To: Downey, Scott[Downey.Scott@epa.gov]; Wroble, Julie[Wroble.Julie@epa.gov]; McClintock, Katie[McClintock.Katie@epa.gov]
From: Koprowski, Paul
Sent: Thur 2/4/2016 6:07:02 PM
Subject: FW: Portland Powell and Twenty Second ave metals monitoring (2).xlsx
Portland Powell and Twenty Second ave metals monitoring (2).xlsx

One of two messages with DEQ data for Bullseye.

Paul

Paul Koprowski

U.S. EPA; Oregon Operations Office

805 SW Broadway, Suite 500

Portland, Oregon 97205

(503) 326-6363

From: ARMITAGE Sarah [mailto:ARMITAGE.Sarah@deq.state.or.us]
Sent: Thursday, February 04, 2016 9:57 AM
To: Koprowski, Paul <Koprowski.Paul@epa.gov>
Subject: Portland Powell and Twenty Second ave metals monitoring (2).xlsx

To: Downey, Scott[Downey.Scott@epa.gov]; McClintock, Katie[McClintock.Katie@epa.gov]
From: Koprowski, Paul
Sent: Thur 2/4/2016 5:16:21 PM
Subject: Teleconference with Richard

Richard isn't available until 11 this morning to talk about Bullseye. Do you have time to talk about it at 11 or 11:15(in case his meeting runs over)?

Paul

Paul Koprowski

U.S. EPA; Oregon Operations Office

805 SW Broadway, Suite 500

Portland, Oregon 97205

(503) 326-6363

To: Downey, Scott[Downey.Scott@epa.gov]
From: McClintock, Katie
Sent: Thur 2/4/2016 4:42:17 AM
Subject: RE: Metal monitoring in moss in SE Portland

Okay, I'll be in at 7 and free until 9. Just come get me when you want to talk.

Have a good night.

Katie

From: Downey, Scott
Sent: Wednesday, February 03, 2016 8:41 PM
To: McClintock, Katie <McClintock.Katie@epa.gov>
Subject: Re: Metal monitoring in moss in SE Portland

Let's try for first thing in the morning. Supposed to be in a RCRA meeting at 8:00 am but I'll see if Cheryl can cover. I'm out Friday.

~~~~~~~~~~~~~~~~~~~~

Scott Downey, Manager

Air and RCRA Compliance Unit

EPA Region 10, OCE-127

1200 6th Ave Suite 900

Seattle, WA 98101

(206) 553-0682

From: McClintock, Katie
Sent: Wednesday, February 3, 2016 8:36 PM
To: Downey, Scott
~~~~~~~~~~~~~~~~~~~~

Subject: RE: Metal monitoring in moss in SE Portland

Yep, I agree. Should I make time with you tomorrow or Friday since I'll be out next week?

From: Downey, Scott
Sent: Wednesday, February 03, 2016 8:36 PM
To: McClintock, Katie <McClintock.Katie@epa.gov>
Subject: Fw: Metal monitoring in moss in SE Portland

The metals issue was discussed with the R10 air managers this afternoon. Rob was there for Mahbubul and shared this. I read the article. Much to discuss on next steps and OCE role.

~~~~~~~~~~~~~~~~~~~~

Scott Downey, Manager

Air and RCRA Compliance Unit

EPA Region 10, OCE-127

1200 6th Ave Suite 900

Seattle, WA 98101

(206) 553-0682

From: Elleman, Robert
Sent: Wednesday, February 3, 2016 4:06 PM
To: Downey, Scott; Matthews, Julie; Hastings, Janis; Suzuki, Debra; Dossett, Donald; Bray, Dave
Cc: Islam, Mahbubul
Subject: Metal monitoring in moss in SE Portland
~~~~~~~~~~~~~~~~~~~~

http://www.lar.wsu.edu/nw-airquest/docs/20150624_meeting/20150625_Donovan_moss.pdf

Robert Elleman

Meteorologist

EPA Region 10, Seattle

(206) 553-1531

elleman.robert@epa.gov

To: Downey, Scott[Downey.Scott@epa.gov]
From: McClintock, Katie
Sent: Thur 2/4/2016 4:36:51 AM
Subject: RE: Metal monitoring in moss in SE Portland

Yep, I agree. Should I make time with you tomorrow or Friday since I'll be out next week?

From: Downey, Scott
Sent: Wednesday, February 03, 2016 8:36 PM
To: McClintock, Katie <McClintock.Katie@epa.gov>
Subject: Fw: Metal monitoring in moss in SE Portland

The metals issue was discussed with the R10 air managers this afternoon. Rob was there for Mahbubul and shared this. I read the article. Much to discuss on next steps and OCE role.

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Scott Downey, Manager

Air and RCRA Compliance Unit

EPA Region 10, OCE-127

1200 6th Ave Suite 900

Seattle, WA 98101

(206) 553-0682

From: Elleman, Robert
Sent: Wednesday, February 3, 2016 4:06 PM
To: Downey, Scott; Matthews, Julie; Hastings, Janis; Suzuki, Debra; Dossett, Donald; Bray, Dave
Cc: Islam, Mahbubul
Subject: Metal monitoring in moss in SE Portland
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http://www.lar.wsu.edu/nw-airquest/docs/20150624_meeting/20150625_Donovan_moss.pdf

Robert Elleman

Meteorologist

EPA Region 10, Seattle

(206) 553-1531

elleman.robert@epa.gov

To: Downey, Scott[Downey.Scott@epa.gov]
From: McClintock, Katie
Sent: Tue 2/2/2016 6:17:23 PM
Subject: RE: Oregon DEQ Media Contact re cadmium, arsenic monitoring near Bullseye Glass, Portland

Rhonda just sent me an email about this too, not sure how they got looped in. I don't see them in echo at all. Their permit is not online since they are minor. Rhonda seems to be concerned about this, do you think it needs further review now? I can see if we have any files on them or try to get the permit from deq.

-----Original Message-----
From: Downey, Scott
Sent: Tuesday, February 02, 2016 8:43 AM
To: Skadowski, Suzanne <Skadowski.Suzanne@epa.gov>
Cc: McClintock, Katie <McClintock.Katie@epa.gov>
Subject: RE: Oregon DEQ Media Contact re cadmium, arsenic monitoring near Bullseye Glass, Portland

Thanks for the heads up. If you track down the web story, we'd like to see.

~~~~~~~~~~~~~~~~~~~~~~~~
Scott Downey, Manager
Air and RCRA Compliance Unit
EPA Region 10, OCE-101
1200 6th Ave, Suite 900
Seattle, WA 98101, (206) 553-0682

-----Original Message-----
From: Skadowski, Suzanne
Sent: Tuesday, February 02, 2016 8:04 AM
To: Downey, Scott <Downey.Scott@epa.gov>; Dossett, Donald <Dossett.Donald@epa.gov>; Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Wilson, Wenona <Wilson.Wenona@epa.gov>; Hastings, Janis <Hastings.Janis@epa.gov>
Cc: Holsman, Marianne <Holsman.Marianne@epa.gov>; Philip, Jeff <Philip.Jeff@epa.gov>
Subject: Oregon DEQ Media Contact re cadmium, arsenic monitoring near Bullseye Glass, Portland

Just FYI for now.

Suzanne Skadowski
Public Affairs Specialist
U.S. Environmental Protection Agency
Region 10 Pacific Northwest | Seattle
Desk: 206-553-2160 Cell: 206-900-3309

-----Original Message-----
From: FLYNT Jennifer [mailto:FLYNT.Jennifer@deq.state.or.us]
Sent: Monday, February 01, 2016 8:17 PM
To: MacIntyre, Mark <Macintyre.Mark@epa.gov>; Skadowski, Suzanne <Skadowski.Suzanne@epa.gov>
Subject: Fwd: Media Contact Metal Monitoring Near Bullseye Glass

-------- Original message --------
From: MONRO David <MONRO.David@deq.state.or.us>
Date: 02/01/2016 7:03 PM (GMT-08:00)
To: ARMITAGE Sarah <ARMITAGE.Sarah@deq.state.or.us>, ALSDORF William H <ALSDORF.William@deq.state.or.us>, DANAB Marcia <DANAB.Marcia@deq.state.or.us>, MCPHERSON Lee <MCPHERSON.Lee@deq.state.or.us>, SVELUND Greg
~~~~~~~~~~~~~~~~~~~~~~~~

<Svelund.Greg@deq.state.or.us>, WHITE Brian <WHITE.Brian@deq.state.or.us>, FLYNT Jennifer <FLYNT.Jennifer@deq.state.or.us>, ARMSTRONG Ken <ARMSTRONG.Ken@deq.state.or.us>, STOCUM Jeffrey <STOCUM.Jeffrey@deq.state.or.us>, MACMILLAN Susan <MacMillan.Susan@deq.state.or.us> Cc: CALDERA Stephanie <caldera.stephanie@deq.state.or.us>, MANEY Ella <MANEY.Ella@deq.state.or.us>, "[All DEQ] Regional Solutions" <RegionalSolutions@deq.state.or.us>, PEDERSEN Dick <PEDERSEN.Dick@deq.state.or.us>, DECONCINI Nina <DECONCINI.Nina@deq.state.or.us>, HAYES-GORMAN Linda <hayes-gorman.linda@deq.state.or.us>, ANDERSEN Keith <ANDERSEN.Keith@deq.state.or.us>, HAMMOND Joni <HAMMOND.Joni@deq.state.or.us>, EMER Lydia <EMER.Lydia@deq.state.or.us>, WILES Wendy <WILES.Wendy@deq.state.or.us>, BARNACK Anthony <BARNACK.Anthony@deq.state.or.us>, BORISENKO Aaron <BORISENKO.Aaron@deq.state.or.us>, COLLIER David <COLLIER.David@deq.state.or.us>, POULSEN Mike <POULSEN.Mike@deq.state.or.us>
Subject: RE: Media Contact Metal Monitoring Near Bullseye Glass

I just got off the phone with Dan. Covered many of the same questions Sarah outlined below, some questions about Bullseye glass (who have we worked with over there, description of their operations); with the addition of a few other questions:
Questions about the permit and what regulations Bullseye must comply with. I explained that the permit implements federal air toxics standards and has limitations that are designed to be protective of the overall airshed. The federal air toxics standard in the permit is a technology based standard that is focused on arsenic; it is also targeted at facilities with higher capacity and production than Bullseye.

How it was that DEQ was blindsided by this? I told him we weren't blindsided, we were using resources, research and partnerships to collect data on air toxics in the Portland area and this kind of thing is the result of our efforts.

If a neighbor knocks on DEQ's door and wants us to shut them down or do something to make them control emissions what can we do? Bullseye is in compliance and the permit program implements the existing rules regulations. Those regulations are focused on implementing federal standards and being protective of the overall airshed, they are not focused on local neighborhood impacts. That's why DEQ puts resources towards efforts like this: to find out where there are problems and then identify solutions.

He thinks they may have something on the web tomorrow; print edition is on Wed.

From: ARMITAGE Sarah
Sent: Monday, February 01, 2016 4:59 PM
To: ALSDORF William H; DANAB Marcia; MCPHERSON Lee; SVELUND Greg; WHITE Brian; FLYNT Jennifer; ARMSTRONG Ken; MONRO David; STOCUM Jeffrey; MACMILLAN Susan
Cc: CALDERA Stephanie; MANEY Ella; [All DEQ] Regional Solutions; PEDERSEN Dick; DECONCINI Nina; HAYES-GORMAN Linda; ANDERSEN Keith; HAMMOND Joni; EMER Lydia; WILES Wendy; BARNACK Anthony; BORISENKO Aaron; COLLIER David; POULSEN Mike
Subject: Media Contact Metal Monitoring Near Bullseye Glass

Date and Time Contacted: 2/1/16, 3:15 pm

Publication/Station: Freelance for Portland Mercury

Reporter's Name and Phone Number: Dan Forbes 503-477-8888

Topic Discussed: Metal monitoring near Bullseye Glass We discussed the steps DEQ has taken to understand the sources of cadmium in Portland, the moss study, our monitoring in the Fred Meyers parking lot, current analysis to understand and map the data, our close work with OHA and Multnomah County Health to determine the significance to public health, what messages we would give to affected people and how we would do it. We also discussed the NESHAP that controls arsenic from glass manufacturing, and that DEQ would be talking with Bullseye and following up very shortly on response actions. I helped Dan find our AQ annual report so he could see how far back we have been measuring

cadmium in Portland (2003) and typical annual averages. Dan asked if we would advise various health related actions (urine testing, avoiding leafy vegetables grown in the area, digging up soil around Cleveland High School) and I said we would need to complete our spatial analysis and consult with OHA for that information. Finally, I let Dan know that we were very concerned that people get accurate information including the extent of the problem, steps for further investigation and appropriate health risk messaging. He said he understood.

Reporter's Deadline: 2/1/16 6pm

Sarah Armitage
DEQ Air Quality Planning
503-229-5186

To: McClintock, Katie[McClintock.Katie@epa.gov]; Downey, Scott[Downey.Scott@epa.gov]
From: Downey, Scott
Sent: Wed 3/2/2016 4:52:00 PM
Subject: Conversation with Katie McClintock

Downey, Scott 8:37 AM:

are you on another call?

Katie McClintock 8:38 AM:

i'm on the JB call

i sent marianne a message

i think it makes more sense for me to be on this one on wednesday

do they need me?

we are going to be discussing Bullseye too

we've got sue and dave from deq on and multunomah

Downey, Scott 8:39 AM:

I'm going to jump on that - I need an update. rec'd another email from Cecilia. no, I gave an update on the meeting yesterday.

Katie McClintock 8:40 AM:

ok

To: McClintock, Katie[McClintock.Katie@epa.gov]; Downey, Scott[Downey.Scott@epa.gov]
From: McClintock, Katie
Sent: Fri 2/19/2016 8:41:55 PM
Subject: Conversation with McClintock, Katie

Katie McClintock 12:17 PM:

i am free at 1 still and have an hour now. Should i gather my thoughts for orcco/apes? I think it would be good to have that convo but don't know if ed has desire/time for it today

Downey, Scott 12:19 PM:

We're still on with Ed as far as I know so gather away unless you need the time for glass work.

Katie McClintock 12:19 PM:

ok, sounds good. there is always work to do but nothing pressing unless OR calls or something. I was going to go to spectrum to pick up data but it isn't ready

Downey, Scott 12:22 PM:

ok, I know the key question for Ed is why you and Zach think source testing is needed at APES when Nina and Dave are so against it. do we still want to push on this? will DEQ's voluntary process get us to the same place? etc

Katie McClintock 12:23 PM:

all of those questions are made harder by the current windstorm (voluntary process is going to be slower for sure), but we can talk about the details.

Downey, Scott 12:23 PM:

yea, I get it.

I think we had the call with Nina just before the storm

Katie McClintock 12:24 PM:

FYI, in case you want to know i have been corresponding directly with the two plant owners for spectrum and uroboros, but because Bullseye lawyered up, my contact is now an attorney. Since julie is out i asked him my questions but we may need to think about whether we need to get lawyers involved here or if that will just make the information gathering adversarial when it doesn't need to be

Downey, Scott 12:26 PM:

right

Katie McClintock 12:26 PM:

i am not feeling outmaneuvered for now, so i think that helps. i'll check with julie monday

Downey, Scott 12:27 PM:

she may be teleworking today and reachable. she usually does on Fridays

Katie McClintock 12:32 PM:

okay, she didn't respond to my other email but it doesn't really matter whether i catch her today or monday. thanks.

i told the perkins attorney the epa people who will be on the phone so he knows. and he will get answers to my clarification questions on their records monday

i just got instructions my iphone is ready!

I plan to be in the office monday to pick it up

Downey, Scott 12:34 PM:

great

One thing Julie and I noticed is that we can't access the one drive from our phones. I going to check with PC support to see if there's a way

To: McClintock, Katie[McClintock.Katie@epa.gov]; Downey, Scott[Downey.Scott@epa.gov]
From: Downey, Scott
Sent: Fri 2/19/2016 12:15:53 AM
Subject: Conversation with Katie McClintock

Downey, Scott 3:58 PM:

do you want to keep the meeting with Ed tomorrow on the APES/ORRCO inspections? not sure you need a lot of prep but want to check

Katie McClintock 3:59 PM:

for now, yes i think but let's see how tomorrow goes

is that what you think or should we just put on back burner a bit

Downey, Scott 4:03 PM:

why don't we keep it on the calendar. we could always use the time to debrief Ed on what you heard at the bullseye meetings. I was going to invite Paul too

Katie McClintock 4:03 PM:

good idea

To: McClintock, Katie[McClintock.Katie@epa.gov]; Downey, Scott[Downey.Scott@epa.gov]
From: McClintock, Katie
Sent: Wed 2/3/2016 5:25:53 PM
Subject: Conversation with McClintock, Katie

Katie McClintock 8:39 AM:

should i bring up the potential rcra find as part of my update

Downey, Scott 8:39 AM:

yes, I think we should. and say we'll follow up with their DEQ RCRA program

Katie McClintock 8:39 AM:

k

Downey, Scott 8:41 AM:

did he say it was state or fed OSHA? now he's interested in data??

Katie McClintock 8:45 AM:

state i think

i think he was very interested last week since someone else is making it happen. he is hoping it means he doesn't have to be the bad guy

so looks like we can reach out to rcra. do you want to do or should we let kevin reach out with his technical prowess to the person as he planned?

Downey, Scott 8:47 AM:

I'll send a note to Audrey the RCRA manager and have Kevin follow up

Katie McClintock 8:49 AM:

sounds good

Katie McClintock 8:52 AM:

do we want to ask about where dave is in the odor protocol since he brought up "moving it forward?"

or should we let rhonda turn to bullseye

Downey, Scott 8:56 AM:

I want to finish reading about the process before challenging him. was able to get through the Report and now want to read the staff strategy

Katie McClintock 8:56 AM:

k

Katie McClintock 9:01 AM:

looked a tiny bit into bullseye, they claim worldwide distribution and may be bigger than your average art glass place

Downey, Scott 9:01 AM:

yep, I perused their website too

Katie McClintock 9:08 AM:

yes, oxygen does change the emissions ;)

Downey, Scott 9:09 AM:

need to school that dude

so even tho they are in compliance, if they are creating a health hazard need to do something, right?

Downey, Scott 9:13 AM:

sounds like Richard is interested.

To: McClintock, Katie[McClintock.Katie@epa.gov]
Cc: Hedgpeth, Zach[Hedgpeth.Zach@epa.gov]
From: Downey, Scott
Sent: Tue 2/16/2016 3:36:45 AM
Subject: Re: Fremont Antique Glass

Makes sense to me. Is Spectrum happening Tuesday?

Sent from my EPA iPhone

On Feb 15, 2016, at 12:00 PM, McClintock, Katie <McClintock.Katie@epa.gov> wrote:

> Fremont Antique Glass has a facility in (Shockingly) Fremont. They don't have a website but according to yelp they make their own glass. It could be interesting to run by here soon (Tuesday if zach has time) or later this week if not to see if they are big enough to merit attention. This quick look would allow me to get a sense of how much beyond the big 8 we will need to go in order to the major sources of potential ambient metals. I can move around my calendar to make it go probably any time.
>
> Thoughts?
>
> Katie McClintock
>
> Air Enforcement Officer
>
> EPA Region 10
>
> 1200 Sixth Avenue, Suite 900, OCE-101
>
> Seattle, WA 98101
>
> Phone: 206-553-2143
>
> Fax: 206-553-4743
>
> Mcclintock.katie@epa.gov

To: McClintock, Katie[McClintock.Katie@epa.gov]; Hedgpeth, Zach[Hedgpeth.Zach@epa.gov]
From: Downey, Scott
Sent: Thur 2/11/2016 2:47:03 AM
Subject: Fwd: Enforcement Confidential - SE Portland air toxics update, 2-10-16

Sent from my EPA iPhone

Begin forwarded message:

From: "Hastings, Janis" <Hastings.Janis@epa.gov>
Date: February 10, 2016 at 6:31:55 PM PST
To: "Kowalski, Ed" <Kowalski.Edward@epa.gov>, "Fleming, Sheila" <fleming.sheila@epa.gov>, "Field, Chris" <Field.Chris@epa.gov>, "Barber, Anthony" <Barber.Anthony@epa.gov>, "Holsman, Marianne" <Holsman.Marianne@epa.gov>
Cc: "Pirzadeh, Michelle" <Pirzadeh.Michelle@epa.gov>, "McLerran, Dennis" <mclerran.dennis@epa.gov>, "Bray, Dave" <Bray.Dave@epa.gov>, "Downey, Scott" <Downey.Scott@epa.gov>
Subject: Enforcement Confidential - SE Portland air toxics update, 2-10-16

The latest information I have from Paul Koprowski is that ODEQ is looking at using emergency authority to deal with Bullseye Glass, and ODEQ is elevating the issue quickly to the Governor's Office. Paul is working at the technical level with Madonna Narvaez, Dave Bray, Julie Wroble, Katie McClintock, and Zach Hedgpeth (OAWT, OCE, and OEA).

The concern extends beyond arsenic and cadmium to hexavalent chromium, which is a serious development. Paul was asked by ODEQ to "keep this under wraps while they vet the response more but he did want to give us a heads up."

We are working closely with the state, and everyone is moving quickly. Katie and Zach did an inspection at the facility today. Paul is keeping us informed of ODEQ's activities. I will send an update to this group (managers) when I have more information. If you have key developments from your staff, please share them.

I'm also copying Mike Koerber, OAQPS, who was named as OAR's point of contact during our call with Janet McCabe this morning. She has offered HQ assistance, and we have ongoing technical discussions at the staff level with OAQPS.

Jan

Janis Hastings, Acting Director

Office of Air, Waste & Toxics

U.S. Environmental Protection Agency, Region 10

1200 Sixth Ave, Ste. 900

Seattle, WA 98101

(206) 553-1582

From: Downey, Scott
Location: R10Sea-Room-12Maple/R10-Rooms-Service-Center
Importance: Normal
Subject: Accepted: hold for bullseye conversation if necessary
Start Date/Time: Mon 2/8/2016 10:00:00 PM
End Date/Time: Mon 2/8/2016 11:00:00 PM

To: Koprowski, Paul[Koprowski.Paul@epa.gov]; McClintock, Katie[McClintock.Katie@epa.gov]
From: Downey, Scott
Sent: Thur 2/4/2016 5:29:50 PM
Subject: RE: Teleconference with Richard

Yes, please call my office then.

~~~~~~~~~~~~~~~~~~~~~~~~~~

Scott Downey, Manager

Air and RCRA Compliance Unit

EPA Region 10, OCE-101

1200 6th Ave, Suite 900

Seattle, WA 98101, (206) 553-0682

From: Koprowski, Paul
Sent: Thursday, February 04, 2016 9:16 AM
To: Downey, Scott <Downey.Scott@epa.gov>; McClintock, Katie <McClintock.Katie@epa.gov>
Subject: Teleconference with Richard

Richard isn't available until 11 this morning to talk about Bullseye. Do you have time to talk about it at 11 or 11:15(in case his meeting runs over)?

Paul

Paul Koprowski

U.S. EPA; Oregon Operations Office

805 SW Broadway, Suite 500
~~~~~~~~~~~~~~~~~~~~~~~~~~

Portland, Oregon 97205

(503) 326-6363

To: McClintock, Katie[McClintock.Katie@epa.gov]
From: Downey, Scott
Sent: Thur 2/4/2016 4:41:29 AM
Subject: Re: Metal monitoring in moss in SE Portland

Let's try for first thing in the morning. Supposed to be in a RCRA meeting at 8:00 am but I'll see if Cheryl can cover. I'm out Friday.

~~~~~~~~~~~~~~~~~~~~

Scott Downey, Manager

Air and RCRA Compliance Unit

EPA Region 10, OCE-127

1200 6th Ave Suite 900

Seattle, WA 98101

(206) 553-0682

From: McClintock, Katie
Sent: Wednesday, February 3, 2016 8:36 PM
To: Downey, Scott
Subject: RE: Metal monitoring in moss in SE Portland

Yep, I agree. Should I make time with you tomorrow or Friday since I'll be out next week?

From: Downey, Scott
Sent: Wednesday, February 03, 2016 8:36 PM
To: McClintock, Katie <McClintock.Katie@epa.gov>
Subject: Fw: Metal monitoring in moss in SE Portland

The metals issue was discussed with the R10 air managers this afternoon. Rob was there for Mahbubul and shared this. I read the article. Much to discuss on next steps and OCE role.

~~~~~~~~~~~~~~~~~~~~

Scott Downey, Manager

Air and RCRA Compliance Unit

EPA Region 10, OCE-127

1200 6th Ave Suite 900

Seattle, WA 98101

(206) 553-0682

From: Elleman, Robert
Sent: Wednesday, February 3, 2016 4:06 PM
To: Downey, Scott; Matthews, Julie; Hastings, Janis; Suzuki, Debra; Dossett, Donald; Bray, Dave
Cc: Islam, Mahbubul
Subject: Metal monitoring in moss in SE Portland

http://www.lar.wsu.edu/nw-airquest/docs/20150624_meeting/20150625_Donovan_moss.pdf

Robert Elleman

Meteorologist

EPA Region 10, Seattle

(206) 553-1531

elleman.robert@epa.gov

To: McClintock, Katie[McClintock.Katie@epa.gov]
From: Downey, Scott
Sent: Thur 2/4/2016 4:35:47 AM
Subject: Fw: Metal monitoring in moss in SE Portland

The metals issue was discussed with the R10 air managers this afternoon. Rob was there for Mahbubul and shared this. I read the article. Much to discuss on next steps and OCE role.

~~~~~~~~~~~~~~~~~~~~

Scott Downey, Manager

Air and RCRA Compliance Unit

EPA Region 10, OCE-127

1200 6th Ave Suite 900

Seattle, WA 98101

(206) 553-0682

From: Elleman, Robert
Sent: Wednesday, February 3, 2016 4:06 PM
To: Downey, Scott; Matthews, Julie; Hastings, Janis; Suzuki, Debra; Dossett, Donald; Bray, Dave
Cc: Islam, Mahbubul
Subject: Metal monitoring in moss in SE Portland

http://www.lar.wsu.edu/nw-airquest/docs/20150624_meeting/20150625_Donovan_moss.pdf

Robert Elleman

Meteorologist

EPA Region 10, Seattle

(206) 553-1531
~~~~~~~~~~~~~~~~~~~~

elleman.robert@epa.gov

To: McClintock, Katie[McClintock.Katie@epa.gov]
Cc: Johnson, Steffan[johnson.steffan@epa.gov]; Fairchild, Susan[Fairchild.Susan@epa.gov]
From: Narvaez, Madonna
Sent: Tue 2/23/2016 8:04:37 PM
Subject: FW: Questions about chromium III reactions
Linak_etal96.pdf

Here is work that the National Risk Management Lab did on chromium reactions at high temperatures. It is possible they may be able to do calculations for higher temperatures.

From: Rosati, Jacky
Sent: Tuesday, February 23, 2016 10:51 AM
To: Nunez, Carlos <Nunez.Carlos@epa.gov>
Cc: McKinney, Doug <Mckinney.Douglas@epa.gov>
Subject: Fw: Questions about chromium III reactions

FYI - we are working on this .....

Dr. Jacky Ann Rosati Rowe

Chief, Air Pollution Technology Branch (APTB)

National Risk Management Research Lab

Air Pollution Protection and Control Division

109 TW Alexander Drive, E305-01

Research Triangle Park, NC 27711

Phone 919.541.9429

Blackberry 919.597-9831

Fax 919.541.0554

rosati.jacky@epa.gov

From: Linak, Bill
Sent: Tuesday, February 23, 2016 1:49 PM

To: Lee, Chun-Wai; Rosati, Jacky
Subject: RE: Questions about chromium III reactions

CW, Jacky:

Back in the early 90s, we were interested in Cr6+ emissions from incineration, and performed modeling (equilibrium calculations) and combustion experiments to examine Cr6+/total Cr behavior in a furnace burning natural gas laced with Cr3+ and Cr6+. The publication from this study is attached.

We incinerated aqueous solutions of Cr3+ (Cr(NO3)3) and Cr6+ (CrO3) separately and in the presence of Cl (1000 and 7000 ppm) and/or S (1000 and 7000 ppm) to examine how those constituents affect Cr speciation.

We were most interested in the possibility of forming stable CrCl6 and/or CrOCl4 (Cr6+) when Cl was present, and if Cr(SO4)3 (Cr3+) might be preferred if S was present. The equilibrium calculations (Fig 1) suggests that CrCl6 is thermodynamically favored at low temperatures, but the presence of even small amounts of S favors Cr(SO4)3. The experimental data (Fig 3) seems to support this.

Please note that the equilibrium calculations do not predict many Cr6+ compounds (dashed curves) at high temperatures, but we did not extend our calculations above 2200 K (1900 C), higher than most peak incineration temperatures. Also, equilibrium calculations only determine the possibility of stable species, and do not include the kinetic rates of reactions to achieve equilibrium. Systems approach equilibrium, but if the reaction kinetics are slow, it may take a very long time to achieve. Chromium species considered in the calculations are listed in Table 1.

The 2800 C temperatures identified below are extremely high, but are consistent with adiabatic flame temperatures for oxy methane, ethane, or acetylene flames. We did not examine this regime, but it might be possible to form stable CrO3 (6+) under these conditions. However, as noted on Fig 3, we burned aqueous CrO3 and measured only small amounts of Cr6+ in the exhaust. That is, CrO3 formed early at high temperatures likely would not survive reactions later in the post flame in a furnace environment. However, from what little I know of artisanal glass making, if CrO3 were formed and then escaped the high temperatures and quickly quenched, it might survive into the environment even though it is not thermodynamically favored.

It's been about 25 years since we did this work. However, I will try to see if we still have a working equilibrium code and see if we might calculate equilibrium for an oxy system at 2800 C.

Bill

From: Lee, Chun-Wai
Sent: Tuesday, February 23, 2016 12:17 PM
To: Linak, Bill <Linak.Bill@epa.gov>
Subject: FW: Questions about chromium III reactions

The request from R10.

CW

From: Rosati, Jacky
Sent: Tuesday, February 23, 2016 9:31 AM
To: Lee, Chun-Wai <Lee.Chun-Wai@epa.gov>
Subject: Fwd: Questions about chromium III reactions

Can you help Rohit?

Sent from my iPhone

Begin forwarded message:

From: "Nunez, Carlos" <Nunez.Carlos@epa.gov>
Date: February 22, 2016 at 8:23:37 PM EST
To: "Rosati, Jacky" <Rosati.Jacky@epa.gov>
Cc: "McKinney, Doug" <Mckinney.Douglas@epa.gov>
Subject: Fwd: Questions about chromium III reactions

Jacky

Is anyone in your branch with experience/knowledge on combustion chemistry of Cr? You can respond directly to Rohit.

Thanks!

Sent from my iPhone

Begin forwarded message:

From: "Mathur, Rohit" <Mathur.Rohit@epa.gov>
Date: February 22, 2016 at 5:42:50 PM EST
To: "Nunez, Carlos" <Nunez.Carlos@epa.gov>
Cc: "Stanek, Lindsay" <Stanek.Lindsay@epa.gov>
Subject: FW: Questions about chromium III reactions

Hi Carlos:

I received the query below. Does anyone in NRMRL work on Cr and combustion chemistry who could help?

Thanks, Rohit

From: Mathur, Rohit
Sent: Monday, February 22, 2016 5:40 PM
To: Narvaez, Madonna <Narvaez.Madonna@epa.gov>

Subject: RE: Questions about chromium III reactions

Hello Madonna:

Thank you for reaching out to us with your question on Cr. Though we have modeled Cr3 and 6 air concentrations, we have essentially treated them as inert tracers in the atmosphere. I and colleagues in my Division am not familiar with the combustion chemistry at 2800 deg C. perhaps a person more familiar with characterizing Cr emissions may know – I'll check with a few colleagues to see if they have any suggestions. You are probably already familiar with the following:

http://www3.epa.gov/airtoxics/hlthef/chromium.html

Also, there is some literature on atmospheric chemical pathways for Cr (see for example):

http://pubs.acs.org/doi/pdf/10.1021/es00001a029

Will let you know if I find anything else.

Rohit

From: Narvaez, Madonna
Sent: Monday, February 22, 2016 12:22 PM
To: Mathur, Rohit <Mathur.Rohit@epa.gov>
Subject: Questions about chromium III reactions
Importance: High

Good morning, Rohit. Anne Pope gave your name as someone who might be an expert or familiar with chromium chemistry in air. We have an art and architecture glass melting facility in Portland, Oregon where the Oregon DEQ has discovered through ambient monitoring some cadmium and arsenic hotspots within 220 meters of the facility, as well as another, smaller art glass melting facility in a different part of the city. We have since learned that the facility uses hexavalent chromium as a dry colorant, as well as trivalent chromium. The furnaces use oxyfuel to increase the temperatures needed to make the glass. They argue that as a result, the reactions are occurring in a reducing environment. They have suspended use of hex chrome and cadmium for the time being, but tell us that to stay in business, they need to start using Cr+3 again. They have not done any stack testing, so we do not know the

emissions actually coming off the furnaces. They want to show by mass balance that the Cr+3 will not result in any Cr+6 emissions. I'm not sure how that can be done, if speciated testing is not done. The monitoring the state has done showed an average of 71.5 ng/m3 of total chromium, with a couple of samples having 406 and 438 ng/m3, both on days that the company said they were not running the furnaces.

I am more familiar with the behavior of chromium in wastewater where the point is to get the C+6 converted to Cr+3, and then the Cr+3 reduced to elemental chromium. I don't know what happens if Cr+3 is subjected to 2800 degree C in the presence of oxygen. Can hexavalent chromium be a product of that reaction? I was trying to look up information but could only find the wastewater information. Thanks for your help!

==========

Madonna Narvaez

Regional Air Toxics Coordinator

USEPA, Region 10

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fax: 206-553-0110

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Follow @EPAnorthwest on Twitter! https://twitter.com/EPAnorthwest

To: Johnson, Steffan[johnson.steffan@epa.gov]; McClintock, Katie[McClintock.Katie@epa.gov]; MONRO David[MONRO.David@deq.state.or.us]
Cc: Doolan, Stephanie[Doolan.Stephanie@epa.gov]; Fairchild, Susan[Fairchild.Susan@epa.gov]
From: Narvaez, Madonna
Sent: Mon 2/22/2016 9:35:47 PM
Subject: RE: Oxyfuel combustion tidbits from the Wool Fiberglass testing

I've read that about oxyfuel using furnaces that they have to have chrome-bearing refractories. Yet, Bullseye insists that they do not have chrome bearing refractories and they rebuild the refractories yearly(?) How often do the fiberglass wool facilities have to rebrick?

From: Johnson, Steffan
Sent: Monday, February 22, 2016 1:11 PM
To: McClintock, Katie <McClintock.Katie@epa.gov>; Narvaez, Madonna <Narvaez.Madonna@epa.gov>; MONRO David <MONRO.David@deq.state.or.us>
Subject: Oxyfuel combustion tidbits from the Wool Fiberglass testing

All,

Susan Fairchild sent along a document titled "Mechanisms of chromium emissions from Wool Fiberglass Furnaces Final.pdf". Here are some tidbits regarding oxyfuel combustion and trivalent chrome conversion. Note that Susan's industry found that trivalent chrome was included in the furnace refractory. Here we have trivalent chrome being added freely to the glass melt.

I believe that the temperature and conditions inside the furnace should be investigated closely before anyone assumes that there is no conversion of trivalent to hex.

Just trying to provide helpful information.

Stef

========== ========== ========== ==========

The oxyfuel furnace has numerous advantages over the air-gas furnace for the glass industry. In both furnace types, the fuel is natural gas (CH_4). Air contains 78.9% nitrogen, which acts as a ballast and reacts with oxides in the glass furnace. The combustion process in the air- gas furnace is:

$CH_4 + O_2 + N_2$ -------→ CO_2, H_2O, NOx, trace gases

The combustion process of the oxyfuel furnace is:

$CH_4 + O_2$ -------→ CO_2, H_2O, trace gases

Because only oxygen and the fuel natural gas are needed in the combustion reaction, nitrogen, which comprises almost 80% of air, is not introduced to the furnace. Several benefits are realized as a result of eliminating N_2 including: increased productivity, greater energy efficiency, enhanced flame stability, reduced exhaust gas volume, and reduced NOx and PM emissions.

The actual flame temperature is determined by the flame radiation efficiency and the combustion system. The best radiation efficiency occurs when both heat absorption of the load and heat refraction of the furnace walls are maximized**. The combustion system is optimized when no products of incomplete combustion remain (i.e., CO and H_2 from partial combustion of CH_4, and unreacted O2 which may occur as a result of chemical dissociation, a common problem at high temperatures.)**

The required fuel input is greatly reduced in the oxyfuel furnace in comparison to the air-gas furnace. The exhaust volume per unit of fuel input is reduced as a function of the elimination of nitrogen, and the available heat increases as a result of the same driver.

"Unlike other fiber glass furnace classes, virtually all of the above-glass refractory in a gas-oxy furnace[12] is also chrome bearing. Currently, there is no material available that is as good as chrome based refractory to resist the chemical corrosion and have the structural integrity at the higher temperature necessary to operate a gas-oxy furnace… Fiber glass furnaces necessarily use chrome-based refractory products. Virtually all of the above-glass refractory in gas-oxy furnaces, unlike other furnace classes, is chrome-based refractory."

Although all glass-melting furnaces are constructed using chromium refractories[14, 15] at and below the line of contact defined by the refractory wall and the molten glass within the glass-melting furnace (the glass/metal line), oxyfuel and some air-gas glass-melting furnaces have other glass-melting furnace parts constructed using chromium refractories, such as the crown and forehearth. The use of chromium refractories above the melt line is necessary to obtain the desired furnace life and reduce the necessity for hot repairs of the furnace. When the hot, corrosive and reactive gases of a gas-fired glass-melting furnace come in contact with the high-chromium refractories lining the area at and above the glass melt in high-temperature glass-melting furnaces, the chromium is available to be oxidized and converted into its hexavalent form.

In the stated opinion of the trade association (NAIMA, February 2012), oxyfuel furnaces have greater chromium emissions than other furnaces because "**the combination of furnace design, glass composition, higher flame temperatures, higher water vapor concentration, and an oxidizing atmosphere with increased concentration of oxides** (filterable and condensable PM) can cause more rapid deterioration of the refractory in a gas-oxy fiber glass insulation manufacturing furnace than in other types of glass furnaces. **The concentration of glass batch ingredient volatiles and water vapor in the oxyfuel furnace environment increases with the reduction in the flue gas volume (as compared to air gas furnaces, which dominated the industry prior to 1990). The peak flame temperatures are up to 40 percent higher than in air gas furnaces which increases the rate of melting, lowers the eutectic point, and drives the reaction of chromium from the trivalent (Cr2O3) state to the hexavalent (Cr2O6) state."**

NAIMA, in their February 2012 letter, added that "**the higher temperature of the gas-oxy burners can volatize the glass batch components more readily than in other furnaces. These glass volatiles that contain alkaline earth oxides reduce the temperature that chrome can be vaporized to as low as 1,832 degrees Fahrenheit. While the chrome must still reach temperatures of 2,700 degrees Fahrenheit to 2,900 degrees Fahrenheit to oxidize the trivalent chromium oxide (i.e., Cr_2O_3 to Cr_2O_6), the potentially increased volatiles can contribute to higher chrome emissions. The 40 percent higher peak flame temperature of oxyfuel burners also raises the probability that available chrome will encounter the conditions that will convert it to the hexavalent form (i.e., Cr_2O_6).** Combined, these differences generate conditions which are more corrosive to chrome refractory and can create favorable conditions for conversion to hexavalent chromium (Cr_2O_6) inside a gas-oxyfueled furnace." According to NAIMA, "These severe conditions do not exist in the other fiber glass furnace classes." Note the flame temperature of the air-gas furnace is sufficient to convert chromium to the hexavalent state, and that the chromium emissions from air-gas furnaces is dependent upon the refractory materials used to construct the furnace at and above the glass melt line.

Stef Johnson | Leader | Measurement Technology Group | Office of Air Quality Planning & Standards | U.S. Environmental Protection Agency | 109 T.W. Alexander Drive | E-143-02 |Research Triangle Park, NC 27711 | Desk: 919.541.4790 | Cell: 919.698.5096 | Fax: 919.541.0516

To: MONRO David[MONRO.David@deq.state.or.us]; Narvaez, Madonna[Narvaez.Madonna@epa.gov]; McClintock, Katie[McClintock.Katie@epa.gov]; DAVIS George[DAVIS.George@deq.state.or.us]
Cc: McCullough, Hugh[McCullough.Hugh@epa.gov]; Fairchild, Susan[Fairchild.Susan@epa.gov]; Johnson, Steffan[johnson.steffan@epa.gov]; Pope, Anne[Pope.Anne@epa.gov]; Dewees, Jason[Dewees.Jason@epa.gov]; Merrill, Raymond[Merrill.Raymond@epa.gov]; Werner, Leslye[Werner.Leslye@epa.gov]
From: Doolan, Stephanie
Sent: Fri 2/19/2016 5:18:41 PM
Subject: RE: do you know a hexavalent chromium expert in OAQPS?
atmospheric fate of Cr+6.pdf

Here is one of the sources I relied upon about behavior of CrVI in air

From: MONRO David [mailto:MONRO.David@deq.state.or.us]
Sent: Wednesday, February 17, 2016 4:45 PM
To: Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Doolan, Stephanie <Doolan.Stephanie@epa.gov>; McClintock, Katie <McClintock.Katie@epa.gov>; DAVIS George <DAVIS.George@deq.state.or.us>
Cc: McCullough, Hugh <McCullough.Hugh@epa.gov>; Fairchild, Susan <Fairchild.Susan@epa.gov>; Johnson, Steffan <johnson.steffan@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>; Werner, Leslye <Werner.Leslye@epa.gov>
Subject: RE: do you know a hexavalent chromium expert in OAQPS?

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David Monro

Air Quality Manager, Northwest Region

office: 503.229.5160

cell: 503.793.9635

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From: Narvaez, Madonna [mailto:Narvaez.Madonna@epa.gov]
Sent: Wednesday, February 17, 2016 12:05 PM
To: Doolan, Stephanie; McClintock, Katie
Cc: McCullough, Hugh; Fairchild, Susan; MONRO David; Johnson, Steffan; Pope, Anne; Dewees, Jason; Merrill, Raymond; Werner, Leslye
Subject: RE: do you know a hexavalent chromium expert in OAQPS?

Thanks, Stephanie!

From: Doolan, Stephanie
Sent: Wednesday, February 17, 2016 11:37 AM
To: McClintock, Katie <McClintock.Katie@epa.gov>
Cc: McCullough, Hugh <McCullough.Hugh@epa.gov>; Fairchild, Susan <Fairchild.Susan@epa.gov>; MONRO David (MONRO.David@deq.state.or.us) <MONRO.David@deq.state.or.us>; Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Johnson, Steffan <johnson.steffan@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>; Werner, Leslye <Werner.Leslye@epa.gov>
Subject: Re: do you know a hexavalent chromium expert in OAQPS?

I'm out of the office today, but can send you the information from our air monitoring efforts. We did monitor for hex chromium with good, low level results. You can make some educated assumptions about how much will be hex, but without data, it's hard to know.

Sent from my iPhone

On Feb 16, 2016, at 11:18 PM, McClintock, Katie <McClintock.Katie@epa.gov> wrote:

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chrome or from conversion of tri chrome) may not persist and hex chrome in the ambient air. If this is the case it would be a wonderful sigh of relief for bullseye who already can't make anything with red, orange and yellow (and green was the killing blow).

I am wondering if one or two people from this great group of hex chrome minds could participate in that call Friday and could pre-meet with ODEQ on Thurdsay. Based on the email traffic today, you all have a lot of knowledge to share with DEQ that would help inform their path forward on chromium.

Please let me know if you are able and if you all decide while I am out on inspections tomorrow, if you could **email David Monro directly as soon as possible** (MONRO.David@deq.state.or.us), that would be perfect!

Thanks.

Katie

From: McCullough, Hugh
Sent: Tuesday, February 16, 2016 1:36 PM
To: Fairchild, Susan <Fairchild.Susan@epa.gov>
Cc: Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Johnson, Steffan <johnson.steffan@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>; McClintock, Katie <McClintock.Katie@epa.gov>; Werner, Leslye <Werner.Leslye@epa.gov>; Doolan, Stephanie <Doolan.Stephanie@epa.gov>
Subject: Re: do you know a hexavalent chromium expert in OAQPS?

Hello all,

I am no longer with the Region 7 air program, but I agree with the points made by Stef. During the RTR for wool fiberglass, we had a couple sources test their Cr6 emissions at the stack with 0061, and I recall from the field that it was challenging for them to get 'good' run.

R7 also conducted ambient air monitoring over a period of a month or two, but unfortunately I am out for training through April and do not have access to my notes. Stephanie Doolan from the R7 air planning group would probably be the best contact for information regarding the QAAP for that monitoring. I should know, but I can't confirm if the monitoring was for total chrome or if it was speciated. I have ccd Stephanie, as well as my previous supervisor, Leslye Werner.

Hope that helps. If there is anything else I can do to help in my limited capacity while I am away, please let me know.

Hugh

Sent from my iPhone

On Feb 16, 2016, at 4:21 PM, Fairchild, Susan <Fairchild.Susan@epa.gov> wrote:

<image002.gif>

Hugh McCullough 913-551-7191

Susan Fairchild

Senior Environmental Scientist

(919) 541-5167

USPS Address:

OAQPS/SPPD/MMG

Mail Code D 243-04

Research Triangle Park, NC 27711

From: Narvaez, Madonna
Sent: Tuesday, February 16, 2016 3:46 PM

To: Johnson, Steffan <johnson.steffan@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>
Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>; McClintock, Katie <McClintock.Katie@epa.gov>
Subject: RE: do you know a hexavalent chromium expert in OAQPS?

What is R7 Hugh's last name?

From: Johnson, Steffan
Sent: Tuesday, February 16, 2016 11:36 AM
To: Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>
Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>
Subject: RE: do you know a hexavalent chromium expert in OAQPS?

Madonna,

In my experience hexavalent forms of chromium are not stable when they are emitted from a source. In fact, EPA has put a good bit of effort into developing a test method designed specifically to capture hex-chrome compounds and keep them in hex form until analysis, as other chromium emissions test methods tend to let the chromium convert to trivalent forms. It is also my understanding (though certainly not the final word on the topic at all) that hex chrome emissions are likely to change state to trivalent chrome post-emission. I believe Jason DeWees and Ray Merrill of my group may also have information to add here, and so I am copying them on this e-mail.

The only reliable test approach that I know to quantify in-stack emissions of hex-chrome is to use a test method known as SW-846-0061. This method uses an alkaline reagent to trap hex-chrome and retain it in hexavalent form until the alkaline solution can be analyzed at a lab. The test method is a bit tricky, but if you need to know in-stack emissions we're certainly available to help you walk through development of a test protocol.

As to ambient sampling for hex chrome, I'll let Hugh in R7 tell you what he knows, my experience stops at the stack.

Please let us know if we can be of further assistance.

Stef

From: Narvaez, Madonna
Sent: Tuesday, February 16, 2016 12:26 PM
To: Pope, Anne <Pope.Anne@epa.gov>
Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Johnson, Steffan <johnson.steffan@epa.gov>
Subject: do you know a hexavalent chromium expert in OAQPS?
Importance: High

Hi, Anne, Susan and Stef. Hope all is well. I don't know if you have heard about the colored glass manufacturer in Portland that DEQ discovered a cadmium hotspot around the facility. In the course of investigations, we discovered that the facility uses Cr+6 as a dry colorant for the glass. Ambient monitoring showed an average of 71.5 ng/m3 of total chromium. I don't know if Katie McClintock, the R10 enforcement contact has asked you for this information yet. If you can point us towards someone, we would really appreciate it. The company uses both Cr+3 and Cr+6, as well as cadmium and arsenic. In the next round of monitoring, the ODEQ will be monitoring for Cr+6 at the day care center, which is 220 meters from the facility. A cadmium hotspot was also detected close to the Harriet Tubman School. A much smaller colored glass mfg facility is close by.

- Katie McClintock did a cursory search for information on the conversion of trivalent chromium to hexavalent chromium and found little information, all of which was talking about smelting and coating. The research confirmed that the use of trivalent chromium alone can still produce hexavalent chromium, but found little data on the conversion rate under various circumstances. We need to develop or find an expert who can read more literature and help interpret the data we find in stack tests and ambient monitoring.

Thanks!

==========

Madonna Narvaez

Regional Air Toxics Coordinator

USEPA, Region 10

1200 Sixth Avenue, Ste 900

MC: AWT-150

phone: 206-553-2117

fax: 206-553-0110

narvaez.madonna@epa.gov

Follow @EPAnorthwest on Twitter! https://twitter.com/EPAnorthwest

To: MONRO David[MONRO.David@deq.state.or.us]; Narvaez, Madonna[Narvaez.Madonna@epa.gov]; McClintock, Katie[McClintock.Katie@epa.gov]; DAVIS George[DAVIS.George@deq.state.or.us]
Cc: McCullough, Hugh[McCullough.Hugh@epa.gov]; Fairchild, Susan[Fairchild.Susan@epa.gov]; Johnson, Steffan[johnson.steffan@epa.gov]; Pope, Anne[Pope.Anne@epa.gov]; Dewees, Jason[Dewees.Jason@epa.gov]; Merrill, Raymond[Merrill.Raymond@epa.gov]; Werner, Leslye[Werner.Leslye@epa.gov]
From: Doolan, Stephanie
Sent: Fri 2/19/2016 5:17:24 PM
Subject: RE: do you know a hexavalent chromium expert in OAQPS?
Chromium VI Air Study QAPP Rev 1 12-05-2011.pdf

Here is the QAPP

From: MONRO David [mailto:MONRO.David@deq.state.or.us]
Sent: Wednesday, February 17, 2016 4:45 PM
To: Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Doolan, Stephanie <Doolan.Stephanie@epa.gov>; McClintock, Katie <McClintock.Katie@epa.gov>; DAVIS George <DAVIS.George@deq.state.or.us>
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Sent: Wednesday, February 17, 2016 12:05 PM
To: Doolan, Stephanie; McClintock, Katie
Cc: McCullough, Hugh; Fairchild, Susan; MONRO David; Johnson, Steffan; Pope, Anne; Dewees, Jason; Merrill, Raymond; Werner, Leslye
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Sent: Tuesday, February 16, 2016 1:36 PM
To: Fairchild, Susan <Fairchild.Susan@epa.gov>
Cc: Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Johnson, Steffan <johnson.steffan@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>; McClintock, Katie <McClintock.Katie@epa.gov>; Werner, Leslye <Werner.Leslye@epa.gov>; Doolan, Stephanie <Doolan.Stephanie@epa.gov>
Subject: Re: do you know a hexavalent chromium expert in OAQPS?

Hello all,

I am no longer with the Region 7 air program, but I agree with the points made by Stef. During the RTR for wool fiberglass, we had a couple sources test their Cr6 emissions at the stack with 0061, and I recall from the field that it was challenging for them to get 'good' run.

R7 also conducted ambient air monitoring over a period of a month or two, but unfortunately I am out for training through April and do not have access to my notes. Stephanie Doolan from the R7 air planning group would probably be the best contact for information regarding the QAAP for that monitoring. I should know, but I can't confirm if the monitoring was for total chrome or if it was speciated. I have ccd Stephanie, as well as my previous supervisor, Leslye Werner.

Hope that helps. If there is anything else I can do to help in my limited capacity while I am away, please let me know.

Hugh

Sent from my iPhone

On Feb 16, 2016, at 4:21 PM, Fairchild, Susan <Fairchild.Susan@epa.gov> wrote:

<image002.gif>

Hugh McCullough 913-551-7191

Susan Fairchild

Senior Environmental Scientist

(919) 541-5167

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Research Triangle Park, NC 27711

From: Narvaez, Madonna
Sent: Tuesday, February 16, 2016 3:46 PM

To: Johnson, Steffan <johnson.steffan@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>
Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>; McClintock, Katie <McClintock.Katie@epa.gov>
Subject: RE: do you know a hexavalent chromium expert in OAQPS?

What is R7 Hugh's last name?

From: Johnson, Steffan
Sent: Tuesday, February 16, 2016 11:36 AM
To: Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>
Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>
Subject: RE: do you know a hexavalent chromium expert in OAQPS?

Madonna,

In my experience hexavalent forms of chromium are not stable when they are emitted from a source. In fact, EPA has put a good bit of effort into developing a test method designed specifically to capture hex-chrome compounds and keep them in hex form until analysis, as other chromium emissions test methods tend to let the chromium convert to trivalent forms. It is also my understanding (though certainly not the final word on the topic at all) that hex chrome emissions are likely to change state to trivalent chrome post-emission. I believe Jason DeWees and Ray Merrill of my group may also have information to add here, and so I am copying them on this e-mail.

The only reliable test approach that I know to quantify in-stack emissions of hex-chrome is to use a test method known as SW-846-0061. This method uses an alkaline reagent to trap hex-chrome and retain it in hexavalent form until the alkaline solution can be analyzed at a lab. The test method is a bit tricky, but if you need to know in-stack emissions we're certainly available to help you walk through development of a test protocol.

As to ambient sampling for hex chrome, I'll let Hugh in R7 tell you what he knows, my experience stops at the stack.

Please let us know if we can be of further assistance.

Stef

From: Narvaez, Madonna
Sent: Tuesday, February 16, 2016 12:26 PM
To: Pope, Anne <Pope.Anne@epa.gov>
Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Johnson, Steffan <johnson.steffan@epa.gov>
Subject: do you know a hexavalent chromium expert in OAQPS?
Importance: High

Hi, Anne, Susan and Stef. Hope all is well. I don't know if you have heard about the colored glass manufacturer in Portland that DEQ discovered a cadmium hotspot around the facility. In the course of investigations, we discovered that the facility uses Cr+6 as a dry colorant for the glass. Ambient monitoring showed an average of 71.5 ng/m3 of total chromium. I don't know if Katie McClintock, the R10 enforcement contact has asked you for this information yet. If you can point us towards someone, we would really appreciate it. The company uses both Cr+3 and Cr+6, as well as cadmium and arsenic. In the next round of monitoring, the ODEQ will be monitoring for Cr+6 at the day care center, which is 220 meters from the facility. A cadmium hotspot was also detected close to the Harriet Tubman School. A much smaller colored glass mfg facility is close by.

- Katie McClintock did a cursory search for information on the conversion of trivalent chromium to hexavalent chromium and found little information, all of which was talking about smelting and coating. The research confirmed that the use of trivalent chromium alone can still produce hexavalent chromium, but found little data on the conversion rate under various circumstances. We need to develop or find an expert who can read more literature and help interpret the data we find in stack tests and ambient monitoring.

Thanks!

==========

Madonna Narvaez

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THE FATE OF HEXAVALENT CHROMIUM IN THE ATMOSPHERE

by
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W. F. Gutknecht
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CARB Contract No. A6-096-32

Prepared for
California Air Resources Board
P. O. Box 2815
Sacramento, California 95812

October 1988

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Grohse, P M
Fate of hexavalent chromium
in the atmosphere

ABSTRACT

A three-phase study was conducted to determine the fate of hexavalent chromium [Cr(VI)] in the atmosphere. Components of the study included the following:

- Identification of the most suitable sampling and analytical methods for Cr(VI)
- Determination, through a series of laboratory reaction chamber tests, the most likely chemical pathways and rate of conversion of hexavalent chromium in ambient air to trivalent chromium [Cr(III)] under simulated atmospheric conditions
- A field test, conducted in California, to support those findings from the laboratory studies

Two general analytical methods were evaluated, a complexation/atomic absorption technique currently utilized by the California Air Resources Board (CARB) and an ion chromatographic method. The atomic absorption method was found to provide the required sensitivity for measurement of atmospheric Cr(VI) [3-10 percent coefficient of variation (C.V.)] and was reasonably precise in the determination of Cr(VI) corresponding to concentrations varying from 0.7 to 5.5 nanograms per cubic meter (ng/m^3).

The ion chromatographic technique was more precise, sensitive, and rapid. The detection limit was 0.1 ng/m^3 with a precision of better than five percent C.V. A modification of this method provided an even greater detection limit (0.1 ng/m^3 and lower) but was more time consuming and complex.

A sampling method currently employed by CARB utilizing polyvinylchloride (PVC) membranes was found to provide low estimates of the true Cr(VI) atmospheric concentrations. Air concentrations approximately ten times higher were measured using an impinger method that provided greater stability of the Cr(VI) species during sampling.

Laboratory reaction chamber tests were conducted that utilized PVC filters spiked with Cr(VI) compounds and exposed to atmospheric reactants typical of the Southern California region. The results indicated that under low atmospheric pH conditions (measurable atmospheric HNO_3, etc.)

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greater than 50% of Cr(VI) species will be reduced in the presence of oxidizable species, such as unsaturated and oxygenated organic compounds, and mono and divalent vanadium [V(I,II)] species over a 24-hour period.

Finally, a two-phase field test conducted in the Los Angeles basin area indicated the following:

- Cr(VI) species exist at measurable levels at distances of up to 0.5 miles or greater from chromium emission sources.
- The rates of reduction of Cr(VI) under true ambient air conditions parallel those seen in the laboratory.

ACKNOWLEDGEMENTS

We wish to express our gratitude to the following persons and organizations for the contributions during this program: Dr. Michael Poore (CARB), who provided valuable information and suggestions regarding analytical methodology and design of an aerosol generation system for the deposition of hexavalent chromium species on membrane filters; Todd Wong (CARB), who provided valuable assistance and equipment in conjunction with the field test effort; in general, the staff of the CARB Environmental Studies Section, Southern Laboratory Branch for field testing performed in conjunction with Entropy Environmentalists, Inc. during October and November 1987; Robert Joyce and Michael Doyle (Dionex Corporation), who provided the ion chromatographic post column reaction method and were extremely helpful in their suggestions for the analytical method; Dr. Joseph Sickles (RTI), who provided essential background information for the design of the laboratory reactivity tests; Doug Van Osdell (RTI), who provided useful suggestions regarding aerosol generation; Dr. Peter McMurry (University of Minnesota), who lent advice regarding reaction chamber design; Christina Davis and Wendy Beverly (RTI) for their secretarial support during the preparation of monthly reports, and this final report.

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1.0 SUMMARY AND CONCLUSIONS

1.1 MEASUREMENT STUDIES

The existing sampling/analytical method proposed by CARB (ADDL006) is flawed primarily in the sampling step. Reaction chamber tests and studies conducted in the field demonstrate that the hexavalent chromium species undergo reduction during sampling presumably due to reaction with oxidizable species such as Fe^{+2}, V^{+}, V^{+2}, organics, etc. under acidic conditions due to CO_2, HNO_3, or other atmospheric species. An ideal sampling device to address this problem has not been identified. Impinger solutions that maintain a neutral or higher pH represent one approach toward stabilizing the Cr(VI) species. These devices show some promise based on some field test data, but are inconvenient to handle and, due to high blank values provided by large volumes of impinger solution and surface problems associated with glassware, they are thus far unsuitable for total chromium determinations. Preliminary data suggest that the most suitable sampling scenario is a filter device that utilizes an alkaline or neutral buffered coating. While PVC or Teflon membranes do not provide suitable surfaces for coating, a material such as paper or glass fiber may hold some promise. Potential problems for these devices include potential sampling inefficiency and reactivity for paper devices and the need for filtering or centrifugation of the paper or glass fiber material following extraction procedures.

At this time, the sampling method of choice appears to be the buffered impinger. The device must provide for the control of the pH of the sampling medium in order to stabilize the oxidation state of the chromium species <u>during</u> sampling. As a consequence, impinger solutions of sodium carbonate (0.02-0.05 M) are currently in use and have provided a much closer approximation of the true Cr(VI) concentration than the previously used PVC membrane. A further improvement might involve the use of plastic impinger devices, if possible, to minimize surface and blank problems associated with glass and allow for Cr(III) quantitation, in addition to Cr(VI) quantitation. A more ideal approach would involve a buffered alkaline coating of a glass fiber or paper filter, but an evaluation of these devices has not been completed.

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Of the analytical methods evaluated in the study, none were found suitable for the in-situ determination of any chromium species. However, at least two analytical methods appear suitable for measurement/speciation of hexavalent chromium in the laboratory--CARB Method ADDL006 and ion chromatography. Both methods appear suitable for the analysis of either impinger solutions or extracts of filter samples. In both cases, however, pH adjustment is essential for recovery of the Cr(VI) species. The CARB method is quite sensitive, capable of detecting atmospheric levels of Cr(VI) of 0.5 ng/m^3, assuming sampling rates of 10 Lpm over a 24-hour period. However, the method is somewhat labor-intensive. If the ion chromatographic (IC) method was used in conjunction with the extract of a suitable filter collection device, Cr(VI) levels of 0.3 ng/m^3 might be determined. The IC detection limit can be lowered to ~0.04 ng/m^3 using a preconcentration technique that is somewhat labor-intensive. This latter technique is also potentially suitable to impinger solution analysis, although the detection limit is then similar to the CARB method. The primary advantage of the IC method is that far fewer sample manipulations are performed during measurement, contamination is minimized, and the method, in general, appears more rugged. The pH adjustment of the sample only requires values greater than 6.8 prior to injection.

The most desirable measurement method at this point appears to be ion chromatography, although further laboratory work is necessary to properly evaluate this technique in conjunction with the sampling device proposed above. Further work refining the preconcentration IC method is required if an impinger approach is to be used in future work. The standard post-column reaction method appears suitable as is, but would require more extensive laboratory evaluation of recovery, accuracy, precision, interferences, etc. At this time, Method ADDL006 appears suitable until such an evaluation is performed, although it appears slightly prone to certain interferences.

1.2 REACTION CHAMBER STUDIES

The experimental design utilized in this phase of the study, namely, exposure of spiked filters to controlled artificial atmospheres of a wide variety of species considered ubiquitous to ambient air, was intended to

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provide an approximation of potential Cr(VI) atmospheric reactions. Semi-quantitative reaction rates have been obtained from individual tests. More quantitative rates would be difficult to obtain, due to the limited conditions/species employed in each test. Some "indicators" suggesting general conditions under which hexavalent chromium is likely to undergo atmospheric conversion are as follows:

1. In the presence of "acidic" species, e.g., HNO_3, Cr(VI) will react with "oxidizable" species such as aldehydes, unsaturated hydrocarbons, substituted aromatic compounds, and inorganic species such as V^{+}, V^{+2}, and Fe^{+2}.

2. "Ambient levels" of Cr(VI) (20-100 ng) demonstrated an average half life [50% conversion to Cr(III)] of 13 hours when exposed to simulated atmospheric reactants. Assuming wind speeds greater than one mile per hour, one might expect the vast majority of Cr(VI) collected within a few miles of a Cr(VI) source to remain in the hexavalent state.

3. Based on the series of chamber tests, no conclusion can be made regarding the humidity factor. For most of the tests, the relative humidity was fixed between 20 to 30 percent.

4. No chamber tests were run to isolate the photochemical input in the conversion of Cr(VI) species. However, later field reaction studies conducted in a manner similar to chamber tests show conversion rates at night were indistinguishable to those found in the daylight hours.

5. The reaction chamber tests tend to be consistent with Cr(VI) behavior in solution. One possible explanation may be in the formation of fine aerosols (droplets) that simulate solution chemistry.

6. Very limited tests in conjunction with literature findings indicate that conversion of trivalent chromium to the hexavalent form is not a likely chemical pathway.

7. The reaction chamber tests provided a field reaction study design that could be easily implemented to provide more realistic Cr(VI) conversion data.

1.3 FIELD STUDY

Samples obtained from the chrome plating facility contained measurable levels of Cr(VI), at distances of at least 0.5 km from the source. Measured Cr(VI) levels ranged from 26.3 ng/m^3 to 315 ng/m^3. These elevated levels are reflective of an improved impinger sampler that allows for some

degree of stabilization of the Cr(VI) species during collection. This type of sampler was utilized as a result of the laboratory reactivity tests, which demonstrated significant reduction on filters during simulated sampling conditions. Previous sampling that had been performed by CARB had featured the use of PVC (or Teflon) membranes to collect Cr(VI), and therefore contained no provision for the fixation of the collected Cr(VI). It is expected that this approach provided estimates of the Cr(VI) atmospheric concentrations that were perhaps only five to ten percent of the true values. This is, in fact, dramatically seen in the results obtained from the CARB measurements performed October 6-9, 1987 at the same general chrome plating site utilized by Entropy Environmentalists during their field test. While levels of hexavalent chromium were measurable at 0.5 Km, most sites at greater distances did not provide sufficient levels to allow for quantitation of a relationship of Cr(VI) to total chromium. It was hoped that if this had been possible, some measure of Cr(VI) reduction with distance from the source could have been obtained. This was not the case, except with one ambient test run.

Levels of hexavalent chromium at the cooling tower site were generally at or near the detection limit. Exceptions are included in this report. Possible contributing factors to low levels at the cooling tower facility include high dilution rates and variable winds.

Field reaction studies that simulated in the field those reactivity tests performed in the laboratory were performed at both sites. Useful data were provided at both sampling sites. PVC filters loaded with 20-100 ng of Cr(VI) at the emission source were taken to an El Monte site (CARB facility) away from the source and exposed to ambient air at a sampling flow rate of 3 Lpm for 24 hours. Hexavalent chromium reduction was observed over this period that paralleled those reduction rates observed in the laboratory under simulated conditions. An average half life of approximately 16 hours was observed over seven field reaction tests conducted at both sites (with a range of 9 to 23 hours). These results corroborated those laboratory chamber tests that demonstrated an average experimental half life of 13 hours (6 to 20 hours).

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2.0 RECOMMENDATIONS

A sampling method has been identified that provides a more accurate estimate of the atmospheric hexavalent chromium burden. The technique, an impinger, provides greater stability for Cr(VI) species during sampling than the currently used PVC membrane, but nevertheless does not provide the ideal conditions for fixing the Cr(VI) species. In addition, it is cumbersome to work with for personnel conducting the sampling. However, handling difficulties might be eased considerably if plastic impinger devices were used. This also would minimize blank problems associated with glass surfaces. If ultrapure or subboiled acids were used during sample preparation, these devices might also allow for Cr(III) quantitation. It is recommended that further work be performed to determine the feasibility of an alkaline- or neutral-buffered coating on a membrane filter. For example, glass (or quartz) fiber material could provide sites for a reagent coating, but would also pass an adequate air flow without sacrificing collection efficiency. In addition, the ease of removal of Cr(VI) species from the membrane must be evaluated. Any potential methods must be evaluated for stability over time; e.g., a 30-day storage period under a variety of conditions.

Further work is needed to evaluate the precision and accuracy of the ion chromatographic (IC) method. If an impinger sampling method is indicated as most suitable, the IC method involving the use of the preconcentration column must be subjected to a full-scale method evaluation as well. In addition to the above mentioned considerations, the technique should be carefully evaluated for potential interferences since the preconcentration column efficiency might be adversely effected by certain species commonly existing in the environment.

The reactivity of trivalent chromium was not closely examined in this study. While not a likely chemical pathway, the potential oxidation of Cr(III) should be studied due to the significance of any possible conversion scenarios. It is recommended that a few selected laboratory reactivity tests be conducted in the presence of manganese dioxide (MnO_2) under varying pH conditions. Subsequent to any findings indicating possible reactivity of Cr(III), additional laboratory tests might be conducted on

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available representative fly ash materials containing Cr(III), likewise in the presence of MnO_2, in order to simulate more realistic conditions.

Should results from these laboratory tests indicate potential Cr(III) reactivity, field tests should be conducted at Cr(III) emission sources [preferably low in Cr(III) emissions] to support these findings. Simultaneously, a field reactivity test might be conducted to parallel the laboratory test design.

3.0 INTRODUCTION

3.1 PURPOSE OF THE STUDY

The health hazards of certain substances have been found to be a function of the chemical forms of these substances. For example, arsenic (V) is carcinogenic, while arsenic (III) is only toxic. The same is true for chromium (VI) and chromium (III), respectively. Chromium (VI) has been identified by the California Air Resources Board (CARB) as an air contaminant and thus poses a potential health hazard. Of concern to CARB is the environmental fate of the chromium (VI) species. That is, airborne hexavalent chromium may be reduced to chromium (III), or it may settle out of the air as particulate matter or be washed out with precipitation. Of these possibilities, the primary concern and thus primary objective of this study, is the determination of the rates of reduction of Cr(VI) to Cr(III) in ambient air. The following three steps have been taken in meeting this objective:

- Identify, evaluate, and validate an accurate and precise methodology for sampling and analyzing the Cr(VI) species.
- Using this measurement methodology, expose Cr(VI)-containing particulate to a variety of potential reducing agents and/or reduction catalysts of the type expected in the ambient air and measure rates of any reduction observed.
- Perform a field measurement study for chromium species at three different sites in California near likely sources of Cr(VI) emissions, with the intent of determining the rate of conversion of Cr(VI) to Cr(III).

There have been a large number of techniques developed for the speciation of hexavalent and trivalent chromium. The most well established methods have been used primarily for samples collected at the chromium sources or in the industrial workplace (1-8). For both cases, chromium levels are much higher than those normally encountered in ambient air, and as a consequence, avoid certain problems frequently peculiar to ambient air analysis such as sensitivity, contamination, and sample (species) stability. However, a few techniques have been developed prior to this study that have shown promise in this particular application (4, 9, 10). CARB Method ADDL006 utilizes a complexation reaction with Cr(VI) followed by isolation

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and acid digestion of the complex. Measurement of the digest is by graphite furnace atomic absorption. An additional ion chromatographic method had been developed by an instrument manufacturer that shows promise.

The second phase of this study presented the greatest challenge. In order to conduct this phase of the study, an understanding of the physical and chemical properties of chromium aerosols was required. Individuals at RTI and elsewhere with atmospheric chemistry experience were consulted. Of primary concern initially was the selection of a suitable reaction chamber design in order to conduct simulated interactions of Cr(VI) and Cr(III) species with a variety of expected atmospheric reactants. RTI has a significant amount of experience with continuously stirred tank reactors (CSTRs) (11, 12). However, several investigators have observed problems with CSTRs when studying aerosols, including severe losses due to the static charge on the particle even when utilizing all metal (aluminized) chambers (13). An alternate configuration utilizes filters spiked with target species that are subsequently exposed to "interferent" atmospheres (14, 15). The degradation of the spiked species is measured over time to establish general reaction rate "trends" as a function of a particular reactant. This approach was utilized during the second phase of the study. Nevertheless, many unanticipated problems were encountered that required changes in design of this phase of the study.

The third phase of the study, the field test, was conducted with the goal of verifying the findings of the second phase in addition to conducting a limited ambient sampling program. CARB utilizes Method ADDL006, which involves sampling utilizing PVC membrane collection. RTI experience during the laboratory reactivity tests indicated that, under typical ambient sampling conditions, more than 50 percent of the Cr(VI) species may be expected to be reduced to trivalent chromium over a 24-hour period. An impinger sampler approach was utilized during the study in order to provide a closer estimate of the Cr(VI) concentrations in the atmosphere. In order to verify those results, a test configuration (similar to that conducted during the laboratory chamber tests) had to be utilized. As a consequence, filters were loaded with Cr(VI) from actual sources and exposed to environmental reactants in a manner analogous to the laboratory test configuration. On the basis of the laboratory reactivity tests, some adjustments

were made immediately before, during, and after this field phase, which pertained mainly to the sampling approach.

3.2 COMPONENTS OF THE STUDY

The following components were included in the study:

- A thorough study of the literature, plus communication with experts to identify methods capable of providing the speciation (identification/measurement) of trivalent and hexavalent chromium in the ambient air samples. In addition, the literature was consulted to determine potential chemical pathways of both hexavalent and trivalent chromium species in atmospheres typical to those encountered in California.

- Testing those analytical methods selected for potential applicability and acceptability (appropriate recovery, precision, detection limit, etc.) by CARB for ambient air applications.

- Constructing an atmospheric test chamber that provides a means of predicting general trends in the atmospheric reactivity of hexavalent and trivalent chromium species, and conducting a series of reactivity tests that provide the general pathways expected in ambient air.

- Validation of the findings of reaction chamber tests through field tests conducted at ambient sites located in the Los Angeles area near two chromium emission sources, one a chrome plating facility and the other a cooling tower.

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4.0 CHEMICAL REACTION SCENARIO BASED ON LITERATURE STUDIES

4.1 INTRODUCTION

A literature study and examination of the chemistry of Cr(VI) and Cr(III) has been performed in order to arrive at a scenario for the potential atmospheric reactions of these species in air. The approach taken has been first to study general inorganic texts and reports dealing with both the general chemistry and also the atmospheric chemistry of chromium. This has been followed by performance of a literature search and contact with experts regarding the atmospheric chemistry of chromium. Data collected includes proposed reactions along with corresponding equilibrium or thermodynamic data, atmospheric concentrations of potential reactants and estimated rates of reaction.

The texts reviewed presented some of the general chemistry of chromium including the acid/base equilibria and various complexation and precipitation reactions. Several major reports on chromium were acquired from the EPA, NTIS, etc. These deal principally with sources of atmospheric chromium (16) and the health effects of chromium (17, 18). They also present some basic inorganic chemistry of various chromium compounds and an overview of methods of analysis. A literature review on occurrence and methodology for determination of chromium species in air prepared by Battelle Columbus Laboratories in 1984 was acquired (19). The only selective analytical procedure for Cr(VI) identified in this study was the ASTM Method utilizing s-diphenylcarbazide as a selective complexing agent.

The most important report identified was that by Christian Seigneur of Systems Applications, Inc., entitled "A Theoretical Study of the Atmospheric Chemistry of Chromium" (20). This report presented a thorough review of the inorganic reactions of Cr(III) and Cr(VI), atmospheric concentrations of potential reactants, and conclusions about the potential reaction scenario for these two species. However, little information was presented about the reactions of these chromium species with organic compounds. Despite, this shortcoming, this report has served as the principal resource for preparation of this chapter.

The literature, though quite thorough, has not revealed any studies of the actual atmospheric chemistry of the chromium species. Several papers

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have indicated that Cr(VI) species would be expected to react with organic material and any reducing species such as Fe^{2+}.

Chromium ranks as the 21st element in the earth's crust in relative abundance and is more abundant than nickel, zinc, and copper. Chromium ion has oxidation states in compounds ranging from -2 to +6, but most commonly occurs as 0, +2, +3, and +6. Only +3 and +6 are found in stable form in natural materials. Cr(III) compounds are relatively stable in aqueous solution. The +3 ion is readily complexed to form octahedral, six-coordinate ions. The chemistry of the +6 oxidation state of chromium (especially CrO_4^{2-}) is very much like that of sulfate. However, free chromic oxide CrO_3 does not exist. In acid solutions, the dichromate ion ($Cr_2O_7^{2-}$) is favored and is a strong oxidizing agent.

The chemistry of the chromium species is quite complex. The type of reactions which can occur include the following:

- Adsorption
- Acid/base equilibria
- Complexation reaction
- Precipitation reactions
- Reduction/oxidation reactions

Each of these will be considered separately with regard to inorganic and organic reactants.

4.2 ADSORPTION

Natural highly oxygenated and/or ion exchange materials such as silicates can adsorb chromium species. A general reaction is as follows:

$$CrO_4^{2-}/Cr_2O_7^{2-} + \text{siliceous particulate} \longrightarrow CrO_4^{2-}/Cr_2O_7^{2-}: \text{siliceous particulate}$$

Quantitative values for the extent of this reaction are not available.

4.3 ACID/BASE EQUILIBRIA

4.3.1 Cr(III)

The Cr(III) may be present in the form of its oxide, Cr_2O_3, or as soluble salts. Cr(III) in water and in the absence of ligands will exist as a

complex molecule with six waters of hydration. Unlike the chromate and dichromate species which act as bases, the Cr(III) species is not basic in nature. It does undergo hydrolysis, however, which is described in a subsequent section.

4.3.2 Cr(VI)

The principal acid/base equilbria for Cr(VI) are as follows:

	k
$H_2CrO_4 \longleftrightarrow HCrO_4^- + H^+$	1.21
$HCrO_4^- \longleftrightarrow CrO_4^{2-} + H^+$	3.0×10^{-7}
$2CrO_4^{2-} + 2H^+ \longleftrightarrow Cr_2O_7^{-2} + H_2O$	4.2×10^{14}
$H_2Cr_2O_7 \longleftrightarrow H^+ + HCr_2O_7^-$	large
$HCr_2O_7^- \longleftrightarrow H^+ + Cr_2O_7^{2-}$	0.85
$2HCrO_4^- \longleftrightarrow Cr_2O_7^{2-} + H_2O$	35.5

At pH less than 0, dihydrogen chromate, H_2CrO_4 , becomes the predominant species. Between pH 1 and 5, which is the principal pH range for atmospheric aerosols, hydrogen chromate and chromate, $HCrO_4^-$ and CrO_4^{2-} , will be the dominant species. At high $HCrO_4^-$ concentration and low pH, dichromate, $Cr_2O_7^{2-}$, will be a major species.

Acidic species in the aerosols may exchange both protons and ligands with the chromium species. Possible reactions are:

	k
$HSO_4^- + HCrO_4^- \longleftrightarrow CrSO_7^{2-} + H_2O$	4.1 M^{-1}
$HSO_3^- + HCrO_4^- \longleftrightarrow CrSO_7^{2-} + H_2O$	36 M^{-1}
$H^+ + Cl^- + HCrO_4^- \longleftrightarrow CrO_3Cl^- + H_2O$	11 M^{-2}
$HCrO_4^- + H_2PO_4^- \longleftrightarrow HCrPO_7^{2-} + H_2O$	2.9 M^{-1}
$HCrO_4^- + H_3PO_4 \longleftrightarrow H_2CrPO_7^- + H_2O$	9.4 M^{-1}

4.4 COMPLEXATION AND LIGAND EXCHANGE REACTIONS

4.4.1 Cr(III)

A major reaction pathway for the Cr(III) species is hydrolysis. Possible reactions are as follows:

	k
$Cr(H_2O)_6^{3+} + H_2O \longrightarrow CrOH^{2+} + H_3O^+$	10^{-4} M
$Cr(H_2O)_5(OH)^{2+} + H_2O \longrightarrow Cr(H_2O)_4(OH)_2^+ + H_3O^+$	2.8×10^{-6} M
$Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3$ (s)	10^{30} M^4
$Cr(OH)_3$ (s) $+ OH^- \longrightarrow Cr(OH)_4^-$	0.40
$2CrOH^{2+} \longrightarrow Cr_2(OH)_2^{4+}$	10^4 M^{-1}

Additional possible reactions with other species likely to be present in the aerosols, including nitrate, sulfate, chloride and fluoride, are as follows:

	k
$Cr^{3+} + 3NO_3^- \longrightarrow Cr(NO_3)_3$ (s)	2.6 M^{-4}
$Cr^{3+} + SO_4^{2-} \longrightarrow CrSO_4^+$	1.38 M^{-1}
$2Cr^{3+} + 3SO_4^{2-} \longrightarrow Cr(SO_4)_3$ (s)	$7.7 \times 10^{+6}$ M^{-5}
$Cr^{3+} + Cl^- \longrightarrow CrCl^{2+}$	2.2×10^{-1} M^{-1}
$CrCl^{2+} + Cl^- \longrightarrow CrCl_2^+$	2.9×10^{-2} M^{-1}
$CrCl_2^+ + Cl^- \longrightarrow CrCl_3$ (s)	1.5×10^{-3} M^2
$CrCl_2^+ + Cr(OH)_2^+ \longrightarrow 2CrClOH^+$	2.5
$CrCl_2^+ + H_2O \longrightarrow CrCl_2OH + H^+$	10^{-6} M^1
$Cr^{3+} + F^- \longrightarrow CrF^{2+}$	2.6×10^4 M^{-1}
$CrF^{2+} + F^- \longrightarrow CrF_2^+$	2.5×10^3 M^{-1}
$CrF_2^+ + F^- \longrightarrow CrF_3$	3.0×10^2 M^{-1}

4.4.2 Cr(VI)

Reactions that involve ligand exchange are presented in Section 4.3.2 since they also involve proton transfer. Complexation reactions which lead to precipitation are presented separately in the following section.

4.5 PRECIPITATION REACTIONS

4.5.1 Cr(III)

Except for chromium oxide, Cr_2O_3, most Cr(III) species are quite soluble. Three possible, though not likely precipitation equilibrium reactions are as follows:

	k_{sp}
$Cr(NO_3)_3$ (s) <---> $Cr^{3+} + 3NO_3^-$	0.4 M^4
$Cr_2(SO_4)_3$ (s) <--> $2Cr^{3+} + 3SO_4^{2-}$	1.3×10^{-7} M^5
$CrCl_3$ (s) <------> $CrCl_2^+ + Cl^-$	1.5×10^{-3} M^2

4.5.2 Cr(VI)

Cr(VI), as compared to Cr(III), forms many relatively insoluble compounds. Possible precipitation equilibrium reactions are as follows:

	k_{sp}
$PbCrO_4$ <------> $Pb^{2+} + CrO_4^{2-}$	1.8×10^{-14}
Ag_2CrO_4 <------> $2Ag^+ + CrO_4^{2-}$	9.0×10^{-12}
$BaCrO_4$ <------> $Ba^{2+} + CrO_4^{2-}$	3.0×10^{-10}
$ZnCrO_4{:}4Zn(OH)_2$ <------> $Zn^{2+} + CrO_4^{2-} + 4Zn(OH)_2$	5×10^{-17}
$ZnCrO_4$ <------> $Zn^{2+} + CrO_4^{2-}$	1.1×10^{-5} M^2
$SrCrO_4$ <------> $Sr^{2+} + CrO_4^{2-}$	3.0×10^{-5}
$CuCrO_4$ <------> $Cu^{2+} + CrO_4^{2-}$	3.6×10^{-6} M^2
$CaCrO_4$ <------> $Ca^{2+} + CrO_4^{2-}$	2.3×10^{-2}
$K_2Cr_2O_7$ <------> $2K^+ + Cr_2O_7^{2-}$	4.9×10^{-3} M^3
K_2CrO_4 <------> $2K^+ + CrO_4^{2-}$	0.23 M^3
Na_2CrO_4 <------> $2Na^+ + CrO_4^{2-}$	3.65 M^3
$(NH_4)_2Cr_2O_7$ <------> $2NH_4^+ + Cr_2O_7^{2-}$	4.0 M^3
CrO_3 (s) <------> CrO_3 (aq)	6.2 M
$(NH_4)_2CrO_4$ <------> $2NH_4^+ + CrO_4^{2-}$	20 M^3
$Na_2Cr_2O_7$ <------> $2Na^+ + Cr_2O_7^{2-}$	5.1×10^2 M^3

4.6 REDUCTION/OXIDATION REACTIONS

4.6.1 Oxidation of Cr(III)

A number of airborne species can react with Cr(III) to form Cr(VI) species, though Cr(III) is not a strong reducing agent. Possible reactions are as follows:

$$5H_2O + 2Cr^{+3} + 3O_3 \longrightarrow 2CrO_4^{2-} + 10H^+ + 3O_2$$

$$2H_2O + 2Cr^{+3} + 3H_2O_2 \xrightarrow{\text{(basic)}} 2CrO_4^{2-} + 10\ H^+$$

$$3H_2O + 2Cr^{+3} + 2MnO_4^- \xrightarrow{\text{(basic)}} Cr_2O_7^{2-} + 2MnO_2 + 6H^+$$

$$H_2O + 2Cr^{+3} + 3PbO_2 \longrightarrow Cr_2O_7^{2-} + 3Pb^{+2} + 2H^+$$

$$2Cr^{3+} + 6Mn^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 6Mn^{2+} + 14H^+$$

4.6.2 Reduction of Cr(VI)

The Cr(VI) species are strong oxidizing agents and thus there are many possible reactions for this oxidation state of chromium. Several of the more likely atmospheric reactions are as follows:

$$3V^{2+} + Cr(VI) \longrightarrow 3V^{3+} + Cr^{3+}$$

$$Cr(VI) + Fe(II) \longrightarrow Cr(III) + Fe(III)$$

$$2HCrO_4^- + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 5\ H_2O$$

$$2HCrO_4^- + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 8H_2O$$

$$2HCrO_4^- + 9I^- + 14H^+ + 4\ H_2O \longrightarrow 2Cr(H_2O)_6^{3+} + 3I_3^-$$

$$2HCrO_4^- + 4HSO_3^- + 6\ H^+ \longrightarrow 2Cr^{3+} + 2SO_4^{2-} + S_2O_6^{2-} + 6H_2O$$

$$2H_2AsO_3^- + 3Cr(VI) \longrightarrow 2Cr^{3+} + 3H_2AsO_4^-$$

$$2HCrO_4^- + 3H_2O_2 + 8H^+ \longrightarrow 2Cr^{3+} + 3O_2 + 8H_2O$$

Though not given major significance by Seigneur, the reduction of the Cr(VI) species by organic compounds is, in fact, a major concern. Two reactions presented by Seigneur are:

$$2Cr(VI) + 3HCOOH \longrightarrow 2Cr(III) + 3CO_2$$

$$2C_2H_5OH + 3Cr(VI) \longrightarrow 2CH_3COOH + 3Cr(III)$$

Other reactions with organic species identified in the literature (21) are as follows:

$$R_3CH + CrO_4^{2-}/Cr_2O_7^{2-} \text{ ------> } R_3COH + Cr^{+3}$$

$$CH_3 + CrO_4^{2-}/Cr_2O_7^{2-} \text{ ------> } RCOOH$$

$$RCHO + CrO_4^{2-}/Cr_2O_7^{2-} \text{ ------> } RCOOH$$

$$\begin{matrix} R^1 \\ H \end{matrix}\!\!>C = C\!<\!\!\begin{matrix} R^2 \\ R^3 \end{matrix} + CrO_4^{2-}/Cr_2O_7^{2-} \text{ ------> } R^1COOH + R^2\text{-}\overset{O}{C}\text{-}R^3$$

$$PAH's + CrO_4^{2-}/Cr_2O_7^{2-} \text{ ------> quinones}$$

4.7 AVAILABILITY OF REACTANTS

The possibility of the reactions given above occurring depends upon the availability of reactants and reaction conditions, as each reaction is thermodynamically favored under conditions of unit activity. Doug Lawson of CARB and Tom Cahill of U.C.-Davis were contacted and air analysis data from a large study conducted in 1986 in the Los Angeles area were acquired. These data are presented in Table 4-1. As noted, metals that form "insoluble" precipitates with chromate, acid, ozone, hydrogen peroxide, and reactive organics are all present. A more comprehensive list found in the Seigneur report is presented in Table 4-2. The extent of reaction will depend both upon the "available" amount of these reactants and the aerosol matrix. The "available" or "reactable" amounts of each of these species is not known. To determine these amounts requires speciation of the inorganics, e.g., lead, and determination of whether the organic molecules are "free," adsorped on (or in) carbonaceous or siliceous material and/or complexed with a metal. The particle or aerosol matrix is also crucial. The two most important factors are the amount of water present and the acidity of this water, as the proposed reactions will occur only in solution. Experts have been contacted, and it appears that no one has determined the "solution" character of an aerosol or "wet" particle.

Despite these severe limitations, speculation about the most likely reactions based on thermodynamics, concentrations and kinetics measured in the laboratory can be made. This has been done by Seigneur and serves as the basis for the following sections.

TABLE 4-1
POTENTIAL REACTANTS IN LOS ANGELES BASIN AIR

Inorganics	Concentrations
Pb	0.1 - 0.4 $\mu g/m^3$
Ca	0.2 $\mu g/m^3$
Mn	0.03 $\mu g/m^3$
Zn	0.015 - 0.385 $\mu g/m^3$
SO_4^{2-}	3.6 - 11.8 $\mu g/m^3$
O_3	~ 200 ppb
H_2O_2	0.1 - 2.5 ppb
HNO_3	1 - 23 ppb

Organics	Concentrations
formaldehyde	4 - 22 ppb
acetaldehyde	2 - 15 ppb
TNMHC*	60% alkanes propane 67.8 ppbC n-pentane 43.5 ppbC isopentane 108 ppbC 15% alkenes ethylene 63.4 ppbC 25% aromatics toluene 116 ppbC benzene 42 ppbC p-xylene 69.6 ppbC
Organic carbon	5 - 9 $\mu g/m^3$
Elemental carbon	3 - 5 $\mu g/m^3$

*1218 ppb C on August 20, 1986

TABLE 4-2
TYPICAL RANGE OF ATMOSPHERIC CONCENTRATIONS OF
CHEMICAL SPECIES INVOLVED IN CHROMIUM CHEMISTRY
(Seigneur)

AEROSOL SPECIES*		GASEOUS SOLUBLE SPECIES	
Chemical Species	Typical Concentrations	Chemical Species	Typical Concentrations
V	0.0013 to 0.022 $\mu g/m^3$	SO_2	10^{-3} to 10^{-2} ppm
Fe	0.026 to 0.59 $\mu g/m^3$	HCOOH	10^{-5} to 10^{-3} ppm
Mn	0.002 to 0.03 $\mu g/m^3$	C_2H_5OH	10^{-6} ppm
Ce	0.00002 to 0.0005 $\mu g/m^3$	H_2S	0 to 0.01 ppm
F	0.001 to 0.01 $\mu g/m^3$	HNO_2	10^{-6} to 10^{-5} ppm
Cl	0.01 to 0.09 $\mu g/m^3$		
Br	0.07 to 0.15 $\mu g/m^3$		
I	0.0004 to 0.003 $\mu g/^3$		
K	0.01 to 0.15 $\mu g/m^3$		
Na	0.05 to 0.35 $\mu g/m^3$		
Pb	0.045 to 0.72 $\mu g/m^3$		
Cu	0.003 to 0.028 $\mu g/m^3$		
Zn	0.007 to 0.10 $\mu g/m^3$		
As	0.0003 to 0.026 $\mu g/m^3$		
SO_4^{2-}	1.0 to 70 $\mu g/m^3$		
NO_3^-	0.0 to 4 $\mu g/m^3$		
NH_4^+	0.2 to 8 $\mu g/m^3$		
Ca^{2+}	0.01 to 0.25 $\mu g/m^3$		

*Concentrations reported are for fine aerosols (less than 2 μm in diameter).

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4.8 REACTIONS BASED ON AVAILABLE THERMODYNAMIC, CONCENTRATION AND KINETIC DATA

4.8.1 Equilibrium Reactions

The report of Seigneur was reviewed and potentially significant reactions identified assuming a maximum upper limit for Cr(III) of 10 $\mu g/m^3$ and 10^{-4} g H_2O/m^3. These equilibrium reactions of Cr(III) are:

Reactant	Concentration	Potential Product	Product Formed?
OH^-	$10^{-10}M$	$Cr(OH)_3$	No
SO_4^{2-}	1 - 70 $\mu g/m^3$	$Cr_2(SO_4)_3$	No
NO_3^-	0 - 4 $\mu g/m^3$	$Cr(NO_3)_3$	No
F^-	0.001 - 0.01 $\mu g/m^3$	CrF^{x3-x}	99+% of Cr^{3+}
Cl^-	0.01 - 0.09 $\mu g/m^3$	$CrCl_3$	No
		$CrCl^{2+}$	30% of Cr^{3+}

Next to be considered are the Cr(VI) equilibrium reactions that are likely to occur based on concentrations available, including Cr(VI) at 10 $\mu g/m^3$ and H_2O at 10^{-4} g/m^3. Again the report of Seigneur was reviewed to identify such reactions; these reactions are:

Reactant	Concentration	Potential Product	Product Formed?
K^+	0.01 - 0.15 $\mu g/m^3$	K_2CrO_4	No
		$KCrO_4^-$	14% of CrO_4^-
		$K_2Cr_2O_7$	No
Na^+	0.05 - 0.35 $\mu g/m^3$	Na_2CrO_4	No
		$Na_2Cr_2O_7$	No
NH_4^+	0.2 - 8 $\mu g/m^3$	$(NH_4)_2CrO_4$	No
		$(NH_4)_2Cr_2O_7$	Only at high Cr(VI))/NH_4^+
Pb^{2+}	0.045 - 0.72 $\mu g/m^3$	$PbCrO_4$	Yes
Cu^{2+}	0.003 - 0.03 $\mu g/m^3$	$CuCrO_4$	No

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Reactant	Concentration	Potential Product	Product Formed?
Zn^{2+}	0.007 - 0.10 $\mu g/m^3$	$ZnCrO_4$	No
		$ZnCrO_4:Zn(OH)_2$	Yes
Ca^{2+}	0.01 - 0.25 $\mu g/m^3$	$CaCrO_4$	No
SO_4^{2-}	1 - 70 $\mu g/m^3$	$CrSO_7^{2-}$	Only at high SO_4^{2-}
SO_2	10^{-3} - 10^{-1} ppm	$CrSO_6^{2-}$	Negligible

4.8.2 Reduction/Oxidation Reactions

The second major type of reaction to consider based on concentration of available reactants and laboratory-determined kinetics are the reduction/oxidation reactions. Potential reactions of Cr(III) to Cr(VI) are as follows:

Reactant	Concentration	Potential Product	Product Formed?
O_3	200 ppb	Cr(VI)	No
H_2O_2	0.1 - 2.5 ppb	Cr(VI)	No
MnO_2	0.03 $\mu g/m^3$	Cr(VI)	Significant if MnO_2 2+% of total Mn

Finally, we consider the oxidation reactions of Cr(VI). The predominant species in the pH 1 - 5 range found in the aerosols will be $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^-$. Seigneur calculated reaction rates based on kinetic data taken from the literature; reactions which could occur at significant rates at Cr(VI) concentration of 10 $\mu g/m^3$, H_2O at 10^{-4} g/m^3 and the reductant at its maximum concentration as presented in Table 4-2 are as follows:

Reactant	Concentration	Potential Product	Reaction Rate
V^{2+}	0.022 $\mu g/m^3$	Cr(III)	Rapid, 100+% per hour
V^{3+}	0.022 $\mu g/m^3$	Cr(III)	Moderate
VO^{2+}	0.022 $\mu g/m^3$	Cr(III)	Moderate
Fe^{2+}	0.59 $\mu g/m^3$	Cr(III)	Rapid

Reactant	Concentration	Potential Product	Reaction Rate
HSO_3^-	0.1 $\mu g/m^3$	Cr(III)	Low
As^{3+}	0.026 $\mu g/m^3$	Cr(III)	•Low

4.9 CONCLUSION

Upon review of this data, it appears that several conclusions can be drawn. The first is that the Cr(III) species will consist principally as the soluble F^- and Cl^- complexes. Second, Cr(VI) will be precipitated as $PbCrO_4$ and probably as $ZnCrO_4:Zn(OH)_2$.

Oxidation of Cr(III) to Cr(VI) by MnO_2 is possible if the MnO_2 concentration is high enough. It is not likely that the MnO_2 concentration is high as it also acts as an oxidizing agent with NO_2, SO_2 and other reducing agents likely to be present. Therefore oxidation of Cr(III) to Cr(VI) is not expected to occur to any significant degree.

The reduction of Cr(VI) to Cr(III) does seem more probable. The reactions with V^{2+}, V^{3+} and VO^{2+} are rapid if such specfes exist in the aerosols. This is not likely since the HVO_4^- species is apparently the major environmental species (22). The reaction with Fe^{2+} is rapid, but again, this is a species not likely to exist in high concentration in the aerosols. One reaction likely to occur is the reaction with HSO_3^-. Finally there is the question of reactions with organic species. The concentrations reported for formic acid and ethanol by Seigneur are low and the reaction rates for these species are about 10^{-9} to 10^{-12} of those for the vanadium species and 10^{-7} to 10^{-8} of those for the HSO_3^- species; however, the concentration for total organic carbon is approximately 10^4 to 10^6 times the levels of these two organic species and 10^2 times the HSO_3^- species. (Table 4-1) This would indicate that the reaction of Cr(VI) with organic species is still slow relative to its reaction with HSO_3^- unless the HSO_3^- were lower than expected and the rates of reaction of the Cr(VI) with organic species other than formic acid and ethanol were much more rapid than those with these two species. In order to answer this question, more fundamental reaction kinetic studies will need to be performed and speciation of other substances which potentially react with Cr(VI) are necessary.

5.0 LABORATORY MEASUREMENT STUDIES

5.1 INTRODUCTION

The initial phase of this study involved the selection of an analytical technique capable of the speciation and measurement of the hexavalent chromium compounds in ambient air. Initially, a literature search was conducted to identify any potential techniques that would conform to the following criteria:

1. The method must provide adequate sensitivity for ambient air levels. Specifically, the method should be capable of detecting Cr(VI) at the approximately 5 ng level for a 15 m^3 air sample (or ~0.3 ng/m^3).

2. The method must be specific for Cr(VI). Cr(III) must not interfere with the method.

3. The method should be free of other interferents (i.e., free of those interferences found in ambient air under all expected conditions).

4. The method should be precise; the precision (C_V) should be ten percent or better at typical low ambient air levels; i.e., ~1 ng/m^3 or a total Cr(VI) sample loading of 10 to 15 ng.

5. The method should be reasonably rapid, and utilize instrumentation that is accessible to the typical small analytical laboratory.

6. The method should be fairly rapid and simple. Considerable care and expertise should not be required by the method.

7. If possible, the method should allow for the "simultaneous" measurement of both Cr(III) and Cr(VI) from the same sample.

8. If possible, the method should allow for the <u>in-situ</u> measurement of Cr(VI).

9. The method must be compatible with a sampling technique capable of collecting <u>and</u> preserving the Cr(VI) species.

Such a Cr(VI) sampling technique must have the following characteristics:

1. The device must be efficient; >95 percent.

2. Filters or impingers should be capable of passing air volumes of up to 15 m^3 in 24 hours or less.

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3. The device must be capable of preserving the chromium oxidation state during the sampling period.

4. The chromium species should be efficiently removed from the sampling device with a minimum of simple manipulation.

5. The sampling material should be readily available and of minimal cost.

The sampling method ideally should be established prior to selection of the analytical/measurement methods. A wide variety of filters have been utilized for collection of ambient air particulate matter. These have included glass and quartz fiber filters, and polyvinylchloride (PVC) and Teflon membranes (23). Also, combinations of the above have been employed, such as Teflon-coated glass fiber (23). In addition, various paper filters have been utilized for the collection of ambient species.

Glass fiber filters generally exhibit excellent efficiency (>99 percent) for particles as small as 0.3 μM (24). However, glass fibers are generally not desirable for the determination of ambient levels of Cr(III) because of the difficulty in obtaining low blank values. In addition, extraction procedures invariably result in solutions that must be centrifuged prior to sample introduction into instrumentation. Cellulose paper filters (such as Scheicher and Schnell Fast Flow papers) tend to leave residues upon extraction, yet they are efficient and exhibit low pressure drops. Such devices have been used even for collection of gaseous species such as SO_2, NH_3, and HNO_3 when a coating has been applied (25-28). Even though such materials are potentially more reactive toward Cr(VI), they can readily accept various coatings that could be useful in Cr(VI) collection.

5.2 SAMPLING

Only two sampling devices were considered early in the study, PVC (5 μM) and Teflon (0.8 μM) membranes. The reasons for this included:

- Both devices were already in use by CARB; PVC for Cr(VI) and Teflon for total chromium sampling.
- Both devices have low background values for species to be collected (<3 ng Cr(VI) for PVC, <2 ng total Cr for Teflon).

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- They do not impart any residue to the resultant extraction solution.
- Impinger solutions are considered relatively inconvenient to manipulate during both sampling and shipping.

PVC membranes were used throughout both the measurement study and the reaction chamber tests. While Teflon membranes are suitable for both species, they are somewhat less convenient to use for Cr(VI) analysis due primarily to the fact that they are not "wet" as easily as PVC by the Cr(VI) extraction solution.

However, it became clear from the results of the chamber tests that membranes (PVC or Teflon) may not be the ideal collection medium for Cr(VI). Throughout the chamber tests, it was consistently apparent that after 24 hours of exposure to a wide variety of typical atmospheric pollutants, Cr(VI) was decaying to Cr(III) at significant rates ranging from 50 percent to more than 90 percent. In addition, the flow rates used during the chamber tests ranged from 3 to 5 liters per minute instead of the 10 to 15 liters per minute used customarily by CARB during 24-hour sampling. Therefore, one might assume that during a typical 24-hour sampling period, one would obtain a very low estimate of the true Cr(VI) content, perhaps as low as ten percent. Since this conclusion was reached during the planning stages for the field study, it was felt that some reference device must be used in conjunction with the PVC filters to provide a comparison. It was felt that such a device must be able to stabilize the Cr(VI) species during collection. Since the scenario for conversion appeared to be low pH conditions in the presence of trace organics, it appeared that the need for some buffering action at neutral or higher pH was necessary. Also, the sample extract or resultant impinger solution should be compatible with both the CARB atomic absorption and the Dionex ion chromatographic measurement methods.

A pH 7 impinger solution appeared to be the most expedient approach to this problem. As a result, three such solutions were evaluated:

- Potassium acetate (0.01 M; pH ~7)
- Sodium acetate (0.01 M; pH ~7; ultra pure)
- CARB Method ADDL006 Buffer with the APDC Cr(VI) complexation reagent

The CARB reagent was prepared in the same manner as would be done during typical sample extractions. Smith-Greenberg impinger trains typically used for stationary source sampling (U.S. EPA Method 5) were employed in these experiments. One hundred milliliters of the test solution were placed in each of three impingers in series. One hundred nanograms of Cr(VI) (as $K_2Cr_2O_7$) was placed in the first impinger. The impinger assembly was placed outside the RTI laboratory and air was drawn through at flow rates of 30 to 40 Lpm for six hours. In parallel to the impinger train containing Cr(VI) was a second impinger train containing no Cr(VI), to serve as a control. Subsequent to sampling, the test solutions were carried through the CARB complexation/atomic absorption analytical method; i.e., pH adjustment to 4.8 followed by extraction, absorption on the Sep-Pak material, desorption, and graphite furnace atomic absorption analysis. The first test compared potassium acetate and Method ADDL006 solutions. After correcting the resultant Cr(VI) levels for the control sample Cr(VI) values, a recovery of 56 percent was obtained for the Method ADDL006 solution, whereas 108 percent of the Cr(VI) was recovered from the potassium acetate solution. An additional test was run under the same conditions. A similar trend was observed--109 percent recovery for the acetate solution and only 24 percent recovery for the CARB buffer. One drawback to the acetate solution was the somewhat high Cr(VI) blank level--approximately twice that of the Method ADDL006 reagent. As a consequence, an ultra pure reagent from Spex Industries, 99.999 percent pure sodium acetate, was purchased. This reagent yielded blank values that were one-third that of the potassium salt. A third test conducted under the same conditions as the first two tests yielded 102.5 percent recovery in the acetate buffer (0.01M) and <20 percent recovery for the CARB buffer. As a consequence, it was felt that an impinger sampler would provide a useful reference value for comparison with the PVC filters, or even be relied upon to provide the bulk of the Cr(VI) data from the subsequent field tests.

In the subsequent field test, personnel from both CARB and Entropy Environmentalists conducted ambient sampling at a chrome plating facility in the Los Angeles area. This field test is further described in the section entitled "Field Studies." Analysis by CARB personnel of the CARB field samples indicated that the RTI-type sampler provided levels of Cr(VI)

that were from four to 27 times that obtained from the CARB PVC filters. These results are included in Appendix A.

5.3 MEASUREMENT

The analytical method developed at CARB involving complexation/extraction followed by graphite furnace atomic absorption (GFAA) was the first to be evaluated. Briefly, the method involves the complexation of Cr(VI) with ammonium pyrollidine dithiocarbamate (APDC) at a pH of 4.5. The complex is then absorbed on a resin and desorbed with acetone. The residue of the evaporated acetone extract is digested in nitric acid and analyzed by GFAA (Appendix B). Initial experiments entailed the spiking of laboratory pure water with chromium levels ranging from 10 to 50 ng (Table 5-1). Blanks showed Cr(VI) levels as high as 70 ng, higher than the highest spiking. Possible sources of contamination considered at this time included the Ultrex nitric acid and the acetone used to extract the chromium complex from the sorbent. Evaporating to dryness two grades of acetone (semiconductor grade and HPLC grade), dissolving the residue with Ultrex nitric acid (0.2 mL) and bringing to two (2) mL volume with laboratory pure water, no significant chromium levels were detected (<5 ng). Three additional sources of contamination were considered:

- Glassware
- APDC
- Buffer solution

When the buffer and APDC solutions used in the procedure were analyzed directly by GFAA, less than one nanogram per milliliter (1 ng/mL) was detected at this time. During a recovery study using spikes of 1 to 40 ng of Cr(VI), high blanks were still observed (>25 ng). Evaluating water as a source of contamination proved to be somewhat problematic. Fifty mL aliquots of water in scrupulously clean glass beakers were brought to near dryness, dissolved in 0.2 mL Baker Instra analyzed or Ultrex HNO_3 and diluted to 2 mL with laboratory pure water. One to eight nanograms of Cr(VI) were detected with no significant difference indicated between Ultrex and Baker Instra analyzed nitric acids. A comparison of several in-house

TABLE 5-1
SOLUTION SPIKING RECOVERY RESULTS

Cr(VI) Spike (ng)	Cr(VI) Spike Recovery (ng)	$\bar{X}$ (ng)
0	17.4, 19.0	18.2
10	19.2, 25.0	22.1
30	19.2, 43.0	31.1
50	49.2, 45.6	47.4

laboratory pure water systems showed no difference or significant water levels--approximately 2 ng per 50 mL of water. Laboratory pure water supplied by CARB contained about 7 ng Cr(VI) per 50 mL versus 6 ng Cr(VI) per 50 mL with RTI pure water.

At this point it was decided to reevaluate the possible contamination of the APDC reagent. One hundred mL of the APDC solution were extracted with 40 mL of chloroform. Subsequent analyses of three blanks yielded acceptably low Cr(VI) values--approximately 4 ng Cr(VI) per 50 mL of extraction solution. A brief recovery study of blanks and 40 ng spikes again showed blanks of 4 ng or less and recoveries of the spikes averaging 92 percent. It can only be speculated that there had been an indeterminate analytical error in the previous analysis of the APDC solution. A series of precision/recovery tests was then conducted using spiked solutions and PVC filters. Again, loadings were in the range of 10 to 50 ng. Results, which are shown in Table 5-2, indicate that recoveries exceeded 95 percent and the precision ranged from 3.0 to 9.8 percent C.V.

A technique based on the EPA Coprecipitation Method 218.5 (29) was evaluated next. This method, which is included in Appendix C, involved the precipitation of Cr(VI) species with lead nitrate at pH 3.5 $\pm$ 0.3, followed by centrifugation, dissolution of the precipitate in nitric acid, and measurement of the digest by GFAA. The initial recovery study performed on spiked solutions ranging from 10 to 80 ng showed poor recoveries below 40 ng (Table 5-3). Three deviations from the method were employed:

- The method was operated at Cr(VI) levels much lower than that for which it was originally designed.
- Plastic (instead of glass) centrifuge tubes were used.
- The final dissolution volume was much lower (2 mL) than the 50 to 100 mL called for in the method.

The use of glass tubes yielded similar recoveries in the 0 to 40 ng range--50 to 69 percent. It was observed from these tests that with normal centrifuging the precipitate was spread around the wall of the tubes instead of at the bottom. Therefore, when the supernatent liquid was decanted, it was proposed that much of the precipitate was carried away, resulting in low recoveries. It was decided to allow the solutions to sit

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TABLE 5-2
RECOVERY STUDY
CARB METHOD ADDL006

Sample		ng Recovered	ng, Blank Corrected	Percent Recovery	
SOLUTIONS					
Blank #1		4.2			
Blank #2		5.4			
10 ng Spike	#1	13.5	8.7	87.0	
	#2	15.1	10.3	103	98.8 ± 9.5
	#3	15.7	10.3	109	CV = 9.5%
	#4	14.4	9.6	96.0	
25 ng Spike	#1	32.9	28.1	112	
	#2	28.0	23.2	92.8	104 ± 10.3
	#3	29.5	24.7	98.8	CV = 9.8%
	#4	33.2	28.4	114	
50 ng Spike	#1	55.4	50.6	101	
	#2	48.8	44.0	88.0	95.5 ± 5.6
	#3	53.8	49.0	98.0	CV = 5.8%
	#4	52.2	47.4	94.8	
FILTERS					
Blank #1		4.1			
50 ng Spike	#1	51.3	46.6	93.2	
	#2	57.5	52.8	106	99.1 ± 5.0
	#3	55.0	50.3	101	CV = 5.0%
	#4	55.2	50.5	101	
	#5	52.3	47.6	95.2	
25 ng Spike	#1	28.2	23.5	94.0	
	#2	29.1	24.4	97.4	$\bar{x}$ = 96 ± 14
	#3	30.8	26.1	104	CV = 14.7%
	#4	23.1	18.4	73.6	
	#5	32.4	27.7	111	w/o Result #4
					$\bar{x}$ = 102 ± 7.5
					CV = 7.4%

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TABLE 5-3
RECOVERY STUDIES
EPA METHOD 218.5

Spiking Level (ng)	Mean Recovery (ng) N=2	Percent Recovery
0	<2	---
10	2.7	27
20	18.2	67
40	34.8	87
80	72.0	90

overnight following the precipitation step to localize the lead chromate precipitate. However, analysis of the resulting precipitate again yielded low recoveries (29 to 57 percent) over the 10 to 80 ng range. It is possible that the use of an ultracentrifuge may overcome the recovery problem at the 0-50 ng level. However, at this point, due to the lack of access to such instrumentation, it was decided to cancel further tests.

The other two analytical methods considered for Cr(VI) speciation involved ion chromatography (IC). Dionex Corporation provided the required equipment for these experiments, as well as the basic chromatography details. These methods are described in detail in Appendices D and E. In summary, hexavalent chromium ions are separated in an ion chromatographic transition metals column possessing both anionic and cationic character. The hexavalent chromium, once separated (by anion exchange), is complexed with the diphenyl carbazide (DPC) color reagent and the visible absorbance is measured photometrically at 520 nm. Although the system is capable of also detecting Cr(III), this latter determination is relatively insensitive for ambient applications. It was assumed that this method would only be suitable for the analysis of filter extracts due to the expected detection limit of 0.3 ng per liter of extract. The analysis of a series of standards in the laboratory yielded a detection limit at least as low as that advertised by Dionex Corporation. If Cr(VI) were collected on a membrane filter and desorbed (for example, in 5 mL of eluent), then the method would have more than adequate sensitivity. Three filters were spiked at the 10 ng level and desorbed in 5 mL of the eluent solution. This was accomplished by placing the filter in a culture tube, adding the solution, covering with parafilm, and manually shaking for one minute. The extract was then manually injected into the ion chromatograph (a Dionex Model 14) equipped with a 250 μL sample loop. Recoveries of 25-50 ng Cr(VI) for two filter types averaged better than 90 percent; the precision was better than seven percent (Table 5-4). It was concluded that the method was rapid [<five minutes elapsed time from sample preparation to measurement of Cr(VI)], sensitive, and precise. A typical chromatogram is shown in Figure 5-1. However, at this time, it was determined in separate experiments that the stability of Cr(VI) on membrane filters was not acceptable during ambient air sampling, and as a consequence, it was felt that a

TABLE 5-4
ION CHROMATOGRAPHY--FILTERS

Sample	ng Recovered	Percent Recovery	
PVC FILTERS			
50 ng Spike #1	50.0	100	
#2	51.7	103	102.2 ± 2.2
#3	52.5	105	CV = 2.1%
#4	50.0	100	
#5	51.7	103	
25 ng Spike #1	24.6	98.2	
#2	23.3	93.1	95.2 ± 3.7
#3	22.4	89.7	CV = 3.9%
#4	24.2	96.6	
#5	24.6	98.2	
1% NA_2CO_3 COATED WHATMAN 41 FILTERS			
50 ng Spike #1	49.1	98.2	
#2	48.2	96.4	99.8 ± 2.7
#3	50.0	100	CV = 2.7%
#4	51.8	104	
#5	50.5	101	
25 ng Spike #1	22.7	90.9	
#2	26.5	106	98.3 ± 6.7
#3	24.6	98.2	CV = 6.8
#4	26.0	104	
#5	23.2	92.7	

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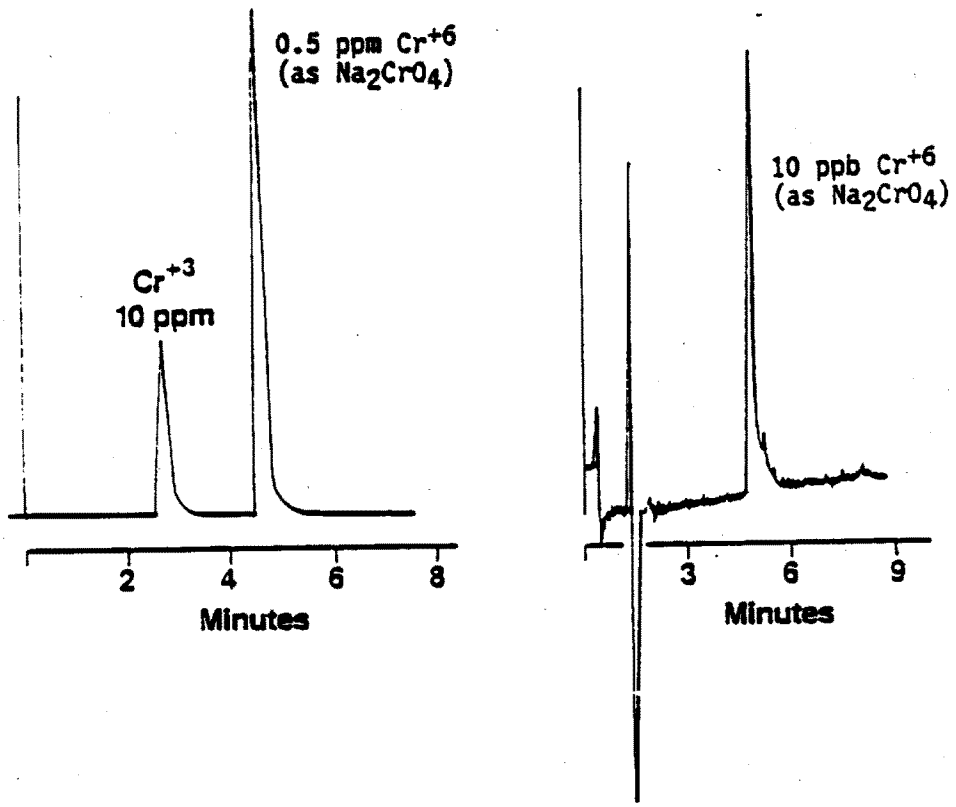
Summary of Conditions

Sample Size:	250 µL
Columns:	HPIC-CG5, Cation Guard Column HPIC-CS5, Cation Separator Column
Eluant Flow Rate:	1.0 mL/min
Post Column Reagent Flow Rate:	0.5 mL/min
Detection:	VIS at 520 nm



(A) Separations of Cr^{+3}, Cr^{+6}

(B) Typical Ambient Air Sample Extract

FIGURE 5-1
TYPICAL POST COLUMN REACTION CHROMATOGRAMS

buffered impinger solution (pH ≥7) that allows for the stabilization of the Cr(VI) species should be employed for sampling. Dionex Corporation recommended that a preconcentration technique be employed prior to injection onto the column to compensate for the larger volume associated with the impinger (30). A schematic of the IC system with and without a concentration column is shown in Figure 5-2. Instead of using a 250 μL injection loop, the Cr(VI) from solution samples of up to 50 mL might be concentrated onto a smaller column initially, then "injected" onto the separator column for separation and photometric detection. Theoretically, this could result in a Cr(VI) concentration factor of up 200X. A calibration curve was prepared in the one to five ng range. The calibration curve linearity was quite acceptable, yielding a correlation coefficient r of >0.999. The limit of detection was calculated to be approximately 0.1 ng corresponding to an air concentration of approximately 0.01 ng/m^3, assuming a 14 m^3 air sample drawn through a membrane filter (assuming a suitable one was developed). However, this level is somewhat unrealistic since the minimum detectable quantity will be related to the blank value of the analyte. One limit to the volume of sample extract used during preconcentration is the strength of buffer used in the extraction of a filter or in an impinger. A solution too high in ionic strength will result in the overloading of the preconcentrator column, or breakthrough of the Cr(VI) species prior to injection of the preconcentrator column contents onto the analytical column. Figure 5-3 depicts this breakthrough effect of Cr(VI) when dissolved in 0.05 M Na_2CO_3. After only two milliliters of solution are loaded onto the preconcentrator column, breakthrough begins to be evident. Based on these tests, it is evident that the weakest possible concentration of buffer required to stabilize Cr(VI) species during sampling must be utilized. Subsequent tests utilizing a 0.02 M Na_2CO_3 sample solution show that the Cr(VI) response is linear to approximately 10 mL.

A brief interference study was conducted utilizing interferent loadings up to 20 times that of typical environmental levels. Experimental parameters shown in Table 5-5 result in less than ten percent change in recovery over the control sample. Analysis of the same samples using CARB AA Method ADDL006 indicate a 20-24 percent loss in recovery compared to the

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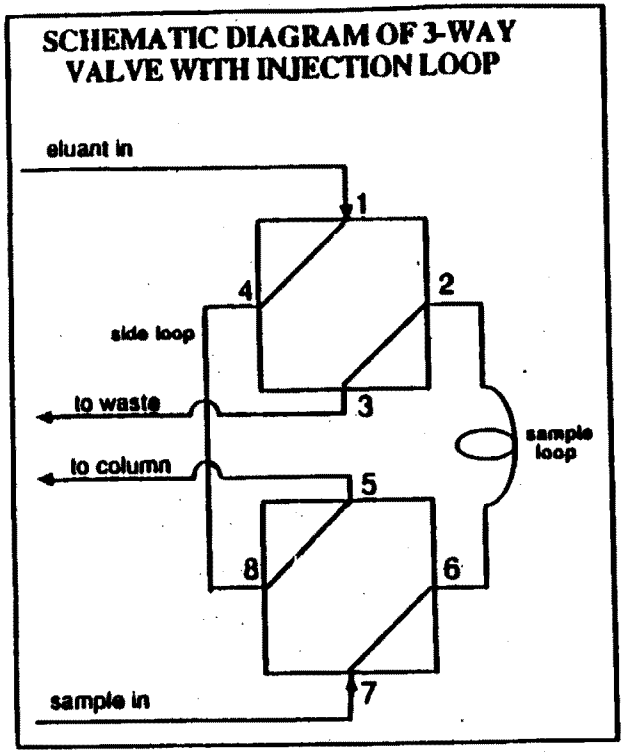

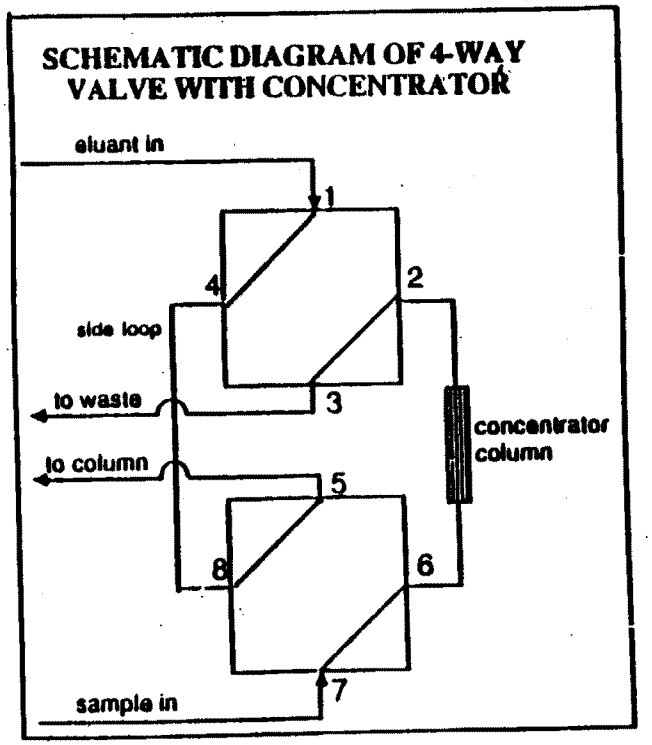

FIGURE 5-2
ION CHROMATOGRAPHIC SCHEMATICS
WITH AND WITHOUT PRECONCENTRATION SAMPLES

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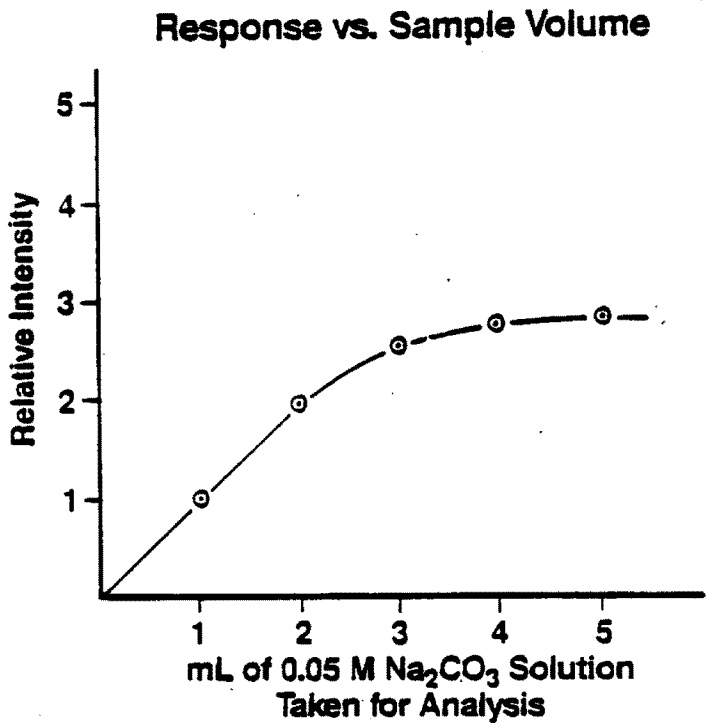

FIGURE 5-3
ION CHROMATOGRAPHY--PRECONCENTRATION METHOD

TABLE 5-5
INTERFERENCE STUDY PARAMETERS

Species	A (ng)	B (ng)
Cr(VI)	25	50
Pb	1,000	2,000
Ag	50	100
Ba	50	100
Ca	50,000	100,000
Mn	50	100
Fe	10,000	20,000
$SO_4^{=}$	25,000	50,000

control samples. A detailed procedure outlining the preconcentration ion chromatographic technique is shown in Appendix E.

A brief stability study was conducted for sample solutions collected using the acetate impinger sampling technique. The study was conducted over a thirty-day period. Two solution types were evaluated--one with Cr(VI) spiked into pure impinger solutions and the second spiked into actual field impinger solutions. Results obtained by ion chromatographic analysis indicated almost complete conversion.

Subsequent studies with 0.02 M Na_2CO_3 buffer solutions demonstrated excellent stability. The reanalyses of four field impinger samples after 60 days in storage demonstrated no measurable conversion (see Table 5-6).

Recently an additional technique has been evaluated by the Texas Air Control Board (31). This method involves collection of the hexavalent species employing a glass fiber high volume sample filter. Plugs are removed with a device such as a cork borer and are desorbed in a weakly alkaline solution containing ethylene diamine. The resulting extract is divided into two portions. To one portion is added an ion exchange resin to selectively remove Cr(VI). The total chromium content in each solution is then measured using inductively coupled plasma emission spectrometry (ICP). The Cr(VI) levels are then obtained by difference between the two values. The method is described as being labor-intensive and, in its present form, appears to lack the required sensitivity for ambient applications. A minimum detectable Cr(VI) air concentration of 5 ng/m^3 is quoted, as opposed to less than 0.5 ng/m^3 for the CARB method or either ion chromatographic technique. In addition, this detection limit is obtained using a 2000 m^3 sample instead of the 10-20 m^3 utilized in the other techniques described in this report. It may be possible to improve this detection limit by utilizing graphite furnace atomic absorption for chromium measurement. However, a major drawback involves the indirect measurement of the Cr(VI) species. If Cr(III) values are high (e.g., greater than 200 ng/m^3), low values of Cr(VI) (e.g., less than 20 ng/m^3) will be difficult to measure. A measurement precision of, e.g., five percent, represents 20 ng/m^3 of Cr(VI) at the 200 ng/m^3 level of total chromium! This latter drawback appears to be the greatest impediment to the method's applicability to ambient air measurements.

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TABLE 5-6
FIELD SAMPLE STABILITY STUDY[a]

	Sample A	Sample B	Sample C
Sampling Date	2/11/88	2/11/88	2/23/88
1st Analysis Date	3/1/88	3/1/88	3/1/88
2nd Analysis Date[b]	4/10/88	4/10/88	4/10/88
1st Analysis (ng/mL)	6.0	8.2	2.7
2nd Analysis (ng/mL)	6.2	8.8	2.9

[a]Samples in 0.02 M Na_2CO_3 matrix, analyzed by ion chromatography, preconcentration method
[b]Samples stored at 4°C (refrigerated)

6.0 REACTION CHAMBER TESTS

6.1 INTRODUCTION

The chamber reaction studies, which were designed to simulate those ambient conditions to which Cr(VI) species would be exposed, were conducted in the following overall manner:

1. Eight or more 37 mm membrane filters (Teflon or PVC) were spiked with levels of Cr(VI) (ranging from 20 ng to 1,000 ng, depending on the test conditions). Initially, this was performed by pipetting known quantities of solutions onto the filter and then drying at room temperature in a vacuum dessicator. Later, the Cr(VI) spiking was performed by creating an aerosol with an inhaler device and allowing the aerosol to merely deposit without pumping onto the filter surface. The aerosol was created inside a plastic can with a fan inside to disperse the aerosol as much as possible, thereby optimizing the uniformity. Nevertheless, since some inhomogeneity was anticipated, CARB suggested the use of a lithium internal standard in the solution to be aspirated. In this way, the lithium content could be measured, in addition to the Cr(VI) species, in order to provide a means of monitoring the variability in the Cr(VI) loadings. A schematic of the aerosol generator is shown in Figure 6-1.
2. Six of these filters were placed in a sampling manifold containing 37 mm polystyrene filter holders with backup pads.
3. The sampling manifold was located in the environmental chamber. Initially, the chamber was one constructed of plexiglass or other plastic materials wherever possible. A schematic of the initial test chamber design is shown in Figure 6-2. Later, the design of the chamber was changed (for reasons to be explained in this section) to that of an all-aluminum design. An aluminum "suitcase" approximately 2 feet x 2 feet x 1 foot was fitted for a gas reactant inlet and for the sampling manifold (Figure 6-3).

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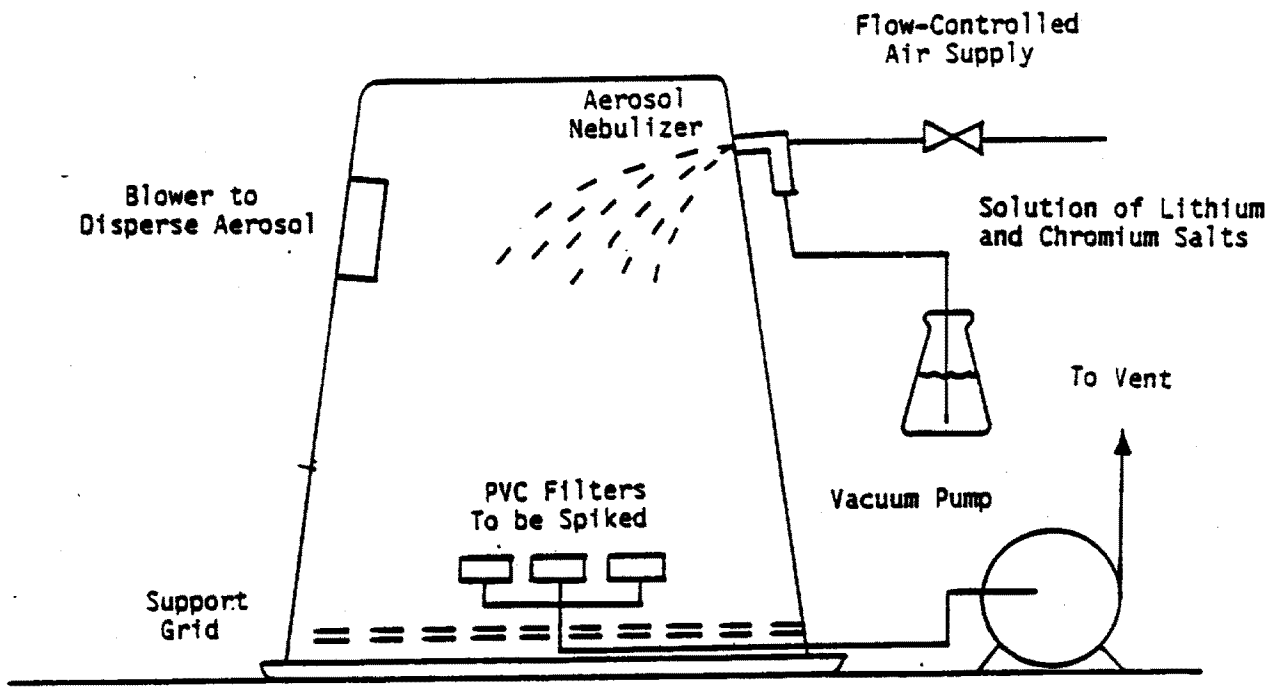

FIGURE 6-1
AEROSOL SPIKING SYSTEM

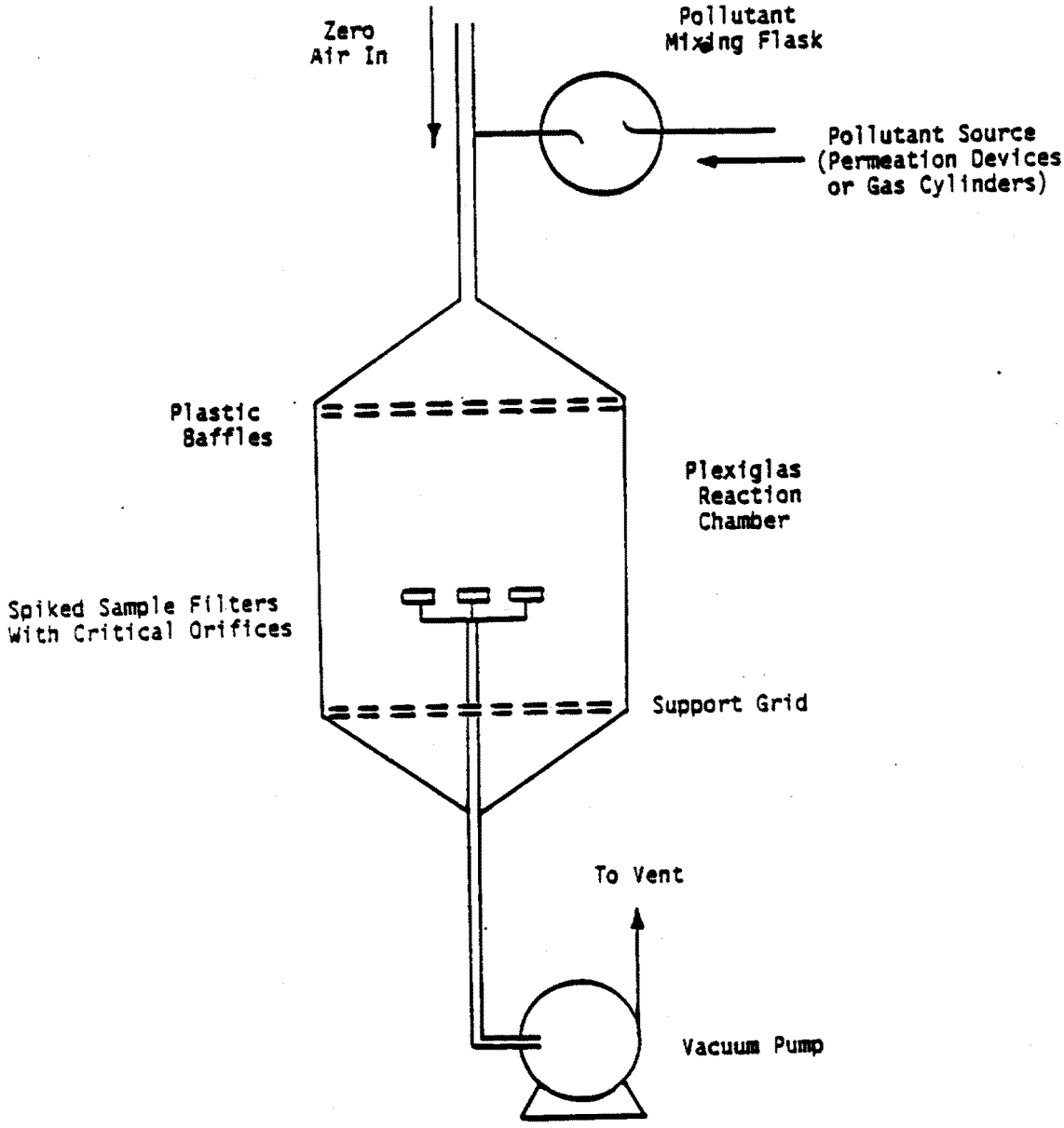

FIGURE 6-2
PLEXIGLAS REACTION CHAMBER

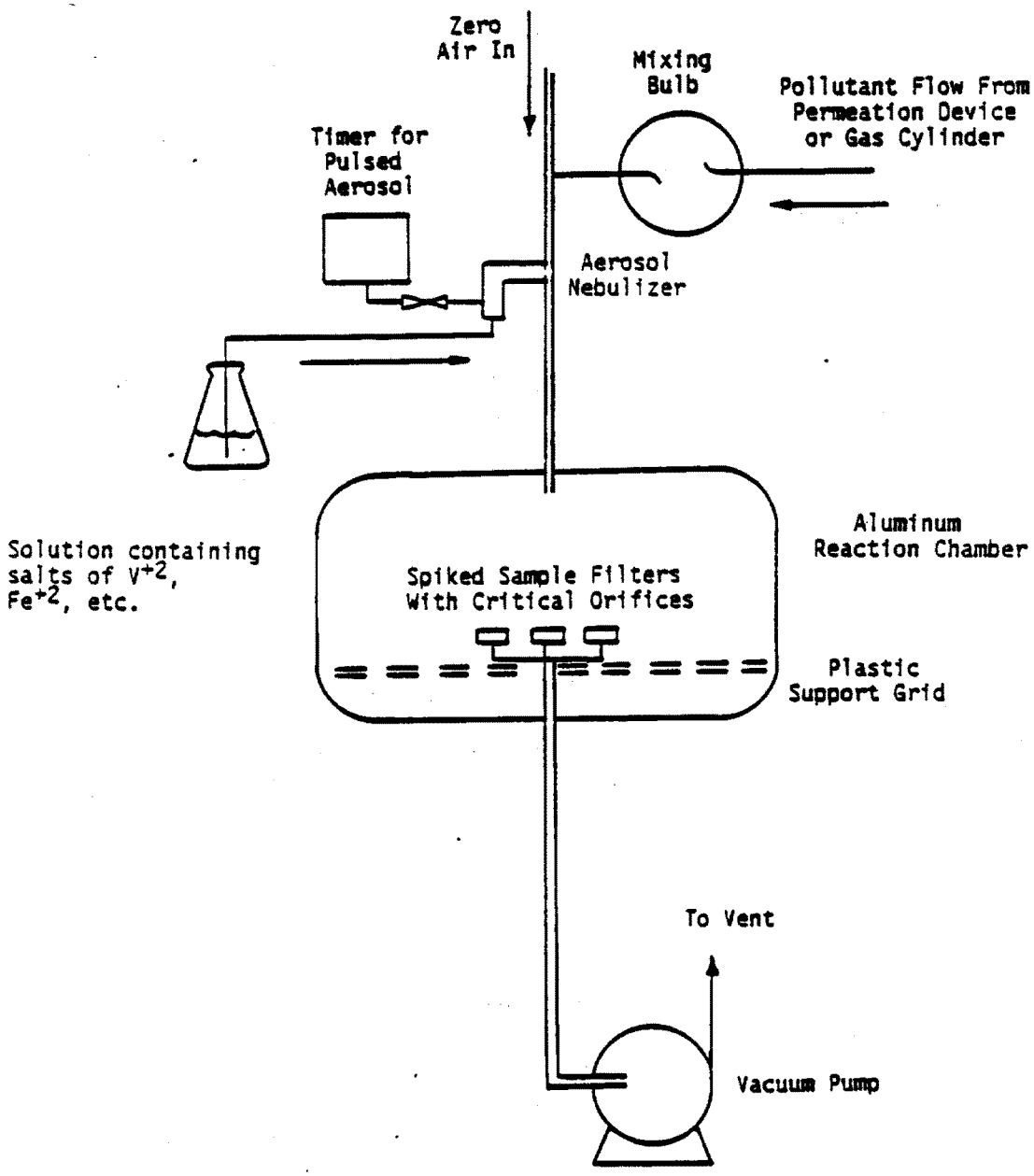

FIGURE 6-3
ALUMINUM REACTION CHAMBER

4. During exposure to the various test reactants, a sampling flow of 3 to 5 Lpm was maintained through each filter. A calibrated critical orifice was used to regulate flow through each filter.
5. Pollutants were introduced into the top of the chamber by a variety of means. Ozone was generated by an ozone generator utilizing pure oxygen irradiated by an ultraviolet source. Atmospheres of species such as SO_2, NO_2, xylene, and benzene were prepared from dilutions of gas cylinder concentrations. Nitric acid (HNO_3) and formaldehyde (HCHO) were generated from permeation devices available from Vici-Metronics (Santa Clara, CA). The verification of HNO_3 concentration was performed by sampling in parallel with a nylon filter, desorbing the filter in an aqueous medium, and performing an ion chromatographic analysis of the resultant nitrate ion. Formaldehyde levels were monitored using hydrogen peroxide impinger samples and subsequent ion chromatographic analysis of the formate ion. A number of other species were evaluated in these tests, and test conditions regarding these potential reactants will be described in detail later in this section.
6. During the test, two filters were removed at each predesignated time interval. For instance, it may have been decided to remove the first two filters after eight hours, two more after 20 hours, and the last two after 40 hours.
7. The filters were then analyzed using CARB Method ADDL006. A portion of the Cr(VI) extract was saved and analyzed for the lithium content to correct for any variability in the aerosol deposition.

6.2 EXPERIMENTAL

The individual tests will be described in detail in this section. Initial tests were conducted to identify the major actors in Cr(VI) reactivity. Levels used were not intended to closely simulate ambient conditions. Also, the early tests served to evaluate the experiment test design and equipment. For instance, after Test 16, the aluminum chamber was used because of large levels of reactive organic species off-gassing from the plastic chamber and adhesives causing considerable Cr(VI) conversion, <u>but</u> only in the presence of HNO_3 or HCl species. It was therefore learned in

these early tests that low pH and the presence of reactive oxidizable species were the major factors in Cr(VI) reduction. Later tests simulated more closely those ambient conditions found in the Los Angeles area in 1986. Table 4-1 provided a basis for the later chamber experimental conditions. However, for simplicity, only one oxidizable species was used at any one time. Since levels of organic species in Los Angeles might be expected to reach more than 200 ppb, this was represented by one compound at the 200-300 ppb level. Generally, species such as HNO_3, O_3, and formaldehyde were maintained at realistic levels. HCl was used in place of HNO_3 in one test to determine if the H^+ contribution from HNO_3 was the major issue or if HNO_3 was playing a more direct role in the oxidation/reduction scenario. (The former appeared to be the case.)

Summary data for the thirty-two test runs are included in Table 6-1. Also, plots of each test showing Cr(VI) loadings versus time are shown in Figures 6-4 through 6-28.

Test 1. Eight filters were spiked with 1 μg Cr(VI) each by means of a 1 mL pipet. The filters were then exposed in the plexiglas chamber to a nitric acid aerosol concentration of eight parts per billion by volume (ppbV) and formaldehyde at a concentration of 68 ppbV. Due to incorrect experimental calculations, an unrealistic level of 3 ppm NO_2 was added to the system. The relative humidity ranged from 78 to 95%. Air temperature in this test and subsequent tests was 25°C. The test atmosphere was drawn through the filters at a rate of 4.7 Lpm. Two filters each were removed and analyzed for Cr(VI) content, after 8, 24, and 48 hours. Two additional unexposed filters were analyzed for a "time zero" reference value (t_0). After 8 hours, 28% conversion was observed, and nearly 98% conversion was detected after 24 hours. It was subsequently determined that the Cr(VI) species ($K_2Cr_2O_7$) had been inadvertently spiked onto cellulose ester membranes instead of PVC. This was significant in light of the following two test results.

Test 2. The test conditions were similar to those for Test 1 except that PVC membranes were spiked (1 μg) and the humidity was less than 10%. Filters were removed at 4, 7, and 24 hours. Eleven (11) percent conversion was observed after 24 hours.

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES

Chamber[a] Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
1	HNO_3--7.7 ppbV HCHO--68 ppbV O_3--100 ppbV NO_2--3,000 ppbV SO_2--25 ppbV RH--80 to 90%	1,000	470 (8 hr)	20 (24 hr)	20 (48 hr)	98
2	HNO_3--6.7 ppbV HCHO--41 ppbV RH--<10%	1,000	870 (4 hr)	830 (7.5 hr)	890 (24 hr)	11
3	HNO_3--8.1 ppbV HCHO--50 ppbV RH--60-90%	1,000 (4 hr)	~1,000 (7 hr)	~1,000 (24 hr)	920	8
4	HNO_3--46 ppbV HCHO--35 ppbV RH--<10%	750	708 (4 hr)	788 (8 hr)	760 (24 hr)	<5
5	HNO_3-none added HCHO--671 ppbV RH--80%	671	601 (4 hr)	636 (8 hr)	555 (24 hr)	17
6	HNO_3--46 ppbV HCHO--35 ppbV RH--70%	21.3	9.3	3.4	1.2	90

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TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Continued)

Chamber[a] Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
7	HNO_3--46 ppbV HCHO--35 ppbV RH--<10%	158	10.1 (16 hr)	2.2 (20 hr)	1.2 (24 hr)	99
8	NOT RUN					
9	HNO_3-none added HCHO--108 ppbV RH--<10%	13.5	23.7 (4 hr)	22.7 (21 hr)	25.6 (24 hr)	<5
10	NOT RUN					
11	HNO_3--43 ppbV HCHO-none added RH--<10%	18.0	9.2 (4 hr)	12.7 (8 hr)	4.4 (24 hr)	76
12	HNO_3--38 ppbV HCHO-none added RH--<10%	54.8	43.5 (4 hr)	35.1 (7 hr)	13.6 (24 hr)	75
13	HNO_3--7 ppbV HCHO-none added RH--25%	117	64 (4 hr)	59 (7 hr)	13 (22 hr)	89

ED_000719_00018483 EPA_000725

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Continued)

Chamber Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
14[a]	HNO_3--12.8 ppbV HCHO-none added RH--19%	303	245 (4 hr)	218 (7.5 hr)	73 (24 hr)	76
15[a]	HNO_3--24 ppbV HCHO-none added RH--20%	(---)[e]	35 (4 hr)	18.3 (7 hr)	5.8 (23 hr)	>80
16[a,f]	$KMnO_4$--~1000 ng O_3--110 RH--20% Cr^{+3}--~100 ng	3.9	5.0 (4 hr)	1.3 (7 hr)	0.1 (24 hr)	<5% (Cr^{+3} o Cr^{+6})
		NO MEASURABLE Cr^{+6} FORMED				
17[g]	HNO_3--18.4 ppbV HCHO-none added RH--23%	50	43 (4 hr)	47 (7 hr)	44 (23 hr)	~10
18	HNO_3--18 ppbV HCHO--15 ppbV RH--20%	71	56 (4 hr)	50 (7 hr)	50 (23 hr)	30
19	HNO_3--18 ppbV HCHO--173 ppbV RH--20%	37	24 (4 hr)	17 (8 hr)	5.6 (72 hr)	~80

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Continued)

Chamber Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
20	HNO_3--22 ppbV Propylene-314 ppbV RH--35%	62	54 (16 hr)	25 (24 hr)	22 (40 hr)	60
21[h]	HNO_3-none added Benzene-293 ppbV RH--15%	21	12 (7 hr)	10 (34 hr)	18 (72 hr)	<20
22[h]	HNO_3-none added m-Xylene-315 ppbV RH--15%	96	(180)[i] (7.3 hr)	80 (18 hr)	75 (21 hr)	<20
23	HNO_3-none added m-Xylene-207 ppbV RH--18%	33	29 (6 hr)	21 (24 hr)	13 (95 hr)	~35
24	NOT RUN					
25	HNO_3-none added V^{+2}---~80 ppbV RH--18%	57	57 (5 hr)	65 (21 hr)	70 (45 hr)	<10

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Continued)

Chamber Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
26	HNO_3--22 ppbV V^{+2}--~80 ppbV RH--18%	23	6 (6 hr)	5 (22 hr)	0.1 (92 hr)	78
27	HNO_3-none added Fe^{+2}--~80 ppbV RH--20%	180	198 (5 hr)	200 (21 hr)	162 (46 hr)	<10
28[j]	HNO_3--17 ppbV HCHO--173 ppbV RH--12% Cr^{+6} from Cooling Tower Water	78	44 (6 hr)	31 (25 hr)	19 (48 hr)	60
29	HNO_3--20 ppbV m-Xylene-337 ppbV RH--15%	NOT RUN Cr^{+6} Aerosol Generator Failure				
30	HNO_3--20 ppbV benzene-315 ppbV RH--20%	NOT RUN Cr^{+6} Aerosol Generator Failure				
31	HNO_3--15 ppbV m-Xylene-313 ppbV RH--30%	50	38 (8 hr)	24 (24 hr)	10 (71 hr)	52

ED_000719_00018483 EPA_000728

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Concluded)

Chamber Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
32[k]	HNO_3--15 ppbV HCHO--320 ppbV RH--30%	55	50 (7 hr)	38 (23 hr)	---	30

[a]Using plastic chamber

[b]analysis by CARB Method ADDL006

[c]n = 2; normalized to Lithium Internal Standard where applicable

[d]Cr^{+6} loading via aerosol deposition for this and subsequent tests

[e]Analytical problem with t_0 filters

[f]Filters spiked w/$KMnO_4$, Cr^{+3} as $CrCl_3$; Cr^{+6} measured

[g]Aluminum chamber used thereafter instead of plastic to minimize "organics" contribution from chamber.

[h]Cr^{+6} results not normalized; no lithium internal standard analysis.

[i]Suspected contamination in one of the t_0 filters.

[j]Filters were aerosol-spiked using actual cooling tower water.

[k]Filters were pipette-spiked using actual chrome plating bath solution

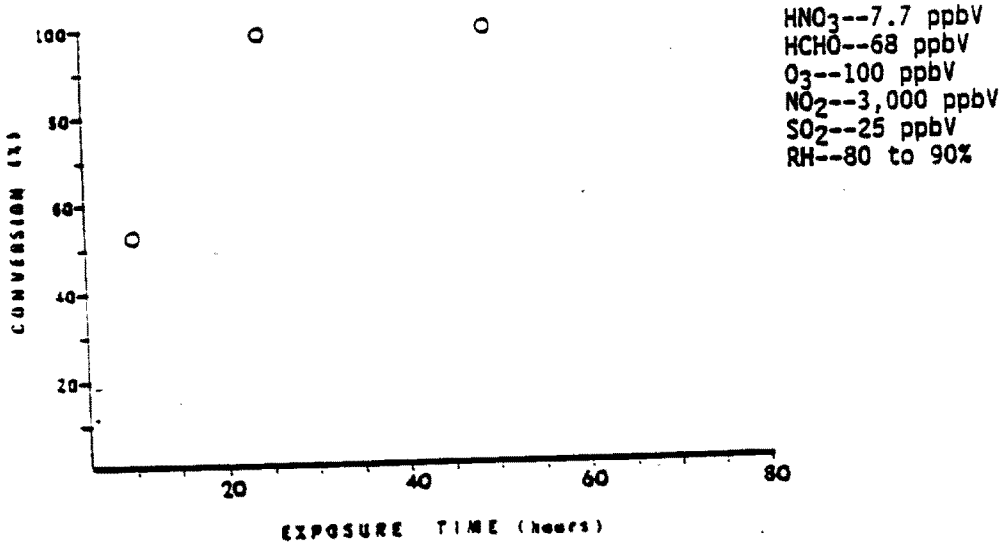

FIGURE 6-4: CHAMBER TEST 1

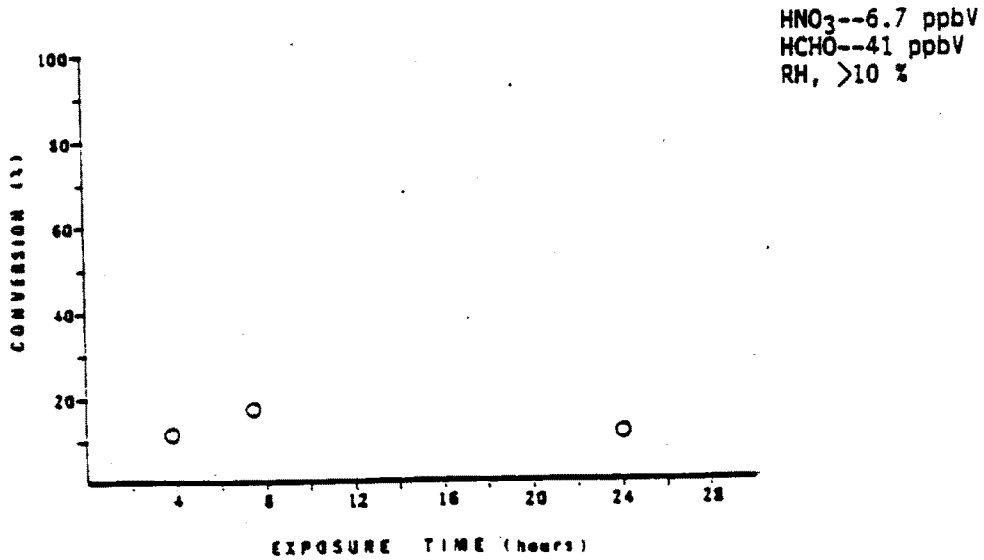

FIGURE 6-5: CHAMBER TEST 2

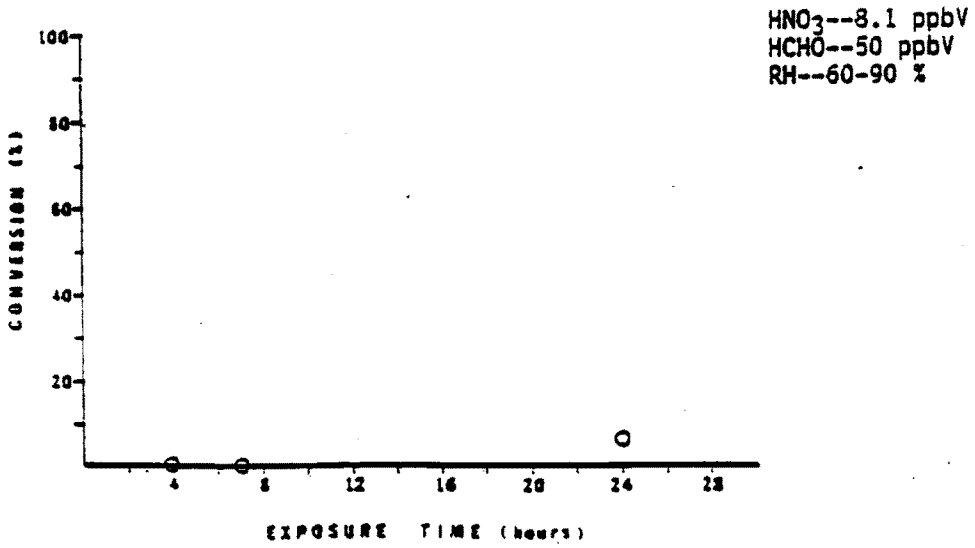

FIGURE 6-6: CHAMBER TEST 3

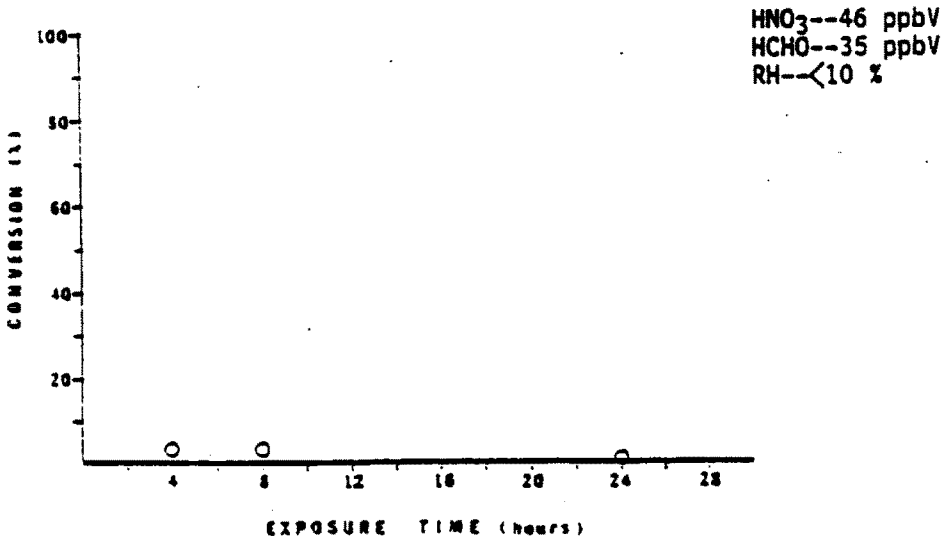

FIGURE 6-7: CHAMBER TEST 4

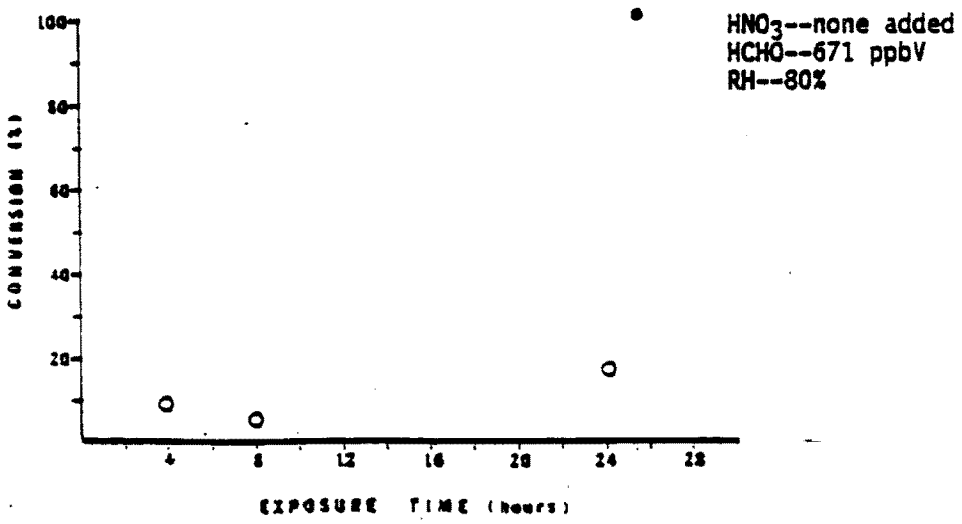

FIGURE 6-8: CHAMBER TEST 5

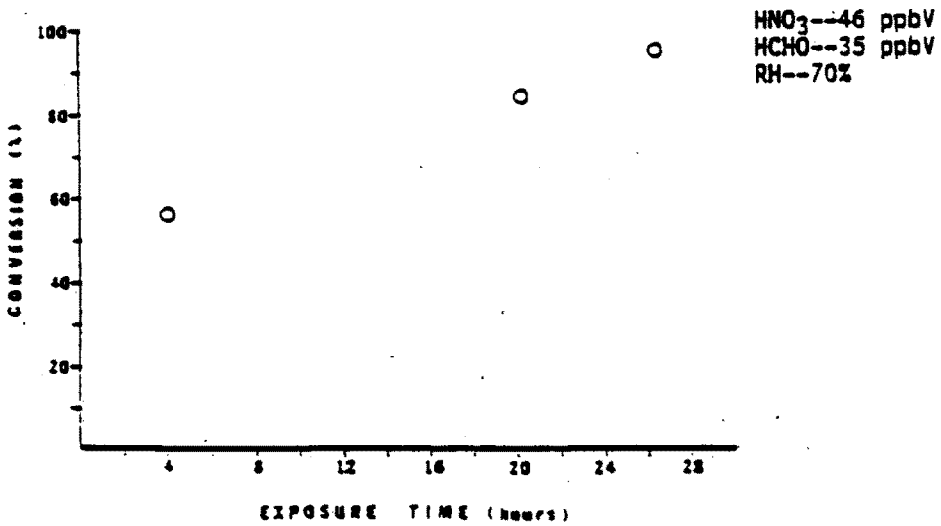

FIGURE 6-9: CHAMBER TEST 6

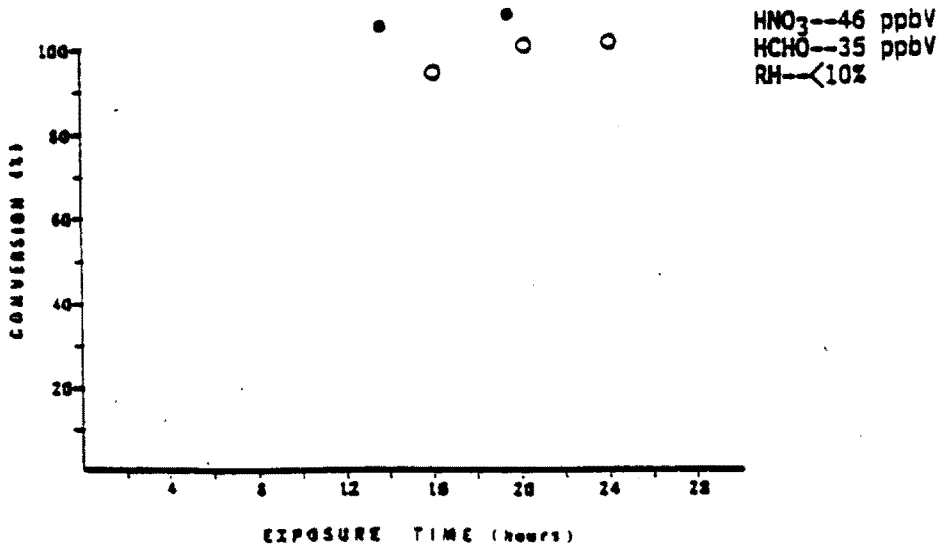

FIGURE 6-10: CHAMBER TEST 7

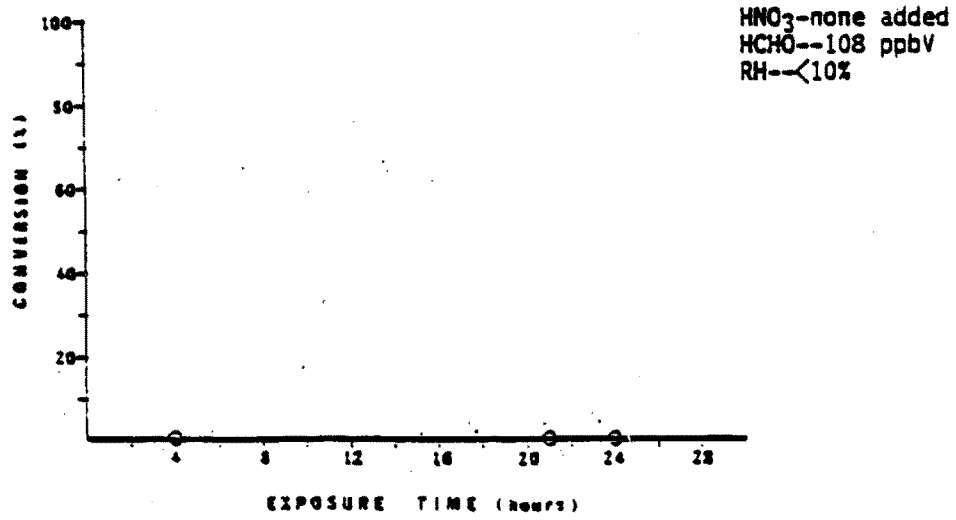

FIGURE 6-11: CHAMBER TEST 9

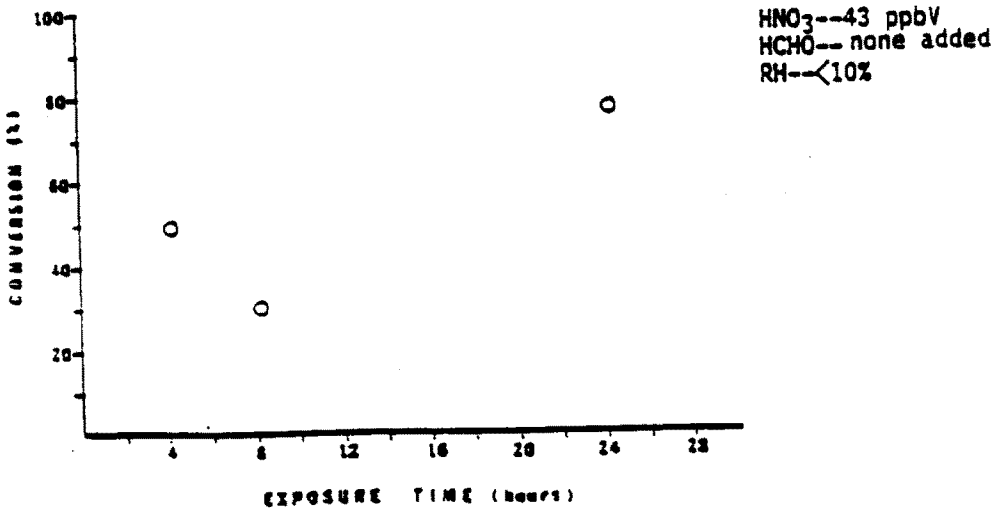

FIGURE 6-12: CHAMBER TEST 11

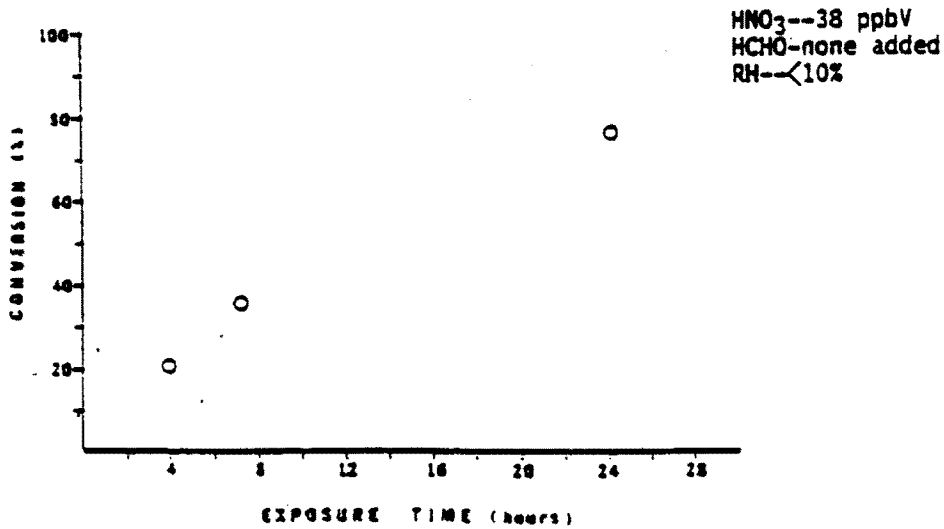

FIGURE 6-13: CHAMBER TEST 12

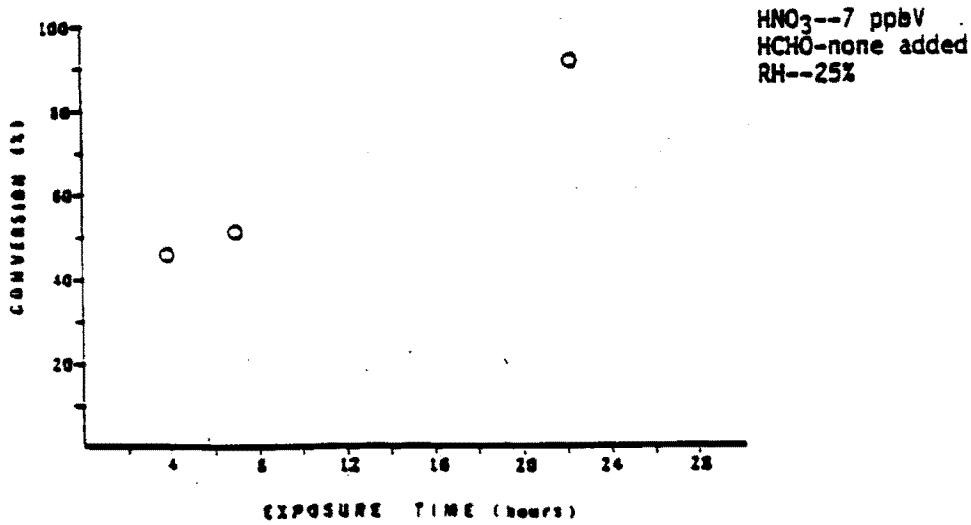

FIGURE 6-14: CHAMBER TEST 13

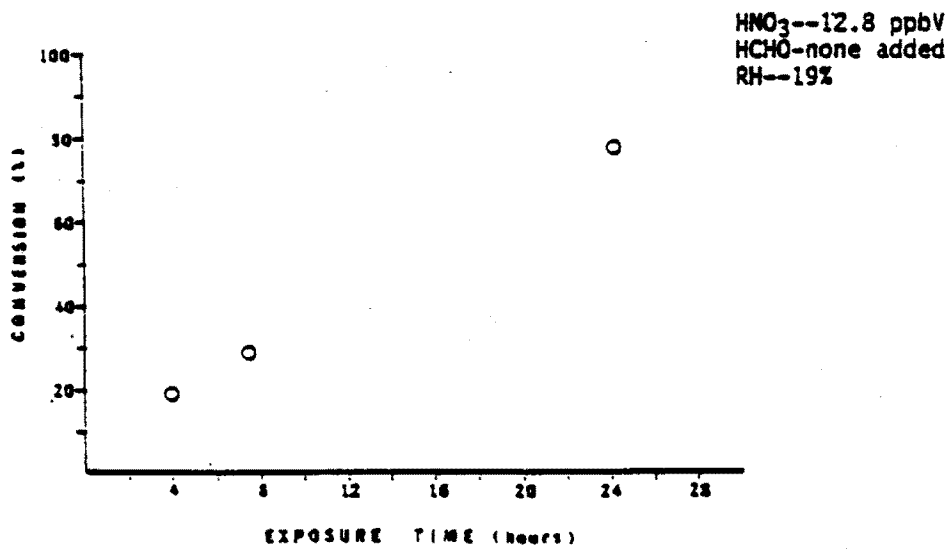

FIGURE 6-15: CHAMBER TEST 14

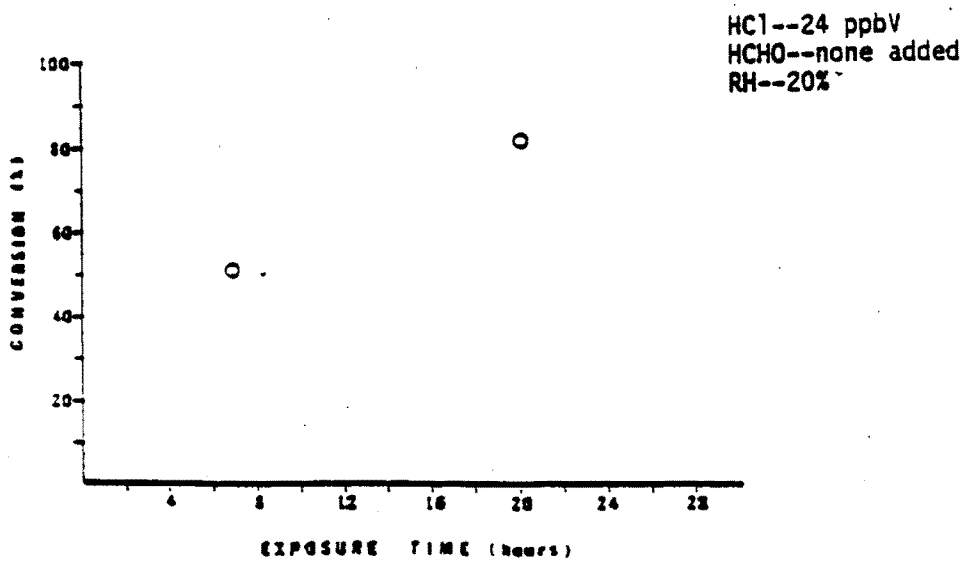

FIGURE 6-16: CHAMBER TEST 15

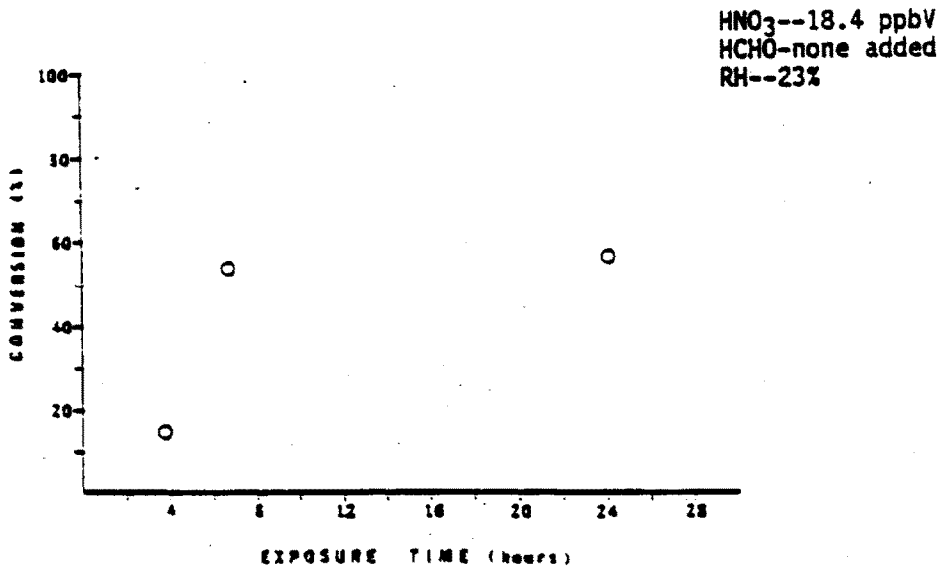

FIGURE 6-17: CHAMBER TEST 17

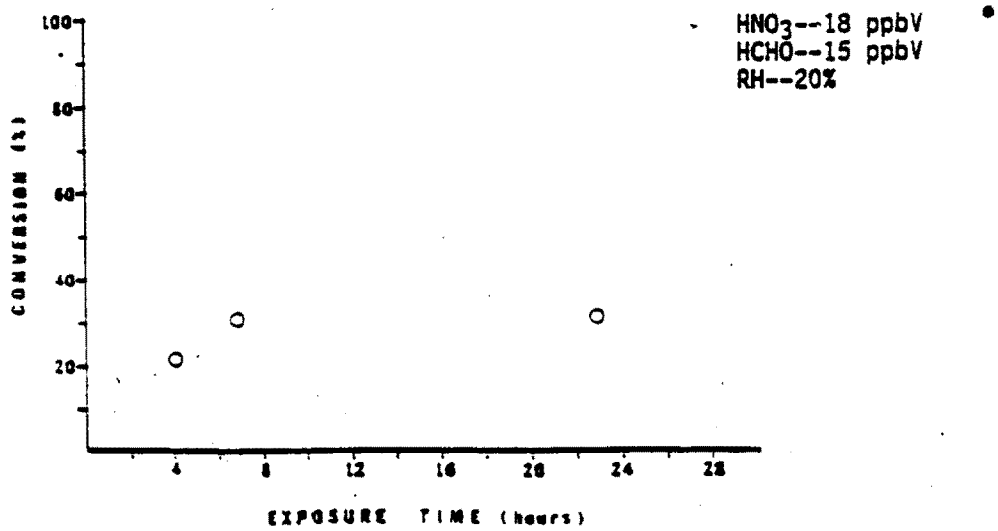

FIGURE 6-18: CHAMBER TEST 18

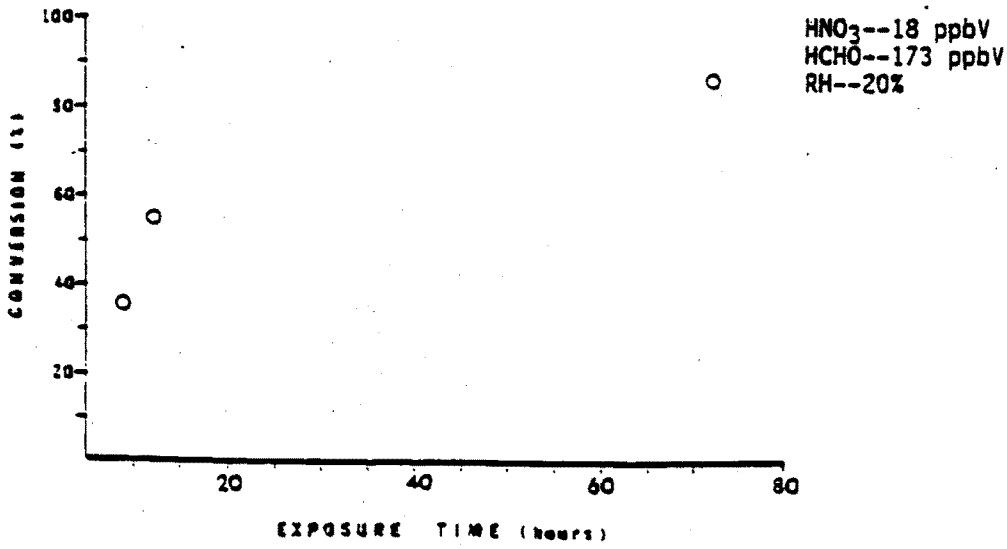

FIGURE 6-19: CHAMBER TEST 19

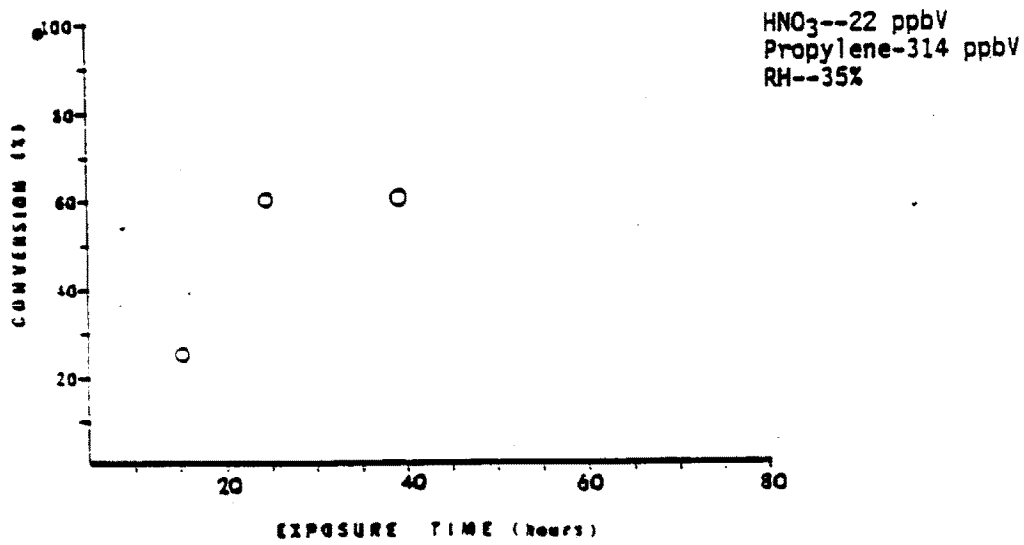

FIGURE 6-20: CHAMBER TEST 20

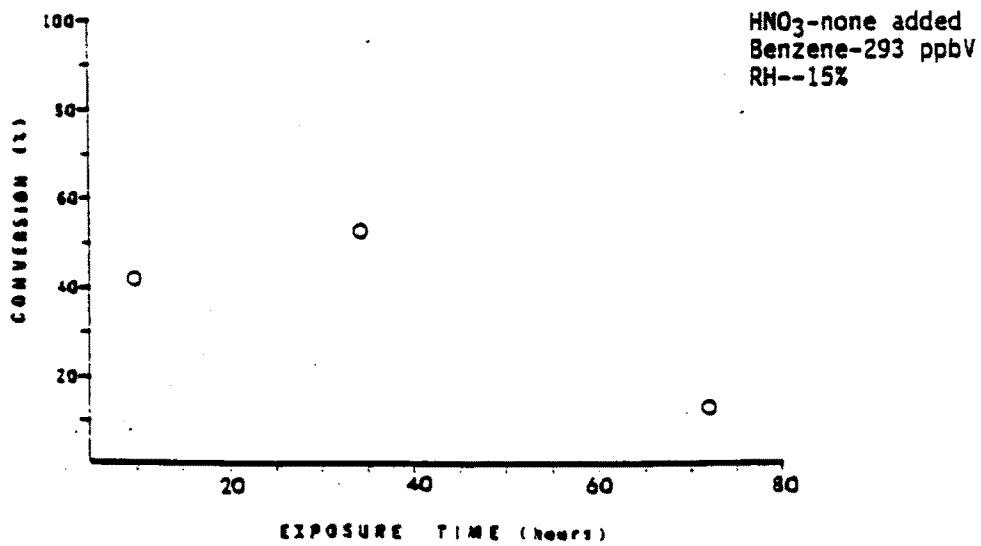

FIGURE 6-21: CHAMBER TEST 21

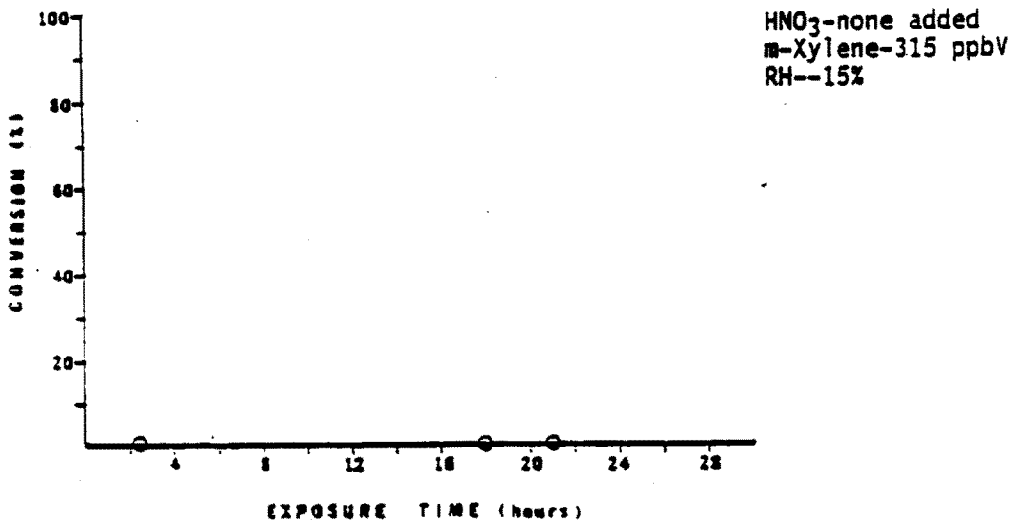

FIGURE 6-22: CHAMBER TEST 22

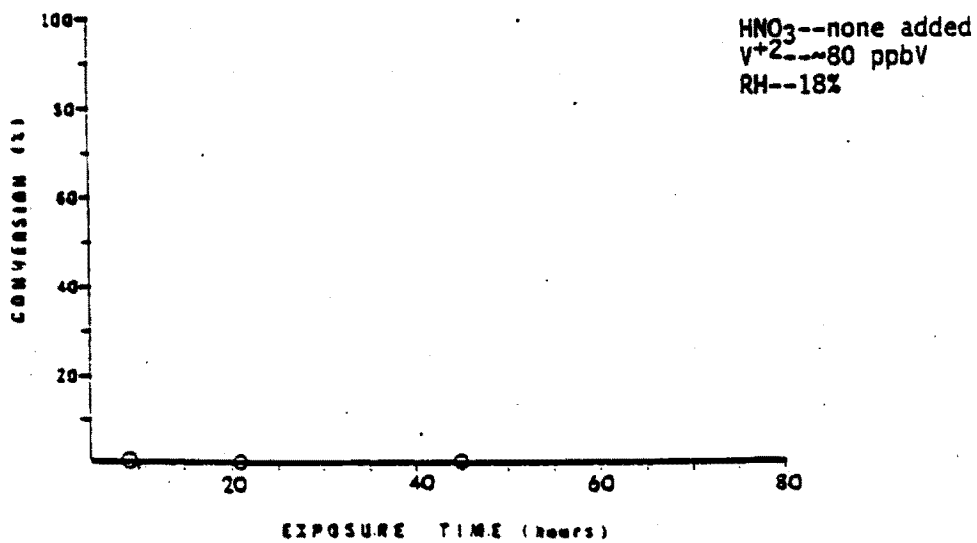

FIGURE 6-23: CHAMBER TEST 25

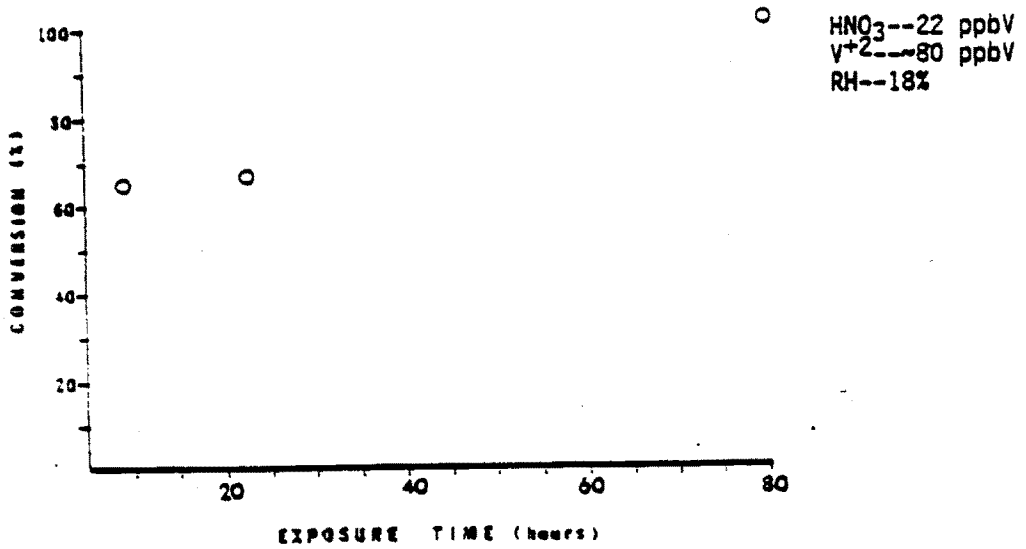

FIGURE 6-24: CHAMBER TEST 26

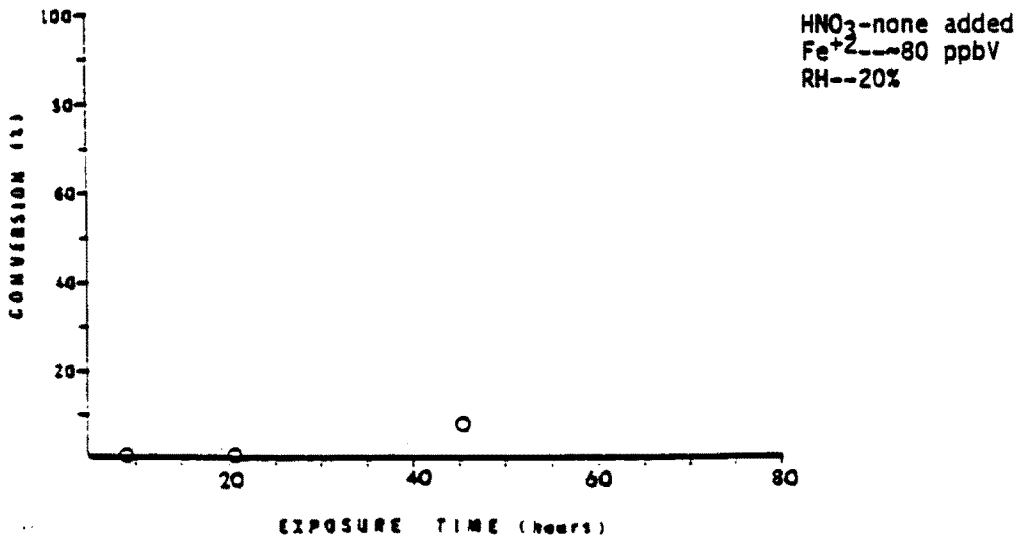

FIGURE 6-25: CHAMBER TEST 27

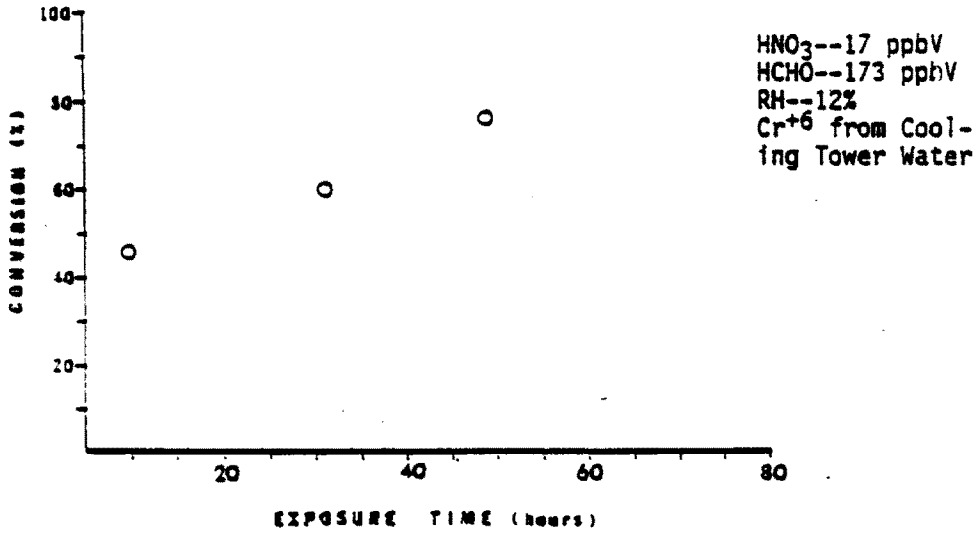

FIGURE 6-26: CHAMBER TEST 28

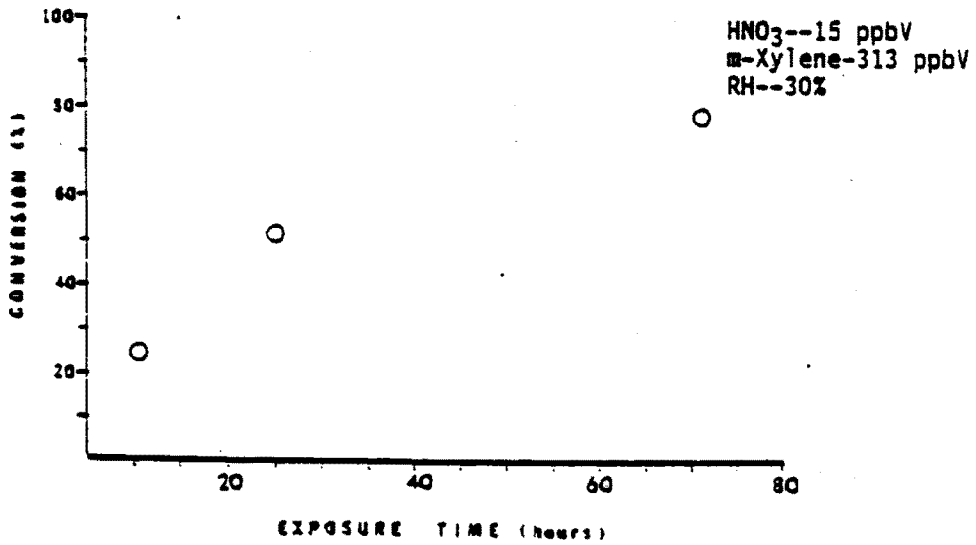

FIGURE 6-27: CHAMBER TEST 31

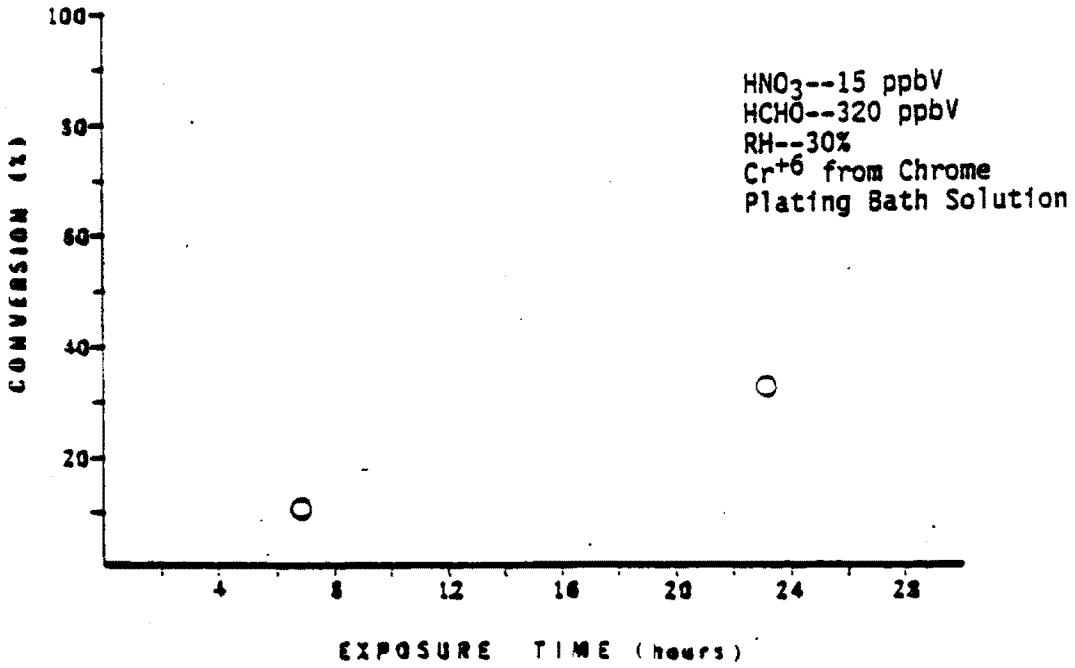

FIGURE 6-28: CHAMBER TEST 32

Test 3. The test conditions were similar to those for Test 2 except that the relative humidity was in the 60-90% range. Filters were removed at 4, 7, and 24 hours. Again, less than 10% conversion was observed after 24 hours. At this point it was assumed that whatever conversion had taken place was minimal in relation to the large quantity of spiked chromium, compared to typical ambient levels. Apparently, the erroneously used cellulose ester membrane (Test 1) provided a considerably reactive surface for the chromium species.

Test 4. The experimental conditions were similar to those of Test 2 (dry conditions). Again, the results indicated that no measurable conversion had taken place. These results are in considerable conflict with Test 7. Two possible explanations are the following:

1. The Cr(VI) level used in Tests 1 to 5 was extremely high (closer to source emission levels). Any Cr(VI) conversion under ambient conditions might well be difficult to measure at the 1 μg Cr(VI) level.

2. The method for Cr(VI) deposition (pipet) may have resulted in a dried droplet that may not have been as easily accessed by the experimental reactants.

As a result of the problems noted above, the aerosolization approach for Cr(VI) deposition was taken after Test 5. This may explain why 150 ppb Cr(VI) was far more reactive than 1,000 ppb Cr(VI).

Test 5. The experimental conditions employed in Test 3 (humid conditions) were repeated in this test. Seventeen (17) percent conversion was observed after 24 hours.

At this point, efforts were made to assemble the aerosol generation system described previously (Figure 6-1). Initially, five filters were exposed to the test aerosol. An aerosol of LiCl generated by aspiration of a 1,000 ppm solution of LiCl showed poor distribution: $\pm$ 60% represented by lithium loadings ranging from 51 to 130 μg (see Table 6-2). To determine if the internal standard technique was feasible for monitoring fluctuations in the aerosol distribution, a solution containing 1,000 ppm lithium and 100 ppm copper was aerosolized. The distribution ratios were quite acceptable, resulting in a correlation coefficient $r = 0.994$ (see Table 6-3).

TABLE 6-2
AEROSOL DISTRIBUTION STUDY
USING A LITHIUM INTERNAL STANDARD

Filter No.	µg/mL Lithium[a]	Total µg
1	13.0	130
2	5.1	51
3	9.0	90
4	12.8	128
5	12.0	120

[a]determined by extraction with 10% HNO_3 and measurement by flame atomic absorption

TABLE 6-3
AEROSOL DISTRIBUTION STUDY
DETERMINATION OF LITHIUM/COPPER RATIO

Filter No.	µg/mL Lithium	µg/mL Copper	Ratio Li/Cu
1	7.9	0.86	.109
2	4.5	0.43	.096
3	7.4	0.77	.104
4	2.6	0.28	.108
5	9.3	1.06	.114

r Li/Cu = correlation coefficient
= 0.994

When an atmosphere containing Li, Cu, and Cr was generated, the correlation was not as acceptable, as shown in Table 6-4. The correlation coefficient between chromium and copper was 0.976, between chromium and lithium was 0.977, but 0.996 between copper and lithium. This implied scatter in the chromium data, possibly due to the much lower levels of Cr. However, it was decided that these data nevertheless provided a means of at least determining a trend in the Cr(VI) data over the 24- to 48-hour period. All subsequent filter loadings for chamber tests were performed in this manner.

Test 6. Using a solution containing 5 μg/mL Cr(VI) (as potassium dichromate) and 1,000 ppm Li (as LiCl), a low level Cr(VI) aerosol was deposited on eight PVC filters (~ 20 ng). Again, two filters were saved for t_0 determination, and additional pairs of filters were removed at 4, 20, and 26 hours. The test atmosphere used contained approximately 50 ppb HNO_3 and 35 ppb formaldehyde. Also, a relative humidity of 70% was used in this test. Fifty-six percent conversion was observed after 4 hours and 84% after 20 hours. Ninety-five percent conversion was indicated after 26 hours.

Test 7. Using a test atmosphere containing similar levels of HNO_3 and formaldehyde, but under dry conditions (<10% RH), six filters containing approximately 150 ng Cr(VI) were exposed and removed after 16, 20, and 24 hours. Ninety-four percent conversion was noted after 10 hours, and greater than 95% was observed after 20 hours.

Test 8. This test was cancelled due to problems with the test atmosphere generation.

Test 9. Samples spiked with the aerosol generator for ten minutes and exposed for up to 24 hours to formaldehyde in the absence of nitric acid indicated no measurable conversion of the Cr(VI) species. Approximately 25 ng were loaded onto the filters. The relative humidity was <10%.

Test 10. This test was cancelled due to problems with the test atmosphere generation.

TABLE 6-4
AEROSOL DISTRIBUTION STUDY
USING LITHIUM/COPPER/CHROMIUM AEROSOL

Filter No.	Cr	Cu	Li	Cr/Li
1	0.55	1.03	26.4	.0210
2	0.50	0.76	19.7	.0253
3	0.62	1.59	38.0	.0163
4	0.52	0.84	21.0	.0247
5	0.63	1.34	33.0	.0191
1B	0.68	1.93	43.5	.0156
2B	0.51	0.73	17.9	.0284
6	0.53	0.84	21.2	.0250

r Cr/Li = 0.977
r Cr/Cu = 0.976
r Cu/Li = 0.996

Test 11. Filters spiked with approximately 20 ng were exposed with nitric acid in the absence of the formaldehyde species but otherwise under the same conditions used in Test 9. After eight hours, 29% of the Cr(VI) species had been reduced. After 24 hours, 76% conversion had taken place.

Test 12. The above conditions (Test 11) were repeated. After seven hours, 36% conversion was observed, while 75% of the Cr(VI) species had undergone decay after 24 hours. These results were regarded as similar to those of Test 11. The relative humidity was <10%.

Test 13. When conducting another test under similar conditions (except relative humidity of 25%), 45% conversion was observed after four hours and 89% after 22 hours.

Test 14. This test was again conducted under similar conditions to establish a chemical explanation for the conversion in the absence of formaldehyde. Since significant conversion was observed in this test as seen in Tests 11 and 12, it was decided that the plexiglas chamber was contributing significant levels of reactive organic species through some off-gassing process. Nevertheless, it was decided to determine if similar results were obtained using an HCl atmosphere instead of the HNO_3 atmosphere in order to determine if the conversion mechanism of the acid species used was essentially a pH phenomenon as opposed to the redox characteristics of HNO_3.

Test 15. When filters were loaded with approximately 30 ng Cr(VI) and exposed to 24 ppb HCl and relative humidity of 20%, the same trends found in Tests 11 to 14 were seen. Approximately 50% conversion was seen after seven hours, and 84% conversion after 23 hours. This appeared to indicate that the H^+ contribution was the major contribution of the HNO_3 species used in previous and subsequent tests, not the HNO_3 molecule itself.

Test 16. In this test, filters were aerosol-spiked with a 5 ppm solution of Cr(III) ($CrCl_3$) in the presence of 50 ppm $KMnO_4$ and exposed to ozone (~100-200 ppb). Exposed filters removed after 4, 7, and 24 hours were analyzed for Cr(VI) content to determine if any Cr(III) oxidation had occurred. However, after 24 hours, none had taken place.

In response to the possibility of contribution of organic species by the plexiglass chamber materials, an alternate chamber (shown in Figure 6-3) was constructed of all aluminum as described previously. At the same time, the atmosphere inside the plexiglass chamber was sampled in an evacuated stainless steel can designed for this application and analyzed for individual gaseous organic compounds by gas chromatography in the flame ionization detection. Organic species found included a variety of unsaturated carbonyl and aromatic organic compounds. The total concentration of these latter species exceeded 300 ppbV, thereby accounting for the measurable Cr(VI) conversion rate, even in the absence of added organic species.

Test 17. Utilizing the new aluminum "chamber," spiked filters were exposed to HNO_3 vapors in the absence of added organic species. Over a 24-hour period, only approximately 10% conversion of the Cr(VI) species was observed. This latter result verified the necessity for the presence of an organic or other oxidizable species under low pH conditions to promote reduction of Cr(VI) species. All subsequent tests were conducted in this aluminum device.

Test 18. Under conditions similar to those in Test 17 but with 15 ppb formaldehyde added, 20% conversion was observed after four hours and 30% conversion was observed after 23 hours. However, the level of formaldehyde used was considered unrealistically low in relation to typical atmospheric organic species concentrations.

Test 19. Noting that the total organic species employed is Test 18 was far below that normally encountered in ambient (200 ppbV or greater), it was decided to utilize far more concentrated HCHO atmospheres. Test 19 results reflect an atmosphere containing approximately 20 ppbV HNO_3 and 175 ppbV formaldehyde. After eight hours, a conversion of 55% was measured. After 72 hours, 85% conversion had taken place.

Test 20. Using an alternate organic species, propylene (at 300 ppb), the following test results were observed. Thirteen percent conversion was observed after 15 hours, 60% after 24 hours, and 65% after 40 hours.

Tests 21 through 23 were inadvertently conducted in the absence of nitric acid. Benzene and meta-xylene were selected as the "oxidizable" organic species. Although a small amount of unexplained conversion was nevertheless observed, the m-xylene test was repeated later (Test 31) to determine what increased effect nitric acid would demonstrate in the reduction process.

Test 25. Divalent or trivalent vanadium species are suspected of promoting Cr(VI) reduction. Efforts to generate an aerosol of V^{+2} were made by pulsing an aspirated 0.5 μg/mL solution of VCl_2 onto exposed filters. It was determined that an approximately 15-hour time period was required to produce a total of 100 μg exposure to the Cr(VI) species. Utilizing no HNO_3 atmosphere, Cr(VI)-spiked filters were exposed to an approximately 200 ng loading of V^{+2}. No measurable conversion was observed.

Test 26. The conditions for Test 25 were reproduced for Test 26, but HNO_3 was added. Seventy-five percent conversion was observed after six hours and no Cr(VI) was detected after 94 hours (>99.5%) conversion). These tests indicated that the V^{+2} compounds were the most reactive species tested to date.

Test 27. Substituting Fe^{+2} species ($FeSO_4$) for V^{+2} species and utilizing an atmosphere containing HNO_3 (nominal 20 ppb) no conversion of the Cr(VI) species was observed.

Test 28. Filters were loaded with an actual cooling tower solution supplied by Entropy Environmentalists. Filters spiked with this solution were exposed to HNO_3 and 300 ppb formaldehyde in the aluminum chamber. Forty-five percent conversion was observed after six hours, 60% after 25 hours, and 75% after 48 hours.

Test 31. Fifty (50) nanograms of Cr(VI) was deposited onto PVC filters by pipette (due to problems with the aerosol generator). The filters were exposed to 310 ppb m-xylene to repeat Test 23 but with 15 ppb HNO_3 added. Fifty-two (52) percent conversion was observed after 24 hours (compared to 35% without HNO_3), and 75% conversion was observed after 71 hours.

Test 32. Hexavalent chromium from an actual chrome plating bath solution was deposited by pipette on filters and subjected to exposure to 320 ppbV formaldehyde and 15 ppbV HNO_3. Thirty percent conversion was observed after 24 hours.

A summary of individual Cr(VI) half life values for those chamber tests deemed to most closely approximate actual ambient conditions is shown in Table 6-5. To qualify for this criteria, the test had to incorporate both an acid species (5 to 50 ppb) and an easily oxidizable species in the 50 to 400 ppb range. The average half life was found to be 12.9 hours ($\pm$ 5.8 hours).

Additional experiments correlating individual particle behavior with reactivity were planned in this study through the use of an electrodynamic balance (32). However, difficulties with the particle balance operation forced RTI investigators to abandon this set of experiments and concentrate efforts more fully on more important questions, such as the chamber reactivity tests.

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TABLE 6-5
ESTIMATED Cr(VI) HALF LIFE DURING CHAMBER TESTS

Chamber Test No.	Cr(VI) ng	Estimated Half Life (Hrs)	Comments[a]
6	21	9	Plastic chamber organics ~300-400 ppb
7	158	7	Plastic chamber organics ~300-400 ppb
11	18	10	Plastic chamber organics ~300-400 ppb
12	55	12	Plastic chamber organics ~300-400 ppb
13	117	7	Plastic chamber organics ~300-400 ppb
14	303	15	Plastic chamber organics ~300-400 ppb
15	35 (est.)	7	Plastic chamber organics ~300-400 ppb
19	37	11	173 ppb HCHO[b]
20	62	24	314 ppb C_3H_6[b]
26	23	15	80 ppb V^{+2}[b]
28	78	15	173 ppb V[b]
31	50	23	313 ppb m-Xylene[b]

Average Half life = 12.9 hrs. (± 5.8 hrs.)

[a]HNO_3 concentration ranged from 7 to 46 ppb; Organics were a variety of species resulting from off-gassing of plastic chamber and adhesives.
[b]Aluminum chamber

7.0 FIELD STUDY

7.1 INTRODUCTION

The third major phase of the study was designed to verify the general Cr(VI) reactivity trends observed in the laboratory reaction chamber tests through the use of actual field samples. This was carried out using two approaches:

- An ambient sampling study near two Cr(VI) sources, a chrome plating facility and a cooling tower, measuring Cr(VI) at distances up to 2 km from each source
- A field reaction study to verify the laboratory chamber tests through the use of true ambient air samples typical of the Los Angeles area

Each analytical method employed in the measurement of the field samples was subjected to a series of quality control/quality assurance procedures. These included the analysis of duplicate aliquots of quality control solutions, spikes, and reagent blanks. Duplicate aliquots of impinger solutions were not available. The entire solution was utilized for each result to provide maximum sensitivity. Spikes results were judged acceptable in the 80-120% recovery range. Duplicates were ± 10% (except at the lower quantifiable limit), quality control sample values were within 10% of the expected value, and blanks in Method ADDL006 were in the 1-3 ng range. Duplicate filter analyses were utilized for the field reaction study.

Quality assurance procedures utilized during field test sampling are indicated in Appendix F.

7.2 THE AMBIENT SAMPLING STUDY

At each Cr(VI) source, one upwind and four potential downwind ambient stations were employed. A meteorological data station was set up near each source to determine wind speed and direction. In addition, sulfur hexafluoride (SF_6) tracer experiments were conducted at each site to verify emission or plume location. Plot plans of each site are shown in Figures 7-1 and 7-2. Each station contained two ambient sampling units for filter sampling and one set of three impinger trains. One filter sampling unit

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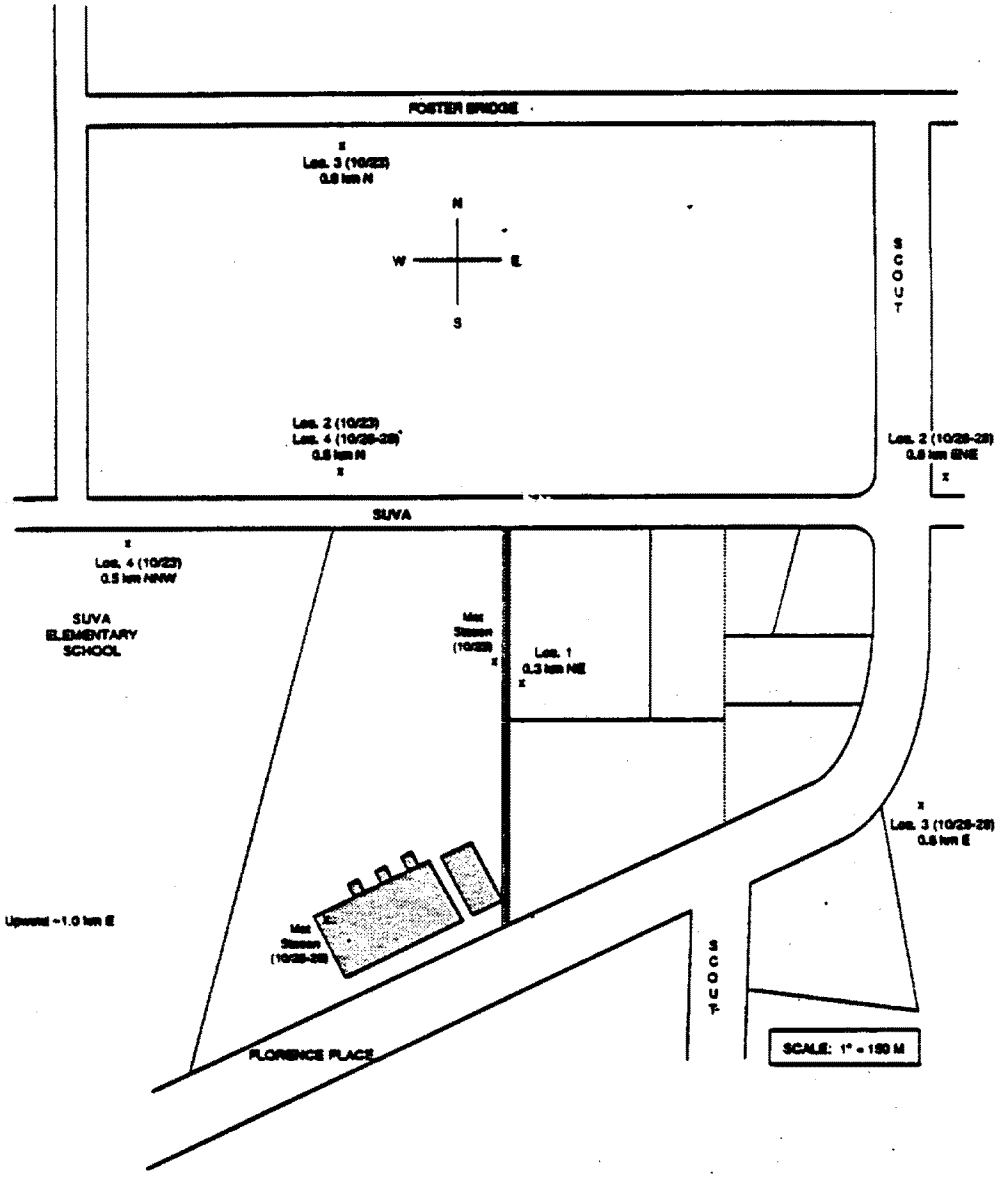

FIGURE 7-1
PLOT PLAN OF CHROME CRANKSHAFT SHOWING SAMPLING LOCATION

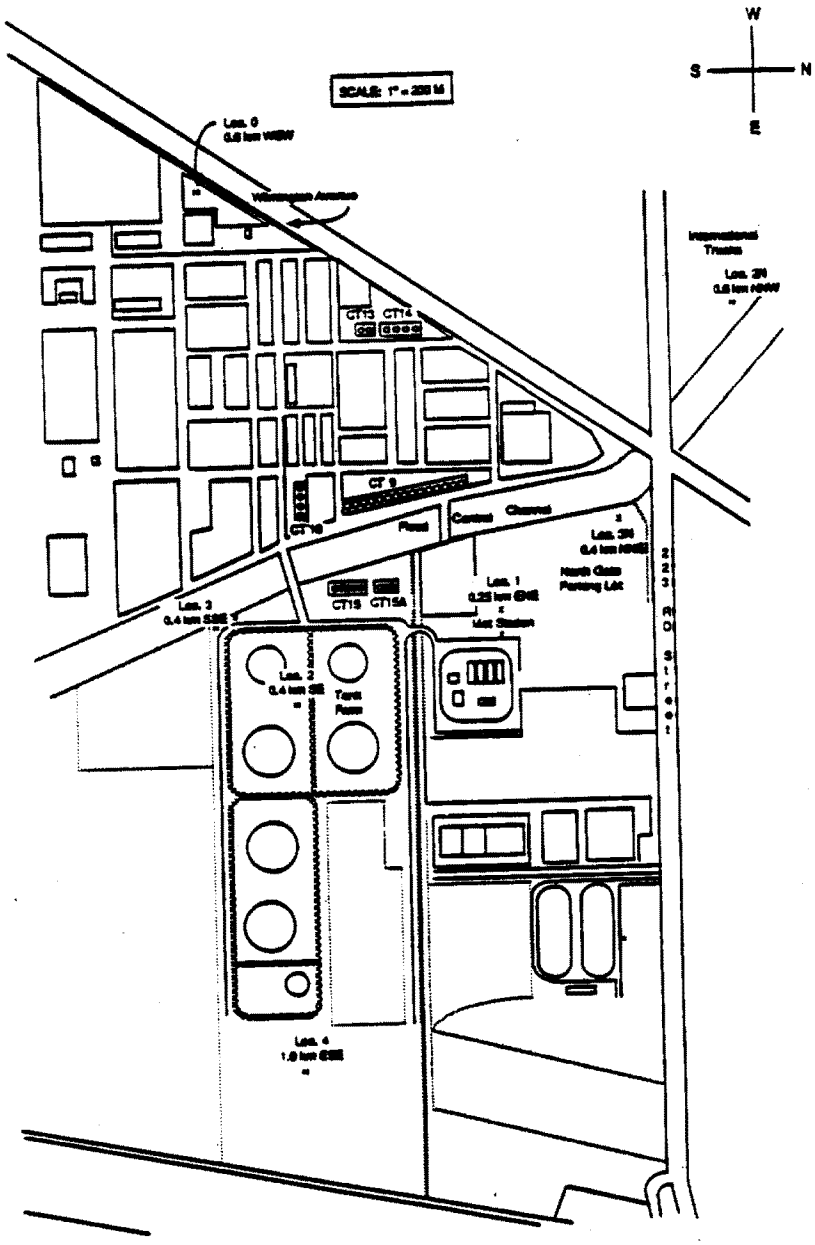

FIGURE 7-2
PLOT PLAN OF THE ARCO REFINERY
SHOWING SAMPLING LOCATIONS (RELATIVE TO CT9)

used polyvinylchloride (PVC) membranes, while the other used Teflon membranes. Teflon membranes were used for total chromium measurements, while PVC membranes were intended for both total chromium and Cr(VI) collection. Impinger samplers were taken using Smith-Greenburg impingers filled with 0.01 M sodium acetate reagent. These devices (depicted in Figure 7-3) were used as a reference method for Cr(VI) sampling. It was expected that some total chromium information might be obtained from these devices, but initial tests indicated a great difficulty in obtaining low blank chromium values.

The information obtained from the ambient study was intended to provide:

- Cr(VI) and Cr(III) levels near the sources
- Some comparison of PVC filters versus sodium acetate impingers in terms of Cr(VI) sampling efficiency
- Some measure of the Cr(VI)/Cr(III) ratio at each downwind sampling site in order to quantitate the rate of conversion

The details of the field test conducted by Entropy Environmentalists are included in the field test report in Appendix F.

7.3 RESULTS

Samples obtained in the vicinity of the chrome plating facility generally contained measurable levels of hexavalent chromium, especially at the "near downwind" sites approximately 0.5 km from the emission source. Of seven tests run at this site, four (4) were judged complete and, from these, Cr(VI) concentrations ranged from 26.3 ng/m^3 to 315 ng/m^3. Results of these four tests are shown in Table 7-1. Although not part of the work plan, the ambient data were also used to calculate the relationship of Cr(VI) to total chromium in order to determine if the ambient data might be used to estimate Cr(VI) conversion rates as a function of distances from the source. Due to the lack of (1) useful total chromium data at the source, and (2) measurable Cr(VI) levels farther than the near downwind sampling position, it is felt that, with the exception of Run 8, the ambient data could not be used to provide conversion estimates. In Run 8, the ratios are likewise somewhat unreliable but indicate that the Cr(VI) levels

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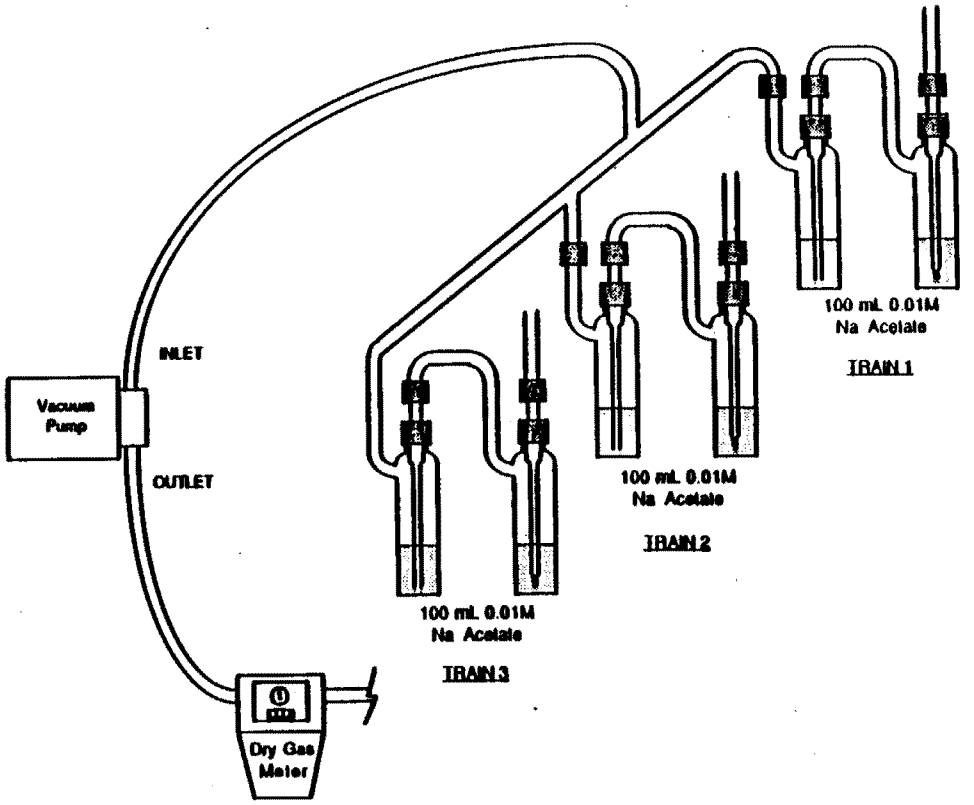

FIGURE 7-3
AMBIENT SAMPLING STATION IMPINGER TRAINS

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TABLE 7-1
AMBIENT SAMPLING TEST RESULTS
NEAR CHROME PLATING SOURCE[a]

Run No.	Position No.	Cr(VI) (ng/m^3)	Total Cr (ng/m^3)	Cr(VI)/Total Cr
3	0-Upwind	2.7	10.3	N/A
	1-Predicted DW	2.3	8.4	0.27
	2-Near DW	33.5	c	---
	3-Far DW	3.7	19.1	0.19
5	0-Upwind	2.6	(153)	N/A
	1-Predicted DW[b]	110	102	~1.0
	2-Far DW	7.6	18.3	0.42
	3-Location 3	1.2	10.9	0.11
	4-Location 4	<0.5	4.8	<0.1
7	0-Upwind	1.9	51.3	N/A
	1-Location 1	26.4	74.7	0.35
	2-Location 2	<0.5	11.7	<0.1
	3-Location 3	<0.5	16.6	<0.1
	4-Location 4	<0.5	4.1	<0.1
8	0-Upwind	2.4	<3	N/A
	1-Predicted/ Near DW	316	340	0.93
	2-Far DW	14.3	24.7	0.58
	3-East of Source	10.3	28.3	0.36
	4-North of Source	13.8	20.7	0.67

[a]Impinger samplers used with Method ADDL006 measurement

[b]Downwind

[c]Defective Sample (no flow)

N/A - Not Applicable

are a significant portion of the total chromium levels at all sampling locations (see Table 7-2).

An additional aspect of the field sampling study was the evaluation of the analytical methodology. There were two goals:

- That the tentatively developed sampling method using the acetate impinger could be compared to the PVC membrane filter presently being used by CARB
- That the CARB Method ADDL006 could be compared to the ion chromatographic methods

It was decided that data from the CARB field test of October 1987 could be utilized for the sampling method comparison. This test did, in fact, involve a comparison of the two methods and indicated that, in general, the impinger technique provided a Cr(VI) estimate of three to 27 times that provided by the PVC membrane. These data are included as Appendix A of this report, and are summarized in Table 7-3. The measurement component of Method ADDL006 was used for all field samples since the method was amenable to both impinger and filter samples. Samples from Runs 2 and 3 were analyzed by both ADDL006 and ion chromatography. The results, shown in Table 7-4, indicate that the IC results are biased 18% higher with respect to Method ADDL006. It should be noted that the IC analyses were conducted using direct injection, which is relatively insensitive. The resulting data are close to the lower quantifiable limit (LQL) for this particular IC method. Additional field sample measurement comparison data, shown in Table 7-5, were obtained from a subsequent Los Angeles area field test in a cooperative effort with the South Coast Air Quality Management District. By contrast, these data show Method ADDL006 to be biased high by an average of 8.8%. These data are perhaps more reliable due to the larger volumes taken for IC analysis. The IC analysis utilized preconcentration prior to sample injection. These data are presented for purposes of measurement comparison only. The sampling data are not available at this time. As a consequence, results from Table 7-5 are unavailable for the purposes of providing ambient test data.

Ambient sampling at the cooling tower facility provided an added difficulty due to Cr(VI) levels that were, in general, close to the detection limit. Measurable levels of Cr(VI) on two days could be provided.

TABLE 7-2
FIELD TEST NUMBER 8

Results in ng (Normalized for flow)*

Sample	Cr(VI)	Total Cr	Cr(VI)/Total Cr
Position 1	1104	1193	0.93
Position 2	93	158	0.59
Position 3	65	179	0.36
Position 4	77	116	0.66

*Cr(VI) results from acetate impinger
Total Cr results from Teflon filters

TABLE 7-3
FIELD TEST COMPARISON OF Cr(VI) COLLECTION DEVICES
PVC FILTERS VS. 0.05 M NA_2CO_3 IMPINGER

Results in ng/m^3[a]

Field Site No.	PVC	Na_2CO_3 Buffered Impinger	Factor (Imp/PVC)
1	1.3	13.9	10.7
2	10.2	47.3	4.6
3	6.5	30.2	4.6
4	0.9	13.3	14.8
5	1.5	41.5	27.7
6	6.9	25.0	3.6
7	4.7	19.2	4.1
8	2.6	26.0	10.0
9	2.4	8.6	3.6
10	7.4	29.0	3.9
11	4.6	19.8	4.3

[a]Method ADDL006

TABLE 7-4
MEASUREMENT METHOD COMPARISON USING FIELD SAMPLES
CARB METHOD ADDL006 VERSUS ION CHROMATOGRAPHY

[ng Cr(VI) Per Sample]

Sample No.	Ion Chromatography[a]	ADDL006
CC-02-IS-11	850	640
CC-02-IS-12	825	600
CC-03-IS-21	175	161
CC-03-IS-22	50	38
CC-03-IS-41	175	165
CC-03-IS-61	200	183
CC-03-IS-62	150	123

[a]Direct injection

TABLE 7-5
MEASUREMENT METHOD COMPARISON--
ADDL006 VERSUS ION CHROMATOGRAPHY
Results in ng Cr(VI)

Sample No.	Ion Chromatography	ADDL006
1	185	229
2	434	423
3	149	190
4	306	353
5	988	1203
6	4550	4260
7	1060	1300
8	270	307
9	133	121

Five (5) other tests were conducted. Hexavalent chromium values were too low to be detected. Total chromium values (obtained from Teflon filters) are provided in Table 7-6. The field test personnel believe that several factors may have contributed to these low Cr(VI) values. The dilution rate from the cooling tower(s) was so great it was difficult to provide adequate quantities of SF_6 to verify the plume location (see Table F-4 in Appendix F).

A summary of wind direction data can be found in Table F-4 of Appendix F. The wind was expected out of the east in the morning. In the afternoon the wind generally came off the ocean. Deviations to this pattern are found in Appendix F(C), which contains wind direction data. An examination of these data indicates that the wind direction at the chrome plating facility was generally steady, while winds at the cooling tower site were highly variable. There were other occasions where sampling personnel felt that they were located downwind of the cooling towers (at least for short periods) but may have not sampled the emission plume due to its altitude. In one test (Run 10), field test personnel could actually feel the mist (drift) from the cooling tower(s). This was not the case during the other tests. However, even for this test, the Cr(VI) values were close to the lower quantifiable limit, or about five to ten times the detection limit.

In general, it was felt that the SF_6 data correlated well with the Cr(VI) ambient data. For example, SF_6 levels for Run 8 were the highest of the chrome plating tests, as were the Cr(VI) levels. This is true also for the cooling tower Run 10. Here again, the levels were among the highest of the cooling tower tests. Runs 11 to 15 yielded nearly nondetectable levels of SF_6. A summary of SF_6 tracer results can be found in Table F-4 of Appendix F. Again, the SF_6 tracer tests were used to verify, not locate, the emission plume. Had more personnel been available, the SF_6 test may also have provided additional means of locating the plume.

Cr(III) concentrations were high enough to be easily measured but did not correlate well with wind direction and sampler location in relation to nearby cooling towers. Two observations of the total chromium data are

TABLE 7-6
AMBIENT SAMPLING TEST RESULTS
NEAR REFINERY COOLING TOWER[a]

Run No.	Position No.	Cr(VI) (ng/m^3)	Total Cr (ng/m^3)	Cr(VI)/Total Cr
9	0-Upwind	---[b]	77	---[b]
	2-DW	10.4	33	0.32
10	0-Upwind	1.0	42	0.02
	1-Due West of Tower Bank	2.1	30	0.07
	2-Straight DW	9.3	No data	
	3-Drift from Another Tower	8.0	99	0.08
11	0-Upwind	ND (<2)	39	
	1-	ND (<2)	52	
	2-	ND (<2)	43	
	3-	ND (<2)	24	
	4-	ND (<2)	102	
12	0-Upwind	ND (<2)	38	
	1-	ND (<2)	15	
	2-	ND (<2)	22	
	3-	ND (<2)	17	
	4-	ND (<2)	59	
13	0-Upwind	ND (<2)	23	
	1-	ND (<2)	10	
	2-	ND (<2)	179	
	3-	ND (<2)	128	
	4-	ND (<2)	766	
14	0-Upwind	ND (<2)	29	
	1-	ND (<2)	52	
	2-	ND (<2)	2	
	3-	ND (<2)	60	
	4-	ND (<2)	46	
15	0-Upwind	ND (<2)	77	
	1-	ND (<2)	76	
	2-	ND (<2)	241	
	3-	ND (<2)	133	
	4-	ND (<2)	38	

[a]Impinger samplers used with Method ADDL006 measurement

[b]Impinger sample not available

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perhaps worthy of note. First, those samples considered indicative of upwind or background conditions (Location 0) provided chromium values usually equal to or greater than the near downwind samples (Runs 9, 10, 12, 15). Since there were no cooling towers west of Location 0 and this location was probably out of any potential plume from nearby cooling towers, this location probably provided chromium values indicative of the area background levels; i.e., 20 to 80 ng/m^3. Also, the sampling location originally designated as far downwind (4) frequently yielded higher chromium values than those locations considered near downwind (Runs 11, 12, 13). Actually, due to wind shifts, Location 4 frequently was the upwind position. Cooling towers due south and east of location 4 (>1 km) may have contributed to the chromium levels measured at that position. In general, it appears that, due to high dilution rates and variable wind conditions, no distinct plume could be located in this area. This is supported by the SF_6 tracer studies. The Run 13 value of 766 ng/m^3 total chromium [Cr(III)] cannot be explained in light of any of the above mentioned sampling conditions. Run 14 Cr(III) results were slightly lower than those of other tests, probably due to rainy conditions that day.

7.4 THE FIELD REACTION STUDY

The primary goal of the field reaction study was the corroboration of laboratory chamber reactivity tests: "Was the Cr(VI) half life of approximately 13 hours determined from chamber tests applicable to actual field conditions?" An additional goal of the field reaction study was to determine if there was any significant photochemical input in the Cr(VI) conversion process.

As a consequence, the field reaction study was conducted in a manner similar to the laboratory chamber tests. PVC and Teflon membrane filters were "preloaded" at each source with levels ranging from approximately 10 to 60 ng of Cr(VI). Twelve filters were loaded simultaneously in this manner for each run. A diagram depicting the filter holder for this test is shown in Figure 7-4. Two days were spent at each source to determine the optimum filter loading time to achieve the appropriate Cr(VI) loading. Based on samples immediately sent to RTI for Cr(VI) analysis, a five-second filter loading period was determined to be adequate at the chrome plating

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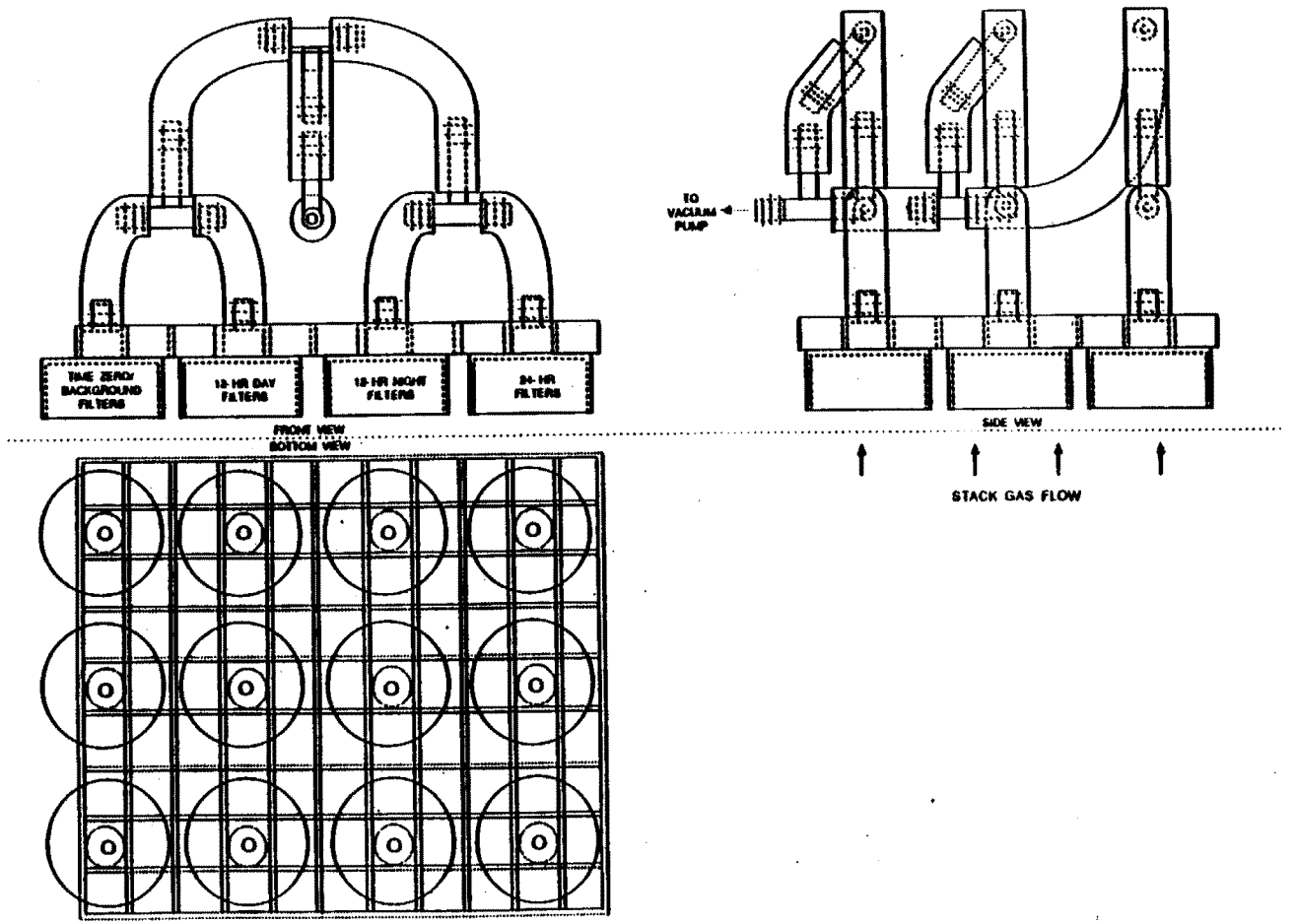

FIGURE 7-4
FIELD REACTION FILTER HOLDER

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site, and a 30-minute period was determined to be appropriate at the cooling tower facility. However, in retrospect, the five-second exposure at the chrome plating site may have been too short, since all filter loadings of Cr(VI) after the first day were less than 20 ng, near the lower quantifiable limit (by Method ADDL006). Once the membrane filters were loaded at the source, they were exposed to ambient air at an upwind or isolated site according to the following scheme:

1. Three (3) filters were set aside for a "t_0" reference Cr(VI) value.
2. Three (3) filters were exposed for 12 hours to night conditions only.
3. Three (3) filters were exposed for 12 hours to daylight conditions only.
4. The remaining three (3) filters were exposed for 24 hours to combined day/night conditions.

Two of three filters for each exposure time were used to provide the average values reported in Table 7-7. The details of the field reaction sampling study sampling are included in Appendix F.

Air quality in the Los Angeles area was generally good with levels of nitrogen oxides (as well as ozone and carbon monoxide) below the clean air standard during the entire field test. From this it could be inferred that potentially reactive species were not at levels that would promote usually rapid Cr(VI) reduction. General air quality indicator data are included in Appendix F(D).

Results of seven (7) field reaction experiments from the chrome plating sites and three (3) from the cooling tower facility are shown in Tables 7-7 and 7-8. Plots depicting Cr(VI) conversion versus time are found in Figures 7-5 through 7-11. Filter loadings ranged from 11 to 49 ng for the chrome plater and 29 to 63 ng for the cooling tower. Over a 24-hour period, the conversion ranged from 49 to 80% for the chrome plating facility and from 39 to 74% for the cooling tower samples. A summary of the estimated Cr(VI) half life for each field reaction test is shown in Table 7-9. Results indicate an average half life of 16 hours ($\pm$ 6.9 hours), in good agreement with that obtained during the laboratory chamber tests. The Run 9 half life value of 30 hours may appear to be somewhat outside of the

TABLE 7-7
FIELD REACTION TESTS OF CHROME PLATING SAMPLES[a]

Run No.	Sample No.	Cr(VI) Recovered (ng)	Percent Conversion
2	Unexposed (t_o)[b]	48.6[c]	---
	12 hr. night	44.3	<10
	12 hr. day	24.8	49
	24 hr.	27.0	44
	Background	<2	
3	Unexposed (t_o)	11.1	---
	12 hr. night	18.3	55
	12 hr. day	34.4	28
	24 hr.	21.1	>80
	Background	<2	
4	Unexposed (t_o)	11.6	
	12 hr. night	9.6	(Inadequate
	12 hr. day	13.3	Sample)
	24 hr.	11.3	
	Background	9.8	
5	Unexposed (t_o)	12.6	---
	12 hr. night	12.3	<10
	12 hr. day	12.3	<10
	24 hr.	4.7	63
	Background	<2	
6	Unexposed (t_o)	24.1	
	12 hr. night	18.3	(Indeterminate
	12 hr. day	34.4	Data)
	24 hr.	21.1	
	Background	<2	
7	Unexposed (t_o)	18.6	---
	12 hr. night	13.5	27
	12 hr. day	15.0	19
	24 hr.	5.2	72
	Background	<2	
8	Unexposed (t_o)	17.5	---
	12 hr. night	5.5	69
	12 hr. day	11.9	32
	24 hr.	5.6	68
	Background	<2	

[a]Values "corrected" for background

[b]Unexposed (t_o)--initial loading at source

[c]All Cr(VI) values are averages of duplicate filter analyses for each time period.

TABLE 7-8
FIELD REACTION TESTS OF COOLING TOWER SAMPLES[a]

Run No.	Sample No.	Cr(VI) Recovered (ng)	Percent Conversion
9	Unexposed (t_o)[b]	62.9 (25)[c]	---
	12 hr. night	43.4 (2.6)[c]	31
	12 hr. day	58.9 (2.6)[c]	<10
	24 hr.	24.2	39
	Background	<2	
10	Unexposed (t_o)	28.5	---
	12 hr. night	13.5	53
	12 hr. day	10.0	65
	24 hr.	7.4	74
	Background	<2	
11	Unexposed (t_o)	31	---
	12 hr. night	17.4	44
	12 hr. day	16.0	48
	24 hr.	23.4	(25)
	Background	4.0	

[a]Values "corrected" for background

[b]Unexposed (t_o)--initial loading at source

[c]Ion chromatographic results 16 days later--these values reflect the instability of Cr(VI) in the acetate impinger

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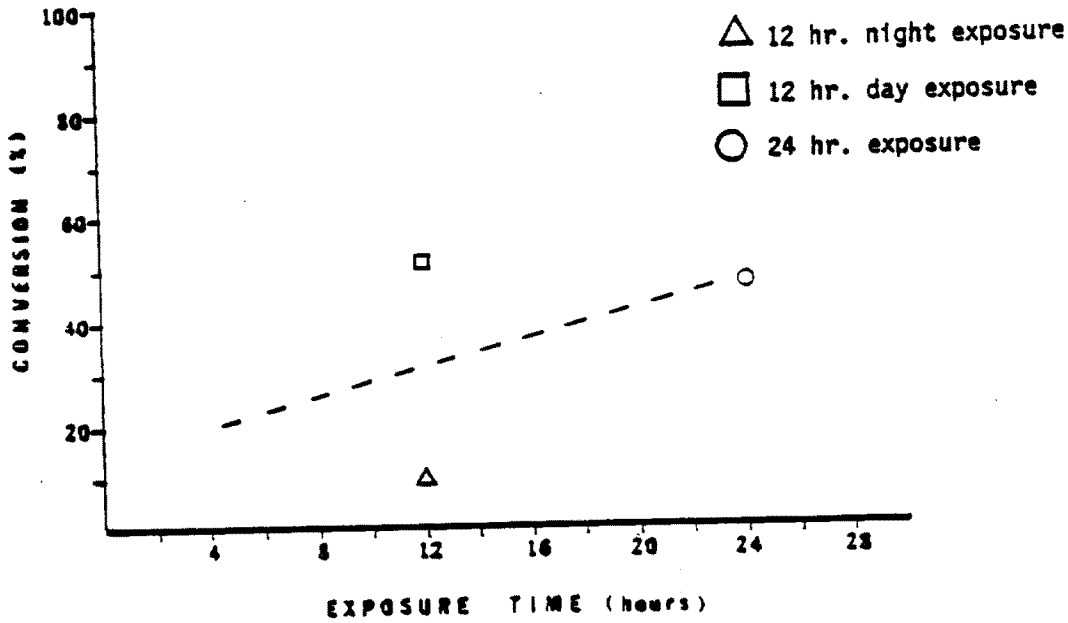

FIGURE 7-5: FIELD REACTION - RUN 2

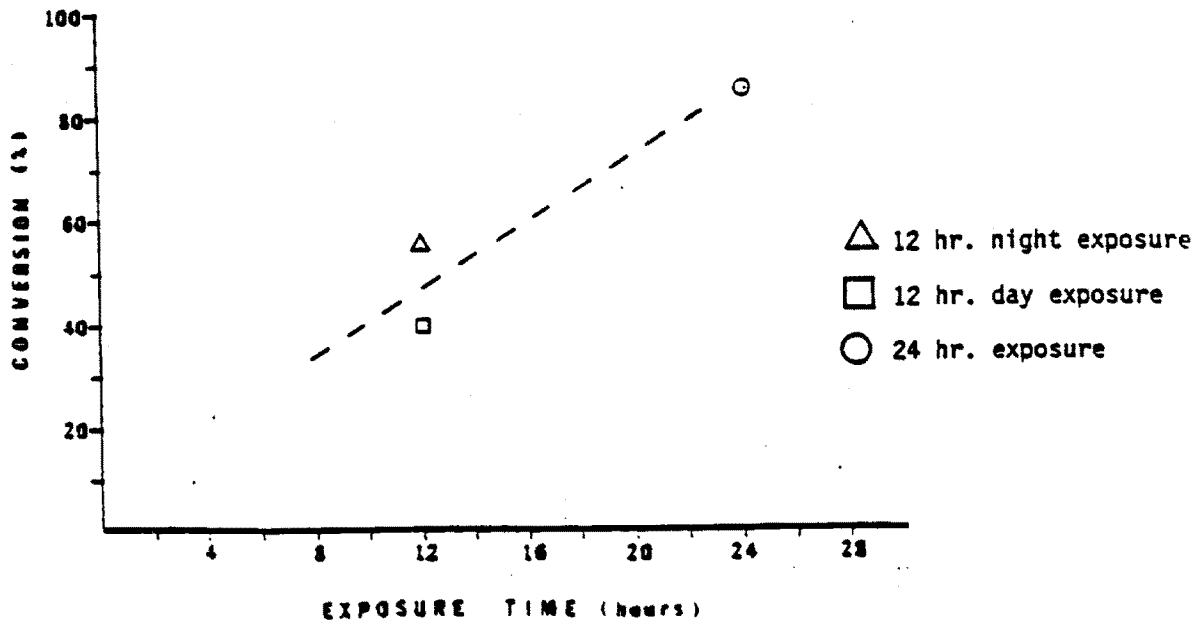

FIGURE 7-6: FIELD REACTION - RUN 3

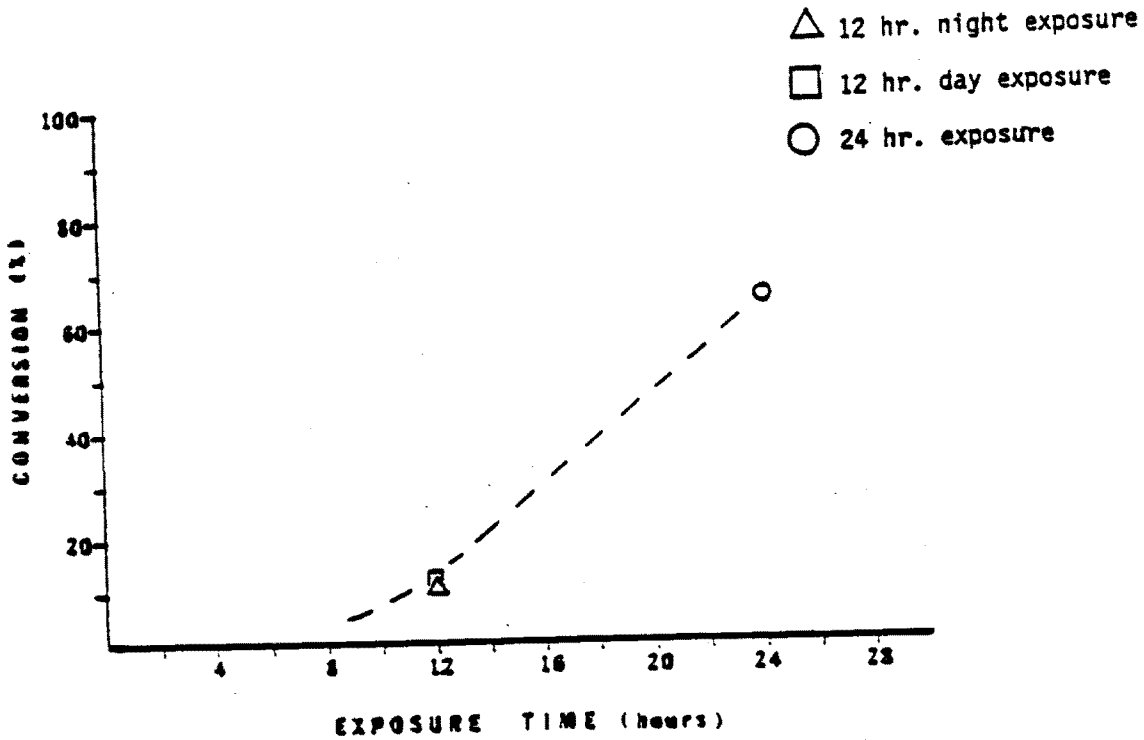

FIGURE 7-7: FIELD REACTION - RUN 5

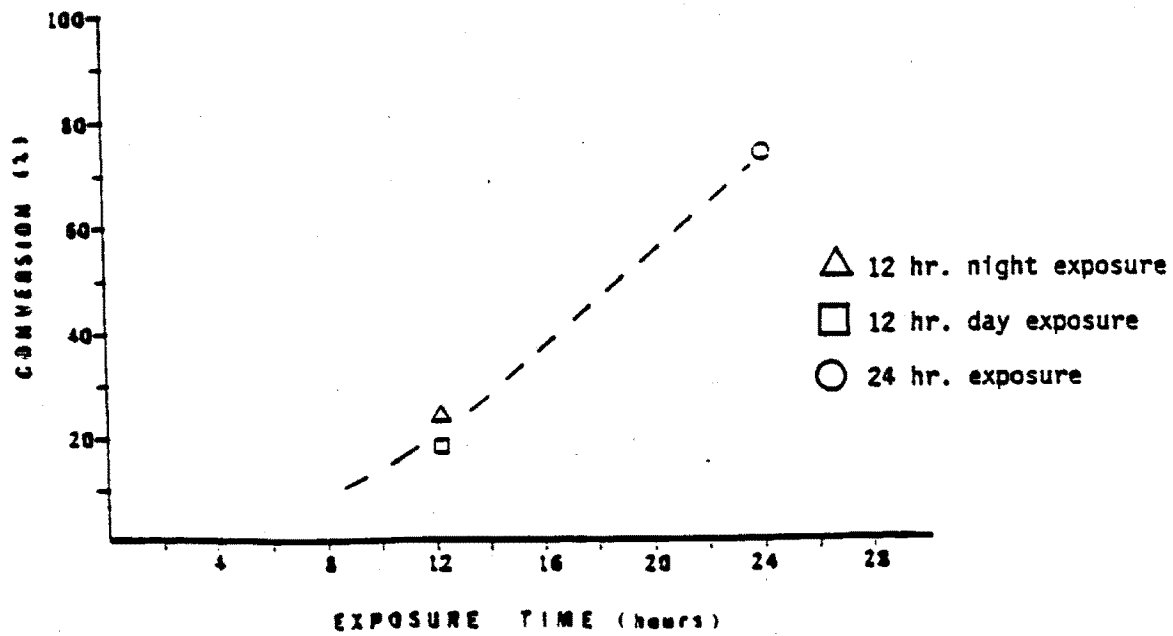

FIGURE 7-8: FIELD REACTION - RUN 7

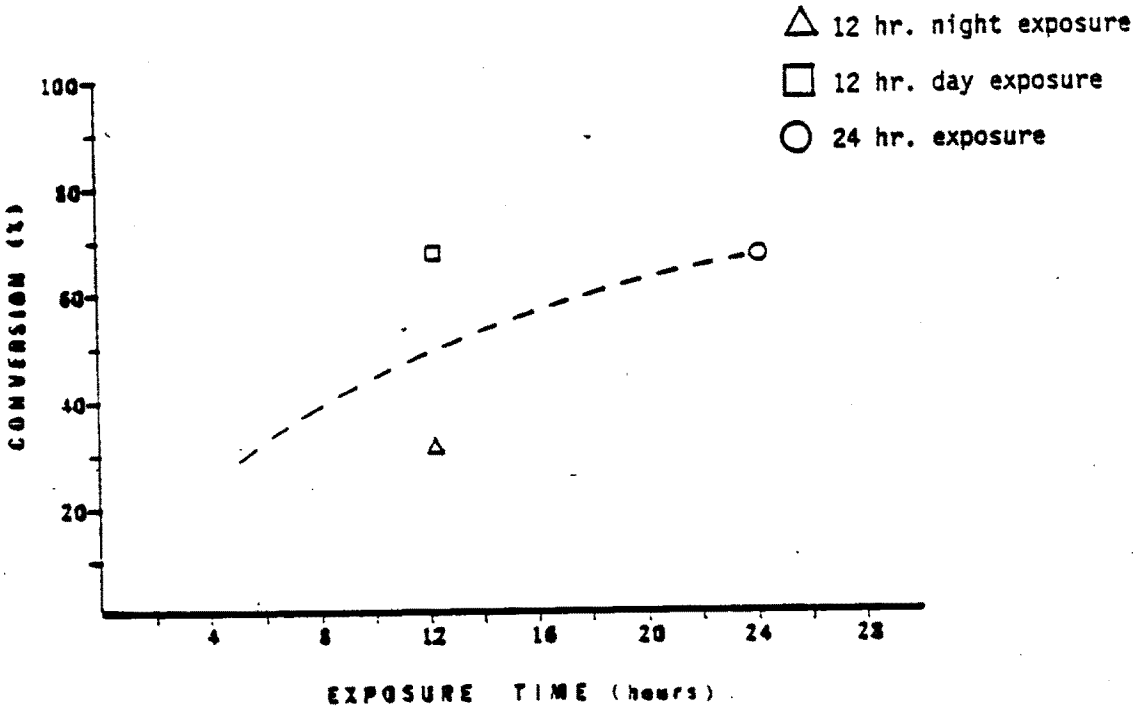

FIGURE 7-9: FIELD REACTION - RUN 8

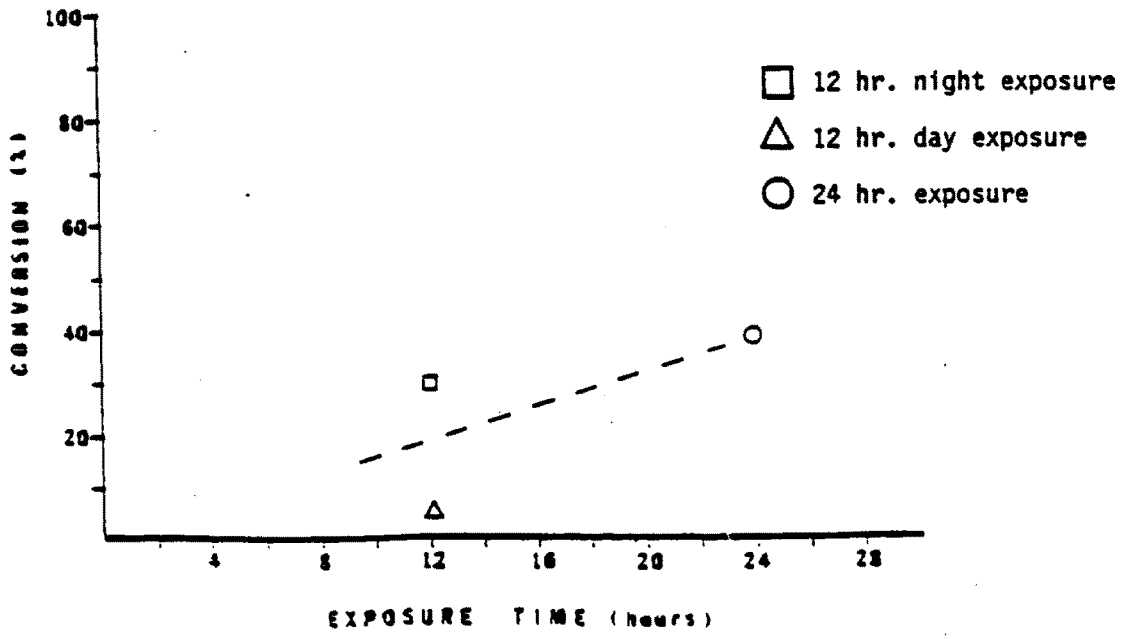

FIGURE 7-10: FIELD REACTION - RUN 9

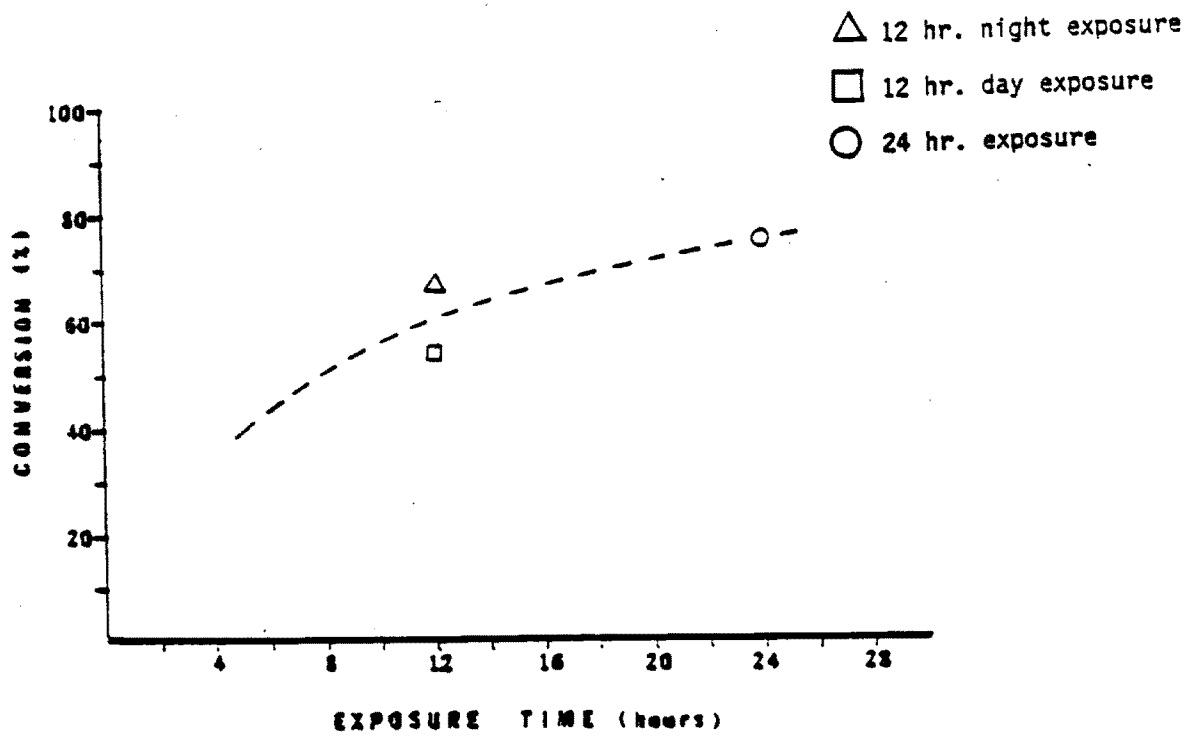

FIGURE 7-11: FIELD REACTION - RUN 10

TABLE 7-9
ESTIMATED Cr(VI) HALF LIFE DURING FIELD REACTION TESTS

Field Reaction Test No.	Estimated Half Life (Hrs.)	Comments
2	12	Chrome Crankshaft
3	14	Chrome Crankshaft
5	21	Chrome Crankshaft
7	20	Chrome Crankshaft
8	13	Chrome Crankshaft
9	~30 (est.)*	ARCO
10	9	ARCO
11	12	ARCO
Average Half life = 16.4 hrs (± 6.9 hrs.)		

*Possible outlier--if excluded the average half life is 14.4 hrs (± 4.4 hrs)--still in excellent agreement with the laboratory results.

expected range over all of the field test results. Analytical problems were evident in this particular run. Duplicate filter results for each time period (T_0, T_{12N}, T_{12D}, T_{24}) demonstrated much more variability than that usually encountered during these analyses. Subsequent IC analyses of the same Run 9 samples indicated Cr(VI) values that had decreased by approximately 30 ng for each time period over that originally obtained by Method ADDL006 due to Cr(VI) instability in the acetate medium. Data from this run might be considered suspect. If the Run 9 data point is discarded, the average Cr(VI) half life for the field test is 14.4 hours (± 4.4 hours), remarkably close to the laboratory half life value of 13 hours. However, this close agreement must be evaluated in relation to previously mentioned rates regarding the generally "good" air quality during the entire study.

Study of the data indicates the following:

- In the absence of more accurate ambient data, field reaction studies indicate that significant reduction of Cr(VI) is likely to take place over hours instead of minutes.
- There is no apparent correlation between photochemical input and Cr(VI) reactivity.
- Both chromium sources demonstrated similar Cr(VI) reduction trends.
- There is a strong parallel between the field reaction study data and that obtained in laboratory tests.

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9.0 GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

CARB	California Air Resources Board
Cr(VI), Cr^{+6}	Hexavalent chromium
Cr(III), Cr^{+3}	Trivalent chromium
ng/m^3	Nanograms per cubic meter
C.V.	Precision, as Coefficient of Variation
PVC	Polyvinylchloride
Fe^{+2}	Ferrous ion
V^{+}, V^{+2}	Reduced vanadium species
Organics	Generic expression referring to those oxidizable organic compounds
CO_2	Carbon dioxide
HNO_3	Nitric acid (atmospheric)
Teflon	Generic expression for chlorofluorocarbon materials
MnO_2	Manganese dioxide
in-situ	Measurement--real time analysis of the desired component--a given
Impinger	A dynamic sampler utilizing the collection of a gaseous or particulate species by passing through liquid absorption medium
Parafilm	A polyneric waxy film used to provide a temporary film on containers
mm	Millimeter
Plexiglass	A generic expression referring to acrylic plastics

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APPENDIX A

REPORT OF FIELD TEST
PERFORMED BY CARB, OCTOBER 1987

CHROME CRANKSHAFT CO
5845 EAST FLORENCE PLACE • BELL GARDENS, CALIF 90201
TELEPHONE 773-5936 AREA CODE 213
POST OFFICE BOX 2126, BELL GARDENS, CALIF. 90201
LOS ANGELES CAL. • CHICAGO, ILL.

December 9, 1986

Frances Cameron, P.E.
Assoc. Air Resources Engineer
State of California
Air Resources Board
Toxic Pollutants Branch/
Compound Evaluation Section
P.O. Box 2815
Sacramento, CA 95812

Re: Scrubber Test Results

Dear Ms. Cameron,

As per your telecon with Mr. Jerry Miller, I am enclosing copies of our recent wet scrubber test results. I trust that this information is as you require to facilitate the successful evaluation procedures toward air emission guidelines.

Thank you for your assistance in these matters and if we can be of further help, please let me know.

Very Truly Yours,

CHROME CRANKSHAFT CO., INC.

David S. Davies
Vice President

DSD
encl.

TRUESDAIL LABORATORIES, INC.

LN 17207

CHROME CRANKSHAFT CO.
10/22/86

Test No: 1(as is make up water)	Scrubber Inlet A	Scrubber Inlet B	Scrubber Outlet
Flue Gas			
Temperature, °F	73	75	61
Velocity, ft/sec	24.6	21.4	26.3
Static pressure, in. H_2O	-0.95	-0.95	-0.50
Flue Diameter, in.	24x24	24x24	27x35
Flue Area, Sq. ft.	4.00	4.00	6.56
Flow Rate, ACFM	5900.	5140.	10,300.
, SCFM	5750.	5000.	10,300.
, DSCFM	5680.	4930.	10,200.
Moisture, % by vol.	1.2	1.1	1.3
Chromium	(11:10-12:10)	(11:10-12:10)	(11:10-12:10)
Sample Volume, DSCF	28.83	27.18	29.28
Concentration			
Total Cr, PPM	5.06	0.22	0.04
, mg/m^3	11.1	0.48	0.08
Cr^{+6}, PPM	3.75	0.16	0.01
, mg/m^3	8.22	0.35	0.03
Emission Rate, lbs/hr			
Total Cr	0.236	0.009	0.003
Cr^{+6}	0.175	0.006	0.001
Removal Efficiency, %			
Total Cr			98.8
Cr^{+6}			99.4

vol. wt. mean mg/m³, TCr 6.17

10^{-4} gr/dscf [illegible]

TRESDAIL LABORATORIES, INC.

LN 17207

CHROME CRANKSHAFT CO.
10/22/86

Test No: Flue Gas	2(ph neutral-make up water)	Scrubber Inlet A	Scrubber Inlet B	Scrubber Outlet
Temperature, °F				
Velocity, ft/sec				
Static pressure, in. H_2O				
Flue Diameter, in.		24x24	24x24	27x35
Flue Area, Sq. ft.		4.00	4.00	6.56
Flow Rate, ACFM				
, SCFM		(from Test 1)		
, DSCFM		5680.	4930.	10,200.
Moisture, % by vol.		1.1	1.5	1.9
Chromium		(13:05-14:05)	(13:05-14:05)	(13:05-14:05)
Sample Volume, DSCF		28.62	26.79	27.94
Concentration				
Total Cr, PPM		3.84	0.39	0.12
, mg/m^3		8.42	0.86	0.27
Cr^{+6}, PPM		2.82	0.28	0.09
, mg/m^3		6.18	0.61	0.20
Emission Rate, lbs/hr				
Total Cr		0.180	0.016	0.010
Cr^{+6}		0.132	0.011	0.008
Removal Efficiency, %				
Total Cr				94.9
Cr^{+6}				94.4
wt. mean mg/m³		4.71		
10^{-1} gr/dscf		2.14		

TRUESDAIL LABORATORIES, INC.

LN 17207

CHROME CRANKSHAFT CO.
10/29/86

Test No: 3 (clean make up water)

Flue Gas	Scrubber Inlet A	Scrubber Inlet B	Scrubber Outlet
Temperature, °F	79	81	69
Velocity, ft/sec	23.6	25.2	27.8
Static pressure, in. H_2O	-0.98	-0.98	-0.43
Flue Diameter, in.	24x24	24x24	27x35
Flue Area, Sq. ft.	4.00	4.00	6.56
Flow Rate, ACFM	5660.	6050.	10,900.
, SCFM	5440.	5800.	10,700.
, DSCFM	5300.	5650.	10,400.
Moisture, % by vol.	2.6	2.6	2.7
	(12:20-13:20)	(12:19-13:19)	(12:20-13:20)
Chromium			
Sample Volume, DSCF	34.71	29.78	32.38
Concentration			
Total Cr, PPM	1.54	0.25	0.01
, mg/m^3	3.39	0.17	0.02
Cr^{+6}, PPM	1.06	0.08	0.01
, mg/m^3	2.32	0.17	0.01
Emission Rate, lbs/hr			
Total Cr	0.072	0.012	0.001
Cr^{+6}	0.050	0.003	0.001
Removal Efficiency, %			
Total Cr			98.8
Cr^{+6}			98.1

vol. wt. mean mg Tcr/m³ .87
10^{-1} gr/dscf 3.8

respectfully submitted,

Truesdail Laboratories. Inc.

S. Hugh Brown

S. Hugh Brown, Supervisor
Air Pollution Testing

EQUIPMENT DESCRIPTION

CHROME CRANKSHAFT CO. 6845 E. Florence Place, Bell Gardens

All tanks have 33 oz./gal. of chromic acid, operating 16 hours/day and 5 days/week, with plating amperage varies between 4000 and 6000 amps.

CHROME PLATING TANKS

TANK 1 - 3'-6"W. X 24'-1"L. X 3'-9"H.
TANK 2 - 3'-4"W. X 20'-0"L. X 3'-8"H.
TANK 3 - 3'-4"W. X 21'-0"L. X 3'-7"H.
TANK 4 - 3'-6"W. X 18'-1"L. X 3'-6"H.
TANK 5 - 3'-6"W. X 18'-0"L. X 3'-6"H.
TANK 6 - 3'-0"W. X 18'-1"L. X 3'-4"H.
TANK 7 - 3'-0"W. X 18'-0"L. X 3'-4"H.
TANK 8 - 3'-0"W. X 18'-0"L. X 3'-5"H.

SCRUBBERS

SCRUBBER 1 - WET SCRUBBER, ERIKSON, 5'-0"W. X 12'-0"L. X 7'-5"H., WITH A 2 HP PUMP AND A 10 HP BLOWER. VENTING TANKS 1 & 2

SCRUBBER 2 - WET SCRUBBER, ERIKSON, 5'-0"W. X 12'-0"L. X 6'-7"H., WITH A 2 HP PUMP AND A 10 HP BLOWER. VENTING TANKS 3 & 4

SCRUBBER 3 - WET SCRUBBER, ERIKSON, 5'-0"W. X 12'-0"L. X 8'-0"H., WITH A 2 HP PUMP AND A 10 HP BLOWER. VENTING TANKS 5 & 6

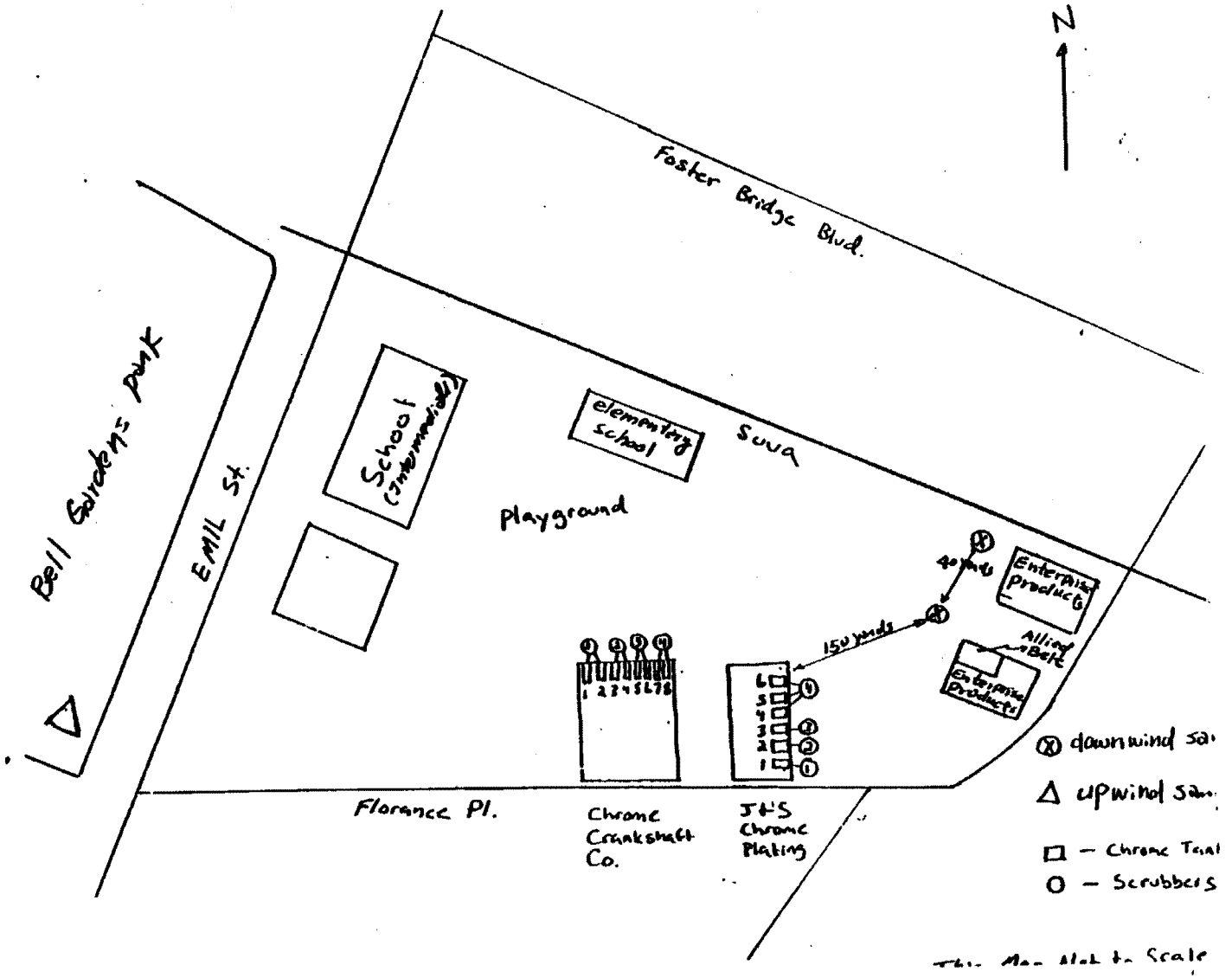
SCRUBBER 4 - WET SCRUBBER, ERIKSON, 5'-0"W. X 12'-0"L. X 7'-11"H., WITH A 2 HP PUMP AND A 15 HP BLOWER. VENTING TANKS 7 & 8

J & S CHROME PLATING CO. 6863 E. Florence Place, Bell Gardens

All tanks have 30 oz./gal.of chromic acid, operating 24 hours/day and 7 days/week, with plating amperage varies between 4200 and 4500 amps.

CHROME PLATING TANKS

TANK 1 - 3'-0"W. X 5'-0"L. X 7'-0"H. VENTED TO SCRUBBER 1.
TANK 2 - 2'-6"W. X 5'-0"L. X 8'-0"H. VENTED TO SCRUBBER 2.
TANK 3 - 2'-6"W. X 7'-0"L. X 7'-0"H. VENTED TO SCRUBBER 3.
TANK 4 - 2'-6"W. X 3'-6"L. X 7'-0"H. VENTED TO SCRUBBER 4.
TANK 5 - 2'-6"DIA. X 2'-7"H. VENTED TO SCRUBBER 4.
TANK 6 - 2'-6"DIA. X 2'-7"H. VENTED TO SCRUBBER 4.



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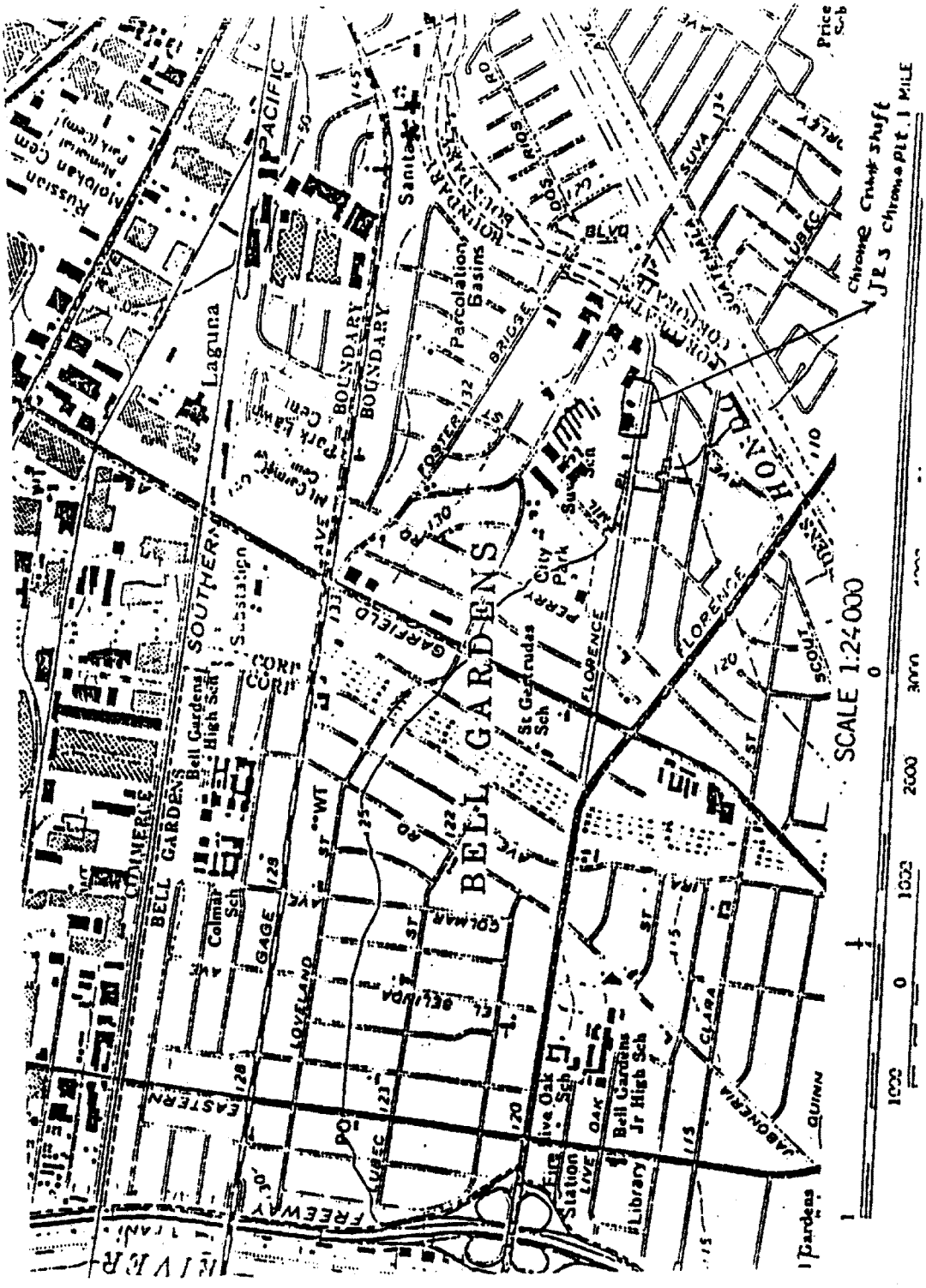

BELL GARDENS
Laguna
Parcolation Basins
City Park
St Gertrudes Sch
Bell Gardens High Sch
Colmar Sch
Bell Gardens Jr High Sch
Live Oak Sch
Fire Station
Library
Substation
Russian
Molokan Cem
Price Sch
Chrome Crew shift
J R S chrome pit 1 MILE
SCALE 1:24000
0
1000
2000
3000
1
0
1000
2000
3000
Gardens

State of California

M E M O R A N D U M

To : Gary Murchison, Manager
SSD, Process Evaluation Section

Date : November 2, 1987

Subject : Chromium +6
Analysis

Bob Kuhrman, Manager
MLD, Laboratory Services Section

From : Air Resources Board

Attached are the data for chromium +6 analyses you requested for the J & S Plating and Chrome Crankshaft study. Based on our preliminary analysis of the data, the impinger method appears to give consistently higher results than the PVC filter method. This relationship is comparable to that reported by Research Triangle Institute in their September 1987 progress report to Research Division for the Cr+6 methods comparison contract. Note that one point (site A PVC), taken on 10/7/87 appears to be an outlier. It is the only PVC sample that shows a daily site A sample lower than a site B sample. It also showed an abnormally low PVC/impinger ratio. While this sample was re-analyzed and the original result validated, the field sampling conditions are unknown and could not be duplicated. In addition, the analysis of the upwind PVC sample taken on 10/8/87 was below our analytical detection limit of 0.4 ng/M3. These two points were removed and a least squares analysis plot of the remaining points is presented in Figure 1.

Caution should be used in interpreting these results. While the study design included a laboratory blank and a trip blank, no impinger blank was provided. Dr. Peter Grohse of RTI has reported high Cr+6 in impinger blanks analyzed for their current South Coast Air Quality Management District study. Our laboratory has also seen Cr+6 in new glassware and has adopted a cleaning procedure involving a soak with concentrated nitric acid prior to use in Cr+6 analysis methods. In short, we do not know the history of the impinger glassware. It is possible that the impinger sample results reflect a positive Cr+6 artifact.

Based on this preliminary analysis, we recommend that future studies be designed to include an impinger blank. Additional samples should be taken to confirm the validity of the method results.

cc. Todd Wong
Catherine Dunwoody
Mike Poore
Dave Hartmann

Sacramento Laboratory Sample Analysis Request/Report Form
Monitoring & Laboratory Division - Laboratory Services Section

Division/Section Submitting Request:	Date Submitted:	Control Number:
SSD/TPS	October 1, 1987	13834 - 13872
Name of Requestor:	**Phone Number:**	**Expected Sample Receipt Date:**
Gary Murchison	2-8521	October 12, 1987

Analytical Service Requested:

AAS quantitative analysis of 12 filter samples, 13 buffered impinger samples and 13 dilute acid impinger rinse samples.

Expected Sample Turn-Around Time: 2 weeks

Description of Sample (how and where taken, purpose of sampling):
During the week of October 6-10, 1987, ambient air samples were taken near two sources - J & S Plating and Chrome Crankshaft. An upwind site was monitored for each source. The methods used to collect the samples were the PVC filter method and the impinger method, which uses a buffered solution of sodium acetate. Sample runs averaged 6 hours at an average volume of 7 M^3.

Specific Compounds/Elements/Ions to Analyze for or Identify:
Analysis of PVC filters and impinger solution samples for hexavalent chromium.
Analysis of impinger acid rinse samples for total chromium.

RESULTS

Analyst's Signature:	Phone Number:	Date Completed:	Instrument/Method:
	4-6863	October 21, 1987	AAS/NLS 006

Qualitative Information/Quantitative Data:

See attachment.

Description of Methods Used:

Refer to NLS006 (former ADDL006) for the analytical description. The buffered impinger solution samples were adjusted to pH 5 with 10% HNO_3 before beginning the method's Cr + 6 complexation procedure. The acid rinses did not require preanalytical preparation.

Supervisor's Approval:	Phone Number:	Date:
R. Kuhlman	2-6042	10/30/87

cc: Todd Wong
P. Venturini

(9-22-87)

J & S Plating and Chrome Crankshaft Study

Los Angeles - October 6-10, 1987

Hexavalent Chromium Results for PVC and Impinger (Buffer) Solution Samples

Method NLS006

Date	Sample #	Lab #	Sample Type	Cr^{+6} ng/M^3
10/6	001	13834	Upwind Buffer	13.9
	003	13836	Site A Buffer	47.3
	005	13838	Site B Buffer	30.2
	279872	13842	Upwind PVC	1.3
	279872A	13843	Site A PVC	10.2
	279872B	13844	Site B PVC	6.5
10/7	009	13845	Upwind Buffer	13.3
	011	13847	Site A Buffer	41.5
	013	13849	Site B Buffer	25.0
	280872	13852	Upwind PVC	0.9
	280872A	13853	Site A PVC	1.5
	280872B	13854	Site B PVC	6.9
10/8	015	13855	Upwind Buffer	15.2
	017	13857	Site A Buffer	19.2
	019	13859	Site B Buffer	26.0
	281872	13861	Upwind PVC	<0.4[2]
	281872A	13862	Site A PVC	4.7
	281872B	13863	Site B PVC	2.6

10/9	021	13864	Upwind Buffer	8.6
	023	13866	Site A Buffer	29.0
	025	13868	Site B Buffer	19.8
	282872	13870	Upwind PVC	2.4
	282872A	13871	Site A PVC	7.4
	282872B	13872	Site B PVC	4.6

Notes:

1. Trip Blank Buffer 4.2 ng (0.6 ng/M^3*) Cr^{+6}

   Lab Blank Buffer 3.6 ng (0.5 ng/M^3*) Cr^{+6}

   Lab Blank Spiked 25 ng/mL 21.4 ng/mL (86% recovery)

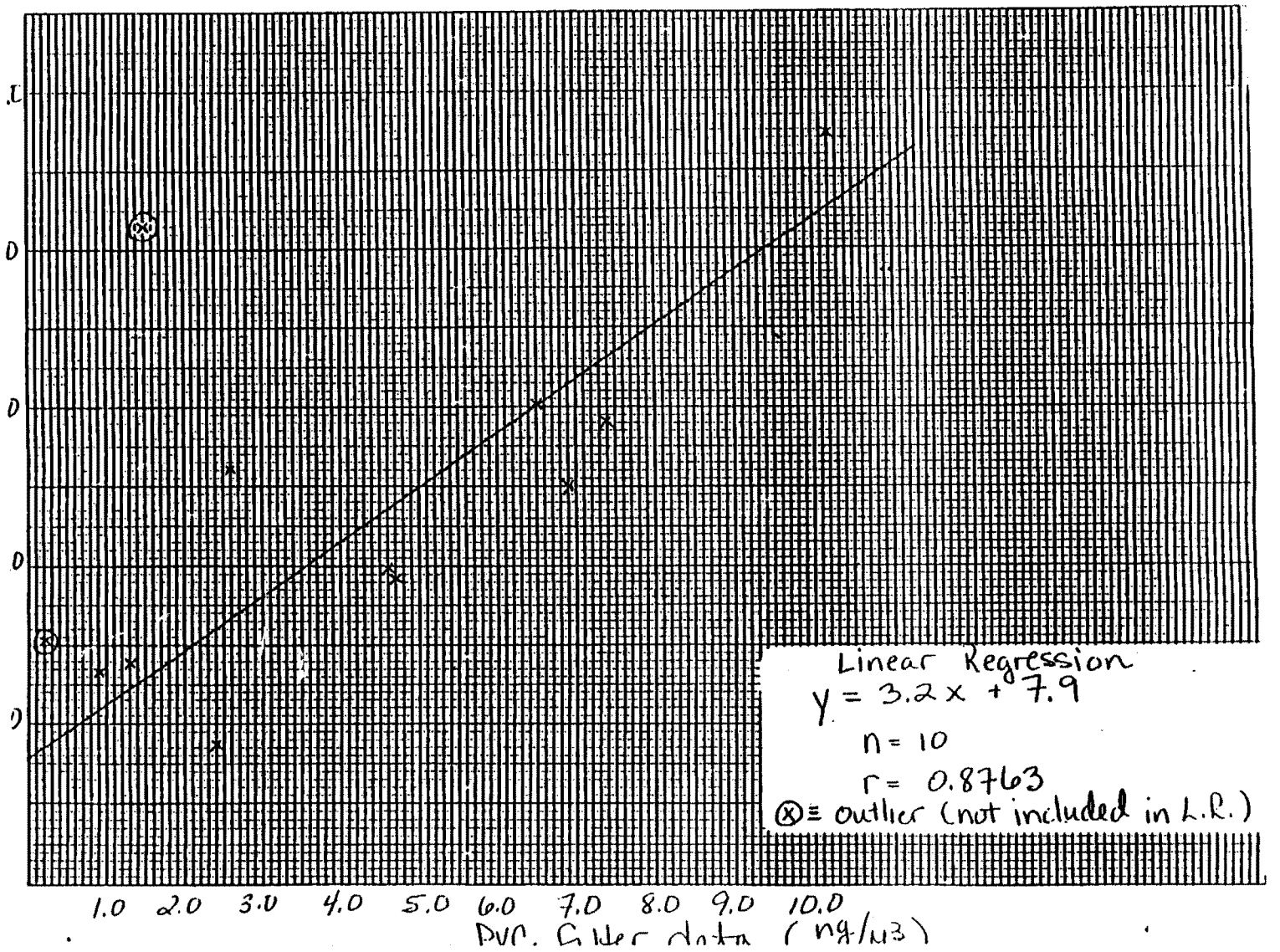
   *equivalent concentration assuming 7M^3 volume

2. Cr^{+6} Method detection limit is 0.4 ng/M^3 based on a volume of 7M^3.

Total Chromium Results for Impinger Acid Rinse Samples

All of the impinger acid rinse analysis total chromium results fell below the Method's detection limit of 3 ng/mL.

Impinger Data vs. PVC Filter Data
J & S Plating and Chrome Crankshaft Study



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State of California

AIR RESOURCES BOARD

DRAFT PROTOCOL: Ambient Air Monitoring Study of Hexavalent Chromium Sources in Bell Gardens, California.

I. TEST PROGRAM

A hexavalent chromium air monitoring study near two chrome plating facilities in Bell Gardens, California will be conducted by the Air Resources Board staff during the week of October 5-9, 1987. The two sources have plating operations that can release hexavalent chromium emissions into the ambient air.

The objectives of the study are:

1. Compare the measurement methods and results using the present ARB filter method and the RTI impinger solution method.

2. Measure the ambient concentrations of hexavalent chromium upwind and downwind of the sources.

Specific meterological conditions will also be monitored during the sampling periods.

II. SAMPLING LOCATIONS

The sampling plan consists of two downwind monitoring sites which will be located approximately 150 and 200 yards to the east/northeast of the chrome plating facilities in an industrial park parking lot. The upwind site will be placed at the City of Bell Gardens corporation yard. This site is approximately 1/4 mile to the south/southwest of the plating facilities. Figure 1 shows the locations of the monitoring sites.

III. MEASUREMENT METHODS

In this monitoring study, the ARB staff will use two different sampling methods. The first is the filter method which is currently used by the ARB to sample hexavalent chromium for the ARB toxic monitoring network. This will involve the use of Xontech samplers which will contain a 37 mm PVC filter and a 37 mm teflon filter. The second method is the proposed RTI impinger solution method which contains 3 Smith-Greenberg impingers in series, with the first two impingers containing 100 ml of 0.05 M buffered sodium bicarbonate solution.

Both sampler types will operate in parallel at each monitoring site for 5 to 7 hours (depending on prevailing winds) at approximately 20 liters per minute. One run will be conducted each day starting on Tuesday, October 6, 1987 and ending on Friday, October 9, 1987. For the impinger sampling, the impinger will be kept in ice baths and teflon tubing will be used to sample the air at about 8 feet above the ground.

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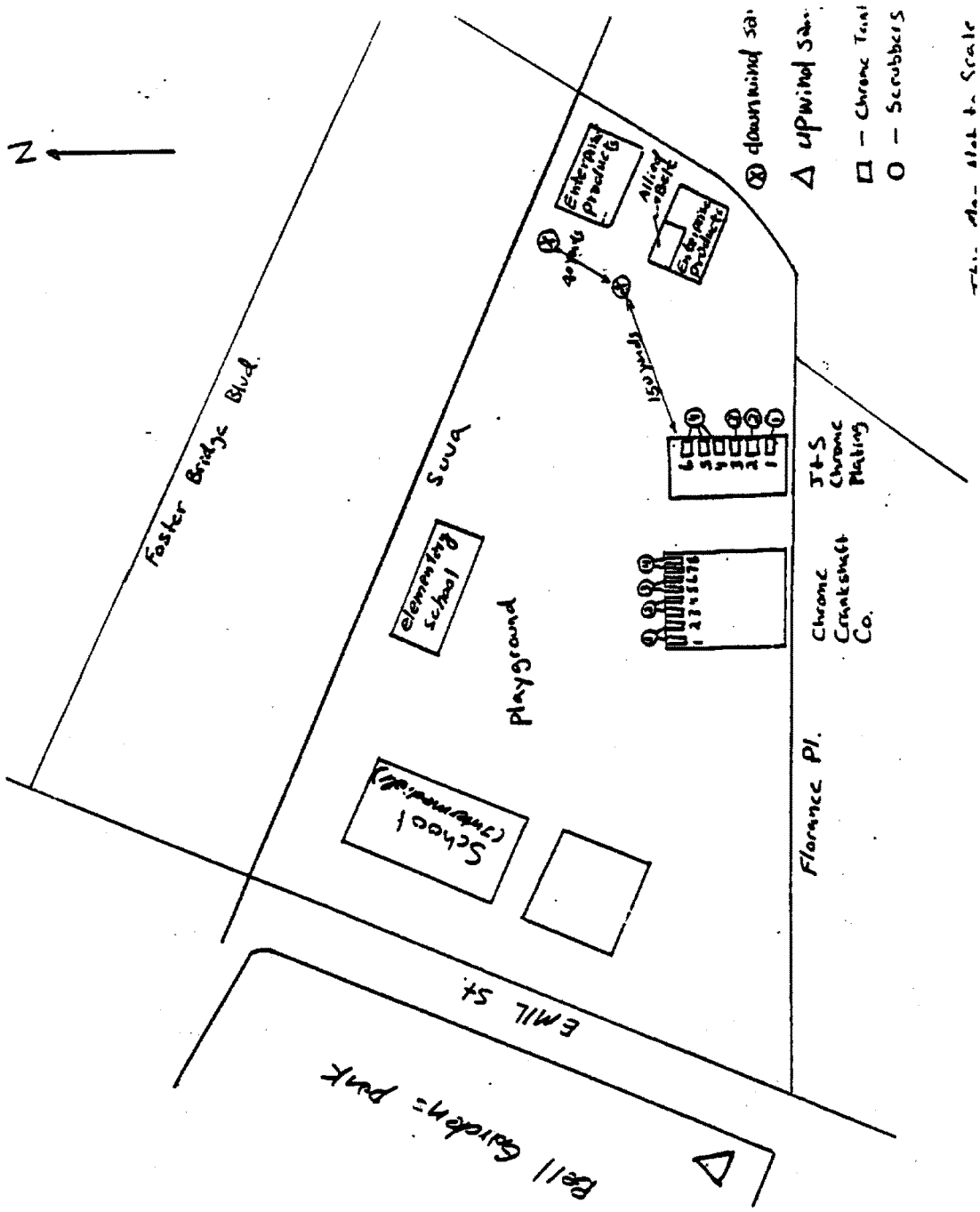
N
Foster Bridge Blvd.
Suva
elementary school
Playground
School (intermediate)
Enterprise Products
Alliance Bank
Enterprise Products
40 yards
150 yards
J+S Chrome Plating
Chrome Crankshaft Co.
Florence Pl.
EMIL St.
Bell Gardens Park
downwind sa
upwind sa
Chrome Tank
Scrubbers

Following the collection of the filter samples, cassettes containing filters will be stored in a refrigerator at the Haagen-Smit Laboratory (HSL). The PVC filters will be analyzed by HSL for total chromium concentrations. The teflon filters will be transported back to Sacramento in a cooler containing ice for hexavalent chromium analysis.

After sampling of the impinger solutions, the contents of the first two impingers will be emptied into clean 250 ml polyethylene bottles. Those impingers will be rinsed 3 times with the sodium bicarbonate solution (25 ml for each rinse). After each wash, the rinse solution is emptied into the polyethylene bottle. The impingers will then be acid rinsed 3 times with 0.1 N nitric acid (30 ml) and emptied into another clean polyethylene bottle. All the collected solutions will be stored in the refrigerator at HSL until transport to Sacramento for hexavalent chromium analysis by the Aerometric Data Division Laboratory (ADD). Clean impingers will be used for each sampling run.

IV. LABORATORY ANALYSIS

See Attachment 1 for ARB Method ADDL006.

V. QUALITY ASSURANCE

A set of filters (1 PVC and 1 teflon) will be retained and given to the appropriate laboratories as field blanks. Field blanks for the sodium acetate and the acid rinse solutions will be prepared by rinsing a clean set of impingers with each solution and retaining it in separate polyethylene bottles for later analysis by ADD.

Attachment 1

ARB Method ADDL006

Standard Operating Procedure for the Speciation and Analysis of Hexavalent Chromium at Ambient Atmospheric Levels

STATE OF CALIFORNIA
AIR RESOURCES BOARD
AEROMETRIC DATA DIVISION LABORATORY

Standard Operating Procedure for the Speciation and Analysis of Hexavalent Chromium at Ambient Atmospheric Levels

1. SCOPE

This document describes the determination of chromium $^{+6}$ in aqueous media after sampling ambient air. The procedure has been tailored to concentrations which would be expected in ambient air. Although the procedure described is known to complex other metal ions, the procedure has not been validated for any metal species other than hexavalent chromium.

2. SUMMARY OF METHOD

A low volume air sampler capable of sampling at a constant rate of 13-15 liters-per-minute for at least 24 hours is fitted with a 37 mm Gelman VM-1 (PVC) membrane filter. After sampling, the filter is added to 50 mL of water and the complexation procedure carried out in the presence of the filter.

The aqueous solution is buffered to pH 4.5 and an aqueous solution of APDC added. After mixing, the solution is filtered through a disposable cartridge containing C_{18}-bonded silica gel. The complex is absorbed onto the gel. The water, remaining ions, and uncomplexed APDC are passed through into a filtering flask and discarded. The absorbed Cr^{+6}-complex is desorbed with acetone, the acetone evaporated, and the resultant residue diluted to 2.0 mL as 10% nitric acid in water.

This solution is then analyzed by flameless atomic absorption spectrophotometry (FAAS) for chromium.

3. LIMITATIONS AND INTERFERENCES

3.1 The concentration ranges expected for Cr^{+6} in ambient air (1-5 ng/M^3) require that extreme care must be taken to insure that glassware and reagents do not contribute to the measured levels. Blanks must be analyzed with every batch of samples.

3.2 Trivalent chromium at levels ten times the Cr^{+6} concentration does not interfere in the method. Iron (Fe+3) does not interfere, except that excess ferric ion will compete with Cr^{+6} for available complexing agent. This effect has been minimized by performing the complexation step at pH 4.5. The other metals known to form APDC complexes at pH 4.5 (copper and cobalt) do not occur at sufficiently high levels to deplete the complexing agent.

3.3 Matrix effects have been reduced or eliminated by the extraction of the complex into an organic solvent and matching the final aqueous diluent to the 10% nitric acid solution used for diluting standards.

4. APPARATUS

4.1 Perkin-Elmer: Model 3030B Atomic Absorption Spectrophotometer, HGA-600 Graphite Furnace, AS-60 Autosampler and PR-100 Printer.

4.2 Vacuum filtering apparatus equipped with Sep-Pak C_{18} cartridge adaptor and teflon tubing.

4.3 Conical, graduated centrifuge tube 15 mL capacity.

4.4 Sep-Pak cartridge: Waters Assoc. #51910. Prepare cartridge for use by first filtering 5 mL of acetone through it, then washing with 10 mL distilled water, then 10 mL of Wash Solution, and repeat the acetone and D.I. washings.

5. REAGENTS

5.1 Nitric acid, Ultrex grade.

5.2 Stock standard, 250 mg/L: Dissolve 141.4 mg $K_2Cr_2O_7$ in 10% nitric acid solution and dilute to 200 mL in a volumetric flask. 1 mL = 0.25 mg Cr^{+6}.

5.3 Intermediate standard (I.S.), 0.5 mg/l: Dilute 100 mL of the stock standard in 50 mL of 10% nitric acid in a volumetric flask. 1 mL = 0.5 ug Cr^{+6}.

5.4 Working standard: Dilute 1.0, 3.0 and 5.0 mL of I.S. in 50 mL of 10% nitric acid. These correspond to 10 ng/mL, 30 ng/mL and 50 ng/mL Cr^{+6}. Prepare working standards daily.

5.5 Buffer, pH 4.5: 50 mL 0.1 M $KHC_8H_4O_4$ and 8.7 mL 0.1 M NaOH.

5.6 APDC solution: Dissolve 2.5 gms ammonium pyrrolidine dithiocarbamate in 50 mL distilled water. Filter the solution through a glass fiber filter to remove the insoluble sediment. The resultant solution will be a clear yellow. The APDC used is J. T. Baker's #3337-2.

5.7 Wash solution: 10 mL D.I. water, 5 mL APDC solution and 10 mL pH 4.5 buffer.

6. INSTRUMENT CALIBRATION

6.1 Optimize the instrument for the flameless analysis of chromium following the manufacturer's instructions.

6.2 Use a pyrocoated graphite furnace tube containing a L'vov platform and condition the tubes as per manufacturer's instructions.

6.3 Set the instrument operating conditions as follows:

Step	Furnace Temp (°C)	Time (seconds) Ramp	Hold
1 Dry	120	5	35
2 Ash	1650	5	20
3 Cool	100	2	5
4 Atomize	2600	0	5
5 Clean	2700	2	8
6 Cool	20	1	20

Wavelength 357.9 nm; lamp current 24 mA, Slit 0.7 argon gas flow 1.5 L/minute (gas stop at Atomize), 20 ul sample injection.

6.4 The instrument is calibrated using the three working standards. Recalibrate if values differ by more than ±15%.

6.5 Determine the least squares fit of the calibration data; the analysis must result in a slope of 1.00 ± 15%. Perform a reslope calibration at least every ten samples.

7. SAMPLE ANALYSIS

7.1 Place the filter in a 100 mL graduated beaker, add 50 mL deionized water, 2 mL of buffer, and 1 mL of APDC solution, swirl and let stand for 20 minutes.

7.2 Aspirate aqueous solution through a prepared Sep-Pak C_{18} cartridge.

7.3 Using a 10 mL syringe, desorb the trapped Cr^{+6}-APDC complex with 5 mL acetone directly into a 15 mL conical centrifuge tube.

7.4 Using a hot water bath (more than 80°C), concentrate the acetone solution to dryness. Note: There will be a small liquid residual, mostly residual water. As much acetone must be removed as possible, since it causes problems during the analysis step.

7.5 While hot, add 0.2 mL concentrated Ultrex nitric acid (6 drops), and place back in the heating bath for 30 seconds.

7.6 Dilute to 2.0 mL with D.I. water.

7.7 Inject 20 uL of the concentrate in triplicate for analysis using the calibrated FAAS system.

7.8 Print out the analysis results with identifying laboratory identification number. Record results and calculations in the AAS laboratory workbook. Record the calculated concentration in nanograms/M^3 on the laboratory data sheet. The concentration may be calculated as follows:

$$\text{Chromium +6, ng/M}^3 = \frac{\text{Concentration Found, ng/mL}}{\text{Volume Sampled, M}^3} \times \text{Dilution Factor}$$

8. METHOD VALIDATION

8.1 The calibration curve from 10 ng/mL to 50 ng/mL was constructed. The results of this procedure are shown in Table I.

8.2 The complexing solution was spiked with 10 ng, 30 ng and 50 ng Cr^6.[1] The analysis results are as follows:

Spike, ng	Recovered,[2] ng	Percent Recovery	RSD (Percent)
10	9.2	92	2.2
30	28.3	94	3.4
50	47.3	95	2.1

[1] The Cr^{+6} spike solution had 0.05 M Na_2CO_3 as its matrix.

[2] Results of three separate analysis minus blanks.

8.3 Filters were spiked as above and dried in a dessicator under vacuum. Their analysis resulted in the following:

Spike, ng	Recovered,[3] ng	Percent Recovery	RSD (Percent)
10	10.0	100	2.2
30	24.8	83	1.6
50	43.6	87	5.8

TABLE I

Method Calibration Data

Concentration ng/mL	Average Recovery	RSD (Percent)[4]
10	10.5	1.2
30	31.2	1.8
50	48.6	0.5

[3] Results of three separate analysis minus blanks.

[4] Relative Standard Deviation, n = 4
Correlation Coefficient: 0.998
Slope: 1.050
Intercept: -1.5 ng/mL
LOD: (i + 3 SD) = 3.04 ng/mL or 0.2 ng/M^3 based on a 20 M^3 sample

APPENDIX B

STATE OF CALIFORNIA AIR RESOURCES BOARD
METHOD ADDL006 FOR THE SPECIATION AND ANALYSIS
OF HEXAVALENT CHROMIUM AT AMBIENT ATMOSPHERIC LEVELS

STATE OF CALIFORNIA
AIR RESOURCES BOARD
AEROMETRIC DATA DIVISION LABORATORY

Method for the Speciation and Analysis of Hexavalent•Chromium at Ambient Atmospheric Levels

1. SCOPE

This document describes the determination of chromium $^{+6}$ on membrane filters after sampling ambient air. The method has been tailored to concentrations which would be expected in ambient air. Although the procedure described is known to complex other metal ions, the procedure has not been validated for any metal species other than hexavalent chromium.

2. SUMMARY OF METHOD

A low volume air sampler capable of sampling at a constant rate of 13-15 liters-per-minute for at least 24 hours is fitted with a 37 mm Gelman VM-1 (PVC) membrane filter. After sampling, the filter is added to 50 mL of water and the complexation procedure carried out in the presence of the filter.

The aqueous solution is buffered to pH 4.5 and an aqueous solution of APDC added. After mixing, the solution is filtered through a disposable cartridge containing C_{18}-bonded silica gel. The complex is absorbed onto the gel. The water, remaining ions, and uncomplexed APDC are passed through into a filtering flask and discarded. The absorbed Cr^{+6}-complex is desorbed with acetone, the acetone evaporated, and the resultant residue diluted to 2.0 mL as 10% nitric acid in water.

This solution is then analyzed by flameless atomic absorption spectrophotometry (FAAS) for chromium.

3. LIMITATIONS AND INTERFERENCES

3.1 The concentration ranges expected for Cr^{+6} in ambient air (1-5 ng/M^3) require that extreme care must be taken to ensure that glassware and reagents do not contribute to the measured levels. Blanks must be analyzed with every batch of samples.

3.2 Trivalent chromium at levels ten times the Cr^{+6} concentration does not interfere in the method. Iron (Fe+3) does not interfere, except that excess ferric ion will compete with $Cr^{+}6$ for available complexing agent. This effect has been minimized by performing the complexation step at pH 4.5. The other metals known to form APDC complexes at pH 4.5 (copper and cobalt) do not occur at sufficiently high levels to deplete the complexing agent.

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3.3 Matrix effects have been reduced or eliminated by the extraction of the complex into an organic solvent and matching the final aqueous diluent to the 10% nitric acid solution used for diluting standards.

4. APPARATUS

4.1 Perkin-Elmer: Model 3030B Atomic Absorption Spectrophotometer, HGA-600 Graphite Furnace, AS-60 Autosampler and PR-100 Printer.

4.2 Vacuum filtering apparatus equipped with Sep-Pak C_{18} cartridge adaptor and Teflon tubing.

4.3 Conical, graduated centrifuge tube 15 mL capacity.

4.4 Sep-Pak cartridge: Waters Assoc. #51910. Prepare cartridge for use by first filtering 5 mL of acetone through it, then washing with 10 mL distilled water, then 10 mL of Wash Solution, and repeat the acetone and D.I. washings.

5. REAGENTS

5.1 Nitric acid, Ultrex grade.

5.2 Stock standard, 250 mg/L: Dissolve 141.4 mg $K_2Cr_2)_7$ in 10% nitric acid solution and dilute to 200 mL in a volumetric flask. 1 mL = 0.5 ug Cr^{+6}.

5.3 Intermediate standard (I.S.), 0.5 mg/1: Dilute 100 uL of the stock standard in 50 mL of 10% nitric acid in a volumetric flask. 1 mL = 0.5 ug $Cr^{+}6$.

5.4 Working standard: Dilute 1.0, 3.0 and 5.0 mL of I.S. in 50 mL of 10% nitric acid. These correspond to 10 ng/mL, 30 ng/mL and 50 ng/mL Cr^{+6}. Prepare working standards daily.

5.5 Buffer, pH 4.5: 50 mL 0.1 M $KHC_8H_4O_4$ and 8.7 mL 0.1 M NaOH.

5.6 APDC solution: Dissolve 2.5 gms ammonium pyrrolidine dithiocarbamate in 50 mL distilled water. Filter the solution through a glass fiber filter to remove the insoluble sediment. The resultant solution will be a clear yellow. The APDC used is J. T. Baker's #B337-2. It may be necessary to extract the APDC solution with chloroform to remove trace amounts of chromium.

5.7 Wash solution: 10 mL D.I. water, 5 mL APDC solution and 10 mL pH 4.5 buffer.

6. INSTRUMENT CALIBRATION

6.1 Optimize the instrument for the flameless analysis of chromium following the manufacturer's instructions.

6.2 Use a pyrocoated graphite furnace tube containing a L'vov platform and condition the tubes as per manufacturer's instructions.

6.3 Set the instrument operating conditions as follows:

Step	Furnace Temp (°C)	Time (Seconds) Ramp	Hold
1 Dry	120	5	35
2 Ash	1650	5	20
3 Cool	100	2	5
4 Atomize	2600	0	5
5 Clean	2700	2	8
6 Cool	20	1	20

Wavelength 357.9 nm; lamp current 24 mA, Slit 0.7 argon gas flow 1.5 L/minute (gas stop at Atomize), 20 ul sample injection.

6.4 The instrument is calibrated using the three working standards. Recalibrate if values differ by more than ± 15%.

6.5 Determine the least squares fit of the calibration data; the analysis must result in a slope of 1.00 ± 15%. Perform a reslope calibration at least every ten samples.

7. SAMPLE ANALYSIS

7.1 Place the filter in a 100 mL graduated beaker, add 50 mL deionized water, 2 mL of buffer, and 1 mL of APDC solution, swirl and let stand for 20 minutes.

7.2 Aspirate aqueous solution through a prepared Sep-Pak C_{18} cartridge.

7.3 Using a 10 mL syringe, desorb the trapped Cr^{+6}-APDC complex with 5 mL acetone directly into a 15 mL conical centrifuge tube.

7.4 Using a hot water bath (more than 80°C), concentrate the acetone solution to dryness. Note: There will be a small liquid residual, mostly residual water. As much acetone must be removed as possible, since it causes problems during the analysis step. The acetone will be removed in 10-15 minutes.

7.5 While hot, add 0.2 mL concentrated Ultrex nitric acid (6 drops), and place back in the heating bath for 30 seconds.

7.6 Dilute to 2.0 mL with D.I. water.

7.7 Inject 20 uL of the concentrate in triplicate for analysis using the calibrated FAAS system.

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7.8 Print out the analysis results with identifying laboratory identification number. Record results and calculations in the AAS laboratory workbook. Record the calculated concentration in nanograms/M^3 on the laboratory data sheet. The concentration may be calculated as follows:

$$\text{Chromium}^{+6},\ ng/M^3 = \frac{\text{Concentration Found, ng/mL}}{\text{Volume Sampled, } M^3} \times \text{Dilution Factor}$$

8. METHOD VALIDATION

8.1 The calibration curve from 10 ng/mL to 50 ng/mL was constructed. The results of this procedure are shown in Table I.

8.2 The complexing solution was spiked with 10 ng, 30 ng and 50 ng Cr^6.[1] The analysis results are as follows:

Spike, ng	Recovered,[2] ng	Percent Recovery	RSD Percent)
10	9.2	92	2.2
30	28.3	94	3.4
50	47.3	95	2.1

8.3 Filters were spiked as above and dried in a dessicator under vacuum. Their analysis resulted in the following:

Spike, ng	Recovered,[3] ng	Percent Recovery	RSD Percent)
10	10.0	100	2.2
30	24.8	83	1.6
50	43.6	87	5.8

TABLE I
METHOD CALIBRATION DATA

Concentration ng/mL	Average Recovery	RSD (Percent)[4]
10	10.5	1.2
30	31.2	1.8
50	48.6	0.5

---

1 The Cr^{+6} spike solution had 0.05 M Na_2CO_3 as its matrix.

2 Results of three separate analysis minus blanks.

3 Results of three separate analysis minus blanks.

4 Relative standard Deviation, n = 4
Correlation Coefficient: 0.998
Slope: 1.050
Intercept: -1.5 ng/mL
LOD: (i + 3 SD) = 3.04 ng/mL or 0.2 ng/M^3 based on a 20 M^3 sample

APPENDIX C

U.S. ENVIRONMENTAL PROTECTION AGENCY
METHOD 218.5--CHROMIUM, DISSOLVED HEXAVALENT
(ATOMIC ABSORPTION, FURNACE TECHNIQUE)

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Chromium, Dissolved Hexavalent (Atomic Absorption, Furnace Technique)—Method 218.5

1. Scope and Application

1.1 This method covers the determination of dissolved hexavalent chromium (Cr^{6+}) in drinking and surface waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that potential interferring substances are taken into account. (See 4.1.)

1.2 The method may be used to analyze samples containing from 5 to 100 μg of Cr^{6+} per liter. The range of the method may be extended upward by dilution.

2. Summary of Method

2.1 The method is based on the separation of Cr^{6+} from the sample by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate is drawn off and the Cr^{6} precipitate resolubilized in nitric acid as trivalent chromium (Cr^{3+}) and quantified by furnace atomic absorption.

2.2 Hexavalent chromium may also be analyzed by the chelation/extraction technique (see Method 218.4 or the procedure described in 9.2 of the Atomic Absorption methods found in this manual).

3. Sample Handling and Preservation

3.1 For sample handling, cleaning glassware and the filtration procedure see part 4.1 of the Atomic Absorption Method section of this manual.

3.2 The sample must not be preserved by acidification, but instead transported and stored until time of analysis at 4°C.

3.3 Stability of Cr^{6+} in environmental samples is n ot completely understood at this time. The chemical nature of the sample matrix can have a definite affect on the chemistry of chromium. Therefore, the analysis should be carried out as soon as possible but no longer than 24 hours after collection.

4. Interferences

4.1 The possible interference from other elements which form stable chromates is not known at this time.

4.2 Samples with either sulfate or chloride concentrations above 1000 mg/liter should be diluted before analysis.

4.3 The potential reduction of Cr^{6+} from highly reductive substances increases as pH is lowered. When sulfites and sulfides are present the

sample aliquot taken for analysis should be neutralized and aerated before beginning.

5. Instrument Parameters (General)

5.1 Drying Time and Temp: 30 sec-125°C.

5.2 Ashing Time and Temp: 30 sec-1000°C.

5.3 Atomizing Time and Temp: 10 sec-2700°C.

5.4 Purge Gas Atmosphere: Argon

5.5 Wavelength: 357.9nm

5.6 Other operating parameters should be as specified by the particular instrument manufacturer.

6. Special Apparatus

6.1 Glassware

6.1.1 Filtering flask, heavy wall, 1 liter capacity

6.1.2 Centrifuge tubes, heavy duty, conical, graduated, glass stoppered, 10 mL capacity

6.1.3 Pasteur pipets, borosilicate glass, 5 ¾ inches.

6.2 Centrifuge: any centrifuge capable of reaching 2000 rpm and accepting the centrifuge tubes described in 6.1.2 may be used.

6.3 pH Meter: a wide variety of instruments are commercially available and suitable for this work.

6.4 Test Tube Mixer: any mixer capable of thorough vortex is acceptable.

7. Reagents

7.1 Lead Nitrate Solution: Dissolve 33.1 grams of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.2 Ammonium Sulfate Solution: Dissolve 2.7 grams of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.3 Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.

7.4 Nitric Acid, conc.: Distilled reagent grade or equivalent to spectrograde quality.

7.5 Acetic Acid, Glacial: ACS reagent grade.

7.5.1 Acetic Acid, 10% (v/v): Dilute 10 mL glacial acetic acid to 100 mL with deionized distilled water.

7.6 Ammonium Hydroxide, 10% (v/v): Dilute 10 mL conc ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with deionized distilled water.

7.7 Hydrogen Peroxide, 30%: ACS reagent grade.

7.8 Potassium Dichromate Standard Solution: Dissolve 2.8285 grams of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in deionized distilled water and dilute to 1 liter. 1 mL = 1 mg Cr (1000 mg/L)

7.9 Trivalent Chromium Working Stock Solution: To 50 mL of the potassium dichromate standard solution (7.8) add 1 mL of 30% H_2O_2 (7.7) and 1 mL conc. HNO_3 (7.4) and dilute to 100 mL with deionized distilled water 1 mL = 0.5 mg Cr^{3+}. Prepare fresh monthly or as needed.

8. Calibration

8.1 At the time of analysis prepare a blank and a series of at least four calibration standards from the Cr^{3+} working stock (7.9) that will adequately bracket the sample. The normal working range covers a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard 1 mL 30% H_2O_2 (7.7), 5 mL CONC HNO_3 (7.4), and 1 mL calcium nitrate solution (7.3) for each 100 mL of prepared solution before diluting to final volume. These calibration standard should be prepared fresh weekly or as needed.

8.2 The listed instrumental conditions (5.1 and the stated calibration concentration range are for a Perkin-Elmer HGA-2100 based on the use of a 20µL injection, continous flow purge gas and non-pyrolytic graphite. The use of simultaneous background correction is required for both calibration and sample analysis.

9. Procedure

9.1 Transfer a 50 mL portion of the filtered sample to a 100mL Griffin beaker and adjust to pH 3.5±0.3 by adding 10% acetic acid dropwise. Record the volume of acid added and adjust the final result to account for the dilution.

Note: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to < 3, 10% NH_4OH (7.6) should be used to raise the pH to above 3.

9.2 Pipet a 10 mL aliquot of the adjusted sample into a centrifuge tube (6.1.2). Add 100µL of the lead nitrate solution (7.1), stopper the tube, mix the sample and allow to stand for 3 min

9.3 After the formation of lead chromate, retain the Cr^{3+} complex in solution by addition of 0.5 mL glacial acetic acid (7.5). Stopper and mix.

9.4 To provide adequate lead sulfate for coprecipitation add 100 mL ammonium sulfate solution (7.2), stopper and mix.

9.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2000 rpm in small increments over a period of 5 min. Centrifuge the sample at 2000 rpm for 10 min.

Note 2: The speed of the centrifuge must be increased slowly to insure complete coprecipitation.

9.6 After centrifuging remove the tube and draw off the supernata using the apparatus detailed in Figure 1. As the pasteur pipet is lowered into the tube the supernate is sucked into the filtering flask. With care the supernate can be withdrawn to within approximately 0.1 mL above the precipitate.

9.7 To the remaining precipitate add 0.5 mL conc HNO_3 (7.4), 100µL 30% H_2O_2 (7.7) and 100µL calcium nitrate solution (7.3). Stopper the tube and mix using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10mL, mix and analyze in the same manner as the calibration standard (8.2).

9.8 For the general furnace procedure and calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

10. Verification

10.1 For every sample matrix analyzed verification is necessary to determine that neither a reducing condition nor a chemical interference affecting precipitation is present. This

must be accomplished by analyzing a second 10mL aliquot of the pH adjusted filtrate (9.1) spiked with Cr^{6+} (7.8). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be of less than 30µg Cr^{6+}/L. To verify the absence of an interference the spike recovery should be between 85% and 115%.

10.2 If the addition of the spike extends the concentration beyond the range of the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

10.3 If the verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

11. Analytical Notes

11.1 Nitrogen should not be used as a purge gas because of possible CN band interference.

11.2 The use of pyrolytic graphite should be avoided when possible. Generally, pyrolytic graphite resulted in a more limited analytical working range and in some situations an enhancement effect.

11.3 Pipet tips have been reported to be a possible source of contamination. (See part 5.2.9 of the Atomic Absorption Methods section of this manual.)

11.4 The method of standard addition should not be required in as much as the Cr^{6+} has been separated from the original sample solution and redissolved in a uniform matrix having an absorption response coincident to the calibration curve.

11.5 Data to be entered into STORET (No. 01032) must be reported as µg/L.

12. Precision and Accuracy

12.1 In a single laboratory (EMSL) using a mixed industrial-domestic waste effluent containing 22 µg Cr^{6+}/L and spiked with a concentration of 50 µg Cr^{6+}/L the standard deviations were ± 1.0 and ± 2.7, respectively with a spike recovery of 94%

12.2 Recoveries of a 40 µg Cr^{6+}/L spike in diluted tannery and plating waste effluents were 96% and 93%, respectively.

12.3 Using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 50 µg Cr^{6+}/L the standard deviations were ± 0.7, ±0.6, and ±0.6, respectively. Spike recovery at all three levels was 102%.

12.4 A 1000 µg Cr^{3+}/L standard solution analyzed by this method yielded a result of 8 µg Cr^{6+}/L with a relative standard deviation of 19%.

12.5 The data from 5 µg Cr^{6+}/L tap water spike was used to calculate method detection limit (MDL) with 99% confidence as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, *Environmental Science and Technology*, Vol. 15, Number 12, page 1426, December 1981. The calculated MDL for Cincinnati drinking water is 2.3 µg/L.

APPENDIX D

ION CHROMATOGRAPHIC METHOD FOR THE SPECIATION AND ANALYSIS OF HEXAVALENT CHROMIUM OF AMBIENT ATMOSPHERIC LEVELS

STATE OF CALIFORNIA
AIR RESOURCES BOARD

Proposed Method for the Speciation and Analysis of Hexavalent Chromium at Ambient Atmospheric Levels

Ion Chromatographic Separation, Chromophoric Complexation, Spectrophotometry

1. SCOPE

This document describes the determination of chromium (VI) on membrane filters after sampling ambient air. The method has been tailored to concentrations that would be expected in ambient air. The method is not expected to have significant interferences. While the method is adequately sensitive for ambient air determinations, it has the potential for further significant improvements in sensitivity.

2. SUMMARY OF METHOD

A low volume air sampler capable of sampling at a constant rate of 13-15 liters per minute for at least 24 hours is fitted with a 37 mm Gelman VM-1 (PVC) membrane filter. After sampling, the filter is placed in a container with 10 mL of chromatographic eluent and the hexavalent chromium is extracted using ultrasonication.

The resultant solution is analyzed using an ion chromatographic technique utilizing a separator column normally used for transition metals analysis. The nearly neutral pH of the eluent system ensures that the Cr^{+6} is stabilized. Following chromatographic separation, the Cr^{+6} is reacted with a chromophoric reagent and measured spectrophotometrically at 520 nm.

3. LIMITATIONS AND INTERFERENCES

No significant interferences are expected with this method. Trivalent chromium is separated during the chromatography step.

4. APPARATUS

4.1 Dionex single channel Ion Chromatograph, P/N 37029

4.2 Dionex HPIC-CG5 Cation Guard Column, P/N 37028

4.3 Dionex HPIC-CS5 Cation Separator Column, P/N 37030

4.4 Dionex Reagent Delivery Module (RDM), P/N 35354

4.5 Dionex Membrane Reactor, P/N 35354

4.6 Dionex Visible Detector (VSM), P/N 37044

5. REAGENTS

5.1 2,6-pyridinedicarboxylic acid (PDCA)

5.2 disodium hydrogen phosphate heptahydrate

5.3 sodium iodide

5.4 ammonium acetate

5.5 lithium hydroxide monohydrate

5.6 1,5-diphenylcarbohydrazide (DPC)

5.7 methanol, HPLC Grade

5.8 sulfuric acid, 96%, spectrophotometric grade

5.9 deionized water, 18 M-ohm

5.10 Eluent Stock: Prepare by dissolving the following reagents in 18 M-ohm deionized water. PDCA is slow to dissolve, and heating the solution before addition of the remaining reagents may be used to increase the rate of dissolution.

20.0 mM	(3.34 g/L)	pyridinedicarboxylic acid (PDCA)
20.0 mM	(5.36 g/L)	disodium hydrogen phosphate
100.0 mM	(15.0 g/L)	sodium iodide
500.0 mM	(38.5 g/L)	ammonium acetate
28.0 mM	(1.10 g/L)	lithium hydroxide

5.11 Eluent: Prepare by diluting 100 mL of the eluent stock to 1 L with 18 M-ohm degassed deionized water. The pH of the diluted eluent should be between 6.70 and 6.80.

5.12 Post Column Reagent: Prepare by dissolving 0.49 g of 1,5-diphenylcarbohydrazide (DPC) in 100 mL of methanol. Add to about 500 mL of degassed deionized water containing 25 mL of concentrated sulfuric acid. Dilute to 1 L with degassed deionized water.

6. INSTRUMENT OPERATION

6.1 Assemble the accessories according to the manufacturer's instructions in the individual component manuals.

6.2 Install a 250 µL sample loop on the injection valve.

6.3 Conditions:

Sample Size:	250 µL
Columns:	HPIC-CG5, Cation Guard Column HPIC-CS5, Cation Separator Column
Eluent Flow Rate:	1.0 mL/min
Post Column Reagent Flow Rate:	0.5 mL/min
Detection:	VIS at 520 nm - Filter #5 on wheel

6.4 Establish the recommended eluent and post column reactor flow rates: 1.0 mL/min for the eluent and 0.5 mL/min for the post column reaction reagent are suggested.

6.5 Turn pumps on.

6.6 Set the detector range on 0.005 AU (most sensitive)

7. INSTRUMENT CALIBRATION

7.1 Inject a series of Cr^{+6} standards diluted in eluent reagent in the range of 5 to 50 µg/L.

7.2 Determine the least squares fit. The calibration data should result in a correlation coefficient of 0.995 or better.

7.3 Run a check standard at least every tenth sample.

8. SAMPLE ANALYSIS

8.1 Place the filter in a 100 mL graduated beaker; add 50 mL of eluent, cover with Parafilm.

8.2 Sonicate without heat for 15 minutes.

8.3 Check the pH to ensure that it is 6.8-6.9.

8.4 The resulting solution is now ready for analysis.

8.5 Print out the analysis results with the identifying laboratory identification number. Record results and calculations in the laboratory notebook. Record the calculated concentration in

nanograms/M^3 in the laboratory data sheet. The concentration may be calculated as follows:

$$\text{Chromium}^{+6},\ ng/M^3 = \frac{\text{Concentration Found, ng/mL} \times \text{Dilution Factor}}{\text{Air Volume Sampled, } M^3}$$

9. METHOD EVALUATION

To be performed.

APPENDIX E

ION CHROMATOGRAPHIC METHOD FOR THE SPECIATION AND ANALYSIS OF HEXAVALENT CHROMIUM AT AMBIENT ATMOSPHERIC LEVELS WITH SAMPLE PRECONCENTRATION

APPENDIX E
HEXAVALENT CHROMIUM ANALYSIS USING ION CHROMATOGRAPHY
Preconcentration Technique

Reagent Preparation

Eluent Stock: Prepare by dissolving the following reagents in deionized water. PDCA is slow to dissolve, and heating the solution before adding the remaining reagents may be necessary.

Pyridinedycarboxylic acid (PDCA)	3.34 g/L	20.0 mM
Disodium hydrogen phosphate	5.36 g/L	20.0 mM
Sodium iodide	15.0 g/L	100.0 mM
Ammonium acetate	38.5 g/L	500.0 mM
Lithium hydroxide	1.10 g/L	28.0 mM

Eluent: Dilute 100 ml of Eluent Stock to 1 L with deionized water. The pH of the diluted eluent should be between 6.70 and 6.80.

Post Column Reagent: Dissolve 0.49 g of 1,5-diphenylcarbohydrazide (DPC) in 100 ml of methanol. Add to about 500 ml of degassed deionized water containing 25 ml of concentrated sulfuric acid. Dilute to 1 L with degassed deionized water.

Procedure

1. Fill post column reagent reservoir with post column reagent. Degas using helium by bubbling helium through reagent for ten minutes. At the end of the ten-minute period remove helium tube and cover reagent reservoir.

2. Fill eluent container with eluent. Place container in stand on side of ion chromatograph. Open valve on eluent container to allow eluent flow to pump.

3. Turn on eluent pump.

4. Turn on ion chromatograph power switch.

5. Open compressed air cylinder valve.

6. Measure eluent flow at outlet line to waste container using a 5 ml graduated cylinder and stopwatch. Flow should be 0.8 ml/minute. If not, adjust using dial on pump.

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7. Turn on post column reagent pump. Measure flow at waste outlet line, again using a 5 ml graduated cylinder and stopwatch. Flow should not be 1.2 ml/minute. If not, adjust flow on post column reagent pump using flow control dial.

8. Turn on detector power using switch at read of instrument. Set filter wheel to #4 (520 nm wavelength setting). Allow detector sufficient time to warm up.

9. Turn on recorder. Adjust baseline zero setting.

10. Place sample inlet tube into a beaker containing deionized water.

11. Set valve switch on chromatograph to "Inject."

12. Turn on sample pump and pump deionized water through side loop for a few minutes. Turn off sample pump.

13. Place sample in small plastic cup. Place sample inlet tube into plastic cup.

14. Turn on sample pump and switch valve on chromatograph to "Load" simultaneously.

15. Allow sample to be pumped into inlet tube. When almost dry, fill plastic cup with deionized water using a squirt bottle. Do not allow sample line to draw in air. Continue pumping in deionized water until total sample inlet time is ten minutes or sample has been completely flashed through the tubing system to the concentrator column.

16. When sample and deionized water flush have been pumped into system, turn off sample pump and switch valve on chromatograph to "Inject." This will begin to pump eluent through the concentrator column and through the system column into the detector.

17. Following elution of peaks, turn on the sample pump and pump deionized water through the side loop for two minutes. The next sample can now be run beginning at Step 10.

EXPERIMENTAL CHAMBER TESTS

INTRODUCTION

The chamber reaction studies, which were designed to simulate those ambient conditions to which Cr^{+6} species would be exposed, were conducted in the following overall manner:

1. Eight or more 37 mm membrane filters (Teflon or PVC) were spiked with levels of Cr^{+6} (ranging from 20 ng to 1,000 ng, depending on the test conditions). Initially, this was performed by pipetting known quantities of solutions onto the filter and then drying at room temperature in a vacuum dessicator. Later, the Cr^{+6} spiking was performed by creating an aerosol with an inhaler device and allowing the aerosol to merely deposit without pumping onto the filter surface (Figure 7). The aerosol was created inside a plastic can with a fan inside to disperse the aerosol as much as possible, thereby optimizing the uniformity. Nevertheless, since some inhomogeneity was anticipated, CARB suggested the use of a lithium internal standard in the solution to be aspirated. In this way, the lithium content could be measured, in addition to the Cr^{+6} species, in order to provide a means of monitoring the variability in the Cr^{+6} loadings. A schematic of the aerosol generator is shown in Figure 5.

2. Six of these filters were placed in a sampling manifold containing 37 mm polystyrene filter holders with backup pads.

3. The sampling manifold was located in the environmental chamber. Initially, the chamber was one constructed of plexiglass or other plastic materials wherever possible. A schematic of the initial test chamber design is shown in Figure 6. Later, the design of the chamber was changed (for reasons to be explained in this section) to that of an all-aluminum design. An aluminum "suitcase" approximately 2 feet x 2 feet x 1 foot was fitted for a gas (reactant inlet and for the sampling manifold (Figure 8).

4. During exposure to the various test reactants, a sampling flow of 3 to 5 Lpm was maintained through each filter. A calibrated critical orifice was used to regulate flow through each filter.

5. Pollutants were introduced into the top of the chamber by a variety of means. Ozone was generated by an ozone generator utilizing pure oxygen irradiated by an ultraviolet source. Atmospheres of species such as SO_2, NO_2, Xylene, and benzene were prepared from dilutions of gas cylinder concentrations. Nitric acid (HNO_3) and formaldehyde (HCHO) were generated from permeation devices available from Vici-Metronics (, CA).?? The verification of HNO_3 concentration was performed by sampling in parallel with a nylon filter, desorbing the filter in an

aqueous medium, and performing an ion chromatographic analysis of the resultant nitrate ion. Formaldehyde levels were monitored using hydrogen peroxide impinger samples and subsequent ion chromatographic analysis of the formate ion. A number of other species were evaluated in these tests, and test conditions regarding these potential reactants will be described in detail later in this section.

6. During the test, two filters were removed at each predesignated time interval. For instance, it may have been decided to remove the first two filters after eight hours, two more after 20 hours, and the last two after 40 hours.

7. The filters were then analyzed using CARB Method ADDL006. A portion of the Cr^{+6} extract was saved and analyzed for the lithium content to correct for any variability in the aerosol deposition.

APPENDIX F

ENTROPY TRIP REPORT:
FIELD SAMPLING FOR DETERMINING THE
FATE OF HEXAVALENT CHROMIUM IN THE ATMOSPHERIC

DRAFT

TRIP REPORT:

FIELD SAMPLING FOR DETERMINING THE FATE OF HEXAVALENT CHROMIUM IN THE ATMOSPHERE

CARB Contract No. A-6-096-32

Prepared by:

Scott C. Steinsberger, Ph.D.
CEM/Engineering Division
Entropy Environmentalists, Inc.
Research Triangle Park, North Carolina

Prepared for:

California Air Resources Board

December 1987

Field Sampling for Determining the Fate of Hexavalent Chromium

Field Reaction Samples

The field reaction samples were collected for two purposes: 1) to determine the conversion rate of hexavalent chromium (Cr^{+6}) during a 12-hour daytime period, 12-hour nighttime period, and 24-hour period, and 2) to determine the ratio of hexavalent to trivalent chromium in the emissions being discharged to the atmosphere from the source (time zero samples). The field reaction samples subjected to the conversion studies were collected on filters directly from the source. In addition to the time zero filter samples collected, impinger samples were also collected directly from the source to provide additional time zero Cr^{+6} data. Two impinger samples were collected per day from each source with one being recovered immediately as a time zero sample. The second impinger sample was taken to the upwind ambient sampling site and ambient air was drawn through the second time zero sample simultaneously with the upwind impinger samples. This was done to determine the stability of the hexavalent chromium already present in the impinger reagent.

Preliminary field reaction samples were collected during the first two days of the field study at each source to determine the proper sampling time at that source for optimum chromium loading on the filters. This was done by collecting four sets of three filter samples each over four different time periods. For the hard chrome plating facility, preliminary sampling periods of 5 seconds, 30 seconds, 5 minutes, and 30 minutes were used, with the 5 second sampling time determined to be optimum. For the refinery cooling tower samples, the preliminary sampling periods were 5 minutes, 30 minutes, 1 hour, and 3 hours, with the 30 minute sampling time determined to be optimum.

Each set of field reaction samples consisted of 12 filters fitted to a filter holder (see Figure F.1). The filters were loaded into the filter holders by hand for the first three runs (Runs CC-02-FR, CC-03-FR, and CC-04-FR). After some concern over potential contamination (which turned out to be high blank values for the filters), filter loading was assigned to one individual wearing latex gloves. Initially, 37 mm PVC filters were used exclusively. Later, for the last three field reaction samples collected from the cooling tower, Teflon filters were substituted for two out of each three PVC filters. To collect samples, the loaded filter holder was inserted in the stack directly into the flow of exhaust gas from the source; and the gas sample was simultaneously pulled through all 12 filters for the optimum sampling period using a fiber vane vacuum pump.

The sample flow rate through all 12 filters combined was determined for each run at the cooling tower using a dry gas meter connected to the outlet of the vacuum pump. The flow rate determination during sampling was not conducted at the hard chrome plating facility due to the short sampling period, but was assumed to be the same as the flow rate at the cooling tower. The flow rate during sampling averaged 35.3 liters per minute (lpm) for the filter holder and, assuming even flow distribution, was 2.9 lpm for each filter. The exact flow rate for the field reaction sampling system was not needed since the ratio of hexvalent to trivalent chromium was to be determined, not the actual emission rate of chromium.

Exposure of the field reaction samples to ambient air for the 12-hour day, 12-hour night and 24-hour periods was conducted at the California Air Resources

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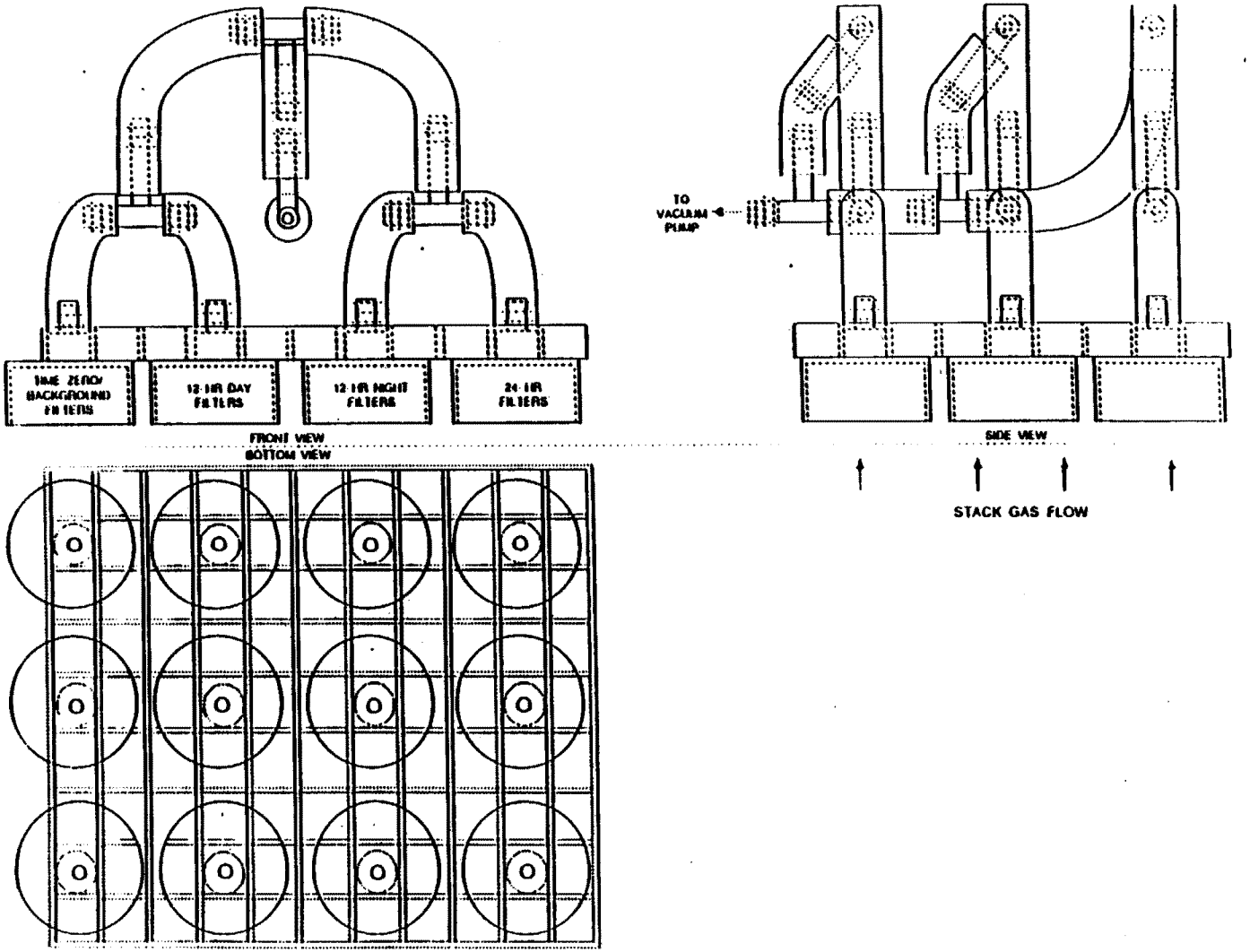

FIGURE F.1 FIELD REACTION FILTER HOLDER

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Board's (ARB) El Monte office. Prior to any ambient exposure, one set of three filters was immediately removed from the filter holder and sealed in the original individual filter holder (see Figure F.1). This set represented both the time zero sample for the ambient study and the time zero sample for the field reaction study. These filters were replaced on the filter holder with new, unexposed filters to determine the background chromium levels over 24-hour ambient exposure period. A positive-displacement vacuum pump was used to pull ambient air through the filters. One set of three filters, designated either 12-hour night or 12-hour day (depending on when the ambient exposure was started), was capped to prevent exposure to ambient air. After 12-hours of exposure to ambient air, the caps were switched to the other set of filters already subjected to a 12-hour exposure. At the end of the 24-hour exposure period, all the filters were removed and sealed.

The flow rate of ambient air through the filters on the holder was determined by measuring the flow at the outlet of the vacuum pump. The flow rate through each filter was intended to reproduce the flow rate used in the original laboratory reaction studies. The flow rate for the filter holder averaged 34.4 lpm and, assuming equal flow through each of the 9 filters, was 3.8 lpm for each filter. Field reaction experiments CC-03-FR and CC-04-FR were run using the XonTech sampling systems with the flow rates set at 1 lpm for each filter. The XonTech channel programmed for the 12-hour day period did not function and no ambient air was pulled through the filters; these 12-hour day period filters were then run concurrently with CC-05-FR.

A total of 14 field reactions were conducted, with 7 field reaction sample sets being collected from each source. A complete sample inventory list for the field reaction study can be found in Appendix A. Efforts to find a source with primarily trivalent chromium emissions in order to conduct additional field reaction studies were not successful.

Ambient Sampling

The ambient sampling portion of the field study involved setting up five ambient sampling stations in the vicinity of each chromium source. The stations were located based on the wind conditions during the afternoon of each test day. Each station consisted of two ambient sampling units (provided by the ARB, El Monte office) for filter samples and one set of three impinger trains (see Figure F.2). Tables F.1 and F.2 summarize the test dates, sampling locations, and sample volumes for the sampling conducted near the chrome plating facilities and at the refinery, respectively.

The Teflon and PVC filter samples were collected using either the newer computer controlled ambient sampling units (XonTechs) or the older units equipped with dry gas meters. The filters were initially loaded into the filter holders with bare hands (Runs CC-02-XT and CC-03-XT). For the remaining runs, the task of filter handling was assigned to one person wearing latex gloves to avoid any potential contamination. (Field blanks and filter blanks collected with bare hands during Run CC-03 did not show any significant contamination). For sample recovery, the filters from the initial runs were placed in nitric acid-rinsed vials; and later the filter samples were placed in the type of plastic petri dishes routinely used by the ARB.

For ambient sampling tests AR-10 through AR-15, three different types of sodium acetate-impregnated filters were used in place of the PVC filters. This was done to evaluate a Cr^{+6} sampling protocol using a filter that would prevent the conversion of the Cr^{+6} collected on the filter.

The impinger sampling trains consisted of a two EPA Reference Method 5 impingers with a Smith-Greenburg tip in the first impinger and a modified Smith-Greenburg tip in the second impinger. The impingers and connecting tubing were prepared prior to the first test run by rinsing with 5% nitric acid followed by deionized water and then a 0.01 M sodium acetate buffer. For sampling, each impinger was charged with 100 ml of the sodium acetate buffer. One train was assembled and immediately recovered for a laboratory proof blank to demonstrate that the sample train components were initially free of contamination.

All three sampling trains at a single location were connected to one fiber vane vacuum pump using a manifold connected to each second impinger outlet. The flow rate for the impinger trains was determined by measuring the flow at the pump outlet using a calibrated dry gas meter. The flow rate was assumed to be equal between the three sampling trains.

Following sampling, impinger samples were recovered into new sodium acetate-rinsed polyethylene storage bottles. Each set of impingers and connecting tubing were rinsed with the sodium acetate buffer and the rinses were added to the appropriate storage bottle. A 5% nitric acid rinse of the impingers and connecting tubing was also performed to remove any insoluble chromium. Initially, the nitric rinses were saved for analysis to determine the total chromium collected; however later rinses were discarded due to a high reagent blank level. Consequently, the impinger samples were used for hexavalent chromium determination only, with the corresponding filter samples providing the total chromium ambient concentration at each sampling location. Deionized water and sodium acetate buffer rinses of the impingers and connecting tubing were performed each day prior to charging the impingers with the sodium acetate reagent.

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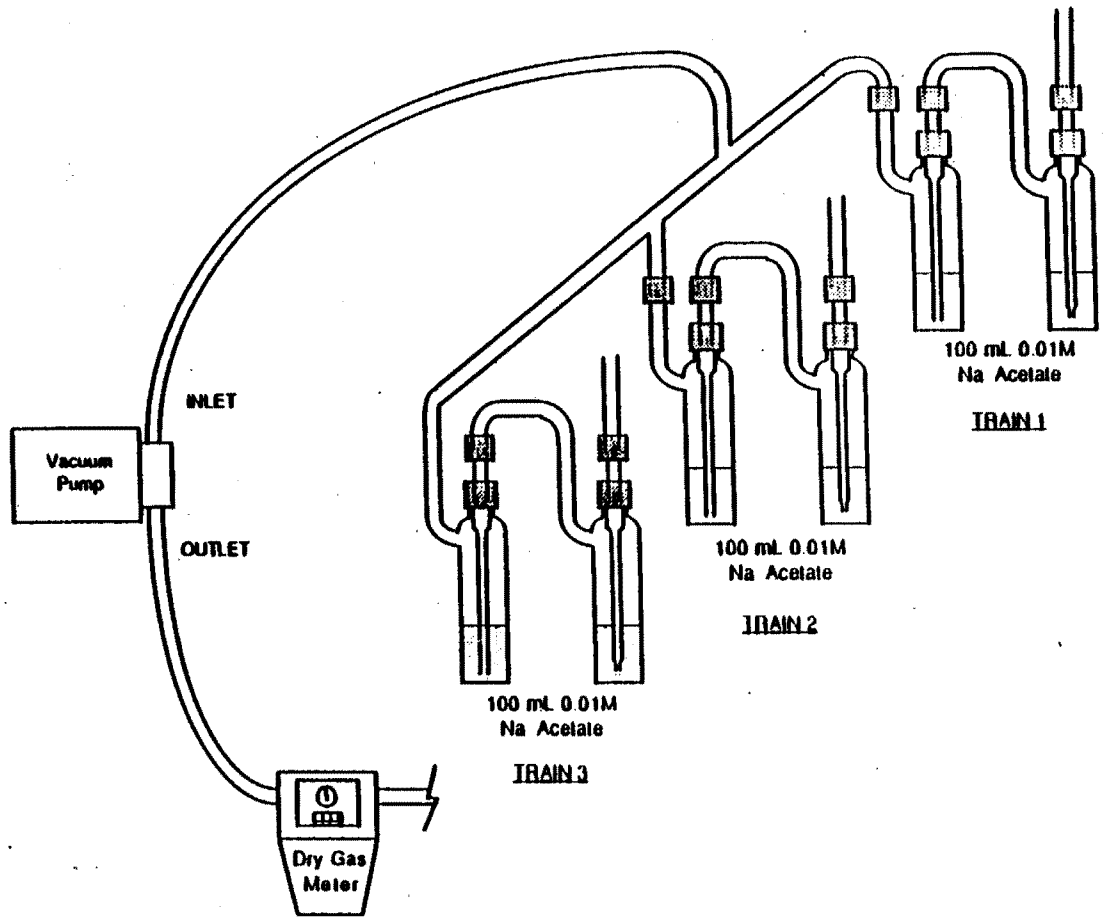

FIGURE F.2 AMBIENT SAMPLING STATION IMPINGER TRAINS

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Table F.1. SUMMARY OF AMBIENT SAMPLING DATA FOR CHROME CRANKSHAFT

Date	Location	Sample Volume (M^3) Teflon	PVC	Impinger	T_{s1}[1] (min.)
10/21	1. 0.3 km NE of CC	4.955		5.95	ND[2]
10/22	0. Upwind	4.668	4.641	7.35	NA[3]
10/22	1. 0.3 km NE of CC	5.575	7.010		11.3
10/23	0. Upwind	3.998	3.974	4.10	NA
10/23	1. 0.3 km NE of CC	3.217	4.548	8.20	2.8
10/23	2. 0.5 km N of CC			4.80	4.7
10/23	3. 0.8 km N of CC	2.462	2.447	5.00	7.5
10/23	4. 0.5 km NNW of CC	5.348	5.043	6.00	4.7
10/26	0. Upwind	3.404	3.309	3.40	NA
10/26	1. 0.3 km NE of CC	4.293	2.270	5.26	1.9
10/26	2. 0.8 km ENE of CC	4.117	4.088	5.41	5.0
10/26	3. 0.6 km E of CC	5.346	5.260	5.65	3.8
10/26	4. 0.5 km N of CC	4.632		5.46	3.1
10/27	0. Upwind	3.999	3.972	4.04	NA
10/27	1. 0.3 km NE of CC	4.316	4.539	6.11	0.9
10/27	2. 0.8 km ENE of CC	5.349	5.257	6.13	2.5
10/27	3. 0.6 km E of CC	5.073	5.112	5.85	1.9
10/27	4. 0.5 km N of CC	5.013		6.19	1.6
10/28	0. Upwind	4.775	4.743	4.90	NA
10/28	1. 0.3 km NE of CC	3.444	3.585	4.30	1.4
10/28	2. 0.8 km ENE of CC	6.459	6.352	6.60	3.8
10/28	3. 0.6 km E of CC	6.336	6.386	6.80	2.8
10/28	4. 0.5 km N of CC	5.610		6.80	2.3

[1] T_{s1} = Calculated reaction time from source to sample location based on mean wind speed for the predominate wind direction.

[2] ND = No Data

[3] NA = Not Applicable

Table F.2. SUMMARY OF AMBIENT SAMPLING DATA FOR ARCO REFINERY

Date	Location	Sample Volume (M^3) Teflon	PVC	Impinger	T_{s1}[1] (min.)
10/29	2, 0.4 km ESE of CT 9	3.180		3.26	ND[2]
10/30	0, Upwind	4.184	4.352[3]	5.16	NA[4]
10/30	1, 0.25 km ENE of CT 9	5.072	5.117[3]	5.44	1.9
10/30	2, 0.4 km SE of CT 9			5.16	3.0
10/30	3, 0.4 km SSE of CT 9	5.178	5.144[3]	5.28	3.0
11/02	0, Upwind	4.365	4.542[3]	5.21	NA
11/02	1, 0.25 km ENE of CT 9	5.713	5.772[3]	4.60	4.7
11/02	2, 0.4 km SE of CT 9	2.436	4.005[3]	2.60	7.5
11/02	3, 0.4 km SSE of CT 9	5.333	5.292[3]	5.44	7.5
11/02	4, 1.0 km ESE of CT 9	2.220		6.04	18.8
11/03	0, Upwind	5.319	5.529[5]	7.44	NA
11/03	1, 0.25 km ENE of CT 9	7.616	7.678[5]	8.16	1.9
11/03	2, 0.4 km SE of CT 9	5.819	5.323[5]	7.02[6]	3.0
11/03	3, 0.4 km NNE of CT 9	6.664	6.630[5]	7.96	3.0
11/03	4, 1.0 km ESE of CT 9	3.108		7.17	7.5
11/04	0, Upwind	5.999	5.773[5]	8.29	NA
11/04	1, 0.25 km ENE of CT 9	7.615	7.679[5]	9.46	3.1
11/04	2, 0.4 km SE of CT 9	6.066	5.525[5]	6.53	5.0
11/04	3, 0.4 km NNE of CT 9	6.488	6.441[5]	7.37	5.0
11/04	4, 1.0 km ESE of CT 9	2.991		7.54	12.5
11/05	0, 0.6 km WSW of CT 9	5.549	5.773[5]	8.29	4.5
11/05	1, 0.25 km ENE of CT 9	6.239	6.290[5]	6.26	1.9
11/05	2, 0.6 km NNW of CT 9	3.785	4.006[5]	4.98	4.5
11/05	3, 0.4 km NNE of CT 9	6.625	6.588[5]	6.69	3.0
11/05	4, 1.0 km ESE of CT 9	2.649		7.20	7.5
11/06	0, Upwind	4.364	4.614[7]	4.91	NA
11/06	1, 0.25 km ENE of CT 9	7.474	7.548[7]	7.25	1.3
11/06	2, 0.4 km SE of CT 9	5.888	5.937[7]	6.14	2.1
11/06	3, 0.6 km NNE of CT 9[8]	5.485	5.483[7]	7.17	3.2
11/06	4, 1.0 km ESE of CT 9	2.200		6.51	5.4

[1] T_{s1} = Calculated reaction time from source to sample location based on mean wind speed for the predominate wind direction.
[2] ND = No Data
[3] NA = Not Applicable
[4] First batch of sodium acetate-impregnated filters
[5] Second batch of sodium acetate-impregnated filters
[6] Maximum sample volume, Actual may be less due to loss of power
[7] Third batch of sodium acetate-impregnated filters
[8] At this location 13:22 to 15:40 and moved, due to wind shift, to 0.4 km SSE of CT 9 from 15:43 to 18:15

Several impinger train runs were selected to determine the collection efficiency of the impinger trains. This involved separate recovery and subsequent analysis of each impinger from the selected trains. The trains were selected for the efficiency checks based on which sampling location was thought to have the greatest chromium catch, with two trains typically selected from this location.

Impinger train field blanks were collected at each source. Collection of the field blanks involved preparing a complete impinger train and immediately recovering the train in the normal manner. Field blanks were collected from an impinger train that had been used during the previous days testing and had been subjected to normal handling. They were taken to demonstrate that sample recovery procedures and subsequent rinses were sufficient to prevent any carry over contamination from sampling runs.

Reagent blanks were collected from each 20 liter batch of sodium acetate buffer.

A complete list of all the ambient samples collected, with the corresponding sampling periods, total sampling times, and sample gas volumes, can be found in Appendix B.

Meteorological Data Station

A meteorological data station was set up near each source tested to continuously collect wind speed and wind direction data during the ambient sampling periods. At the hard chrome plating facility, the meteorological data station was located 10 feet off the ground near sampling location 1 (see Figure F.3) for the first run (CC-03). For the last three sampling runs at the plating facility, the meteorological data station was set up on the northwest corner of the facility's roof. The station was relocated to avoid any potential interference from nearby buildings.

At the refinery, the meteorological data station was located 10 feet off the ground, 40 meters east of sampling location 1 (see Figure F.4).

The wind direction, expressed as a percent of time, and the mean wind speed for each wind direction recorded are summarized in Table F.3. Photocopies of the chart recordings from the meteorological data station are presented in Appendix C.

The ambient air quality from 7 a.m. to 6 p.m., as measured by the South Coast Air Quality Management District and published in the Los Angeles Times, are presented in Appendix D.

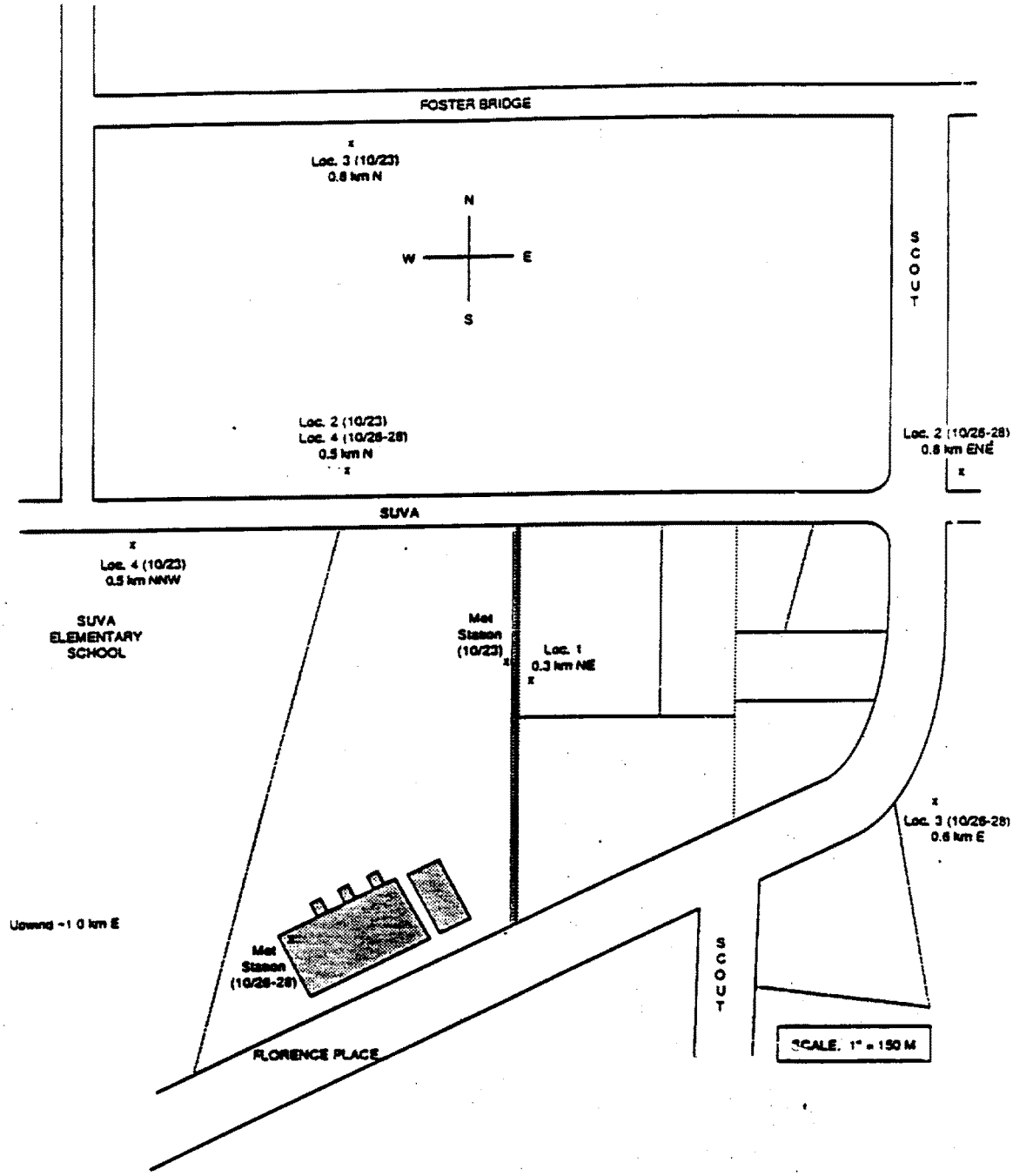

FIGURE F3 PLOT PLAN OF CHROME CRANKSHAFT SHOWING SAMPLING LOCATION

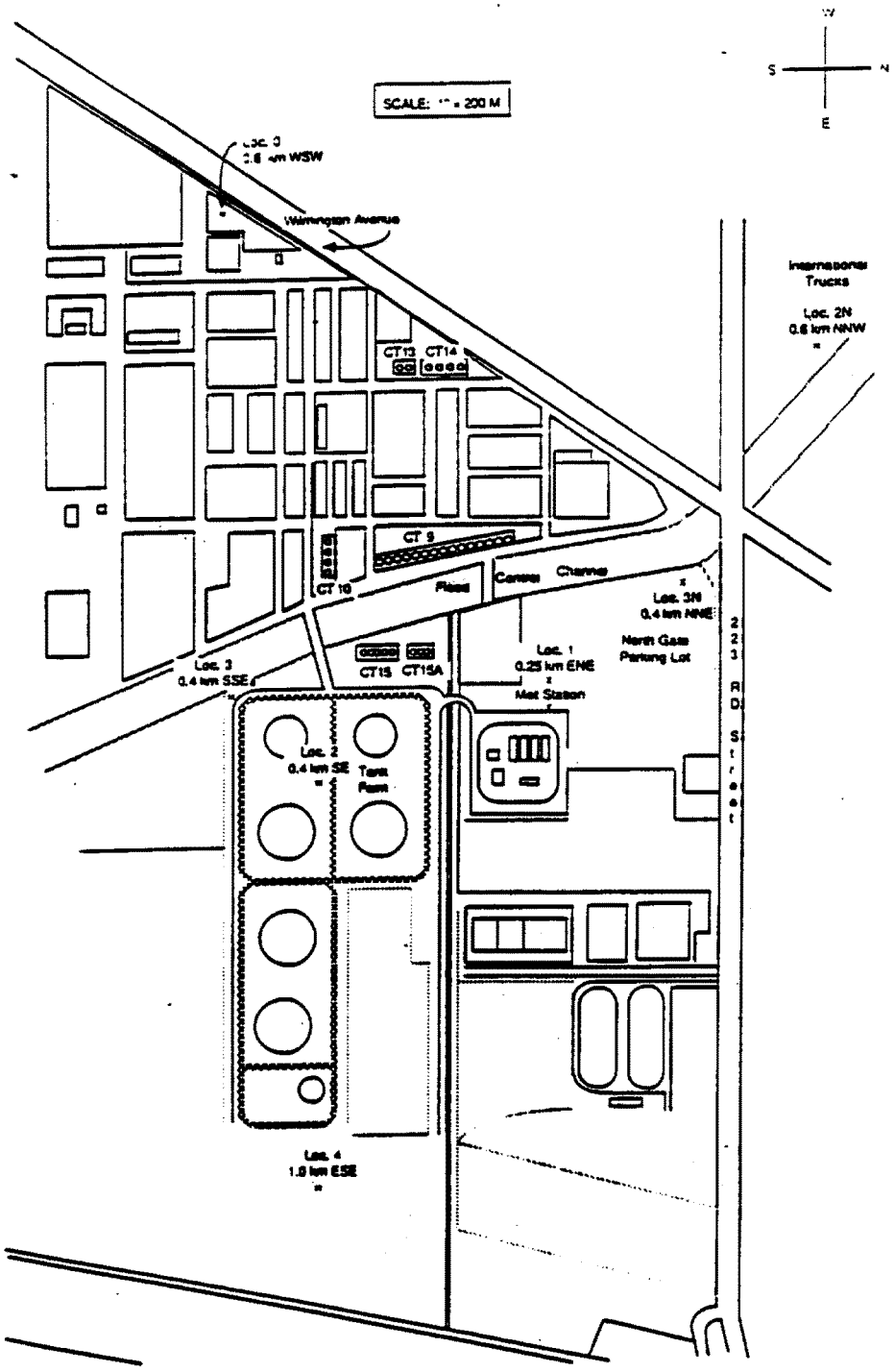

FIGURE F4: PLOT PLAN OF THE ARCO REFINERY SHOWING SAMPLING LOCATIONS (RELATIVE TO CT9).

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Table F.3 WIND DIRECTION AND WIND SPEED DURING AMBIENT SAMPLING

Date	Site	Run	Time Period	Direction	% of Time	Mean Speed
10/23	CC	03	12:00-18:30	SSW	50	4
				E	22	3
				S	20	3
				ESE	4	3
				SE	4	3
10/26	CC	05	12:30-19:00	W	70	6
				SW	15	3
				SE	15	3
10/27	CC	06	12:00-18:00	WSW	56	12
				NNW	13	7
				WNW	10	7
				SW	8	4
				NW	7	6
				W	5	5
				N	1	5
10/28	CC	08	12:00-19:00	W	43	8
				WSW	39	5
				SW	11	4
				WNW	7	5
10/30	AR	10	12:30-18:30	WNW	92	5
				NW	6	5
				W	2	5
11/02	AR	11	12:00-18:00	ESE	41	2
				W	28	5
				S	10	5
				E	8	3
				ENE	7	2
				NE	6	2
11/03	AR	12	12:00-18:00	SE	36	5
				ESE	23	3
				WNW	15	4
				E	15	2
				S	6	2
				N	5	2
11/04	AR	13	12:00-18:30	SE	62	3
				ESE	28	5
				N	7	1
				W	3	1

(continued)

Table F.3 continued

Date	Site	Run	Time Period	Direction	% of Time	Mean Speed
11/05	AR	14	12:00-17:30	SE	64	5
				NNE	29	4
				N	5	3
				E	3	3
11/06	AR	15	12:00-18:00	W	50	7
				SE	36	7
				E	10	3
				ESE	4	3

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Daily Sampling Locations

The ambient sampling stations were located as follows:

Upwind of the chromium source (Location 0)
Predicted downwind approximately 0.3 km from source
Actual near downwind approximately 0.5 km from source
Actual far downwind approximately 1.0 km from source
Alternate downwind approximately 0.5 km from source

Some variations on this general deployment scheme were used depending on the wind conditions for a particular day and the logistics of locating an ambient sampling station at the desired location. The typical wind pattern was for the wind to shift from the east to the west around midday as the land mass warmed and the wind would come in off of the ocean. The sampling locations were selected once the wind appeared to be coming steadily out of one direction. The decision was usually made by 13:00.

Chrome Plating Facilities - The first full day of testing at the hard chrome plating facilities (see Figure F.3) was on October 23. At the start of the testing, the wind was primarily out of the south as opposed the predicted westerly direction. The upwind sampling location (Location 0) was located approximately 1.0 km east of the source. The predicted downwind sampling location (Location 1) was set up 0.3 km northeast of the source at the same location used two weeks earlier by the ARB. The near and far downwind sampling locations (Loaction 2 and 3) were set up 0.5 km and 0.8 km, respectively, north of the facility with the alternate downwind location (Location 4) being setup 0.5 km to the north northwest of the facility.

For the testing conducted on October 26 through October 28, the wind was primarily out of the west. This allowed the predicted downwind sampling location (Location 1) to become the actual near downwind location. A far downwind location (Location 2) was setup 0.8 km east northeast of the source, being set up as close as possible in a direct line with the near downwind station and the source. The other two locations were setup 0.6 km to the east and 0.5 km to the north of the source (Locations 3 and 4, respectively).

Refinery Cooling Tower - At the refinery (see Figure F.4) for the first full day of testing (October 30), the wind was primarily out of the west northwest. Location 2 was set up as the near downwind location 0.4 km southeast of cooling tower. Locations 1 and 3 were 0.25 km east northeast and 0.4 km south southeast, respectively, of cooling tower 9. A far downwind sampling station was not set up on this day due to limitations in power supplies. The upwind station was located 0.65 km west southwest of cooling tower 9.

On the second day of testing at the refinery (November 2), the wind was initially out of the west but shifted to the east southeast at about 14:30. Sampling locations 1 and 2 and the upwind station were at the same location as on October 30. Location 3 was moved to 0.4 km north

northeast of cooling tower 9 (designated as Location 3N in Figure F.4). A far downwind station was established at 1.0 km east southeast of cooling tower 9.

On November 3, the wind was primarily out of the southeast to east southeast. The wind shifted to the west for the last hour of sampling (17:00 to 18:00). The sampling locations were the same as those used on November 2.

On November 4, the wind was primarily out of the south during most of the test period. Again, the sampling locations were the same as those used on November 2.

On November 5, the wind was primarily out of the southeast. Rain began at 15:30 coinciding with a shift in the wind to out of the north. Sampling Location 2 was set up at the start of the test period 0.6 km north northeast of cooling tower 9 (designated as Location 2N in Figure F.4). All other sampling locations were the same as those used on November 2. Tracer experiments, described below, suggest that cooling tower 9 may have had some impact on the upwind location during this test period. Consequently, location 4 may be considered as the upwind location for this day. However, the impact of some cooling towers due south of Location 4 should also be considered.

On November 6, the wind was initially out of the southeast. At 15:00, the wind changed distinctly and came from the west for the remainder of the test. Initially, the sampling locations were the same as those used on November 2. With the wind shift at 15:00, Location 3N was for the remainder of the test moved back to the original Location 3, used on October 30.

Sulfur Hexafluoride Tracer Experiments

Sulfur hexafluoride (SF_6) was chosen as the compound to conduct tracer experiments at each chromium source. SF_6 is a stable nontoxic gas capable of being detected at sub part-per-billion (ppb) concentrations using a gas chromatograph equipped with an electron capture detector (GC/ECD). The GC/ECD used for the SF_6 tracer experiments was a Hewlett-Packard 5890 equipped with a Porapak Q column. The carrier gas, SF_6 tracer gas, and 100-ppb SF_6 calibration gas were all obtained from a commercial vendor (Scott Specialty Gases, San Bernardino, CA). The output from the GC/ECD was recorded on a strip chart recorder.

Calibration of the GC/ECD was done using the 100-ppb SF_6 calibration gas. A standard curve was established by in-situ dilution of the 100-ppb calibration gas in a gas-tight syringe.

Ambient samples were collected in 250-ml amber low-density polyethylene bottles, each outfitted with screw cap with an integral teflon-lined rubber septa. Samples were collected in the bottles by first repeatedly purging the bottles 30 seconds prior to the sample actual collection time by squeezing and allowing the bottles to refill with ambient air. At the appropriate time the final purge would be made and the bottle sealed with the cap described above.

The SF_6 releases were conducted in-stack at each source. The SF_6 was routed through a rotameter to measure the release flow rate and then flowed through Tygon tubing to the stack for release. At the hard chrome plating facility, the releases were made in stack 4. At the refinery, the releases were made on cooling tower 9 in fan cell 9. The releases were typically 5 minutes in length.

The downwind sampling for SF_6 occurred at one or two minute intervals starting three or four minutes after beginning the release, depending on the wind speed and the distance from the release point. Typically, two of the ambient sampling locations were selected for sampling during each release and five samples were collected at each location. The samples were analyzed on-site immediately after collection with the GC/ECD.

Using the estimated flow rate of the stack receiving the SF_6 and the flow rate of the SF_6 into the stack, an in-stack dilution factor was calculated. The peak concentration at each sampling location was used to calculate the total dilution of the pure SF_6 release gas. The total dilution of SF_6 was divided by the in-stack dilution to calculate the downwind dilution.

A summary of the SF_6 tracer experiments is presented in Table _.4. At the chrome plating facility ground effects were evident presumably caused by neighboring buildings. At the refinery, the in-stack dilution was 20 times higher than at the chrome plating facility even at the maximum release rate of SF_6. As a result, the SF_6 was either not detected or found in trace quantities at only one sampling location (9 ppb at 0.4 km ESE).

For some of the tracer experiments, a Gaussian distribution was seen for the five samples taken at a particular sampling location. An example chromatogram is presented in Figure _.5.

Table F.4. SUMMARY OF SULFUR HEXAFLUORIDE TRACER EXPERIMENTS

Date	Site[1]	Time	Wind Speed and Direction	Location[2]	Peak Conc. (ppb)	Calculated Downwind Dilution
10/26	CC	14:55	SW/WSW 5 mph	0.8 km ENE	ND[3]	------
10/26	CC	14:55	SW/WSW 5 mph	0.5 km N	80	3,364
10/26	CC	16:15	West 7 mph	0.6 km E	ND[3]	------
10/26	CC	16:15	West 7 mph	0.3 km NE	15	16,840
10/27	CC	14:20	W/WSW 15 mph	0.3 km NE	120	2,119
10/27	CC	14:20	W/WSW 15 mph	0.8 km ENE	20	12,870
10/27	CC	15:40	WNW/W 6 mph	0.6 km E	ND[3]	------
10/27	CC	15:40	WNW/W 6 mph	0.5 km N	107	2,361
10/28	CC	13:50	WSW/SW 7 mph	0.3 km NE	25	9,980
10/28	CC	13:50	WSW/SW 7 mph	0.5 km N	trace	------
10/28	CC	15:00	WSW/SW 8 mph	0.8 km ENE	16	14,850
10/28	CC	15:00	WSW/SW 8 mph	0.6 km E	trace	------
10/28	CC	15:55	WSW 9 mph	0.8 km ENE	10	26,260
10/28	CC	15:55	WSW 9 mph	0.3 km NE	500	500
10/30	AR	16:30	WNW 5 mph	0.4 km SSE	ND[3]	------
10/30	AR	16:30	WNW 5 mph	0.4 km ESE	9	1,178
11/03	AR	16:00	SSE 5 mph	0.25 km ENE	trace	------
11/03	AR	16:00	SSE 5 mph	0.4 km NNE	trace	------
11/04	AR	15:10	SSE 2 mph	0.4 km NNE	0.1[4]	100,000
11/04	AR	17:00	SSE 3 mph	0.4 km NNE	0.1[4]	100,000
11/04	AR	17:00	SSE 3 mph	0.65 km WSW	0.1[4]	100,000
11/05	AR	15:00	SSE 5 mph	0.4 km NNE	0.1[4]	100,000
11/05	AR	15:00	SSE 5 mph	0.6 km NW	ND[3]	------
11/06	AR	15:05	W 7 mph	0.4 km NNE	ND[3]	------
11/06	AR	15:05	W 7 mph	0.4 km NE	ND[3]	------

[1] CC = Chrome Crankshaft; AR = ARCO Refinery
[2] Location relative to Chrome Crankshaft or center of cooling tower 9 at ARCO Refinery
[3] ND = Not Detected
[4] Estimated concentration

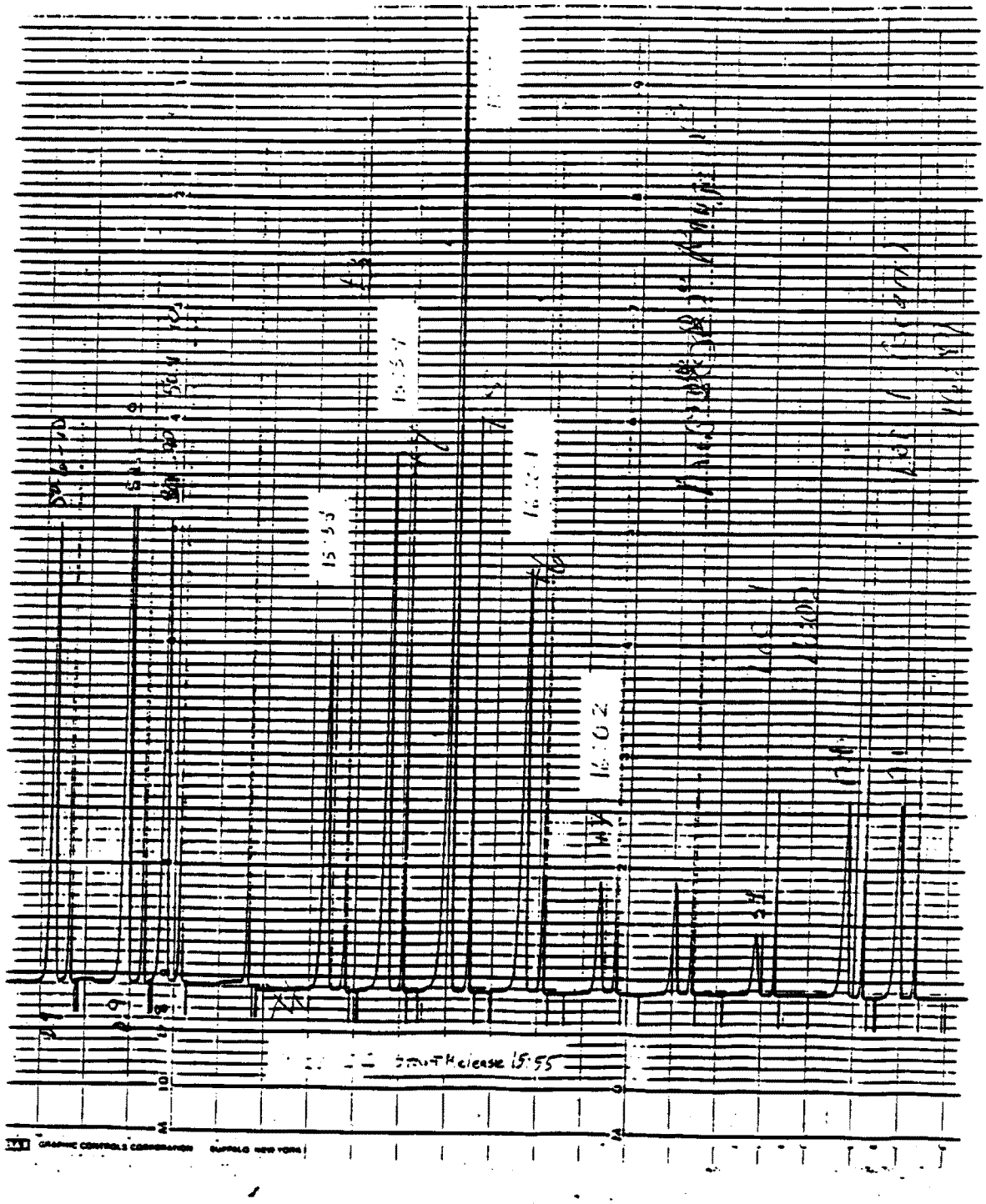


Figure F.5. Example chromatogram showing Gaussian distribution of SF_6

APPENDIX A.

Inventory of Field Reaction Samples

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
10/19	CC 01 FR 01 A	5 Second Exposure - Stack 4	
10/19	CC 01 FR 01 B	5 Second Exposure - Stack 4	
10/19	CC 01 FR 01 C	5 Second Exposure - Stack 4	
10/19	CC 01 FR 02 A	30 Second Exposure - Stack 4	
10/19	CC 01 FR 02 B	30 Second Exposure - Stack 4	
10/19	CC 01 FR 02 C	30 Second Exposure - Stack 4	
10/19	CC 01 FR 03 A	5 Minute Exposure - Stack 4	
10/19	CC 01 FR 03 B	5 Minute Exposure - Stack 4	
10/19	CC 01 FR 03 C	5 Minute Exposure - Stack 4	
10/19	CC 01 FR 04 A	30 Minute Exposure - Stack 4	
10/19	CC 01 FR 04 B	30 Minute Exposure - Stack 4	
10/19	CC 01 FR 04 C	30 Minute Exposure - Stack 4	
10/19	CC 01 FR 00 -	Blank	
10/20	AR 01 FR 01 A	5 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 01 B	5 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 01 C	5 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 02 A	30 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 02 B	30 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 02 C	30 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 03 A	1 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 03 B	1 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 03 C	1 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 04 A	3 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 04 B	3 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 04 C	3 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR BLANK	Blank	
10/22	CC 02 FR 01	Time zero - Instack - Top	
10/22	CC 02 FR 02	Time zero - Instack - Middle	
10/22	CC 02 FR 03	Time zero - Instack - Bottom	
10/22	CC 02 FR 11	12 hour night	
10/22	CC 02 FR 12	12 hour night	
10/22	CC 02 FR 13	12 hour night	
10/22	CC 02 FR 21	12 hour day	
10/22	CC 02 FR 22	12 hour day	
10/22	CC 02 FR 23	12 hour day	
10/22	CC 02 FR 31	24 hour	
10/22	CC 02 FR 32	24 hour	
10/22	CC 02 FR 33	24 hour	
10/22	CC 02 FR 41	24 hour - background	
10/22	CC 02 FR 42	24 hour - background	
10/22	CC 02 FR 43	24 hour - background	
10/26	CC 03 FR 01	Time zero Instack (top filter)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
10/26	CC 03 FR 02	12:00 (mid filter)	
10/26	CC 03 FR 03	10/23 (bottom filter)	
10/26	CC 03 FR 11	12 hour night (top filter)	
10/26	CC 03 FR 12	19:00-7:00 (Middle Filter)	
10/26	CC 03 FR 13	10/24-10/25 (Bottom Filter)	
10/26	CC 03 FR 21	12 hour day (top filter)	
10/26	CC 03 FR 22	9:00-21:00 (Middle Filter)	
10/26	CC 03 FR 23	10/26 (Bottom Filter)	
10/26	CC 03 FR 31	24 hour day/night (top filter)	
10/26	CC 03 FR 32	19:00-19:00 (Middle Filter)	
10/26	CC 03 FR 33	10/24-10/25 (Bottom Filter)	
10/26	CC 03 FR 41	24 hour background (top filter)	
10/26	CC 03 FR 42	19:00-19:00 (Middle Filter)	
10/26	CC 03 FR 43	10/24-10/25 (Bottom Filter)	
10/26	CC 04 FR 01	Time zero Instack (top filter)	
10/26	CC 04 FR 02	12:05 (mid filter)	
10/26	CC 04 FR 03	10/23 (bottom filter)	
10/26	CC 04 FR 11	12 hour night (top filter)	
10/26	CC 04 FR 12	19:00-7:00 (Middle Filter)	
10/26	CC 04 FR 13	10/24-10/25 (Bottom Filter)	
10/26	CC 04 FR 21	12 hour day (top filter)	
10/26	CC 04 FR 22	9:00-21:00 (Middle Filter)	
10/26	CC 04 FR 23	10/26 (Bottom Filter)	
10/26	CC 04 FR 31	24 hour day/night (top filter)	
10/26	CC 04 FR 32	19:00-19:00 (Middle Filter)	
10/26	CC 04 FR 33	10/24-10/25 (Bottom Filter)	
10/26	CC 04 FR 41	24 hour background (top filter)	
10/26	CC 04 FR 42	19:00-19:00 (Middle Filter)	
10/26	CC 04 FR 43	10/24-10/25 (Bottom Filter)	
10/26	CC 05 FR 01	Time zero Instack (top filter)	
10/26	CC 05 FR 02	12:10 (mid filter)	
10/26	CC 05 FR 03	10/23 (bottom filter)	
10/26	CC 05 FR 11	12 hour night (top filter)	
10/26	CC 05 FR 12	21:00-9:00 (Middle Filter)	
10/26	CC 05 FR 13	10/26-10/27 (Bottom Filter)	
10/26	CC 05 FR 21	12 hour day (top filter)	
10/26	CC 05 FR 22	9:00-21:00 (Middle Filter)	
10/26	CC 05 FR 23	10/26 (Bottom Filter)	
10/26	CC 05 FR 31	24 hour day/night (top filter)	
10/26	CC 05 FR 32	9:00-9:00 (Middle Filter)	
10/26	CC 05 FR 33	10/26-10/27 (Bottom Filter)	
10/26	CC 05 FR 41	24 hour background (top filter)	
10/26	CC 05 FR 42	9:00-9:00 (Middle Filter)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
10/26	CC 05 FR 43	10/26-10/27 (Bottom Filter)	
10/27	CC 06 FR 01	Time zero Instack (top filter)	
10/27	CC 06 FR 02	(mid filter)	
10/27	CC 06 FR 03	(bottom filter)	
10/27	CC 06 FR 11	12 hour night (top filter)	
10/27	CC 06 FR 12	21:10-9:00 (Middle Filter)	
10/27	CC 06 FR 13	10/27-10/28 (Bottom Filter)	
10/27	CC 06 FR 21	12 hour day (top filter)	
10/27	CC 06 FR 22	9:30-21:10 (Middle Filter)	
10/27	CC 06 FR 23	10/27-10/27 (Bottom Filter)	
10/27	CC 06 FR 31	24 hour day/night (top filter)	
10/27	CC 06 FR 32	9:30-9:00 (Middle Filter)	
10/27	CC 06 FR 33	10/27-10/28 (Bottom Filter)	
10/27	CC 06 FR 41	24 hour background (top filter)	
10/27	CC 06 FR 42	9:30-9:00 (Middle Filter)	
10/27	CC 06 FR 43	10/27-10/28 (Bottom Filter)	
10/28	CC 07 FR 01	Time zero Instack (top filter)	
10/28	CC 07 FR 02	(mid filter)	
10/28	CC 07 FR 03	(bottom filter)	
10/28	CC 07 FR 11	12 hour night (top filter)	
10/28	CC 07 FR 12	21:00-9:00 (Middle Filter)	
10/28	CC 07 FR 13	10/28-10/29 (Bottom Filter)	
10/28	CC 07 FR 21	12 hour day (top filter)	
10/28	CC 07 FR 22	9:00-21:00 (Middle Filter)	
10/28	CC 07 FR 23	10/28-10/28 (Bottom Filter)	
10/28	CC 07 FR 31	24 hour day/night (top filter)	
10/28	CC 07 FR 32	9:00-9:00 (Middle Filter)	
10/28	CC 07 FR 33	10/28-10/29 (Bottom Filter)	
10/28	CC 07 FR 41	24 hour background (top filter)	
10/28	CC 07 FR 42	9:00-9:00 (Middle Filter)	
10/28	CC 07 FR 43	10/28-10/29 (Bottom Filter)	
10/28	CC 08 FR 01	Time zero Instack (top filter)	
10/28	CC 08 FR 02	(mid filter)	
10/28	CC 08 FR 03	(bottom filter)	
10/28	CC 08 FR 11	12 hour night (top filter)	
10/28	CC 08 FR 12	20:15-9:35 (Middle Filter)	
10/28	CC 08 FR 13	10/29-10/30 (Bottom Filter)	
10/28	CC 08 FR 21	12 hour day (top filter)	
10/28	CC 08 FR 22	9:32-20:15 (Middle Filter)	
10/28	CC 08 FR 23	10/29-10/29 (Bottom Filter)	
10/28	CC 08 FR 31	24 hour day/night (top filter)	
10/28	CC 08 FR 32	(Middle Filter)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
10/28	CC 08 FR 33	(Bottom Filter)	
10/28	CC 08 FR 41	24 hour Background (top filter)	
10/28	CC 08 FR 42	9:32-9:35 (Middle Filter)	
10/28	CC 08 FR 43	10/29-10/30 (Bottom Filter)	
10/28	CC 08 FR B	Blank Lot #5288037	
10/29	AR 09 FR 01	Time zero Instack 60 min (top)	
10/29	AR 09 FR 02	(mid filter)	
10/29	AR 09 FR 03	(bottom filter)	
10/29	AR 09 FR 11	12 hour night (top filter)	
10/29	AR 09 FR 12	20:15-9:35 (Middle Filter)	
10/29	AR 09 FR 13	10/29-10/30 (Bottom Filter)	
10/29	AR 09 FR 21	12 hour day (top filter)	
10/29	AR 09 FR 22	9:40-20:15 (Middle Filter)	
10/29	AR 09 FR 23	10/30-10/30 (Bottom Filter)	
10/29	AR 09 FR 31	24 hour day/night (top filter)	
10/29	AR 09 FR 32	20:15-20:15 (Middle Filter)	
10/29	AR 09 FR 33	10/29-10/30 (Bottom Filter)	
10/29	AR 09 FR 41	24 hour Background (top filter)	
10/29	AR 09 FR 42	20:15-20:15 (Middle Filter)	
10/29	AR 09 FR 43	10/29-10/30 (Bottom Filter)	
10/29	AR 09 FR B	Blank, Lot #8002908	
10/30	AR 10 FR 01	Time zero 30 min Instack (top)	
10/30	AR 10 FR 02	(mid filter)	
10/30	AR 10 FR 03	(bottom filter)	
10/30	AR 10 FR 11	12 hour night (top filter)	
10/30	AR 10 FR 12	21:38-9:01 (Middle Filter)	
10/30	AR 10 FR 13	11/1-11/2 (Bottom Filter)	
10/30	AR 10 FR 21	12 hour day (top filter)	
10/30	AR 10 FR 22	9:03-21:37 (Middle Filter)	
10/30	AR 10 FR 23	11/2-11/2 (Bottom Filter)	
10/30	AR 10 FR 31	24 hour day/night (top filter)	
10/30	AR 10 FR 32	21:38-21:37 (Middle Filter)	
10/30	AR 10 FR 33	11/1-11/2 (Bottom Filter)	
10/30	AR 10 FR 41	24 hour Background (top filter)	
10/30	AR 10 FR 42	21:38-21:37 (Middle Filter)	
10/30	AR 10 FR 43	11/1-11/2 (Bottom Filter)	
10/30	AR 10 FR 71	2 min Instack Time Zero	
10/30	AR 10 FR 72	2 min Instack Time Zero	
10/30	AR 10 FR 73	2 min Instack Time Zero	
10/30	AR 10 FR B	Blank	
11/2	AR 11 FR 01	Time zero 40 min Instack (top)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
11/2	AR 11 FR 02	(mid filter)	
11/2	AR 11 FR 03	(bottom filter)	
11/2	AR 11 FR 11	12 hour night (top filter.)	
11/2	AR 11 FR 12	21:37-8:57 (Middle Filter)	
11/2	AR 11 FR 13	11/2-11/3 (Bottom Filter)	
11/2	AR 11 FR 21	12 hour Day (top filter)	
11/2	AR 11 FR 22	8:57-9:30 (Middle Filter)	
11/2	AR 11 FR 23	11/3-11/3 (Bottom Filter)	
11/2	AR 11 FR 31	24 hour day/night (top filter)	
11/2	AR 11 FR 32	9:38-9:30 (Middle Filter)	
11/2	AR 11 FR 33	11/2-11/3 (Bottom Filter)	
11/2	AR 11 FR 41	24 hour Background (top filter)	
11/2	AR 11 FR 42	9:38-9:30 (Middle Filter)	
11/2	AR 11 FR 43	11/2-11/3 (Bottom Filter)	
11/2	AR 11 FR 71	2 min Instack Time zero	
11/2	AR 11 FR 72	2 min Instack Time zero	
11/2	AR 11 FR 73	2 min Instack Time zero	
11/2	AR 11 FR B	Blank Teflon FR filter 11/02	
11/4	AR 12 FR 01	Expose 30 min - Time zero Instack (top f.)	
11/4	AR 12 FR 02	(mid filter)	
11/4	AR 12 FR 03P	(bottom filter) PVC	
11/4	AR 12 FR 11	12 hour night (30 min Instack exp.) (top f.)	
11/4	AR 12 FR 12	21:30-8:56 (Middle Filter)	
11/4	AR 12 FR 13P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 12 FR 21	12 hour Day (30 min Instack exp.) (top f.)	
11/4	AR 12 FR 22	8:58-21:30 (Middle Filter)	
11/4	AR 12 FR 23P	11/5-11/5 (Bottom Filter) PVC	
11/4	AR 12 FR 31	24 hour day/night (30 min instack exp.) (top f.)	
11/4	AR 12 FR 32	8:58-8:56 (Middle Filter)	
11/4	AR 12 FR 33P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 12 FR 41	24 hour Background (30 min instack exp.) (top f.)	
11/4	AR 12 FR 42	8:58-8:56 (Middle Filter)	
11/4	AR 12 FR 43P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 12 FR BP	Blank PVC Lot #5242027	
11/4	AR 12 FR BT	Blank Teflon Lot #2617	
11/4	AR 13 FR 01	Expose 30 min - Time zero Instack (top filter)	
11/4	AR 13 FR 02	(mid filter)	
11/4	AR 13 FR 03P	(bottom filter) PVC	
11/4	AR 13 FR 11	12 hour night (30 min Instack exp.) (top filter)	
11/4	AR 13 FR 12	21:30-8:56 (Middle Filter)	
11/4	AR 13 FR 13P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 13 FR 21	12 hour Day (30 min Instack exp.) (top filter)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
11/4	AR 13 FR 22	8:58-21:30 (Middle Filter)	
11/4	AR 13 FR 23P	11/5-11/5 (Bottom Filter) PVC	
11/4	AR 13 FR 31	24 hour day/night (30 min instack exp.) (top f.)	
11/4	AR 13 FR 32	8:58-8:56 (Middle Filter)	
11/4	AR 13 FR 33P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 13 FR 41	24 hour Background (30 min instack exp.) (top f.)	
11/4	AR 13 FR 42	8:58-8:56 (Middle Filter)	
11/4	AR 13 FR 43P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 13 FR BP	Blank PVC Lot #5242027	
11/4	AR 13 FR BT	Blank Teflon Lot #2617	
11/5	AR 14 FR 01	Expose 30 min - Time zero Instack (top filter)	
11/5	AR 14 FR 02	(mid filter)	
11/5	AR 14 FR 03P	(bottom filter) PVC	
11/5	AR 14 FR 11	12 hour night (30 min Instack exp.) (top filter)	
11/5	AR 14 FR 12	20:14-9:30 (Middle Filter)	
11/5	AR 14 FR 13P	11/6-11/7 (Bottom Filter) PVC	
11/5	AR 14 FR 21	12 hour Day (30 min Instack exp.) (top filter)	
11/5	AR 14 FR 22	9:31-20:12 (Middle Filter)	
11/5	AR 14 FR 23P	11/6-11/6 (Bottom Filter) PVC	
11/5	AR 14 FR 31	24 hour day/night (30 min instack exp.) (top f.)	
11/5	AR 14 FR 32	9:31-9:30 (Middle Filter)	
11/5	AR 14 FR 33P	11/6-11/7 (Bottom Filter) PVC	
11/5	AR 14 FR 41	24 hour Background (30 min instack exp.) (top f.)	
11/5	AR 14 FR 42	9:31-9:30 (Middle Filter)	
11/5	AR 14 FR 43P	11/6-11/7 (Bottom Filter) PVC	
11/5	AR 14 FR 71	Instack 2 min sampling	
11/5	AR 14 FR 72	Instack 2 min sampling	
11/5	AR 14 FR 73P	Instack 2 min sampling	
11/5	AR 14 FR BP	Blank PVC Lot #5242027	
11/5	AR 14 FR BT	Blank Teflon Lot #2617	
11/6	AR 15 FR 71	Instack 2 min sampling	
11/6	AR 15 FR 72	Instack 2 min sampling	
11/6	AR 15 FR 73P	Instack 2 min sampling	

APPENDIX B.

Inventory of Ambient Samples

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/21	CC 01 IS LPB	Impinger Train Lab Proof Blank			
10/21	CC 01 IS 01 A	Loc. 1. C train 1st Imp.	13:45-18:00	255	6.0
10/21	CC 01 IS 01 B	Loc. 1. C train 2nd Imp.			
10/21	CC 01 IS 02 A	Loc. 1. B train 1st Imp.	13:45-18:00	255	6.0
10/21	CC 01 IS 02 B	Loc. 1. B train 2nd Imp.			
10/21	CC 01 IS 03 A	Loc. 1. A train 1st Imp.			
10/21	CC 01 IS 03 B	Loc. 1. A train 2nd Imp.	13:45-18:00	255	6.0
10/21	CC 01 NR 04	A,B,C Train Nitric Rinse			
10/21	CC 01 XT 01	Teflon Filter Sample	13:45-18:00	255	4.955
10/22	CC 02 IS 01	Upwind Impinger Train 1	11:30-15:00	210	7.4
10/22	CC 02 IS 02	Upwind Impinger Train 2	11:30-15:00	210	7.4
10/22	CC 02 IS 11	In-stack 3 seconds			0.0035
10/22	CC 02 IS 12	In-stack 10 seconds			0.0116
10/22	CC 02 IS 13	In-stack 30 seconds			0.035
10/22	CC 02 NR 03	Upwind IS 01 + 02 Nitric Rinse			
10/22	CC 02 NR 14	3 + 10 second IS Nitric rinse			
10/22	CC 02 NR 15	30 second IS Nitric rinse			
10/22	CC 02 XT 01	Upwind TEFLON Filter	11:30-15:00	210	4.668
10/22	CC 02 XT 02	Upwind PVC Filter	11:30-15:00	210	4.641
10/22	CC 02 XT 21	Loc. 1 Teflon - Lot 2089	13:18-18:30	312	5.575
10/22	CC 02 XT 22	Loc. 1 PVC - Lot 5288037	12:24-18:30	366	7.010
10/23	CC 03 IS 01	Upwind Impinger Train 1	12:05-15:05	180	4.1
10/23	CC 03 IS 02	Upwind Impinger Train 2	12:05-15:05	180	4.1
10/23	CC 03 IS 11	Pred. Downwind (Loc. 1) Train 1	14:35-18:35	240	8.2
10/23	CC 03 IS 12	Pred. Downwind (Loc. 1) Train 2	14:35-18:35	240	8.2
10/23	CC 03 IS 21	Near Downwind (Loc. 2) Train 1	14:40-18:50	211	4.8
10/23	CC 03 IS 61	Stack 10 sec. time zero Nitric Rinse			
10/23	CC 03 IS 61	Stack 10 sec. time zero			0.0116
10/23	CC 03 IS 62	10 sec stack sample + 3 hr amb.	12:05-15:05	180	4.1
10/23	CC 03 IS 22	Near Downwind (Loc. 2) Train 2	14:40-18:50	211	4.8
10/23	CC 03 IS 23	Near Downwind (Loc. 2) Train 3	14:40-18:50	211	4.8
10/23	CC 03 IS 31	Far Downwind (Loc. 3) Train 1	14:35-18:30	220	5.0
10/23	CC 03 IS 32	Far Downwind (Loc. 3) Train 2	14:35-18:30	220	5.0
10/23	CC 03 IS 33	Far Downwind (Loc. 3) Train 3	14:35-18:30	220	5.0
10/23	CC 03 IS 41	Alt. Downwind (Loc. 4) Trains 1	14:30-18:55	265	6.0
10/23	CC 03 IS 42	Alt. Downwind (Loc. 4) Trains 2	14:30-18:55	265	6.0
10/23	CC 03 IS 43	Alt. Downwind (Loc. 4) Trains 3	14:30-18:55	265	6.0
10/23	CC 03 NR 03	Upwind Train 1 + 2 Nitric Rinse			
10/23	CC 03 NR 62	Time Zero + 3 hr amb. Nitric Rinse			
10/23	CC 03 NR 13	Loc. 1 Train 1 + 2 Nitric Rinse			
10/23	CC 03 NR 24	Loc. 2 Trains 1,2, & 3 Nitric Rinse			
10/23	CC 03 NR 34	Loc. 3 Trains 1,2, & 3 Nitric Rinse			
10/23	CC 03 NR 44	Loc. 4 Trains 1,2, & 3 Nitric Rinse			

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM · Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/23	CC 03 XT 01	Upwind Teflon Filter	12:05-15:05	180	3.998
10/23	CC 03 XT 02	Upwind PVC Filter	12:05-15:05	180	3.974
10/23	CC 03 XT 11	Pred. Downwind (Loc. 1) Teflon Filter	15:30-18:30	180	3.217
10/23	CC 03 XT 12	Pred. Downwind (Loc. 1) PVC Filter	14:35-18:35	240	4.584
10/23	CC 03 XT 21	Near Downwind (Loc. 2) Teflon Filter	No Flow		
10/23	CC 03 XT 22	Near Downwind (Loc. 2) PVC Filter	No Flow		
10/23	CC 03 XT 31	Far Downwind (Loc. 3) Teflon Filter	16:15-18:30	135	2.462
10/23	CC 03 XT 32	Far Downwind (Loc. 3) PVC Filter	16:15-18:30	135	2.447
10/23	CC 03 XT 41	Alt. Downwind (Loc. 4) Teflon Filter	14:55-18:55	240	5.348
10/23	CC 03 XT 42	Alt. Downwind (Loc. 4) PVC Filter	14:50-18:50	230	5.043
10/23	CC 03 XT FB 01	XT Teflon Field Blank Ch 1 Loc. 1			
10/23	CC 03 XT FB 02	XT PVC Field Blank Ch 2 Loc. 1			
10/23	CC 03 XT RB 01	Teflon Filter Blank			
10/23	CC 03 XT RB 02	PVC Filter Blank			
10/26	CC 04 IS 11	Loc. 1 48 imp. sample	21:00-21:00	2880	54.015
10/26	CC 04 NR 11	Nitric Rinse Loc. 1 48 imp. sample	11/23-11/25		
10/26	CC 04 XT 11	Loc. 1 48 hours Teflon	21:00-21:00	2880	51.494
10/26	CC 04 XT 12	Loc. 1 48 hours PVC	11/23-11/25	2880	54.551
10/26	CC 05 IS 01	Upwind samp. loc. Train 1	12:48-15:18	150	3.4
10/26	CC 05 IS 02	Upwind samp. loc. Train 2	12:48-15:18	150	3.4
10/26	CC 05 IS 11	Pred. Sam.Loc.(Loc. 1) Train 1	13:50-17:50	240	5.3
10/26	CC 05 IS 12	Pred. Sam.Loc.(Loc. 1) Train 2	13:50-17:50	240	5.3
10/26	CC 05 IS 13	Pred. Sam.Loc.(Loc. 1) Train 3	13:50-17:50	240	5.3
10/26	CC 05 IS 21	Far Downwind (Loc. 2) Train 1	13:45-17:50	240	5.4
10/26	CC 05 IS 22	Far Downwind (Loc. 2) Train 2	13:45-17:50	240	5.4
10/26	CC 05 IS 23a	Far Downwind (Loc. 2) Train 3 Imp 1	13:45-17:50	240	5.4
10/26	CC 05 IS 23b	Efficiency Check Train 3 Imp 2			
10/26	CC 05 IS 31	Loc 3 Scout+Florance P1. Train 1	13:50-17:50	240	5.7
10/26	CC 05 IS 32a	Loc 3 Train 2 Imp 1	13:50-17:50	240	5.7
10/26	CC 05 IS 32b	Efficiency Check Train 2 Imp 2			
10/26	CC 05 IS 33	Loc 3 Scout+Florance P1. Train 3	13:50-17:50	240	5.7
10/26	CC 05 IS 41	Loc 4 Suva at Box Co Train 1	13:34-17:34	240	5.5
10/26	CC 05 IS 42	Loc 4 Suva at Box Co Train 2	13:34-17:34	240	5.5
10/26	CC 05 IS 43	Loc 4 Suva at Box Co Train 3	13:34-17:34	240	5.5
10/26	CC 05 IS 61	10 sec. In stack Time zero			0.0116
10/26	CC 05 IS 63	Instack sample+2.5 hr upwind samples	12:48-15:18	150	3.4
10/26	CC 05 NR 03	Nitric Rinse Loc. 0 Trains			
10/26	CC 05 NR 14	Nitric Rinse Trains 1,2,3 Loc1			
10/26	CC 05 NR 24	Nitric Rinse Trains 1,2,3 Loc 2			
10/26	CC 05 NR 34	Nitric Rinse Trains 1,2,3 Loc 3			
10/26	CC 05 NR 44	Nitric Rinse Trains 1,2,3 Loc 4			
10/26	CC 05 NR 62	Nitric Rinse -In stack Time zero			

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/26	CC 05 NR 64	Nitric Rinse Time Zero + 2.5 hr amb			
10/26	CC 05 XT 01	Upwind Teflon	12:48-15:18	150	3.404
10/26	CC 05 XT 02	Upwind PVC	12:48-15:18	150	3.309
10/26	CC 05 XT 11	Pred. Loc. 1 (near downwind) Teflon	13:50-17:50	240	4.293
10/26	CC 05 XT 12	Pred. Loc. 1 (near downwind) PVC	15:50-17:50	120	2.270
10/26	CC 05 XT 21	Far downwind (Loc. 2) Teflon	13:50-17:50	240	4.117
10/26	CC 05 XT 22	Far downwind (Loc. 2) PVC	13:50-17:50	240	4.088
10/26	CC 05 XT 31	Loc 3 (East of source) Teflon	13:50-17:50	240	5.346
10/26	CC 05 XT 32	Loc 3 (East of source) PVC	13:50-17:50	240	5.260
10/26	CC 05 XT 41	Loc 4 (North of source) Teflon	13:34-17:34	240	4.632
10/27	CC 07 IS 01	Imp. sample, Loc 0 Train 1	12:21-15:21	180	4.0
10/27	CC 07 IS 02	Imp. sample, Loc 0 Train 2	12:21-15:21	180	4.0
10/27	CC 07 IS 11	Imp. sample, Loc 1 Train 1	13:00-17:00	240	6.1
10/27	CC 07 IS 12a	Loc 1 Eff. Check Train 2 Imp 1	13:00-17:00	240	6.1
10/27	CC 07 IS 12b	Loc 1 Eff. Check Train 2 Imp 2			
10/27	CC 07 IS 13	Imp. sample, Loc 1 Train 3	13:00-17:00	240	6.1
10/27	CC 07 IS 21	Imp. sample, Loc 2 Train 1	13:10-17:10	240	6.1
10/27	CC 07 IS 22	Imp. sample, Loc 2 Train 2	13:10-17:10	240	6.1
10/27	CC 07 IS 23	Imp. sample, Loc 2 Train 3	13:10-17:10	240	6.1
10/27	CC 07 IS 31	Imp. sample, Loc 3 Train 1	13:05-17:05	240	5.9
10/27	CC 07 IS 32	Loc 3 Eff. Check Train 2 Imp 1	13:05-17:05	240	5.9
10/27	CC 07 IS 33a	Loc 3 Eff. Check Train 2 Imp 2			
10/27	CC 07 IS 33b	Imp. sample, Loc 3	13:05-17:05	240	5.9
10/27	CC 07 IS 41	Imp. sample, Loc 4	13:00-17:00	240	6.2
10/27	CC 07 IS 42	Imp. sample, Loc 4	13:00-17:00	240	6.2
10/27	CC 07 IS 43	Imp. sample, Loc 4	13:00-17:00	240	6.2
10/27	CC 07 IS 61	Time zero, 10 sec. stack sample			0.0116
10/27	CC 07 IS 63	10 sec. Time zero + 3 hr upwind amb	12:21-15:21	180	4.0
10/27	CC 07 IS FB	Field Blank / Acetate			
10/27	CC 07 IS RB	Reagent Blank / Acetate Batch 2			
10/27	CC 07 NR 03	Imp. sample, Loc 0 Nitric Rinse			
10/27	CC 07 NR 12c	Imp. sample, Loc 1 Eff. Check			
10/27	CC 07 NR 14	Imp. sample, Loc 1 Nitric Rinse			
10/27	CC 07 NR 24	Imp. sample, Loc 2 Nitric Rinse			
10/27	CC 07 NR 34	Imp. sample, Loc 3 Nitric Rinse			
10/27	CC 07 NR 44	Imp. sample, Loc 4 Nitric Rinse			
10/27	CC 07 NR 62	Nitric Rinse -In stack Time zero			
10/27	CC 07 NR 64	Nitric Rinse Time Zero + 3 hr amb			
10/27	CC 07 NR RB	Field Blank / 5% Nitric Acid Rinse			
10/27	CC 07 NR RB	Reagent Blank / 5% Nitric Acid			
10/27	CC 07 XT 01	Upwind Teflon	12:21-15:21	180	3.999
10/27	CC 07 XT 02	Upwind PVC	12:21-15:21	180	3.972
10/27	CC 07 XT 11	Pred. Loc. 1 (near downwind) Teflon	13:00-17:00	240	4.361
10/27	CC 07 XT 12	Pred. Loc. 1 (near downwind) PVC	13:00-17:00	240	4.539

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/27	CC 07 XT 21	Far downwind (Loc. 2) Teflon	13:10-17:10	240	5.349
10/27	CC 07 XT 22	Far downwind (Loc. 2) PVC	13:10-17:10	240	5.257
10/27	CC 07 XT 31	Loc 3 (East of source) Teflon	13:05-17:05	240	5.073
10/27	CC 07 XT 32	Loc 3 (East of source) PVC	13:05-17:05	240	5.112
10/27	CC 07 XT 41	Loc 4 (North of source) Teflon	13:00-17:00	240	5.013
10/28	CC 08 IS 01	Imp. sample, Loc 0 Time Zero?	11:25-13:45	140	3.2
10/28	CC 08 IS 02	Imp. sample, Loc 0 Time Zero?	11:25-13:45	140	3.2
10/28	CC 08 IS 03	Imp. sample, Loc 0 Time Zero?	11:25-13:45	140	3.2
10/28	CC 08 IS 11a	Loc 1 Eff. Check Train 1 Imp 1	13:50-17:00	190	4.3
10/28	CC 08 IS 11b	Loc 1 Eff. Check Train 1 Imp 2			
10/28	CC 08 IS 12a	Loc 1 Eff. Check Train 2 Imp 1	13:50-17:00	190	4.3
10/28	CC 08 IS 12b	Loc 1 Eff. Check Train 2 Imp 2			
10/28	CC 08 IS 12c	Loc 1 Eff. Check Train 2 Imp 3			
10/28	CC 08 IS 13	Imp. sample, Loc 1 Train 3	13:50-17:00	190	4.3
10/28	CC 08 IS 21	Imp. sample, Loc 2 Train 1	12:10-17:00	290	6.6
10/28	CC 08 IS 22	Imp. sample, Loc 2 Train 2	12:10-17:00	290	6.6
10/28	CC 08 IS 23	Imp. sample, Loc 2 Train 3	12:10-17:00	290	6.6
10/28	CC 08 IS 31	Imp. sample, Loc 3 Train 1	12:05-17:05	300	6.8
10/28	CC 08 IS 32	Imp. sample, Loc 3 Train 2	12:05-17:05	300	6.8
10/28	CC 08 IS 33	Imp. sample, Loc 3 Train 3	12:05-17:05	300	6.8
10/28	CC 08 IS 41	Imp. sample, Loc 4 Train 1	11:55-16:55	300	6.8
10/28	CC 08 IS 61	Time Zero instack sample 10 seconds			0.0116
10/28	CC 08 NR 04	Imp. sample, Loc 0 Nitric Rinse			
10/28	CC 08 NR 14	Imp. sample, Loc 1 Nitric Rinse			
10/28	CC 08 NR 24	Imp. sample, Loc 2 Nitric Rinse			
10/28	CC 08 NR 34	Imp. sample, Loc 3 Nitric Rinse			
10/28	CC 08 NR 44	Imp. sample, Loc 4 Nitric Rinse			
10/28	CC 08 NR 62	10 sec. Time Zero Nitric Rinse			
10/28	CC 08 XT 01	Upwind Teflon	11:25-15:00	215	4.775
10/28	CC 08 XT 02	Upwind PVC	11:25-15:00	215	4.743
10/28	CC 08 XT 11	Pred. Loc. 1 (near downwind) Teflon	13:50-17:00	190	3.444
10/28	CC 08 XT 12	Pred. Loc. 1 (near downwind) PVC	13:50-17:00	190	3.585
10/28	CC 08 XT 21	Far downwind (Loc. 2) Teflon	12:10-17:00	290	6.459
10/28	CC 08 XT 22	Far downwind (Loc. 2) PVC	12:10-17:00	290	6.352
10/28	CC 08 XT 31	Loc 3 (East of source) Teflon	12:05-17:05	300	6.336
10/28	CC 08 XT 32	Loc 3 (East of source) PVC	12:05-17:05	300	6.386
10/28	CC 08 XT 41	Loc 4 (North of source) Teflon	11:55-16:55	300	5.610
10/29	AR 09 IS 21	Imp. Sample, Loc 2 Downwind	14:54-17:15	141	3.3
10/29	AR 09 IS 22	Imp. Sample, Loc 2 Downwind	14:54-17:15	141	3.3
10/29	AR 09 IS 23	Imp. Sample, Loc 2 Downwind	14:54-17:15	141	3.3
10/29	AR 09 IS 61	Loc 6, Instack 70 min	15:00-16:10	70	2.4
10/29	AR 09 IS 62	Loc 6, Instack 70 min	15:00-16:10	70	2.4
10/29	AR 09 XT 21	Loc 2, Teflon	14:54-17:15	141	3.180

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/29	AR 09 XT 22	Loc 2, Teflon	14:54-17:15	141	3.180
10/30	AR 10 IS 01	Upwind (Loc. 0)	14:08-17:58	230	5.2
10/30	AR 10 IS 02	Upwind (Loc. 0)	14:08-17:58	230	5.2
10/30	AR 10 IS 11	Downwind (Loc 1) Train 1	13:38-17:38	240	5.4
10/30	AR 10 IS 12	Downwind (Loc 1) Train 2	13:38-17:38	240	5.4
10/30	AR 10 IS 13	Downwind (Loc 1) Train 3	13:38-17:38	240	5.4
10/30	AR 10 IS 21	Downwind (Loc 2) Train 1	13:22-15:22	230	5.2
10/30	AR 10 IS 22	Downwind (Loc 2) Train 2	13:22-15:22	230	5.2
10/30	AR 10 IS 23	Downwind (Loc 2) Train 3	13:22-15:22	230	5.2
10/30	AR 10 IS 31	Downwind (Loc 3) Train 1	13:54-17:54	233	5.3
10/30	AR 10 IS 32	Downwind (Loc 3) Train 2	13:54-17:54	233	5.3
10/30	AR 10 IS 33	Downwind (Loc 3) Train 3	13:54-17:54	233	5.3
10/30	AR 10 IS 61	30 min instack Time zero	11:00-11:30	30	1.0
10/30	AR 10 IS 62	30 min Time zero + 230 min Loc. 0	14:08-17:58	230	5.2
10/30	AR 10 XT 01	Upwind Teflon	14:08-17:58	230	4.184
10/30	AR 10 XT 02	Upwind NaAc PVC	14:08-17:58	230	4.352
10/30	AR 10 XT 11	Downwind Left (Loc 1) Teflon	13:38-17:38	240	5.072
10/30	AR 10 XT 12	Downwind Left (Loc 1) 1st NaAC PVC	13:38-17:38	240	5.117
10/30	AR 10 XT 31	Downwind Right (Loc 3) Teflon	13:54-17:54	233	5.178
10/30	AR 10 XT 32	Downwind Right (Loc 3) 1st NaAc PVC	13:54-17:54	233	5.144
11/2	AR 11 IS 01	Loc 0 Upwind Train 1	13:20-17:10	230	5.2
11/2	AR 11 IS 02	Loc 0 Upwind Train 2	13:20-17:10	230	5.2
11/2	AR 11 IS 11a	Loc 1 Downwind Train 1 1st imp	13:10-17:10	240	4.6
11/2	AR 11 IS 11b	Loc 1 Downwind Train 1 2nd imp			
11/2	AR 11 IS 12a	Loc 1 Downwind Train 2 1st imp	13:10-17:10	240	4.6
11/2	AR 11 IS 12b	Loc 1 Downwind Train 2 2nd imp			
11/2	AR 11 IS 13	Loc 1 Downwind Train 3	13:10-17:10	240	4.6
11/2	AR 11 IS 21	Loc 2 Downwind Train 1	13:58-15:56	118	2.6
11/2	AR 11 IS 22	Loc 2 Downwind Train 2	13:58-15:56	118	2.6
11/2	AR 11 IS 23	Loc 2 Downwind Train 3	13:58-15:56	118	2.6
11/2	AR 11 IS 31	Loc 3 Downwind Train 1	13:20-17:20	240	5.4
11/2	AR 11 IS 32	Loc 3 Downwind Train 2	13:20-17:20	240	5.4
11/2	AR 11 IS 33	Loc 3 Downwind Train 3	13:20-17:20	240	5.4
11/2	AR 11 IS 41	Loc 4 Far Downwind Train 1	13:40-17:44	244	6.0
11/2	AR 11 IS 42	Loc 4 Far Downwind Train 2	13:40-17:44	244	6.0
11/2	AR 11 IS 43	Loc 4 Far Downwind Train 3	13:40-17:44	244	6.0
11/2	AR 11 IS 61	30 min Instack Time Zero	11:00-11:30	30	1.1
11/2	AR 11 IS 62	Instack Time Zero + 230 min amb	13:20-17:10	230	5.2
11/2	AR 11 IS FB	Sample Train Field Blank			
11/2	AR 11 IS RB	NaAcetate Reagent Blank Batch 3			
11/2	AR 11 XT 01	Upwind (Loc 0) Teflon	13:10-17:10	240	4.365
11/2	AR 11 XT 02	Upwind (Loc 0) 1st NaAc PVC	13:10-17:10	240	4.542
11/2	AR 11 XT 11	Downwind Left (Loc 1) Teflon	13:00-17:30	270	5.713

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

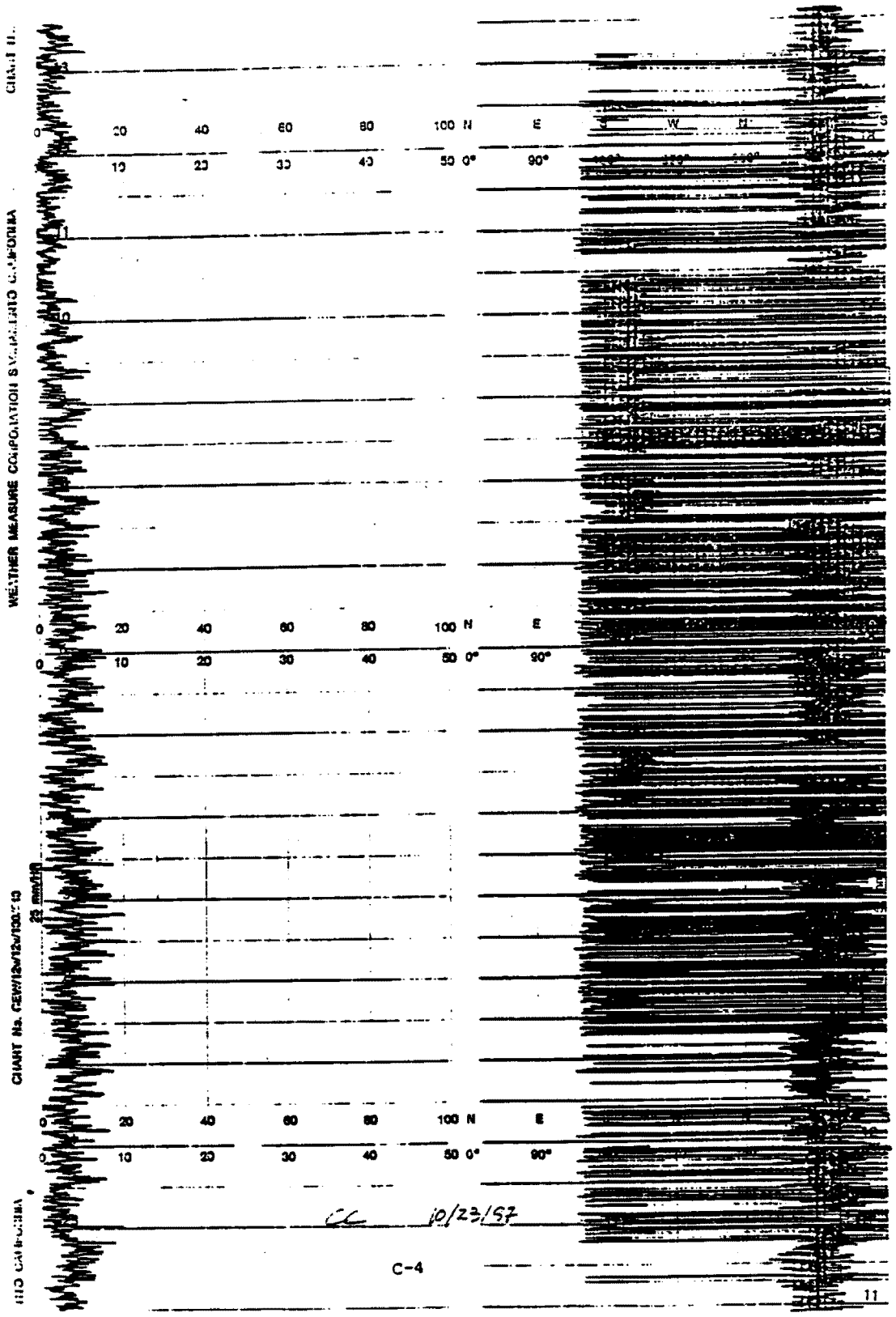
Date	Sample Number	Description	Time	Minutes	Cu.Meters
11/2	AR 11 XT 12	Downwind Left (Loc 1) 1st NaAC PVC	13:00-17:30	270	5.772
11/2	AR 11 XT 21	Downwind (Loc 2) Teflon	13:58-15:56	118	2.436
11/2	AR 11 XT 22	Downwind (Loc 2) 1st NaAc PVC	13:58-15:56	118	4.005
11/2	AR 11 XT 31	Downwind Right (Loc 3) Teflon	13:20-17:20	240	5.333
11/2	AR 11 XT 32	Downwind Right (Loc 3) 1st NaAc PVC	13:20-17:20	240	5.292
11/2	AR 11 XT 41	Far Downwind (Loc. 4) Teflon	13:41-17:44	243	2.220
11/2	AR 11 XT B	1st Batch Blank Na Acetate Filter			
11/3	AR 12 IS 01	Loc 0, Upwind Train 1	12:45-17:45	293	7.4
11/3	AR 12 IS 02	Loc 0, Upwind Train 2	12:45-17:45	293	7.4
11/3	AR 12 IS 11	Loc 1, East of CT 9 Train 1	11:50-18:00	370	8.2
11/3	AR 12 IS 12	Loc 1, East of CT 9 Train 2	11:50-18:00	370	8.2
11/3	AR 12 IS 13	Loc 1, East of CT 9 Train 3	11:50-18:00	370	8.2
11/3	AR 12 IS 21	Loc 2, In Tank Farm Train 1	12:52-17:52	<300	<7.0
11/3	AR 12 IS 22	Loc 2, In Tank Farm Train 2	12:52-17:52	<300	<7.0
11/3	AR 12 IS 23	Loc 2, In Tank Farm Train 3	12:52-17:52	<300	<7.0
11/3	AR 12 IS 31	Loc 3N, NW corner of Lot Train 1	13:05-18:05	300	8.0
11/3	AR 12 IS 32	Loc 3N, NW corner of Lot Train 2	13:05-18:05	300	8.0
11/3	AR 12 IS 33	Loc 3N, NW corner of Lot Train 3	13:05-18:05	300	8.0
11/3	AR 12 IS 41	Loc 4, Far Downwind Train 1	11:44-17:06	322	7.2
11/3	AR 12 IS 42	Loc 4, Far Downwind Train 2	11:44-17:06	322	7.2
11/3	AR 12 IS 43	Loc 4, Far Downwind Train 3	11:44-17:06	322	7.2
11/3	AR 12 IS 61	Instack Time zero, (30 min)			1.1
11/3	AR 12 IS 62	Time zero + 293 min at Loc 0	12:45-17:45	293	7.4
11/3	AR 12 XT 01	Upwind (Loc 0) Teflon	12:45-17:45	293	5.309
11/3	AR 12 XT 02	Upwind (Loc 0) 2nd NaAc Filter	12:45-17:45	293	5.529
11/3	AR 12 XT 11	Loc 1, East of CT 9 Teflon	11:50-17:50	360	7.616
11/3	AR 12 XT 12	Loc 1, East of CT 9 2nd NaAc Filter	11:50-17:50	360	7.678
11/3	AR 12 XT 21	Loc 2, In Tank Farm Teflon	12:52-17:52	300	5.819
11/3	AR 12 XT 22	Loc 2, In Tank Farm 2nd NaAc Filter	12:52-17:52	300	5.323
11/3	AR 12 XT 31 N	Loc 3N, NW corner of Lot Teflon	13:05-18:05	300	6.664
11/3	AR 12 XT 32 N	Loc 3N, NW corner 2nd NaAc Filter	13:05-18:05	300	6.63
11/3	AR 12 XT 41	Loc 4, Far Downwind Teflon	11:44-17:06	322	3.108
11/3	AR 12 XT BGF	Blank Na Acetate Filter 2nd Batch			
11/3	AR 12 XT BT	Blank Filter Teflon Lot #2089			
11/4	AR 13 IS 01	Loc 0, Upwind Train 1	12:30-18:00	330	8.3
11/4	AR 13 IS 02	Loc 0, Upwind Train 2	12:30-18:00	330	8.3
11/4	AR 13 IS 11	Loc 1, West of CT 9 Train 1	12:00-18:00	360	9.5
11/4	AR 13 IS 12	Loc 1, West of CT 9 Train 2	12:00-18:00	360	9.5
11/4	AR 13 IS 13	Loc 1, West of CT 9 Train 3	12:00-18:00	360	9.5
11/4	AR 13 IS 21	Loc 2, In Tank Farm Train 1	12:36-17:22	286	6.5
11/4	AR 13 IS 22	Loc 2, In Tank Farm Train 2	12:36-17:22	286	6.5
11/4	AR 13 IS 23	Loc 2, In Tank Farm Train 3	12:36-17:22	286	6.5
11/4	AR 13 IS 31a	Loc 3N, Train 1, Imp 1	12:40-17:40	292	7.4

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
11/4	AR 13 IS 31b	Loc 3N, Train 1, Imp 2			
11/4	AR 13 IS 32a	Loc 3N, Train 2, Imp 1	12:40-17:40	292	7.4
11/4	AR 13 IS 32b	Loc 3N, Train 2, Imp 2			
11/4	AR 13 IS 33	Loc 3, NW corner of lot, Train 3	12:40-17:40	292	7.4
11/4	AR 13 IS 41	Loc 4, Far downwind Train 1	12:00-17:15	315	7.5
11/4	AR 13 IS 42	Loc 4, Far downwind Train 2	12:00-17:15	315	7.5
11/4	AR 13 IS 43	Loc 4, Far downwind Train 3	12:00-17:15	315	7.5
11/4	AR 13 IS 61	Instack Time zero,(30 min CT-9,FC 13)	10:39-11:09	30	1.1
11/4	AR 13 IS 62	Time Zero + 330 min. amb. at Loc. 0	12:30-18:00	330	8.3
11/4	AR 13 XT 01	Loc 0, Teflon Filter	12:30-18:00	330	5.999
11/4	AR 13 XT 02	Loc 0, NaAcetate Filter 2nd Batch	12:30-18:00	330	6.241
11/4	AR 13 XT 11	Loc 1, Teflon Filter	12:00-18:00	360	7.615
11/4	AR 13 XT 12	Loc 1, NaAcetate Filter 2nd Batch	12:00-18:00	360	7.679
11/4	AR 13 XT 21	Loc 2, Teflon Filter	12:36-17:22	286	6.066
11/4	AR 13 XT 22	Loc 2, NaAcetate Filter 2nd Batch	12:36-17:22	286	5.525
11/4	AR 13 XT 31	Loc 3, Teflon Filter	12:40-17:40	292	6.488
11/4	AR 13 XT 32	Loc 3, NaAcetate Filter 2nd Batch	12:40-17:40	292	6.441
11/4	AR 13 XT 41	Loc 4, Teflon Filter	12:00-17:15	315	2.991
11/5	AR 14 IS 01	Loc. 0 Previous Upwind Train 1	12:50-17:55	305	7.9
11/5	AR 14 IS 02	Loc. 0 Previous Upwind Train 1	12:50-17:55	305	7.9
11/5	AR 14 IS 03	Loc. 0 Previous Upwind Train 1	12:50-17:55	305	7.9
11/5	AR 14 IS 11	Loc. 1 W of CT 9 Train 1	12:10-17:05	295	6.3
11/5	AR 14 IS 12	Loc. 1 W of CT 9 Train 2	12:10-17:05	295	6.3
11/5	AR 14 IS 13	Loc. 1 W of CT 9 Train 3	12:10-17:05	295	6.3
11/5	AR 14 IS 21	Loc 2N Int. Truck Park. lot, Train 1	13:06-16:36	210	5.0
11/5	AR 14 IS 22	Loc 2N Int. Truck Park. lot, Train 2	13:06-16:36	210	5.0
11/5	AR 14 IS 23	Loc 2N Int. Truck Park. lot, Train 3	13:06-16:36	210	5.0
11/5	AR 14 IS 31a	Loc 3N, Train 1 1st Imp	12:25-17:22	298	6.7
11/5	AR 14 IS 31b	Loc 3N, Train 1 2nd Imp			
11/5	AR 14 IS 32a	Loc 3N, Train 2 1st Imp	12:25-17:22	298	6.7
11/5	AR 14 IS 32b	Loc 3N, Train 2 2nd Imp			
11/5	AR 14 IS 33	Loc 3N, NW corner of lot Train 3	12:25-17:22	298	6.7
11/5	AR 14 IS 41	Loc 4 Prev. Far Downwind Train	12:30-17:13	283	7.2
11/5	AR 14 IS 42	Loc 4 Prev. Far Downwind Train	12:30-17:13	283	7.2
11/5	AR 14 IS 61	30 min Instack Time Zero (CT 9,FC 13)	10:56-11:26	30	1.1
11/5	AR 14 IS 62	Time Zero + 283 min. amb. at Loc 4	12:30-17:13	283	7.2
11/5	AR 14 IS RB	NaAc Reagent blank Batch 4			
11/5	AR 14 XT 01	Loc 0 Previous upwind Teflon	12:50-17:55	305	5.549
11/5	AR 14 XT 02	Loc 0 NaAcetate Filter 2nd Batch	12:50-17:55	305	5.773
11/5	AR 14 XT 11	Loc 1, Teflon Filter	12:10-17:05	295	6.239
11/5	AR 14 XT 12	Loc 1, NaAcetate Filter 2nd Batch	12:10-17:05	295	6.290
11/5	AR 14 XT 21	Loc 2N, Teflon Filter	13:06-16:36	210	3.785
11/5	AR 14 XT 22	Loc 2N, NaAcetate Filter 2nd Batch	13:06-16:36	210	4.006
11/5	AR 14 XT 31N	Loc 3N, Teflon Filter	12:25-17:22	298	6.625

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
11/5	AR 14 XT 32N	Loc 3N, NaAcetate Filter 2nd Batch	12:25-17:22	298	6.588
11/5	AR 14 XT 41	Loc 4, Teflon Filter	12:30-17:13	283	2.649
11/5	AR 14 XT RB 2	2nd Batch NaAcetate Filter Blank			
11/5	AR 14 XT RB 1	Teflon Filter Blank Lot #2089			
11/6	AR 15 IS 01	Loc 0, Original Upwind Train 1	13:42-17:42	240	4.9
11/6	AR 15 IS 02	Loc 0, Original Upwind Train 2	13:42-17:42	240	4.9
11/6	AR 15 IS 11	Loc 1, W of CT 9 Train 1	12:10-18:02	354	7.3
11/6	AR 15 IS 12	Loc 1, W of CT 9 Train 2	12:10-18:02	354	7.3
11/6	AR 15 IS 13	Loc 1, W of CT 9 Train 3	12:10-18:02	354	7.3
11/6	AR 15 IS 21	Loc 2, Tank Farm Train 1	13:30-17:55	265	6.1
11/6	AR 15 IS 22	Loc 2, Tank Farm Train 2	13:30-17:55	265	6.1
11/6	AR 15 IS 23	Loc 2, Tank Farm Train 3	13:30-17:55	265	6.1
11/6	AR 15 IS 31	Mobile DW 13:22 to 15:40 NE corner	13:22-18:15	290	7.2
11/6	AR 15 IS 32	of lot (Loc. 3N), from 15:43 to 18:15	13:22-18:15	290	7.2
11/6	AR 15 IS 33	at roadway corner (Loc. 3)	13:22-18:15	290	7.2
11/6	AR 15 IS 41	Far downwind of Loc 2 Train 1	13:29-18:07	278	6.5
11/6	AR 15 IS 42	Far downwind of Loc 2 Train 1	13:29-18:07	278	6.5
11/6	AR 15 IS 61	30 min. Instack Time zero (CT9,FC13)	11:00-11:30	30	1.3
11/6	AR 15 IS 62	Time zero + 240 min. amb. at Loc 0	13:42-17:42	240	4.9
11/6	AR 15 XT 01	Loc 0, Teflon Filter	13:42-17:42	240	4.364
11/6	AR 15 XT 02	Loc 0, NaAcetate Filter 3rd Batch	13:42-17:42	240	4.614
11/6	AR 15 XT 11	Loc 1, Teflon Filter	12:10-18:02	354	7.474
11/6	AR 15 XT 12	Loc 1, NaAcetate Filter 3rd Batch	12:10-18:02	354	7.548
11/6	AR 15 XT 21	Loc 2, Teflon Filter	13:30-17:55	265	5.888
11/6	AR 15 XT 22	Loc 2, NaAcetate Filter 3rd Batch	13:30-17:55	265	5.937
11/6	AR 15 XT 31	Loc 3N and 3, Teflon Filter	13:22-18:15	290	5.485
11/6	AR 15 XT 32	Loc 3N and 3, NaAc Filter 3rd Batch	13:22-18:15	290	5.483
11/6	AR 15 XT 41	Loc 4, Teflon Filter	13:29-18:07	278	2.502
11/6	AR 15 XT RB 2	3rd Batch NaAcetate Filter			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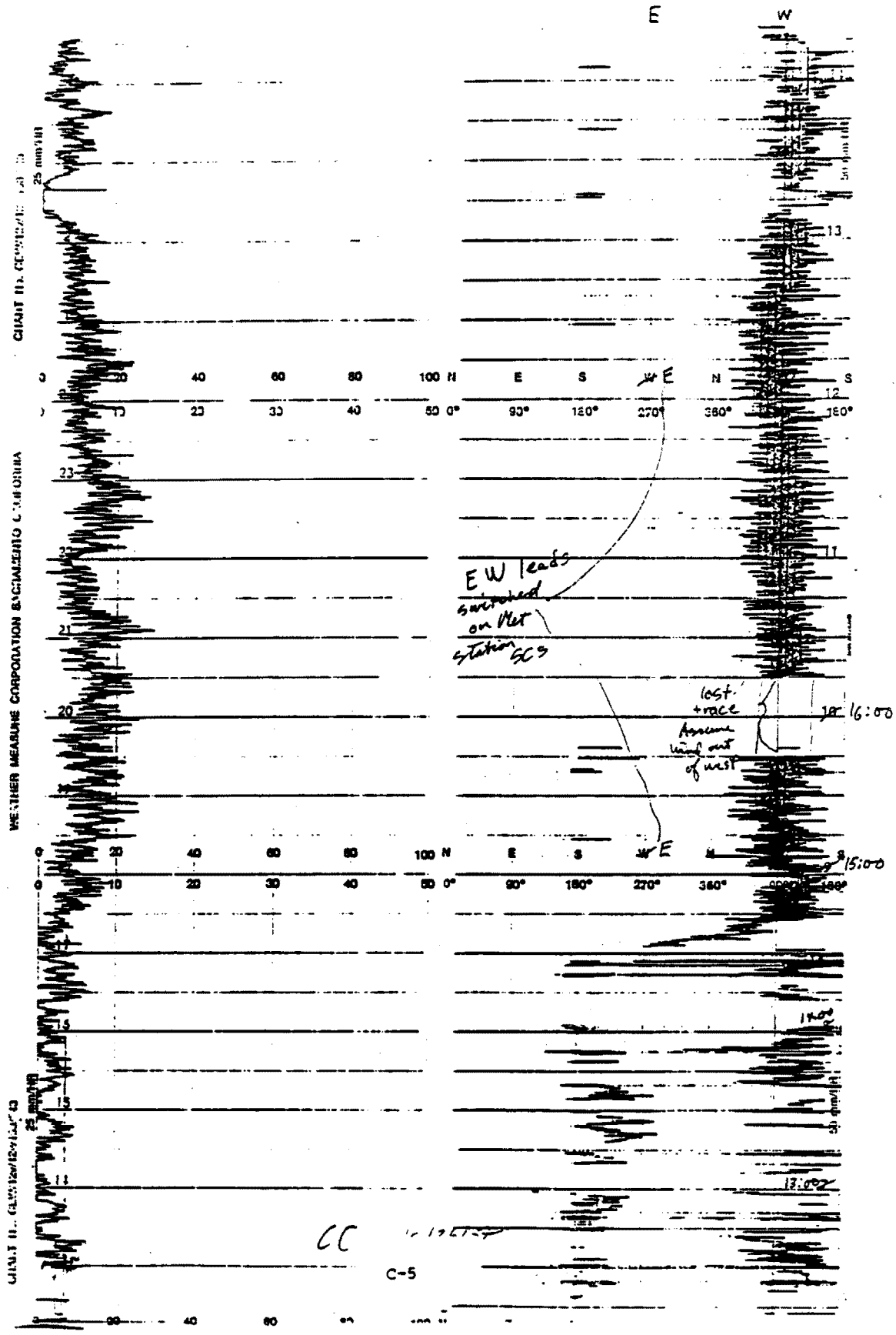
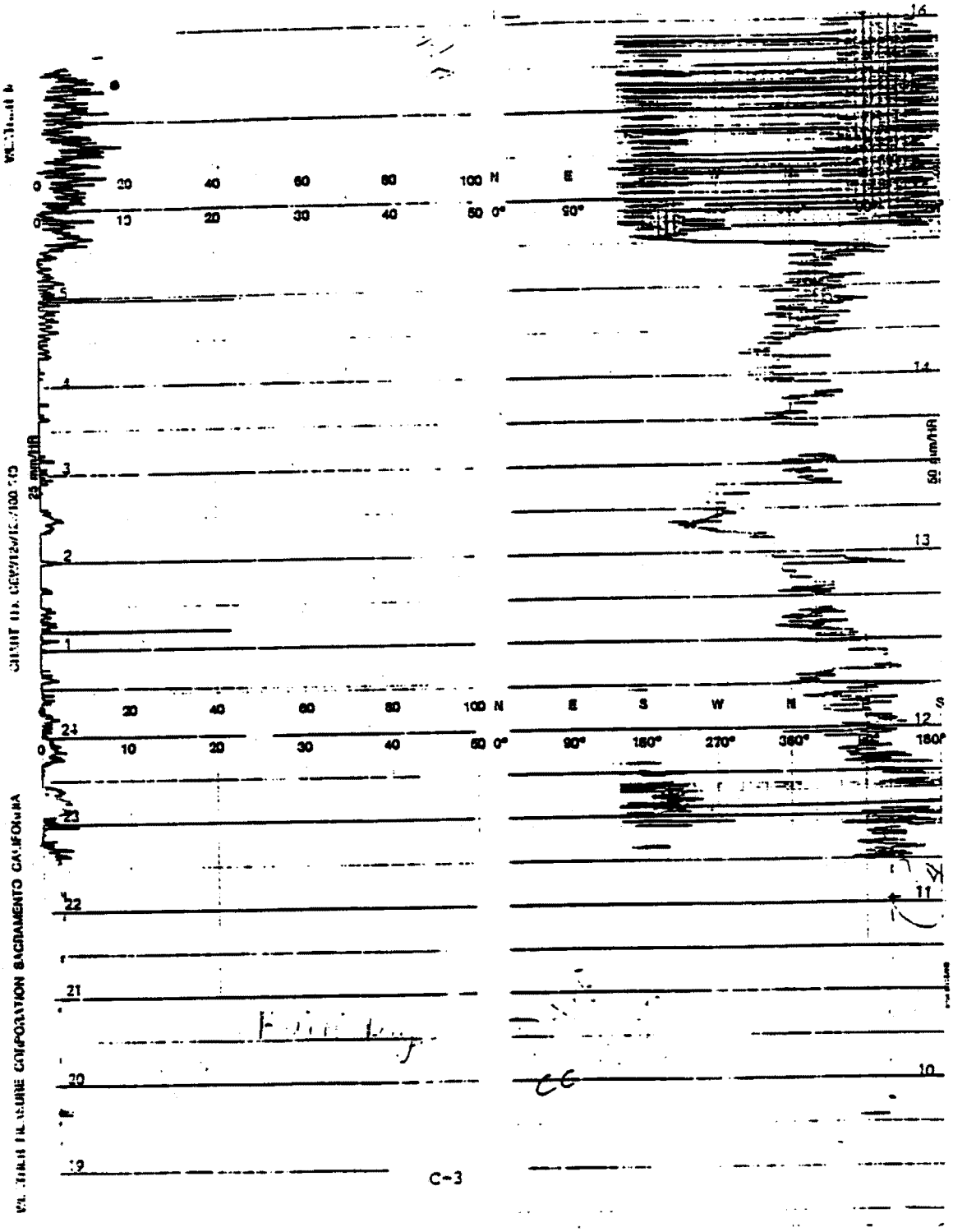
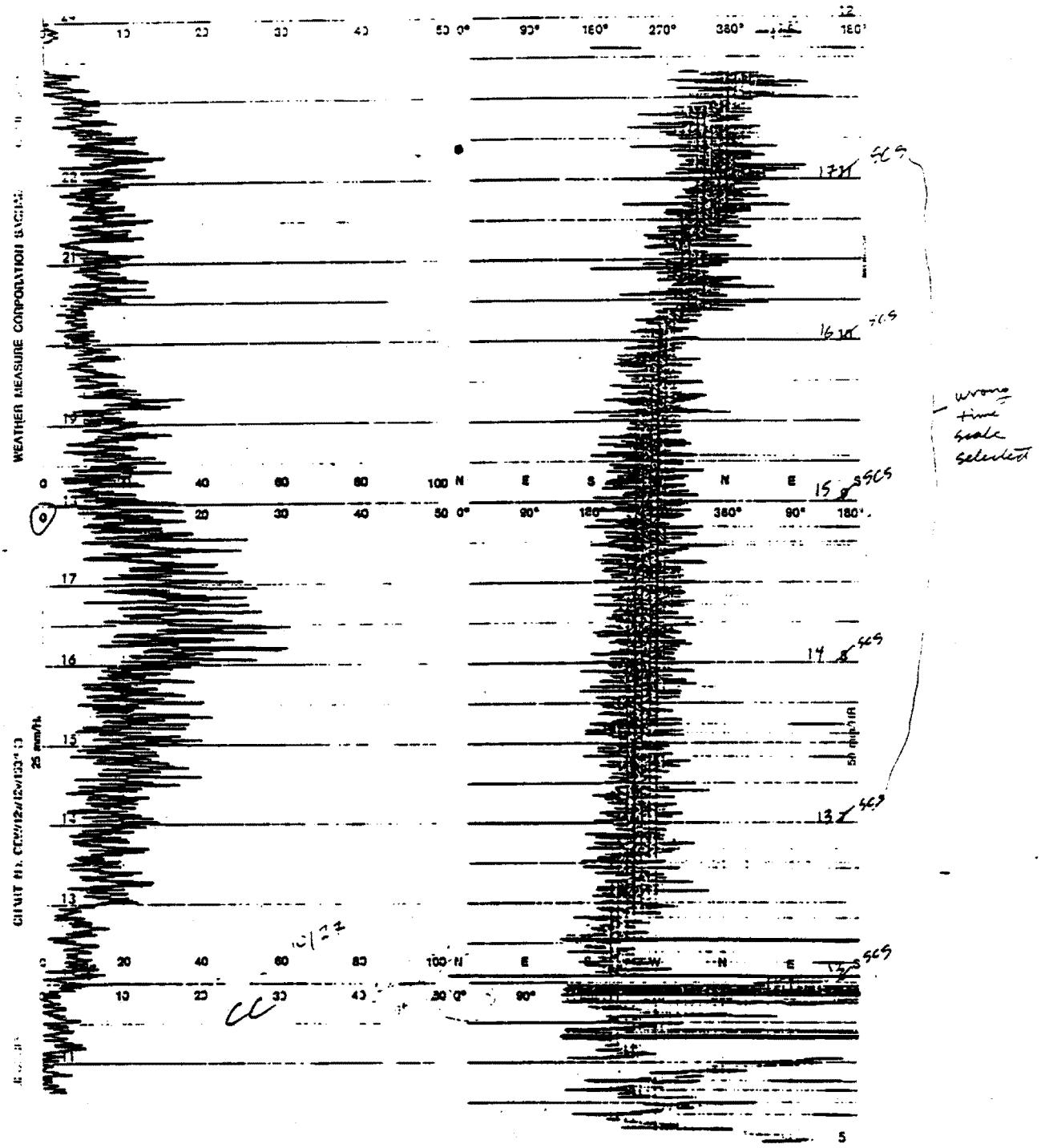
0 10 20 30 40 50 0° 90°
CC 10/23/97
C-4
11

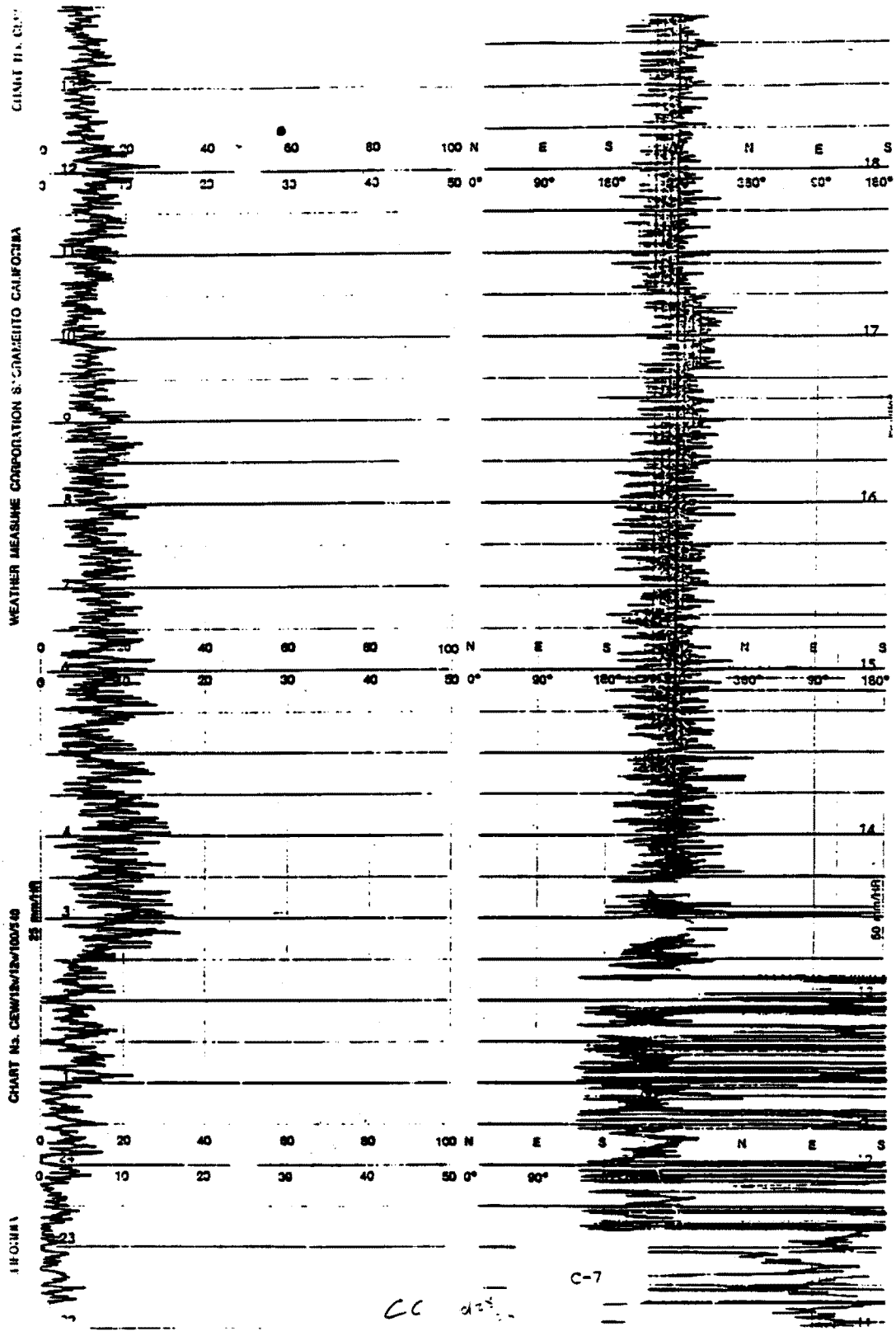

E
W
EW leads switched on Met station SC3
lost trace
Assume wind out of west
16:00
15:00
14:00
13:00
CC
C-5

APPENDIX C.

Meteorological Data Station Strip Charts


0 20 40 60 80 100 N E
0 10 20 30 40 50 0° 90°
20 40 60 80 100 N E S W N S
0 10 20 30 40 50 0° 90° 180° 270° 360° 180°
25 mm/HR
50 gm/HR
C-3


WEATHER MEASURE CORPORATION
wrong time scale selected



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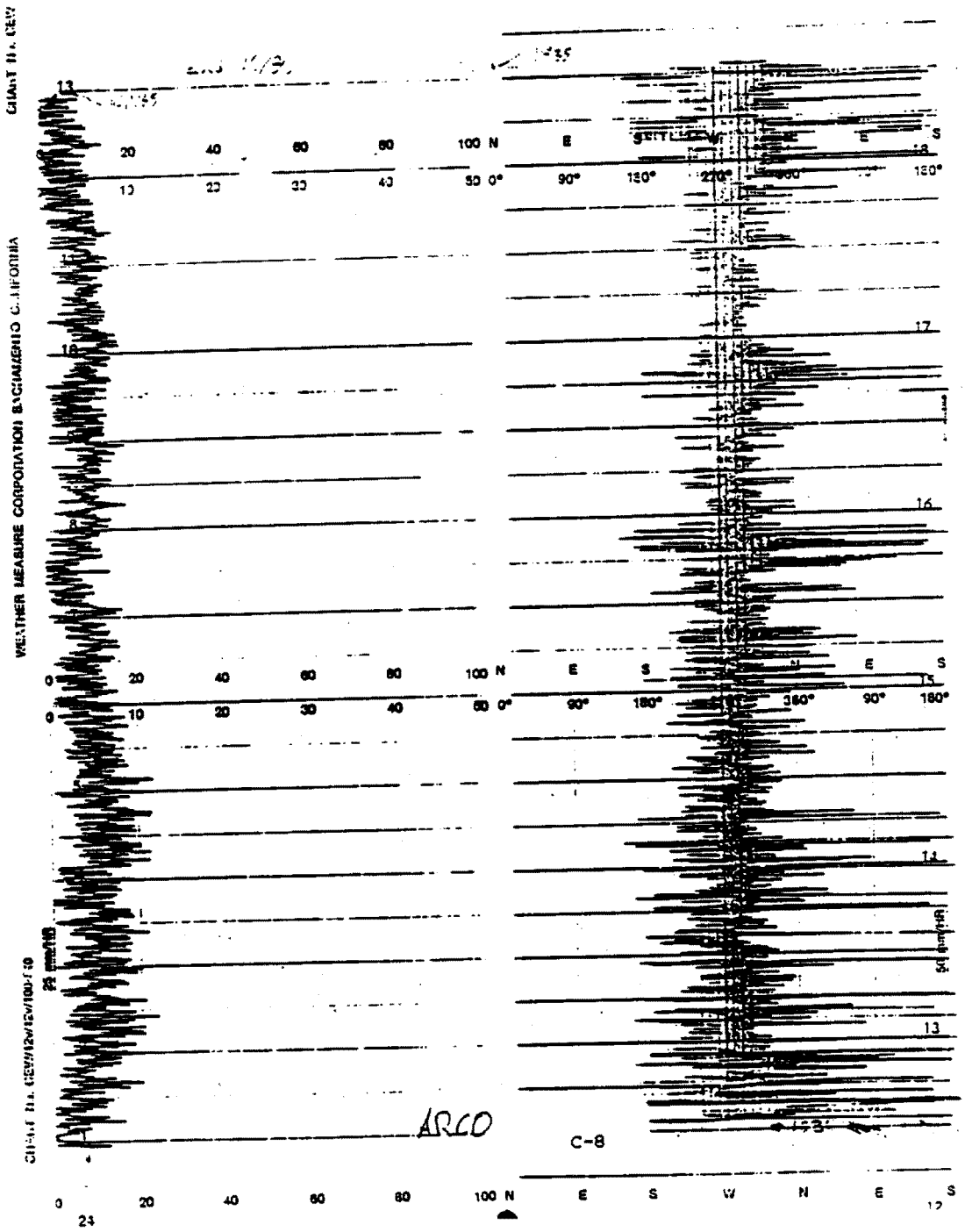
ASSET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ARCO
C-8

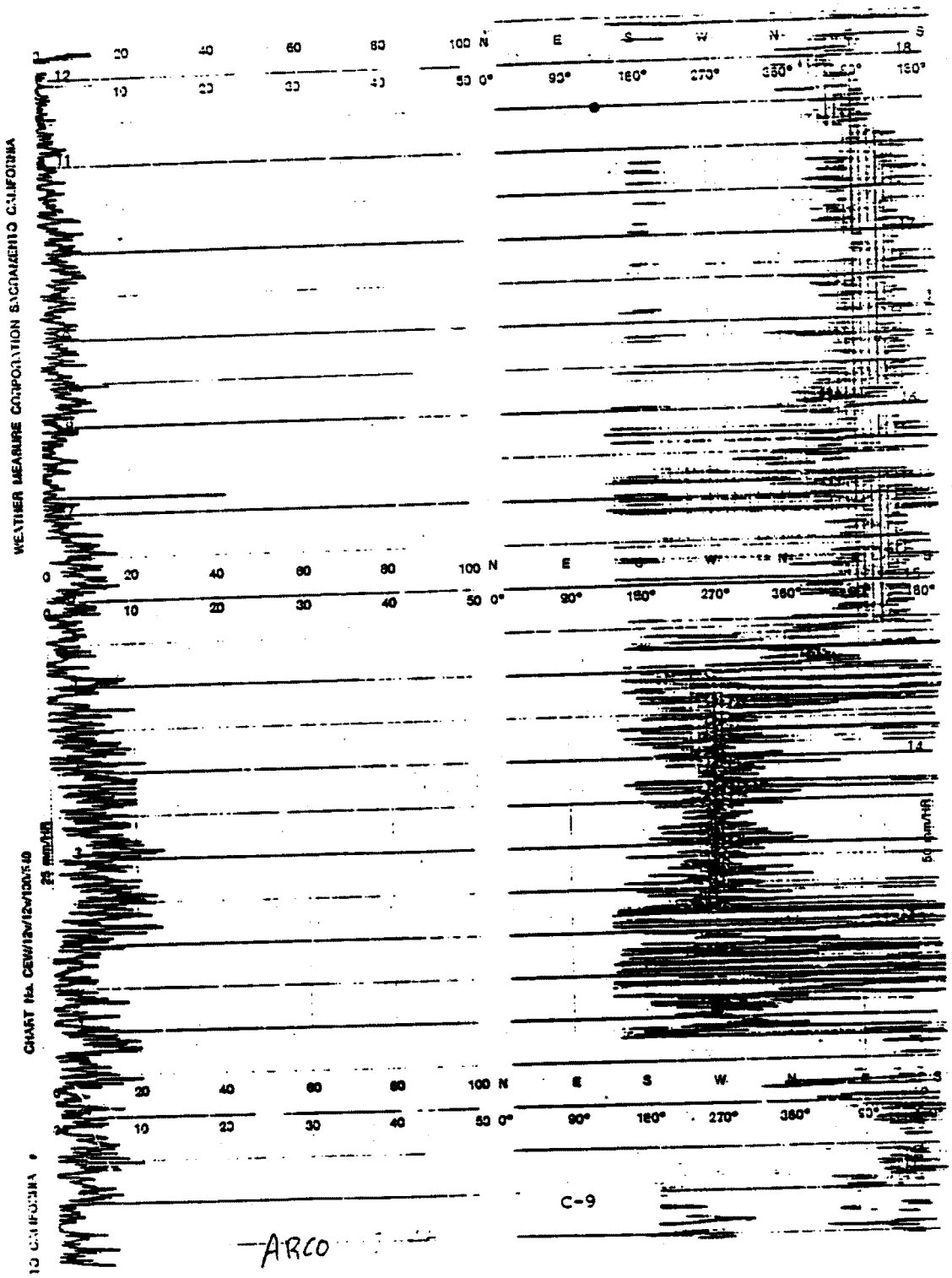
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CHART No. CEW/12w/12w/100/540
25 mm/HR
50 mm/HR
TO CALIFORNIA
C-9
ARCO

Quality Assurance Project Plan for Chromium (VI) Air Study Kansas City, Kansas

U. S. EPA Region 7
Air Program
November 2011

Stephanie Doolan, Program Lead
AWMD/APDB, EPA Region 7

11/07/2011
Date

Leland Grooms, Technical Lead
ENSV/ASRS, EPA Region 7

11/15/2011
Date

Mark Smith, Chief
AWMD/APCO, EPA Region 7

11/7/11
Date

Diane Harris (approved w/ condition)
Diane Harris
Regional Quality Assurance Manager

11/28/2011
Date

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Appendix A

Figure 1 – Site Map & Proposed Air Sampler Location
Figure 2 – Air Modeling Results – Predicted Risk
Figure 3 – Air Modeling Results – Cr(VI) Predicted Concentration
Figure 4 – Air Sampler Detail

Appendix B

Eastern Research Group, Inc. Quality Assurance Plan

Appendix C

Standard Operating Procedure for Measurement of Hexavalent Chromium using the BGI PQ167R Low Volume Sampler, School Air Toxics Study, August 14, 2009

Appendix D

"Collection and Analysis of Hexavalent Chromium in Ambient Air," ERG, January 9, 2007

Appendix E

Region 7 Standard Operating Procedure No. 2314.06A, "Measurement of Hexavalent Chromium Using the BGI PQ167R Low Volume Sampler," November 7, 2011

A. Project Management

A3. Distribution List

Stephanie Doolan, Air Program Lead	AWMD/APDB, EPA Region 7
Leland Grooms, Technical Lead	ENSV/ASRS, EPA Region 7
Todd Phillips, Risk Assessment Support	ENSV/EAMB, EPA Region 7
Mike Jones, Analytical Contract Support	Office of Air Quality Planning Standards (OAQPS)
Julie L. Swift, Program Manager/Chemist	Eastern Research Group (ERG)
Miles Stotts, Air Program Lead	Kansas Department of Health & Environment (KDHE)

A4. Project/Task Organization

This project is being managed by the Air and Waste Management Division (AWMD), Air Planning and Development Branch (APDB), and administered by the Environmental Services Division (ENSV), Air Sampling and Services (ASRS) Branch, EPA Region 7. Field data collection, sample management, and reporting for the Chromium (VI) Air Study under this Quality Assurance Project Plan (QAPP) will be conducted by EPA Region 7. Air sample analysis will be conducted by Eastern Research Group, Inc. (ERG) under contract to the EPA's Office of Air Quality Planning and Standards (OAQPS) in Research Triangle Park, North Carolina.

EPA, Region 7

Stephanie Doolan, Program Lead
RCAP/AWMD (913) 551-7719
Responsibilities: Project management, laboratory coordination, and data validation and reporting

Leland Grooms, Technical Lead
EMWC/ENSV (913) 551-5010
Responsibilities: Receipt of sampling supplies, sample collection, shipment to laboratory, and data validation

Todd Phillips, Risk Assessment Support
ENSV/EAMB (913) 551-7438
Responsibilities: Developing site-specific action levels, sampling project design, technical support to program lead and field team

Mike Jones, Contract Officer Representative and Technical Support
OAQPS (919) 541-0528
Responsibilities: Contract fixed laboratory sample analyses, technical support

Julie Swift, Program Manager/Chemist
ERG (919) 468-7924
Responsibilities: Laboratory coordination including shipment of sampling supplies, sample management, quality assurance and data reporting

Miles Stotts
Kansas Department of Health and Environment
(785) 296-1615
Responsibilities: Act as a liaison with state regulatory agency.

A5. Problem Definition/Background

The purpose of this Quality Assurance Project Plan (QAPP) is to describe the procedures to be used for outdoor air sampling for hexavalent chromium [Cr(VI)] at a location in Kansas City, Kansas, predicted by modeling to represent the highest risk for human exposure. Outdoor air sampling is to measure Cr(VI) concentrations in ambient air in a residential neighborhood downwind from the source of the Cr(VI) emissions, and to determine whether further action is necessary to protect human health and the environment.

The source of the Cr(VI) emissions is the CertainTeed wool fiberglass manufacturing facility at 103 Funston Road, Kansas City, Kansas, in what is commonly known as the "Fairfax District." During the rule revision of the Wool Fiberglass National Environmental Standards for Hazardous Air Pollutants (NESHAP), CertainTeed conducted a stack test in November 2010 for Cr(VI). The stack test data, validated by CertainTeed in February 2011, indicate that the facility emits approximately 840 pounds of Cr(VI) per year combined from two process stacks known as the "K1stack" and "K2 stack." OAQPS notified Region 7 of this information in June 2011. The Cr(VI) is believed to be emitted by the facility from the degradation of high-chrome refractory brick inside the furnaces that melt the silica and other substrates to form the fiberglass. Under high (3,000 degrees F) temperatures and a corrosive environment, the refractory brick degrades and Cr(VI), in the form of particulates, is emitted from the stacks that vent the kilns. By comparison, the next largest source of Cr(VI) in the wool fiberglass source category emits 56 lbs per year of Cr(VI).

Modeling was conducted by both OAQPS and Region 7 staff using AERMOD, EPA's preferred air dispersion model. Inputs to the model include five years of meteorological data (2006 – 2010) from Kansas City's Wheeler Airport, emissions data from the 2010 stack test conducted by CertainTeed, terrain and elevation data, and building and stack heights and dimensions to determine release heights of the Cr(VI) emissions and to evaluate potential "downwash" of contaminants from structures near the location the Cr(VI) is released. The outcomes of the model (Appendix A, Figures 2 and 3) indicate that the closest human receptors are in the Oak Grove Neighborhood to the southwest of the CertainTeed facility, that the Maximum Individual Risk (MIR) to the exposed population is approximately a 40-in-one-million (or 4×10^{-5}) cancer risk, and that the predicted maximum annual concentration averaged over five years (the number of years of meteorological data used to input the model) for Cr(VI) in the area of the Oak Grove Neighborhood is 2.4 nanograms per cubic meter (ng/m^3). For comparison, the EPA Air Program typically considers carcinogenic risks greater than 100-in-one-million (or 1×10^{-4}) to require further action. Based on EPA's Integrated Risk Information System (IRIS) database, the Region 7 toxicologists have recommended the following screening level for Cr(VI) listed in Table 1 below in outdoor air for a 70-year (e.g., lifetime) exposure.

Table 1. Cr (VI) Cancer Screening Levels[1]

Risk Level	Screening Level (ng/m^3)	Modeled Concentration (ng/m^3)[2]	Analytical Detection Level (ng/m^3)
100 in 1 Million	8	2.4	0.0039[3]
10 in 1 Million	0.8		
1 Million	0.08		

[1] - Assumes 70 year continuous exposure to outdoor (ambient) air
[2] – This value represents the modeled concentration at the closest human receptor.
[3] – The Analytical Detection Limit listed is from the laboratory's Method Detection Limit (MDL) study which corresponds to 21.6 m^3 of air.

Table 2. Cr (VI) Non-Cancer Screening levels[1]

Duration	Screening Level (ng/m^3)	Modeled Concentration (ng/m^3)[2]	Analytical Detection Level (ng/m^3)
Chronic Exposure (≥ 6 – 7 years)[3]	100	2.4	0.0039[4]

[1] - Assumes chronic/long-term continuous exposure. Generally applies to exposures greater than 6 to 7 years.
[2] – This value represents the modeled concentration at the closest human receptor.
[3] - Source: EPA's Integrated Risk Information System (IRIS) chronic reference concentration (RfC) for particulates.
[4] – The Analytical Detection Limit listed is from the laboratory's Method Detection Limit (MDL) study which corresponds to 21.6 m^3 of air.

Based on the predicted outcomes of the model and comparison with relevant human health screening criteria presented above, EPA intends to collect outdoor air data to confirm that the risk for the closest receptors does not exceed levels EPA has determined to be protective of human health. Note that for conservatism EPA is comparing the model predicted values for Cr(VI) to risk levels based on 70 years of continuous exposure. It is important to note that, based on available information, EPA believes that Cr(VI) emissions from the CertainTeed facility have only been elevated since 2004 when the facility reports that it re-bricked its furnaces with higher chrome content refractory brick.

In the initial phase of outdoor air sampling, EPA plans to collect multiple rounds of samples to determine the outdoor air concentration of Cr(VI) in the Oak Grove Neighborhood area, and to compare actual concentrations to the human health screening levels and predicted results of the model listed in Tables 1 and 2 above. Because wind direction and speed, relative humidity, and outdoor temperature can greatly affect the results of outdoor air sampling, EPA will initially collect samples at a frequency of one sample per every three days (1/3) from both of the collocated samplers for a period of six months. At the end of six months, EPA will evaluate the initial results and determine whether the frequency of sampling needs to be adjusted, the sampling needs to be continued, and if the number and location of samplers is appropriate. If the initial data indicate the need to adjust the sampling regime, this QAPP will be revised accordingly.

A public hearing and availability session is being planned for November 2011 to discuss the proposed Risk and Technology Review for Wool Fiberglass facilities, the new standards for Cr(VI) emissions from the CertainTeed facility, the results of EPA's risk modeling, and the plan to conduct this study to gather actual outdoor air data for Cr(VI) in the area of highest predicted risk for human receptors.

The former Garland Park Landfill is the selected location for sampling because it lies within the same contours for MIR and Cr(VI) concentration as the nearest residences, e.g., a measured concentration at the landfill is representative of Cr(VI) that may be measured at nearby residences. The former landfill site is open so that there are no obstructions from trees or buildings between samplers and the CertainTeed stacks emitting the Cr(VI), and it is fenced to limit access and tampering with the air samplers. Figure 1 in Appendix A depicts the proposed location of the air samplers. The Unified Government of Wyandotte County and Kansas City, Kansas, the current owners of the landfill property, have agreed to grant access for the sampling. At this time, discussions are occurring to determine whether electrical power for the samplers can be arranged or if the samplers will need to be powered by marine cycle batteries. Electrical power is preferable to battery power if possible due to the consistency in the power source, especially during cold winter months.

Analytical work will be performed by ERG, Inc., a contractor to OAQPS for air sample analysis. The laboratory's QAPP is provided as Attachment B. The analytical SOP for the specific analysis for Cr(VI) is proprietary; however, a copy will be made available to the Region 7 RQAM upon request. The analytical method for Cr(VI) is based on the California Air Resources Board (CARB) Method 039 and the paper provided as Appendix D titled, "Collection and Analysis of Hexavalent Chromium in Ambient Air," transmitted from ERG to Mike Jones, EPA OAQPS, in a letter dated January 9, 2007.

A6. Project/Task Description

The project is designed to:

- Measure concentrations of Cr(VI) in ambient air in areas where human exposures may occur;
- Assess whether exposure to Cr(VI) concentrations in outdoor air exceed human health risk-based criteria; and
- Determine whether further action is necessary.

To determine if exposure poses a potential human health risk, data will be compared with the risk-based screening levels presented in Tables 1 and 2 above, for cancer and non-cancer risks, respectively.

The data from this study will be submitted by the contract laboratory, ERG, to Mike Jones, EPA OAQPS, and Stephanie Doolan, EPA Region 7. If the average results for Cr (VI) over the first six months are found to exceed risk-based screening criteria listed above in Tables 1 and 2, further action may be deemed necessary. Further action could include, but is not limited to, additional sampling, an investigation of other possible sources of Cr (VI) in the surrounding area, and regulatory options, including enforcement, to reduce Cr (VI) emissions from the facility.

A7. Quality Objectives and Criteria for Measurement Data

By following the QAPP, the ERG contract statement of work, the EPA SOP, and the laboratory quality assurance plan, the quality objectives of this air sampling and analysis plan are to provide valid data of known and documented quality such that:

- Data will be collected in a manner to result in an accurate average annual 24-hour concentration of Cr(VI) in outdoor air;
- Data will be collected for comparison with risk based screening levels based on chronic/long-term exposure;
- Data will be used to determine the need for possible future actions; and
- Samples will be representative of seasonal and temporal variability of local meteorological conditions and operating conditions at the facility.

The data quality indicators to be used are identified below. Note that field collection best practices are detailed within the sampling SOP and methodology provided in Appendices C and E, and criteria for measurement data are embedded within the analytical methods.

- Representativeness will be addressed by collecting, analyzing, and reporting the data as described in this document, the attached SOP, and the analytical method.

- Comparability will be addressed by collecting, analyzing, and reporting the data as described in this document, the attached SOP and the analytical method.

- Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. The completeness objective for this project will be not less than 90%.

- Method accuracy will be assessed by laboratory analysis of calibration and control standards with known concentrations of the analyte of interest.

Method accuracy performance will be considered acceptable if daily quality control sample results fall within the normal range of acceptable values as indicated by the laboratory quality assurance plan (Appendix B). Sample specific and batch QA/QC will be reported in the data package received from the contract laboratory.

Field precision will be assessed by collection of collocated samples (two samplers located together). Field precision performance will be considered acceptable if sample results fall within +/- 70 Relative Percent Difference (RPD).

A8. Special Training Requirements/Certification

Experienced EPA air sampling personnel will be deployed to set up sampling equipment and retrieve samples for this project. Field personnel must be experienced in the operation of low volume particulate air samplers.

A9. Documentation and Records

The Program Lead is responsible for ensuring that the QAPP currently represents the sample collection activities in the field and that the most current version of the QAPP has been distributed to the list in Section A.3. For field documentation see section B3.

The records retention schedule for this project is as follows:

Function Code	Schedule	Disposition	Description
304-104-06	185a	Disposable 10 years after file closure	Collection of approved Quality Assurance Plans, QAPP
108-25-01-01-02	484a	Disposable 10 years after file closure	Data Records
305-109-01	258a(1)	Disposable 20 years after file closures	Final Deliverable and Reports

B. Measurement/Data Acquisition

B1. Sampling Process Design

To collect representative data great care must be taken during the field sampling to ensure proper purging, leak testing, and vacuum of the sample collection systems. Note that it is well reported in the literature that outdoor air samples have a high degree of variability. Factors that can influence air quality include distance from the source, source characteristics such as building dimensions and stack heights, topographic elevation of the source and receptors, and seasonal weather variations such as outdoor air temperature, wind speed and direction, and relative percent humidity.

As stated above, samples will be collected from two, collocated air samplers at a frequency of one per every three days, for a duration of a minimum of six months. The first phase of sampling will result in approximately 56 outdoor air samples (28 samples from each sampler). Initially, a minimum of 20 field blanks will be collected. Depending on the results of the initial 20 field blanks, as discussed above, the number of field blanks collected may be reduced. For the purposes of this QAPP, it is estimated that field blanks will be collected biweekly, for a total number of 24. The project team will evaluate the data after six months and decide whether to continue, reduce or expand the study.

The Technical Lead will be responsible for identifying and implementing any corrective action in the field, and as a part of sample handling and shipment. All corrective actions taken must be documented in the field logbook. Issues and corrective action taken that affect the quality and usability of the data must be reported to the Program Lead to ensure that data are validated appropriately and usability is considered as a part of decision making.

B2. Sampling Methods Requirements

Samples will initially be collected from two collocated low volume particulate air samplers in accordance with Appendix E, "Measurement of Hexavalent Chromium Using the BGI PQ167R Low Volume Sampler (U. S. EPA, 2011), which is based on Appendix C, "Standard Operating Procedure for Measurement of Hexavalent Chromium using the BGI PQ167R Low Volume Sampler, School Air Toxics Study," (U. S. EPA 2009). Per the study conducted by ERG (Appendix D), the following sample preservation procedures need to be employed:

- Teflon filters must be used to collect the samples;
- Filter media must be pre-washed with acid and rinsed before coating with sodium bisulfate to prevent Cr(VI) background interference;
- Samples must be retrieved within 24-hours after collection to prevent sample loss; and
- All samples must be delivered to the laboratory frozen to reduce sample loss.

The Technical Lead is responsible for ensuring that these field procedures are strictly adhered to, and documenting and reporting any deviations from these procedures that may affect data quality and usability.

B3. Sample Handling and Custody Requirements

Sample containers, preservation, and holding times will be those found in the EPA SOP (Appendix C) and the procedures listed in B.2 above that are from the "Collection and Analysis of Hexavalent Chromium in Ambient Air," transmitted from ERG to Mike Jones, EPA OAQPS, in a letter dated January 9, 2007 (Appendix D).

Chain-of-Custody documentation will be recorded on the form provided by ERG similar to the example provided on page 19 of the SOP found in Appendix C. This form also records the date and time of collection, location, total sampling time, meteorological conditions, and air sample volume. The field team will record this information and other site-specific observations in a field logbook using indelible ink.

B4. Analytical Methods Requirements

Air sample analysis for Cr(VI) will be conducted by ERG in accordance with a modified CARB SOP 039 in accordance with ERG's quality assurance plan. This analytical method employs the use of both Ion Chromatography (IC) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Results from this study will be compared to the cancer and non-cancer risk screening values as provided in Tables 1 and 2 above. As noted above, the SOP for the method is proprietary; however, it will be made available to EPA personnel upon request.

Correction action for analytical quality control issues is the responsibility of the laboratory to conduct in accordance with its Quality Assurance Plan (Appendix B). However, it is the responsibility of the Laboratory Program Manager/Chemist to inform the Program Lead of issues requiring corrective action, actions taken and the affect, if any, on the analytical data reported.

The turnaround time for sample analysis is 30 days from sample receipt, per the laboratory's contract.

B5. Quality Control Requirements

Collocated samples and trip blanks will be collected during the project. Two collocated samples will be collected on each day of sampling. The collection of two collocated samples will provide measurement of sampling precision and environmental variability.

Field blanks (sample media handled, exposed to outdoor air briefly, and shipped to the contract laboratory for analysis along with the collocated field samples) will be prepared and analyzed initially at a frequency with every shipment of field samples to the laboratory. The field blanks will be used to assess sampling accuracy and the potential for cross-contamination to occur during sample handling and shipment. As the study progresses, the frequency of field blank preparation and analysis may be reduced to biweekly if the following conditions are met: 20 trip blank samples have been submitted for analysis and the results are less than field sample results; the collocated field sample data do not indicate the potential for cross-contamination of samples; and the laboratory blank sample results analyzed as a part of the batch including the field samples indicate no significant laboratory contamination issues.

Laboratory quality control elements, including spikes and blanks will be performed in accordance with the ERG quality assurance plan (Appendix B).

B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The field equipment instrumentation testing, inspection, and maintenance will be performed in accordance with the field SOPs (Appendix C). Analytical instrumentation testing, inspection, and maintenance will be performed in accordance with the ERG quality assurance plan (Appendix B).

B7. Instrument Calibration and Frequency

Field equipment and analytical instrument calibrations will be performed in accordance with the appropriate referenced analytical or sample collection SOP and manufacturer's recommendations. Analytical instrumentation calibration will be performed in accordance with the ERG quality assurance plan (Appendix B).

B8. Inspection/Acceptance Requirements for Supplies and Consumables

The Technical Lead will be responsible for receipt and inspection of sample media and containers for return shipment to the laboratory. As described in B.2 above, the sample media need to be shipped to the field coated with sodium bisulfate. Rejection of sampling media and supplies needs to be reported to Mike Jones, OAQPS, with a copy to the Program Lead, because these are contract requirements that must be resolved by the EPA Contracting Officer for the analytical contract with ERG.

B9. Data Acquisition Requirements

Acquired data for this project include modeling results that were generated using an EPA-approved model, AERMOD, using protocols that are established in 40 CFR Part 58, Appendix W. Thus, the quality and reliability of the modeling is assured by using an approved model and following a prescriptive process.

B10. Data Management

Analytical data management will be in accordance with EPA's national contract for air sample analysis with ERG. Data will be reported both to Mike Jones, the EPA Contract Officer Representative, and Region 7's Program Lead. The Program Lead will review and validate the data, and transmit it to the project team for further review and analysis.

C. Assessment/Oversight

C1. Assessments and Response Actions

The EPA Region 7 QA Manager (RQAM) or designee may conduct an audit of the field activities for this project if requested by the EPA Program Lead or Technical Lead. The EPA RQAM will have the authority to issue a stop work order upon finding a significant condition that would adversely affect the quality and usability of the data. The EPA Technical Lead will have the responsibility for initiating and implementing response actions associated with findings identified during the on-site audit. Once the response actions have been implemented, the EPA RQAM will perform a follow-up audit to verify and document that the response actions were implemented effectively.

C2. Reports to Management

A six-month technical report will be prepared by the Program Lead and Technical Lead with support from the Regional Risk Assessor. The report shall incorporate the results form EPA air sampling and shall be distributed in accordance with section A3. The six-month report will contain environmental sampling results and will compare the results with the respective human health risk-based levels. The six-month report will also recommend whether additional sampling is needed.

D. Data Validation and Usability

D1. Data Review, Validation, and Verification Requirements

The data will be reviewed and reported by the contract laboratory in accordance with its procedures documented in the quality assurance plan (Appendix B). The EPA Program Lead and Technical Lead will be responsible for overall validation and final approval of the data in accordance with project purpose and use of the data.

D2. Validation and Verification Methods

ERG, the contract laboratory performing the analysis will input the data to EPA's Air Quality System (AQS). AQS contains outdoor air data collected by EPA, state, local, and tribal air pollution control agencies from thousands of monitoring stations. AQS also contains meteorological data, descriptive information about each monitoring station (including its geographic location and its operator), and data quality assurance/quality control information. OAQPS staff review and validate AQS using air program guidelines before release on the publically available portion of the AQS website.

The EPA Program Lead and Technical Lead will perform the final review and approval of the data prior to it being reported to the project team for decision making. The final review will consist of verifying that the sample collection and analyses were performed in accordance with the approved QAPP, and the SOPs provided in Appendices C and E. Final review and validation will include a review of the results of the collocated samples and trip blanks to ensure they are acceptable and have met precision and accuracy goals set forth in this QAPP. The final review will also compare the sample descriptions with the chain-of-custody/field sheets for consistency and will ensure that any anomalies in the data are appropriately documented.

D3. Reconciliation with User Requirements

Once the results are compiled, the EPA Program Lead and Technical Lead will review the results from collocated samples and trip blanks to determine if they fall within the acceptance limits as defined in this QAPP. Completeness will also be evaluated to determine if the completeness goal for this project has been met (> 90%). If data quality indicators do not meet the project's requirements as outlined in this QAPP (including the accuracy for lab spikes), the data may be discarded and re-sampling may occur. The EPA Program Lead and Technical Lead will evaluate the cause of the failure (if possible) and make the decision to discard the data and re-sample. If the failure is tied to the analysis, calibration and maintenance techniques will be reassessed as identified by the appropriate lab personnel. If the failure is associated with the sample collection and re-sampling is needed, sampling personnel will be retrained or the sampling method modified accordingly to correct the problem.

Data will be compared with meteorological data from the Kansas City Downtown Airport, looking particularly at the data when the predominant wind direction is from the source and toward the samplers. Results for dates when the wind direction is toward the monitors will be compared with the model predicted results. At a minimum, the average, maximum and minimum results will be reported by month and for the duration of the sampling program.

The data from dates when the predominant wind direction is not toward the samplers will be examined to determine whether the CertainTeed facility is the only source of Cr(VI) emissions in the area, or if there are other possible sources unknown to EPA at this time. Should the data indicate other potential sources of Cr(VI), EPA may adjust the number and location of samplers deployed as a part of this study, and/or, in consultation with KDHE, will conduct a more rigorous review of emissions inventory data and industrial classifications for facilities that may be contributing to measured levels of Cr(VI) in outdoor air.

APPENDIX A

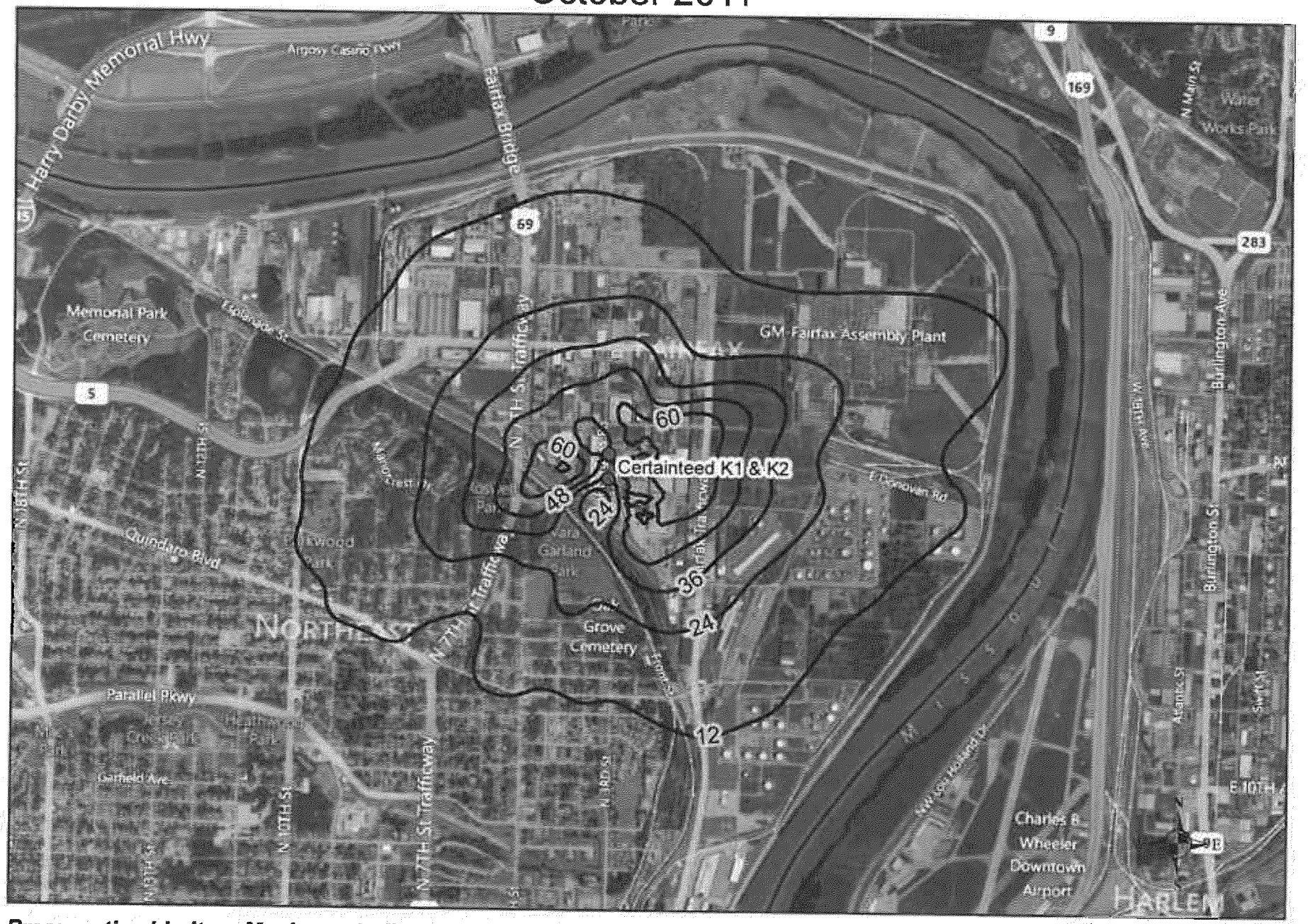
FIGURES

ED_000719_00018485

FIGURE 1 - LOCATION MAP & PROPOSED SAMPLER LOCATION

EPA_000889

Figure 2 Maximum Indiv al Cancer Risk (MIR)
Chromium (VI) Air Study
October 2011



Presumptive Limit on Maximum Individual Risk = 100 in a million
Risk assumes continious 70 year exposure

0 0.2 0.4 0.8 1.2 1.6 Miles

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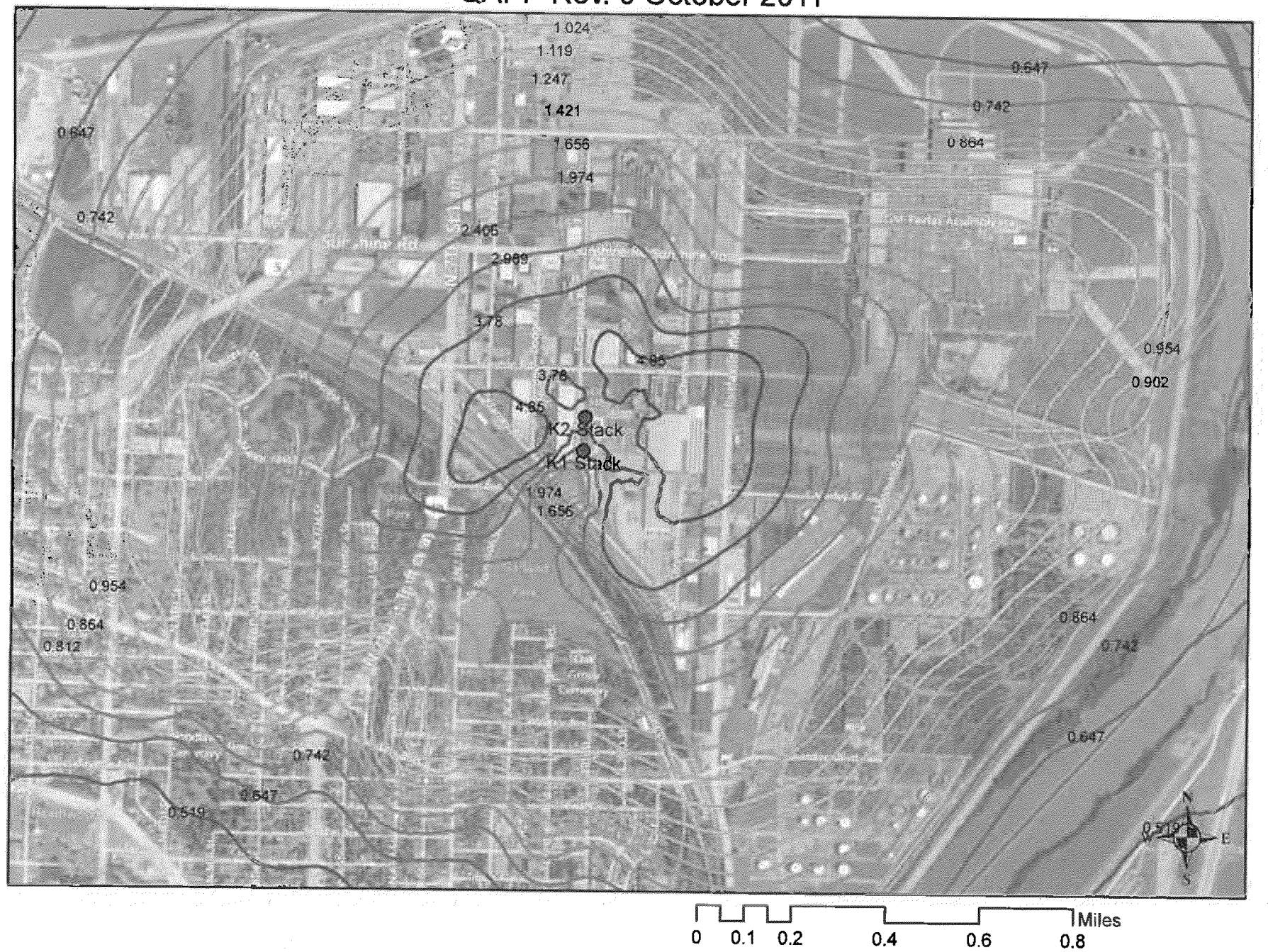
EPA_000890

Figure 3 Ambient Cr (VI) Concentrations (ng/m3)
Chromium (VI) Air Study
QAPP Rev. 0 October 2011



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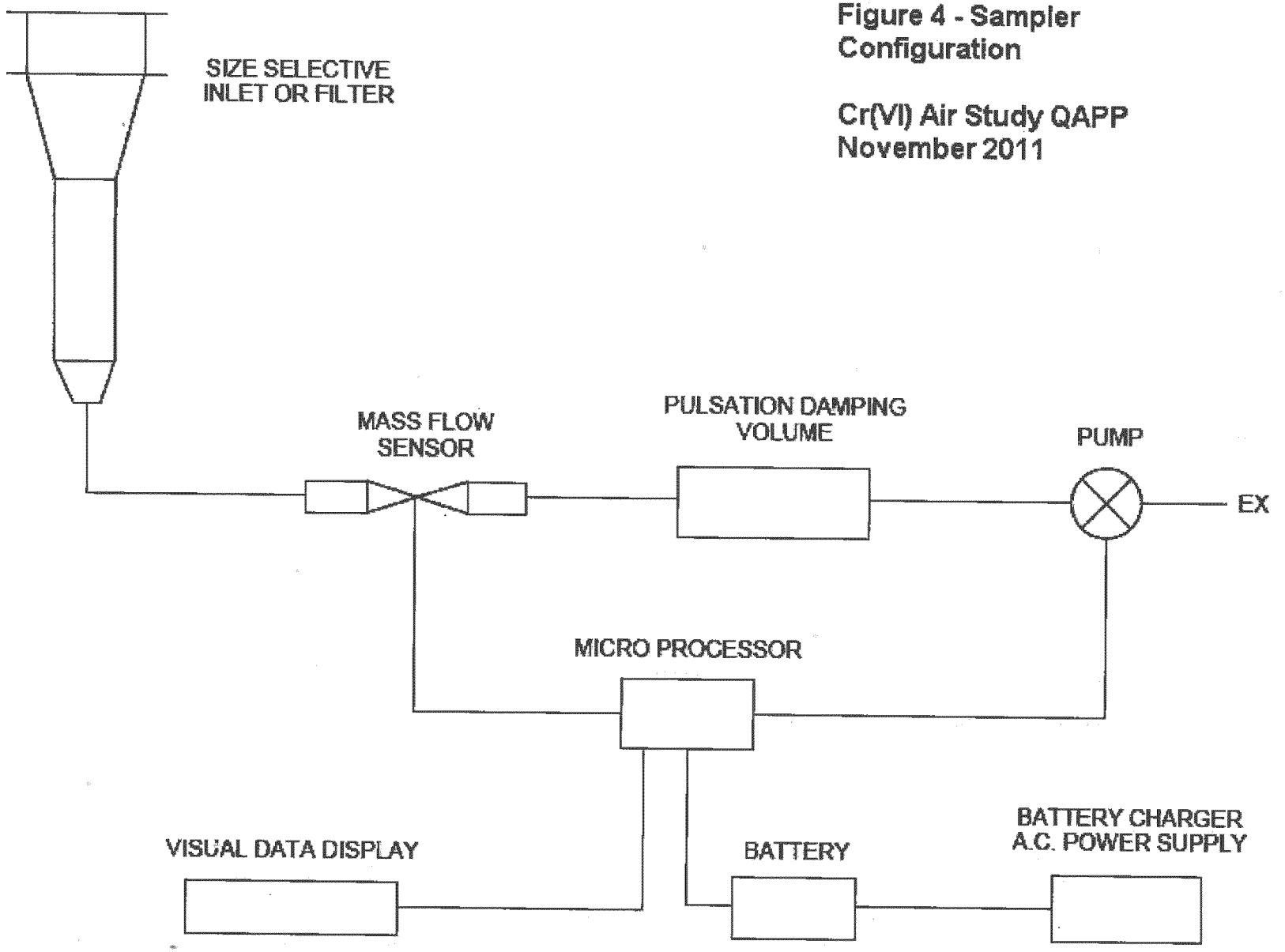

Figure 4 - Sampler Configuration

Cr(VI) Air Study QAPP
November 2011

EPA_000892

APPENDIX B

2011 ERG LABORATORY QUALITY ASSURANCE PLAN

APPENDIX C

STANDARD OPERATING PROCEDURE FOR MEASUREMENT OF HEXAVALENT CHROMIUM USING THE BGI PQ167R LOW VOLUME SAMPLER (U. S. EPA, 2009)

STANDARD OPERATING PROCEDURE FOR MEASUREMENT OF HEXAVALENT CHROMIUM USING THE BGI PQ167R LOW VOLUME SAMPLER

U.S. Environmental Protection Agency
Region 4, Science and Ecosystem Support Division
Athens, Georgia, 30605

ED_000719_00018485 EPA_000895

Acknowledgement

This Standard Operating Procedure (SOP) was developed by EPA Region 4, Science and Ecosystem Support Division. This SOP is based on the Commonwealth of Kentucky's ambient monitoring SOP template. Special thanks to BGI Inc. and ERG for operational content and illustrations.

For questions or comments please contact:

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Mike Jones, EPA-OAQPS-AQAD at jones.mike@epa.gov or 919-541-0528

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I. INTRODUCTION

This procedure is designed to provide instruction on collecting hexavalent chromium (Cr+6) in air using the BGI PQ167R air sampler for metals analysis.

The BGI PQ100 is an "Intelligent Air Pump" that can monitor its own airflow rate and thereby adjust the pump speed to compensate for changes in load pressure and/or other forces which would otherwise hamper the flow of air through a filter (or sample collector). The PQ100 unit can be programmed to begin its sampling job at a specific date, time, and stop sampling after the user defined run time is depleted. However, the sampling time should always be 24 hours for Cr+6 sampling the Toxics in Schools Study.

The PQ100 was designed to operate from 1 standard liter per minute (1000 cc per minute) to 25.0 standard liters per minute and is unaffected by changes in ambient temperature and barometric pressure. The flow rate precision is guaranteed to 2% of the calibration set point.

This SOP is designed to be a step by step method for operating the sampler to be used in conjunction with the manufacturer's operators manual. Laboratory Analysis Methodology may be referenced by contacting the Eastern Research Group (ERG) directly at 919-468-7800 or by email Julie.Swift@erg.com. Maintenance and troubleshooting should be conducted using the BGI167R operator's manual.

FIGURE 1. Schematic of PQ167 Sampling System
(Cr+6 filter holder apparatus replaces PM10 inlet head)

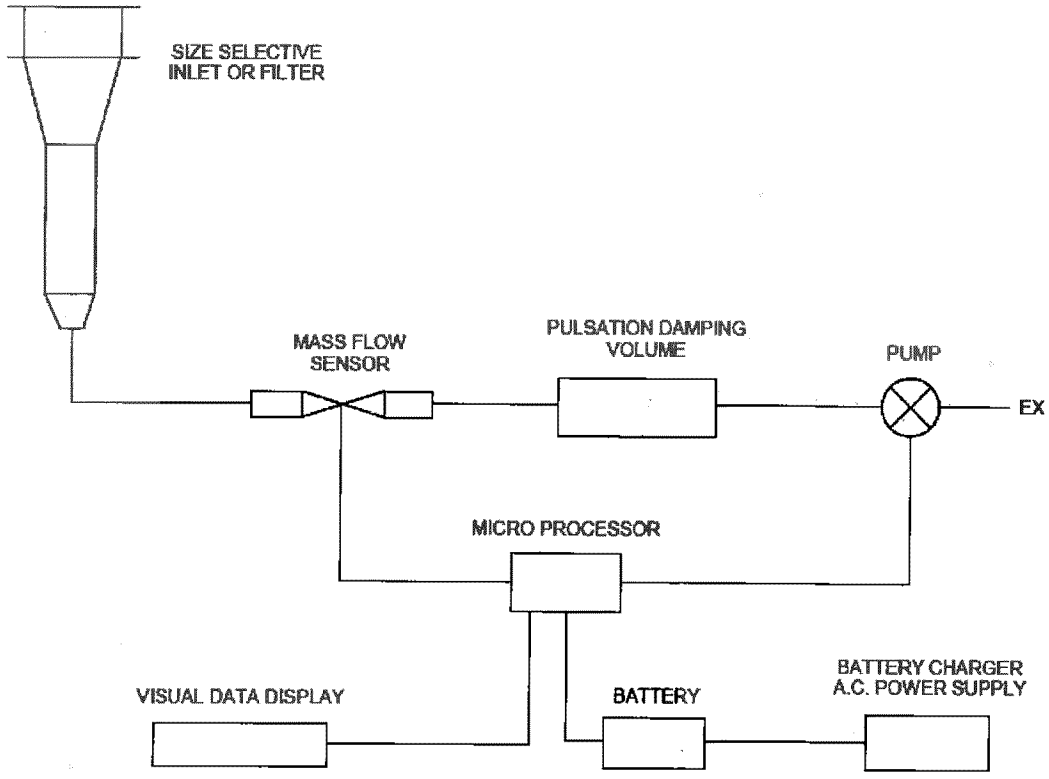
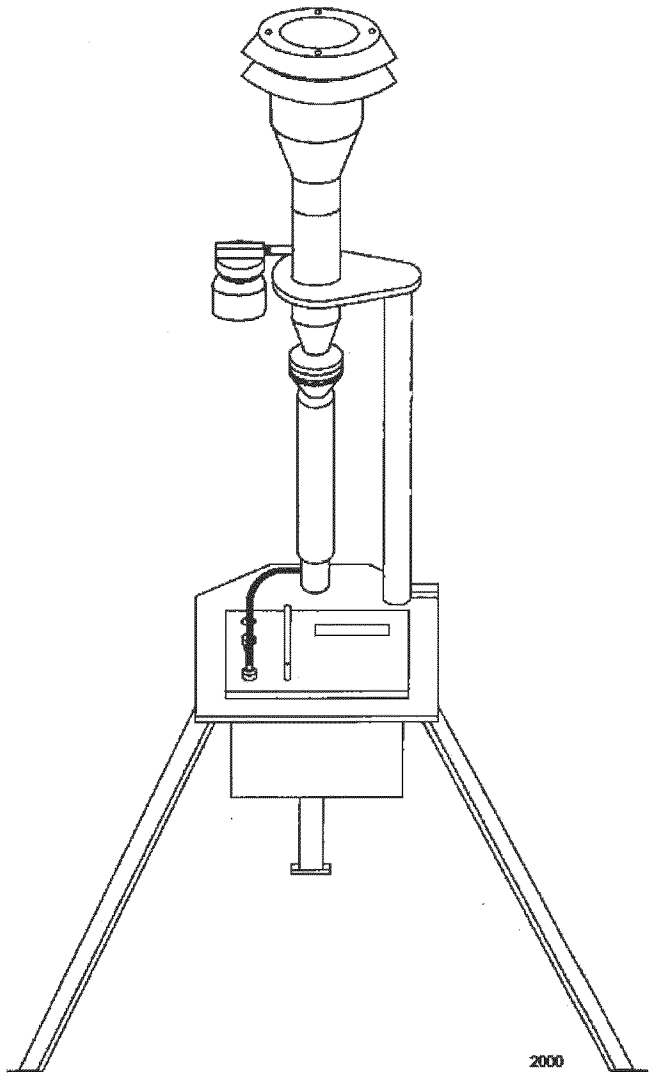


FIGURE 2. PQ167R with Mounting Stand
(Cr+6 filter holder apparatus replaces PM10 inlet head and filter cassette module and downtube assembly brace are not used)



II. INSTALLATION

A. Sampler Siting

Check the areas for safety. Ensure there will be enough room for the operator to move freely while working, and ensure physical conditions of the location will allow the operator to work safely.

The sampler should be set in a location unobstructed from any side. No tree limbs or other hanging obstructions should be above the sampler. It is suggested that the horizontal distance from the sampler to the closest vertical obstruction higher than the sampler be at least twice the height of the vertical obstruction. There should be no sources located nearby that may bias sampling measurements.

Locate the sampler on a reasonably level structure at a height between two (2) and fifteen (15) meters above the ground.

B. Sampler Installation

Assemble the sampler according to Figure 3 below omitting the installation of the PM10 inlet head, filter cassette holder assembly, and downtube assembly brace. For detail and illustration, refer to the BGI PQ167 Quick Start document, pages 2 through 8.

Cr+6 Retrofit Instructions

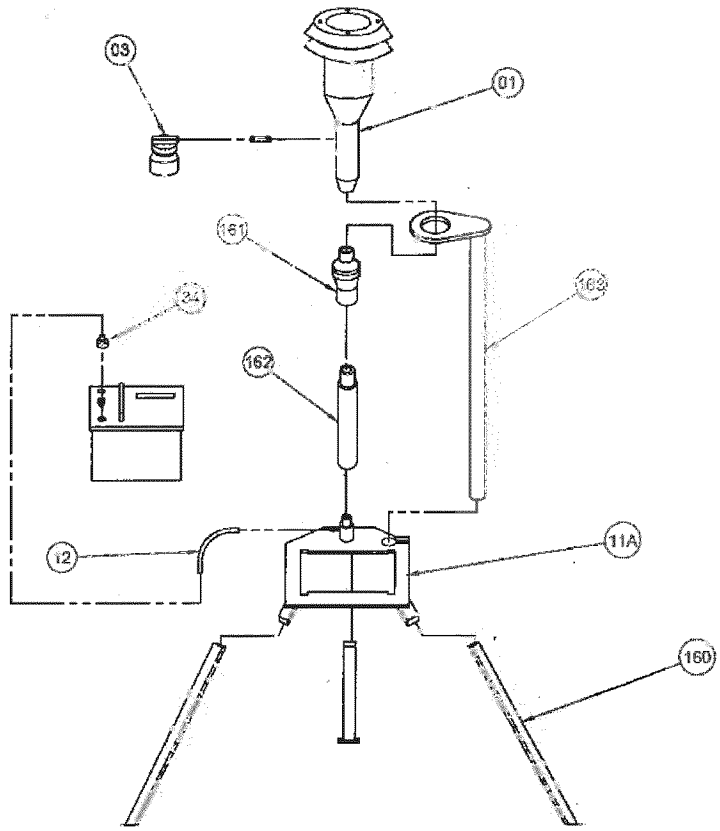
1. The sampling unit, at this point, should have legs mounted on the stand, and the pump and power components should be secured in the stand according to the PQ167 Quick Start document. The downtube, PM10 inlet head, and filter cassette holder assembly should NOT be installed.

2. Install the downtube on the top of the cylindrical mount on the stand. The mount should have tubing leading from the port on its side to the inlet on the pump module.

3. The total ERG Cr+6 filter holder apparatus consists of a BGI flow adapter with shut-off valve, stainless steel connector fitting, a length of "U" shaped stainless steel ¼ inch tubing, ERG filter assembly, and a glass funnel. **The ERG filter assembly and glass funnel will be provided for each sampling run and should not be installed until a sampling run is setup.** Place this apparatus (without ERG filter assembly) on the top of the downtube, and ensure that the shut-off valve is in the open position.

4. The open end of the stainless steel tubing should be capped when sampling is not in progress to prevent contamination.

Figure 3. Sampler Assembly Diagram
(Cr+6 filter holder apparatus replaces PM10 inlet head and filter cassette module and downtube assembly brace are not used)



01	PM10 Inlet head
03	Water collection bottle
11A	Tripod frame
12	Rubber hose
34	Hose adapter
160	Sampler leg
161	Filter cassette holder assembly
162	Downtube
163	Downtube assembly brace

Place and level the sampler on site. To secure the sampler and protect membrane roofs, 2 x 4 wooden studs may be cut into one foot sections and fastened to the feet of the legs using lag bolts. Place sand bags on these skids to prevent tipping of the sampler.

Connect the sampler to a grounded electrical outlet with 115 volts, and at least 5 amp service. Protect the connector from precipitation by fastening beneath the sampler or wrapping it with plastic tape.

If operating using a deep cycle marine battery for power, install the external power cord by screwing the round harness into the "utility adapter" port on top of the sampler. Attach the positive and negative contacts to the deep cycle marine battery and secure. A fully charged battery should provide power for at least 2 sampling runs. Depending on the battery available, more consecutive runs may be possible. Store the battery in a plastic container near the sampler to conceal and protect it from the weather.

If collocated samplers will be located at the site, the two samplers must be within four (4) meters of each other, but outside of two (2) meters. The inlet heights must be within one (1) meter vertically.

III. OPERATING PROCEDURE

A. Equipment and Supplies

BGI PQ167R
ERG Cr+6 filter holder apparatus
Flow calibrator
Logbook
ERG filter assembly with glass funnel
Cooler with ice substitute
Powderfree gloves
ERG sample paperwork

B. Sampler and Sample Media Receipt Activities

1. Plug sampler into AC power and charge the internal battery for at least 24 hours.

2. Check parts and components against the packing list.

3. After charging, ensure sampler will power up and that the main screen is operational.

4. The sampler may arrive with a default flow rate of 16.7 Lpm. **If**

during the initial verification, the sampler's target flow rate is displayed as 16.7 Lpm, it must be changed to 15 Lpm. Proceed directly to the calibration section of the SOP for direction in making the change.

5. The ERG Cr+6 Filter Holder Modules will arrive to the field office in a cooler with frozen ice substitutes. The modules will have paperwork designating them for a specific site and run day. **The modules must be kept in a freezer prior to sampling and kept cold during transport to the monitoring site for run preparation.**

6. It is highly recommended that there be as little time as reasonably possible between preparing the sampler for the next run (i.e. loading the sample media); the day prior is optimal.

7. **Samples must be retrieved the day following sampling, *preferably NLT NOON LST*, and returned to ERG cold using the ice substitutes provided.**

C. Verification

NOTE: THE PQ100 DOES *NOT* REQUIRE A LEAK TEST. CUTTING OFF THE FLOW OF AIR BY COVERING OR RESTRICTING THE AIR FLOW TO THE INLET WILL CAUSE DAMAGE TO THE INTERNAL PUMP AND WILL VOID THE WARRANTY.

To VERIFY flow:

1. Install a test ERG Cr+6 filter holder module if available. If a test module is not available, the module to be used for the next sample day is acceptable; however, the module must be used immediately following the verification/calibration.

2. Attach a NIST traceable flow standard to the inlet of the filter module. Ensure the flow standard is on and has equilibrated to ambient conditions.

3. Turn on the PQ167R by pushing the "ON/OFF" button. If a message is blinking on the display, press "ENTER" to proceed to the "MAIN IDLE DISPLAY".

   The screen display should read:

   ET0000Min TS00.00M (Date)
   Q(Flow)Lpm T(Time) Bty(Capacity)%

   (Date) – today's date in military notation; e.g., 01JAN= January 1st

(Flow) - the current flow rate selected to be regulated.
(Time) - military time; e.g., 13:08= 13 Hours 8 Minutes or 1:08 PM
(Capacity) - remaining charge in the internal battery.

4. Press SETUP three times until the Set START DATE and TIME screen appears: The screen should appear as below:

   Set START DATE and TIME
   (Date) (Time) Off

5. The word, "Off", should be displayed in the lower right corner of the screen. The bottom line of the display should be flashing. If "On" is displayed, press the "ENTER" button until "On" stops flashing. Then toggle to "Off" by pressing the + or – buttons.

6. Press the "SETUP" button twice to get to the "MAIN IDLE DISPLAY"

7. Press the "RUN/STOP" button to activate the pump.

8. Allow the pump to stabilize for at least 2 minutes.

9. If the measured flow and the flow indicated on the flow standard are within 4%, the sampler's calibration is acceptable. If the flow is outside 4%, the unit must be recalibrated.

10. Press the "RUN/STOP" button to turn off the pump.

D. Calibration

NOTE: THE PQ100 DOES *NOT* REQUIRE A LEAK TEST. CUTTING OFF THE FLOW OF AIR BY COVERING OR RESTRICTING THE AIR FLOW TO THE INLET WILL CAUSE DAMAGE TO THE INTERNAL PUMP AND WILL VOID THE WARRANTY.

To CALIBRATE flow:

1. Install a test ERG Cr+6 filter holder module if available. If a test module is not available, the module to be used for the next sample day is acceptable; however, the module must be used immediately following the verification/calibration.

2. Press "SETUP". The screen will read; "Select FLOW RATE"

3. From the "MAIN IDLE DISPLAY" press the "Setup" key once until the message below appears;

Select FLOW RATE

The Target Q should read 15.0 Lpm. If it does not read 15.0 Lpm, set TARGET FLOW RATE to 15.0 Lpm by pressing ENTER. The whole number value will remain on constant while the tenths still blink); use "+" or "-" to increase or decrease until 15 is displayed. Press ENTER (Tenths value will now remain constant while whole number blinks); use "+" or "-" to increase or decrease until .0 is displayed.

4. From the "Select FLOW RATE" message screen, press both the "Reset" key and the "Run/Stop" key simultaneously to enter the calibration mode and the message below will appear:

   CALIBRATE Target=15.0 Lpm

5. Press the "RUN/STOP" button to activate the pump and the message below will appear:

   CALIBRATE Target = 15.0 Lpm
   Reference Q.. XX.X

   The Reference Q is an approximate flow rate used only as a visual aid in finding the corrected flow on the calibration device. This value may indicate 5 to 15% error. This is for reference only!

6. Use the "+/-" keys to move the pump speed up or down until the calibration device indicates the desired flow rate.

7. When a stable reading has been achieved, press the "ENTER" key to store the flow rate.

8. Exit the Setup menu and return to the "MAIN IDLE DISPLAY". CALIBRATIONS ARE NOT AFFECTED UNTIL THE ENTER KEY IS PRESSED AND THE PUMP IS RUNNING.

9. Record pre- and post- flow measurements and adjustments in the logbook.

E. Conducting the Sampling Event

Site Arrival Daily Activities

1. Visually inspect and ensure all O-rings are in place and secure. Replace if necessary.

2. Always ensure that samples and unused ERG Cr+6 Filter Holder Modules are transported to and from the site cold.

3. Confirm all cables (electrical connections) are secure, and that exterior connections are protected from the elements.

4. Record activities, site observations, and maintenance activities in logbook.

Preparing Sampler for a Sampling Event

1. Prepare sample paperwork. On the ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET, complete the "Lab Pre-Samp." and "Field Setup" sections. Record any pertinent observations in the notes section at the bottom of the form.

2. Turn on the PQ167R by pushing the "ON/OFF" button. If a message is blinking on the display, press "ENTER" to proceed to the "MAIN IDLE DISPLAY". Then press "RESET" to clear prior run data.

3. Conduct an initial flow check (verification) by following the instructions in section **C. Verification.** Record the measurement from the flow standard on the ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET under the "Field Setup" section on the "Initial Rotameter Setting".

4. Following the flow check, the screen display should read:

   ET0000Min TS00.00M (Date)
   Q(Flow)Lpm T(Time) Bty(Capacity)%

   (Date) – today's date in military notation; e.g., 01JAN= January 1st
   (Flow) - the current flow rate selected to be regulated.
   (Time) - military time; e.g., 13:08= 13 Hours 8 Minutes or 1:08 PM
   (Capacity) - remaining charge in the internal battery.

5. Press "SETUP". The screen will read; "Select FLOW RATE" The flow rate value will be blinking.

6. The flow rate should read 15.0 Lpm. If it does not read 15.0 Lpm, the unit must be calibrated to 15.0 Lpm. See calibration section for adjusting target flow rate and calibration.

7. Press "SETUP". This is the date and time screen.

   The screen should read;

Set DATE and TIME
(dd) (mmm) (yyyy) (time)

To change the Date and Time;

TIP: Only the field not blinking can be adjusted. Push enter to move to the next field.

a. DAY: Press ENTER and change by pressing the + or - key. When the day is correct, press ENTER.

b. MONTH: To change, press + or - key. When correct, press ENTER.

c. YEAR: To change, press + or - key. When correct, press ENTER.

d. TIME (hrs): To change, press + or - key. When correct, press ENTER.

e. TIME (min): To change, press + or - key. When correct, press ENTER.

8. When date and time are correct press "SETUP"

9. This is the sample start screen which reads;

Set START DATE and TIME
(dd) (mmm) 00:00 Off

This screen allows you to set a start date and time for a sampling run. The default is set to midnight the next day. To designate your own start date and time:

a. DAY: Press ENTER and change by pressing the + or - key. When the day is correct, press ENTER.

b. MONTH: To change, press + or - key. When correct, press ENTER.

c. YEAR: To change, press + or - key. When correct, press ENTER.

d. TIME (hrs): To change, press + or - key. When correct, press ENTER.

e. TIME (min): To change, press + or - key. When correct, press ENTER.

f. Enable the run by setting the "On/Off" function on the screen to "On".

WARNING: The sampler will not automatically activate if this option is set to "Off".

10. Press "SETUP"

The screen will read;

Set RUN TIME
Hours: 24 Min: 00 On

Set to 24 hours 0 minutes. The default is always 24 hrs 0 min, the required sample duration. If the sample time needs to be modified, adjust as instructed in step 6 and 8.

11. Press "SETUP". The screen will return to the "MAIN IDLE DISPLAY"

WARNING: DO NOT PRESS THE RESET BUTTON AT THIS TIME AS THE START TIME AND RUN TIME WILL DEFAULT.

12. Press "RUN/STOP"

If the START TIME ENABLE is set to "On" then the message "Alarm Triggered Run..." followed by "PQ100 Powering Down.." will appear briefly. The PQ100 is now waiting for the internal real time clock to achieve the designated start time and will then power itself on and begin the sampling run. If the START TIME ENABLE is set to "Off" then the pump will begin to run immediately. If this occurs, press RUN/STOP and begin back at step 2 ensuring START TIME ENABLE is set to "On".

Installing the ERG Cr+6 Filter Holder Module

NOTE: Gloves must be changed for each sample, i.e. between retrieving a sample and preparing a new run gloves MUST be changed to prevent cross contamination.

1. Remove the sample inlet cover on the stainless steel probe and make sure there is no contamination on the probe.

2. Put on a clean pair of powderfree gloves

3. Take the ERG Cr+6 Filter Holder Module storage container from the cooler and carefully remove the module. The module may be in a plastic bag. Return the bag to the container for use in the collection procedure.

4. Make sure the glass funnel is securely attached to the filter holder. Loosen the small top nut on the filter container. Arrows will be present on the filter holder showing air flow direction and they should always point to the end of the sample probe line.

5. Holding the module with the glass funnel facing down, slide the probe into the top fitting of the filter module and tighten the nut. Tighten the nut until the ERG Cr+6 Filter Holder Module is securely fastened to the probe. Do not overtighten the plastic nut.

   NOTE: If running a field blank, repeat steps 1 through 5, count to 10, and then remove the field blank filter holder module and place it back into the antistatic bag. Label the bag to designate the filter module as a field blank. Log the filter ID as field blank in the comments section of the ERG Hexavalent Chromium Sample Data Sheet. The field blank must be run before the sample filter module is fastened to the probe.

Sample Recovery and Data Collection

NOTES:

I. **Samples must be retrieved the day following sampling, *preferably NLT NOON LST*, and returned to ERG cold using the ice substitutes provided.**

II. **Gloves must be changed for each sample, i.e. between retrieving a sample and preparing a new run, to prevent cross contamination.**

1. On the ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET, fill in the "Field Recovery" section. Be sure to fill in the "Recovery Date", "Recovery Time", "Elapsed Time" (ETXXXXMin from sampler), and circle a "Status" selection. This information will be on the "MAIN STATUS SCREEN".

2. Conduct a final flow check (verification) by following the instructions in section **C. Verification.** Record the measurement from the flow standard on the ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET under the "Field Setup" section, "Final Rotameter Reading".

3. Put on a clean pair of powderfree gloves

4. Take the module storage container from the cooler, open, and set aside.

5. While holding the ERG Cr+6 Filter Holder Module, loosen the top nut holding the module to the sample inlet and slide the module off the stainless steel probe.

6. Place the ERG Cr+6 Filter Holder Module including glass funnel in the plastic bag and place back into the storage container. Place the storage container into a cooler with ice substitutes.

7. Place cover back on end of probe line.

8. Data may be downloaded to a laptop using the PQ100/200 DOWNLOAD SOFTWARE. ERG does not require this data, but direction can be found in the BGI PQ167 Quick Start document, pages 16 and 17.

Sample Shipping

The ERG Cr+6 Filter Holder Module container must be packed in a cooler with ice substitutes and shipped overnight cold to ERG. The sample paperwork must be included in the shipment. Use the pre-filled out FedEx label provided by ERG, and fill out the "Sender" section with the sampling agency's address and phone number. Send priority overnight to ERG.

If the shipping form is lost, use the address below for shipping to ERG, and contact them directly for the FedEx accounting.

Address: ERG
601 Keystone Park Drive
Suite 700
Morrisville, NC 27560
919-468-7924

IV. QUALITY ASSURANCE

To ensure that quality data is being collected the following checks should be considered:

A. Flow Calibration

A flow verification must be completed at the beginning of the study period. If the verification does not compare within 4%, the flow must be calibrated. Document all quality assurance activities in the logbook.

B. Flow Verifications

The flow must be verified or checked at the beginning and end of the sampling event to determine an average sample flow. Document all quality assurance activities and observations in the logbook.

C. Independent Audits

If possible, it is recommended that an independent flow check of the sampler be conducted at some point during the study. This check may be conducted by a state or local agency's quality assurance team or independent audit program.

V. DATA FORMS

All sample related run data forms will be supplied by ERG. Check the data sheets for completion after every setup or retrieval event. The operator is expected to keep a logbook to document all site activities, quality assurance activities, and sampling activities. The ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET is attached below.

ERG Ambient Hexavalent Chromium Sample Data Sheet

ERG Lab ID # _____

AMBIENT HEXAVALENT CHROMIUM DATA SHEET

Lab Pre-Sampling

Site Code: _____ Collection Date: _____
City/State: _____ Primary Event (Y/N): _____
AQS Code: _____ Collocated Event (Y/N): _____

Field Setup

Site Operator: _____ System #: _____
Set-Up Date: _____ Elapsed Timer Reset (Y/N): _____
Collection Date: _____
Batch I.D. No.: _____
Initial Rotameter Setting (C.O. B.): _____ (After 5 minutes warm-up)
Programmed Start Time: _____ Programmed End Time: _____

Field Recovery

Recovery Date: _____ Recovery Time: _____
Final Rotameter Reading (C.O.B.): _____ (After 5 minutes warm-up)
Elapsed Time: _____ Status: Valid Void (Circle one)

Lab Recovery

Received by: _____ Date: _____ Refrigerator No: _____
Status: Valid Void (Circle one) Temperature: _____
If void, why: _____
Collection Time (Minutes): _____
Flowrate (L/min): _____
Total Volume of Air Sampled (m^3): _____

Comments: _____

White: Sample Traveler Canary: Lab Copy Pink: Field Copy

APPENDIX D

COLLECTION AND ANALYSIS OF HEXAVALENT CHROMIUM IN AMBIENT AIR

ERG

www.erg.com

January 9, 2007

Mr. Michael Jones
Emissions, Monitoring and Analysis Division (C339-02)
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Mr. Jones:

I have enclosed a copy of the paper we recently presented for "Collection and Analysis of Hexavalent Chromium in Ambient Air". We presented this paper at the NEMC in Washington, DC (August, 2006), and the QA Region 6 Conference, in Dallas, TX (October, 2006).

If you have any questions or comments, please call me at (919) 468-7924.

Sincerely,

Julie L. Swift

Julie L. Swift
Senior Program Manager

cc: Dennis Mikel, EPA

601 Keystone Park Drive, Suite 700, Morrisville, NC 27560 • Phone (919) 468-7924 • Fax (919) 468-7803
Arlington, VA • Atlanta, GA • Austin, TX • Boston, MA • Chantilly, VA • Chicago, IL • Fairfield, CT
Harrisburg, PA • Kansas City, KS • Lexington, MA • Nashua, NH • Research Triangle Park, Morrisville, NC • Sacramento, CA
San Francisco, CA • Tampa, FL

Collection and Analysis of Hexavalent Chromium in Ambient Air

Prepared by J. Swift, M. Howell, D. Tedder
Eastern Research Group, 601 Keystone Park Drive, Suite 700, Morrisville, NC 27560

ABSTRACT

Hexavalent chromium (Cr^{6+}) is one of the top four pollutants of concern in the EPA National Air Toxics Trends Stations (NATTS) Program. The Environmental Protection Agency (EPA) worked in conjunction with Eastern Research Group (ERG) to improve the California Air Resource Board (CARB) Method 039 for Cr^{6+} monitoring. Attempts to sample and analyze Cr^{6+} at NATTS with improved sensitivity uncovered challenges in the sampling procedures. Issues with background contamination on filters and stability of field samples were the most important contributors to bias and imprecision. Different filters and filter preparations were studied to minimize background Cr^{6+} on filters. A standardized method for media preparation and storage will be discussed. A stability study was performed to determine the best storage conditions to maintain Cr^{6+} stability with less than 30 Relative Percent Difference (RPD). The stability of Cr^{6+} was also evaluated using collocated samplers with spiked and blank filters. Data, using improvements to the Cr^{6+} sampling and analysis procedure for the NATTS, will be presented to show the recent history of Cr^{6+} recovery from field samples.

INTRODUCTION

Chromium is a natural constituent of the earth's crust and is present in several oxidation states. Trivalent chromium (Cr^{3+}) is naturally occurring, environmentally pervasive and a trace element in man and animals. Hexavalent chromium is anthropogenic from a number of commercial and industrial sources. It readily penetrates biological membranes and has been identified as an industrial toxic and cancer substance. Hexavalent chromium is a known inhalation irritant and associated with respiratory cancer. Exposure occurs primarily in the chrome plating and anodizing process, and emissions from chromate treated cooling towers.

METHOD DEVELOPMENT

Previous sampling and analysis studies for Cr^{6+} at NATTS have shown a variety of issues including filter contamination and storage stability issues. High filter background concentrations are due to manufacturing processes or contamination in storage. Background contamination results in small differences between measured and blank values, which make data interpretation at low concentrations less confident.

Determining the Sampling Media

Four types of filter media were examined to determine which performed best in terms of background contamination and stability. These filters were prepared using the CARB Standard

Operating Procedure (SOP) 039 to determine if the chromium leaching off the filters at ambient temperatures would cause contamination. The filters used in this study were:

- Cellulose;
- Binderless Quartz;
- Teflon®; and
- Polyvinyl Chloride (PVC).

The results of this study show that the best media is the cellulose filters. The Teflon® filter results are questionable because the coating solution does not adhere to these filters. The results for all of the filters are presented in Table 1 below.

Table 1: Chromium Filter Background Contamination – Assessing the Filter Media

	Filter Media Concentrations (total ng)			
Sample Name	**Cellulose**	**Binderless Quartz**	**PVC**	**Teflon®**
Day 0 – 1	Not Detected	8.42	2.43	0.320
Day 0 – 2	Not Detected	6.95	2.03	0.370
Day 0 – 3	Not Detected	8.22	3.00	0.400
Day 6 – 1	Not Available	21.9	Not Available	Not Available
Day 6 – 2	Not Available	47.7	Not Available	Not Available
Day 6 – 3	Not Available	28.3	Not Available	Not Available
Day 12 – 1	1.44	Not needed	15.9	0.430
Day 12 – 2	1.12	Not needed	14.6	ND
Day 12 – 3	0.760	Not needed	14.4	ND

ERG treated the cellulose filters selected from initial evaluation of filter media in an attempt to reduce the background below the detection limit of the analysis method. Filters were cleaned with nitric acid to remove hexavalent chromium prior to filter preparation before sampling. Once cleaned, hexavalent chromium was not detected on any unspiked filters. Recovery on spiked filters was from 92 to 100 percent. Based on these results, the acid washed filters are determined to have no associated chromium contamination.

Temporal Stability Study

A temporal study was performed on cellulose and Teflon filters because of the low recovery of background Cr^{6+} in the background contamination study. To determine if the preferred filter preparation method would interfere with recovery of Cr^{6+} samples, 32 bicarbonate coated cellulose and 32 Teflon filters were prepared and spiked. All filters were spiked with 2.5 total ng Cr^{6+} and placed on the laboratory countertop. The experimental design for each filter media included:

- Four spiked filters were analyzed the day they were spiked and four were placed in the freezer.
- Four spiked filters were analyzed the day after spiking (Day 2) and four were placed in the freezer.
- Four spiked filters were analyzed two days after spiking (Day 3) and four were placed in the freezer.
- Four spiked filters were analyzed three days after spiking (Day 4) and four were placed in the freezer.

Table 2 shows the spiked filter results.

Table 2: Cr^{6+} Filter Stability Study

Spiked Samples	Cellulose Filters		Teflon Filters	
	Average Concentration (total ng)	**Percent Recovery**	**Average Concentration (total ng)**	**Percent Recovery**
Stored at Room Temperature				
Day 1	2.17	87 ± 3%	2.05	89 ± 5%
Day 2	2.20	88 ± 4%	2.25	98 ± 6%
Day 3	2.28	91 ± 3%	2.27	99 ± 35%
Day 4	1.93	**77** ± 10%	2.53	110 ± 3%
Stored at -18°C				
Day 1	2.62	105 ± 3%	NA	NA
Day 2	2.66	107 ± 3%	NA	NA
Day 3	2.74	109 ± 7%	2.46	108 ± 8%
Day 4	2.58	103 ± 7%	NA	NA
Day 7	2.75	110 ± 8%	NA	NA
Day 8	2.54	102 ± 4%	NA	NA
Day 9	2.57	103 ± 1%	NA	NA
Day 10	2.60	104 ± 4%	NA	NA
Day 11	2.71	108 ± 2%	NA	NA
Blanks	ND	NA	ND	NA

NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%.

One of the purposes of this study is to determine whether it is feasible to have the filters stored in the field for more than one day after sampling. The cellulose filters stored at room temperature had a reduced recovery from 87 percent on Day 1 to 77 percent on Day 4. The recoveries for the Teflon filters stored at room temperature varied from Day 1 to Day 4 by approximately 15 percent. Once the cellulose filters were stored at -18°C before analysis, however, the percent recovery varied 102 to 110 percent. Because only one set of Teflon filters was frozen for the stability study, limited data is available for conclusions; however, the recovery for Day 3 is 108 percent. This study shows that the cellulose filters would need to be recovered within 1 day to determine the best recovery, whereas the Teflon filter could be recovered up to 4 days without

any significant loss. Also, once frozen, the Cr^{6+} can be considered stable and can be left on the cellulose filters for up to 11 days.

Interfering Element Check

Possible interfering compounds were added to the filters and to determine if there were any positive or negative interference when analyzing for Cr^{6+}. All filters were spiked with 10 total ng of Cr^{6+}. Four separate sets of filters were spiked with 10 total ng of Cr^{3+}, Fe, and Mg. All recoveries were within 95% ± 13%, indicating that these elements do not pose any interference for the analysis of Cr^{6+}.

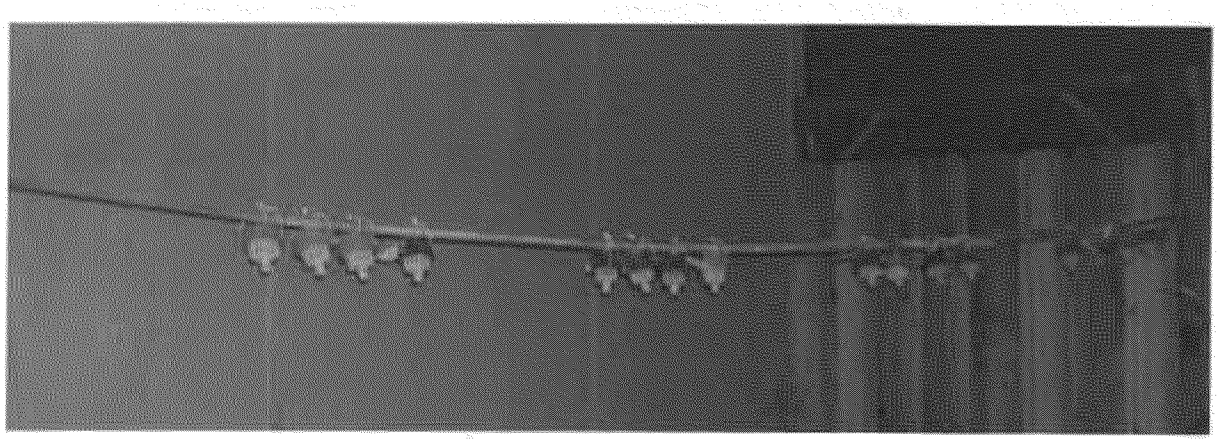
Method Validation

Field studies were performed to validate the filter preparation and storage study determined acceptable under laboratory conditions.

Cr^{6+} Sample Stability Study

In order to determine the stability of a sample in field before retrieval, filters were spiked and left in the field for up to 4 days. All filters were spiked with 2.5 total ng Cr^{6+}. Filters were installed on a line in the field. Four filters were prepared for each batch of samples and are shown in Figure 1.

Figure 1. Field Cr6+ Sample Stability Study



The filters were left for 33 hours – 24 hours (based on 1 day) plus 9 hours (needed for sample retrieval). All samples were analyzed on the day the samples were recovered, as presented in Table 3.

Table 3: Cr^{6+} Filter Stability Study – Sample Stability (Cellulose Filters)

Spiked Samples in Field	Average Concentration (total ng)	Percent Recovery	Average Relative Percent Difference (RPD)	Coefficient of Variation (CV)
Spiked and placed in Freezer after Days presented and analyzed after sample pickup.				
33 Hours	1.76	**70%**	30% ± 6%	8%
57 Hours	1.27	**51%**	49% ± 6%	13%
81 Hours	1.19	**48%**	53% ± 4%	9%
105 Hours	1.05	**42%**	58% ± 5%	11%

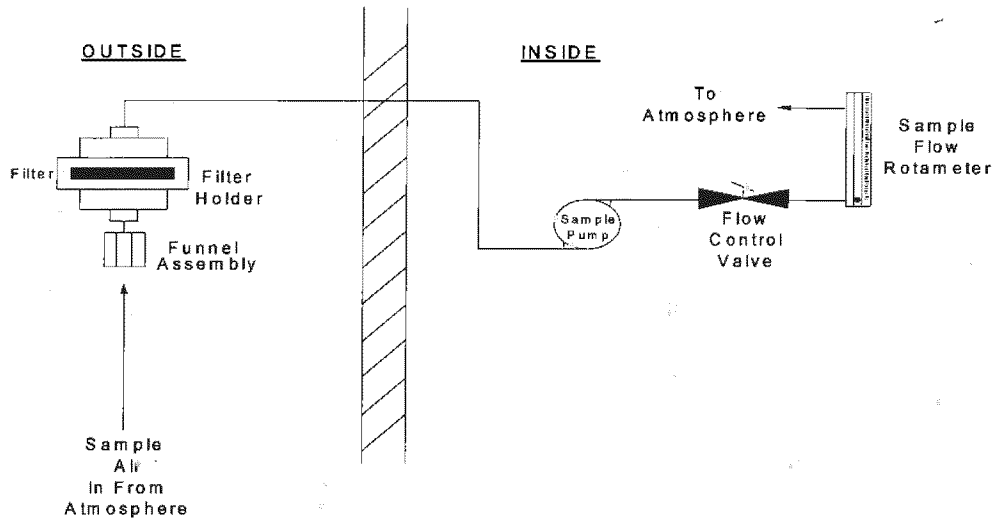
NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%.

The purpose of this study was to determine whether it is practical to leave the cellulose filters in the field for more than one day after sampling. The cellulose filters stored in the field had reduced recoveries from 70 percent for 33 hours (24 hours + 9 hours for recovery) to 42 percent for 105 hours (24 hours times 4 days + 9 hours for recovery). This study shows that the cellulose filters would need to be recovered within 1 day in order to allow the best recovery possible. Once frozen, however, the Cr^{6+} can be considered stable and can be left on the cellulose filters for up to 11 days (as presented in Table 2).

Cr^{6+} Sampling Study

To continue evaluating the preparation and stability of these filters, a field sampling study was performed. A hexavalent chromium sample is collected by pulling ambient air through the prepared filter at a known flow rate for a period of 24 hours. The hexavalent chromium sampling system is designed to automatically perform a 24-hour filter collection and is automated using a digital timer to initiate sample collection at a flow rate of 15 Lpm. The prepared filter assembly is attached to the inlet of the probe, and the funnel is attached to the inlet of the filter assembly. At the end of the 24-hour collection period, the filter assembly containing the exposed filter is removed from the sampler. The Teflon rod stock plugs are reinserted into the inlet and outlet. Figure 1 presents a standard Cr6+ sampling layout.

Figure 1. Cr^{6+} Sampler Layout



Cr^{6+} Sampling Study – Cellulose Filters

A sampling site was chosen for the initial study which included a collocated sampler loaded with either spiked or unspiked filters. For the initial study, each sample sets collected the following cellulose filters:

- One filter unspiked. (Background Sample)
- One filter spiked at 2.5 total ng. Total spiked amount in a 21.6 m^3 sample is 0.12 ng/m^3. This value is 10 times the current detection limit, but is assumed an appropriate average result from samples collected in the field. (Spike)
- One trip blank (stored in cooler during sampling period). (Trip Blank)
- One filter spiked at 2.5 total ng and left in the filter container. This filter was stored in the freezer while the samples were taken to the field. It was taken out of the freezer immediately before analysis. (Matrix Spike)

All samples were analyzed the day after collection. The results are presented in Table 4 below. All passive and trip blank samples had no detectable hexavalent chromium. The recoveries of spiked samples are slightly better during cold, wet days.

Table 4: Ambient Monitoring Study – Cellulose Filters

Sample Set	Conditions				RPD	% Recovery
	Sample Volume (m^3)	Humidity	Temperature	Comments		
1	21.57	88% (58% - 96%)	48.8°F (44.1°F - 57.9°F)	Rain	**28**	72%
MS – 1					3.2	103%
2	21.66	81% (38% - 100%)	41.3°F (37°F – 59°F)	Rain	6.4	94%
MS – 2					4.0	96%
3	21.7	76% (37% - 100%)	37.8°F (34°F – 42.1°F)	Overcast to Clear	**73**	27%
MS – 3					9.1	109%
4	21.7	42% (24% - 61%)	35.3°F (27°F – 45°F)	Cloudy to Clear	**58**	42%
MS - 4					0	100%

NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%.
MS = Matrix Spike

The cellulose filters showed varying recoveries on the samples taken. Two of the 8 spiked filters recovered under 70%, with a total average recovery at 80%.

Cr^{6+} Sampling Study – Teflon® Filters

A comparison study was performed to reproduce the sampling completed on the cellulose filters. This study is presented in Table 5 and is described below:

- Teflon Set 1 through 3 followed same procedures as the cellulose study (spiked at 2.5 total ng),
- Teflon Set 4 through 7 collected using a lower flow rate at 8 L/min (spiked at 2.5 total ng for 4 and 5, 5.0 total ng for 6 and 7),
- Teflon Set 8 and 9 collected at 15 L/min with a particulate filter before the spiked filter (spiked at 2.5 and 5.0 total ng, respectively),
- Teflon Set 10 and 11 collected using an ozone scrubber cartridge (used for TO-11A sampling) that would take out ozone as well as particulate (spiked at 2.5 total ng).

Table 5: Spiked Teflon Filter Study (with rough polypropylene support)

Sample Set	Setup	RPD	% Recovery
Teflon Set 1	Standard conditions at 15 L/min	**24**	76%
Teflon Set 2		**64**	**36%**
Teflon Set 3		4.0	96%

Sample Set	Setup	RPD	% Recovery
Teflon Set 4	Flow at 8 L/min	1.2	101%
Teflon Set 5		**83**	**17%**
Teflon Set 6		9.0	109%
Teflon Set 7		**60**	**41%**
Teflon Set 8	Collected a particulate filter before spiked filter	1.9	98%
Teflon Set 9		5.6	94%
Teflon Set 10	Collected using an ozone scrubber before spiked filter	13	113%
Teflon Set 11		6.3	94%

NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%.

The Teflon also showed varying recoveries. Three of the 11 spiked filters recovered under 70%, with a total averaged recovery at 80%. This indicated a close comparison of the Teflon to the cellulose filter Cr^{6+} collection.

Cr^{6+} Sampling Study – Interferants

In order to distinguish other possible interferants, another set of experiments were preformed:

- Volume Check - the rate of collection was too high by reducing the overall sample volume to 11.5 m^3,
- Particulate Check - the particulate reacted with the Cr^{6+} to reduce it to Cr^{3+} by having a Teflon filter inline before the spiked filter, and
- Ozone Check – ozone reacts to oxidize other agents that could reduce the Cr^{6+} to Cr^{3+}.

As presented in Table 6, the Cr^{6+} recovery was not affected by changing any of these parameters (volume, particulate and ozone).

Table 6: Physical interferants check for Cr^{6+} sampling.

Sample	Spiked in total ng	Results in total ng	Percent Recovery
Volume Check – collected at 11.5 m^3 (instead of standard 21.6 m^3)			
Run 1	2.5	2.53	101%
Run 2	5.0	5.45	109%
Particulate Check – collected particulate before ambient air crossed spiked filter			
Run 1	2.5	2.45	98%
Run 2	5.0	4.72	94%
Ozone Check – scrubbed ozone and particulate before ambient air crossed spiked filter			
Run 1	2.5	2.82	113%
Run 2	5.0	4.68	94%

Comparison Sampling using Cellulose and Teflon Filters

The optimal way to confirm the performance using either filter is to collect collocated sets of cellulose and Teflon filters. ERG sent five different NATTS sites the standard cellulose and Teflon filters as a means to evaluate the performance of the Teflon filters. These sites were selected based on recent history of Cr^{6+} in their samples. The results are presented in Table 7 below.

Table 7: Comparison of Cr^{6+} Recovery on Cellulose and Teflon Filters

Site	Total # of Samples	Cellulose Concentration Higher (>30% RPD)	Similar Results on Cellulose and Teflon (±30% RPD)	Teflon Concentration Higher (>30% RPD)
Boston, MA	3	100%	0%	0%
Detroit, MI	5	80%	20%	0%
Seattle, WA	4	25%	75%	0%
Tampa, FL	5	80%	0%	20%
Washington, DC	4	75%	0%	25%
Average	4	72%	19%	9%

Note: Sampling was conducted from June to August 2005.

This table shows the total number of samples collected at each site and compares the Cr^{6+} recoveries of the cellulose to the Teflon filters. For example, the site in Detroit sampled 5 sets of collocated filters (one cellulose and one Teflon filter) during the same sampling period. One of these filter sets had similar recoveries on the cellulose and Teflon filters, and the other 4 filter sets had higher Cr^{6+} recoveries on the cellulose filters. The lower recovery on the Teflon filters could be due to other reducing agents in the ambient air that would convert the Cr^{6+} to Cr^{3+}. This is prevented on the cellulose filters because of the sodium bicarbonate coating. In Seattle, WA, the air stream is blown from the west, off the Pacific Ocean. Because of the lower interference from mobile and emission sources, the difference between the cellulose and Teflon filters is minimal. The other 4 sites (Boston, Detroit, Tampa, and Washington, DC) are in highly populated areas where these emissions could reduce the Cr^{6+} significantly. Based on the results of this sampling study, ERG determined that collection on the acid washed, sodium bicarbonate coated cellulose filters would recover the Cr^{6+} more efficiently for real-world ambient samples.

FIELD SAMPLE RESULTS FOR HEXAVALENT CHROMIUM

Twenty-two National Monitoring Program (NMP) sites collected Cr^{6+} samples from January 2005 to December 2005. Some monitors were placed near the centers of heavily populated cities (e.g., Chicago, IL and Detroit, MI), while others were placed in moderately populated areas (e.g., Madison, WI and Hazard, KY). Hexavalent Chromium concentrations measured during this time varied significantly from monitoring location to monitoring location. The proximity of the monitoring locations to different emissions sources, especially industrial facilities and heavily traveled roadways, often explains the observed spatial variations in ambient air quality.

Table 8 presents the frequency of detects, maximum value, minimum detected value, median, and average.

Table 8: Analytical Results for samples collected between January 2005 and December 2005.

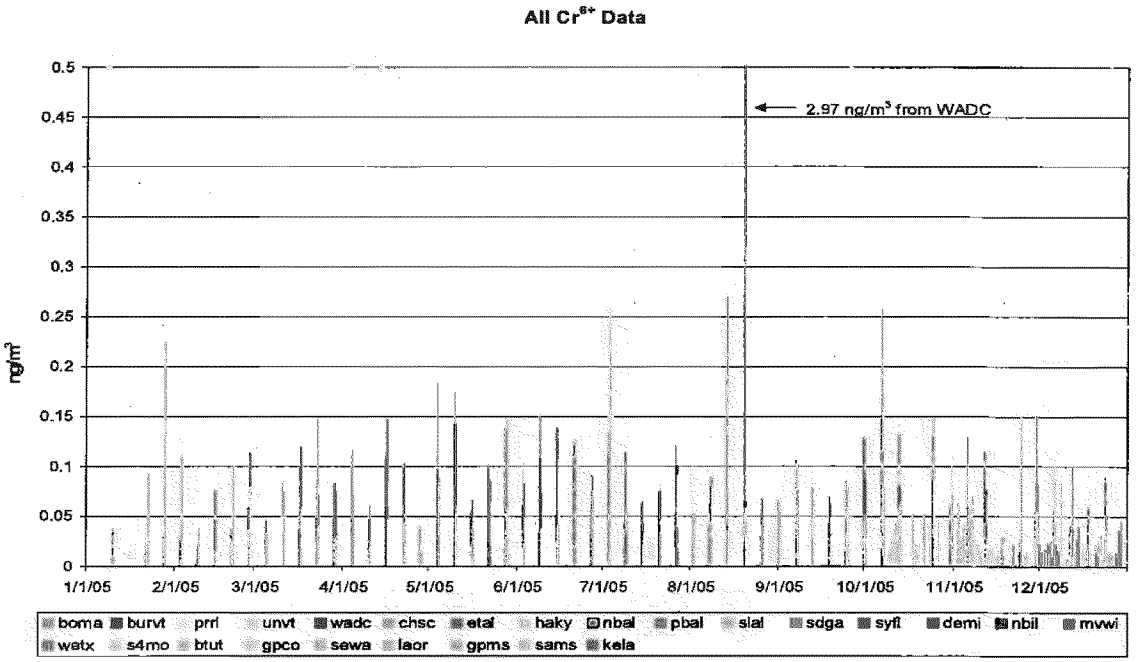
Sites	% Frequency	Maximum Value (ng/m^3)	Minimum Value (ng/m^3)	Median (ng/m^3)	Average (ng/m^3)
Roxbury, MA	78%	0.269	0.017	0.048	0.071
Burlington, VA	80%	0.147	0.003	0.054	0.065
Providence, RI	100%	0.119	0.006	0.023	0.028
Underhill, VT	32%	0.101	0.005	0.027	0.034
Washington, DC	54%	2.970	0.010	0.026	0.156
Chesterfield, SC	40%	0.147	0.006	0.024	0.034
Birmingham, AL (site 1)	73%	0.081	0.020	0.041	0.049
Hazard, KY	43%	0.103	0.011	0.029	0.036
North Birmingham, AL	67%	0.100	0.016	0.046	0.050
Providence, AL	50%	0.026	0.004	0.019	0.016
Birmingham, AL (site 2)	56%	0.104	0.029	0.044	0.052
S. Dekalb Co., GA	100%	0.116	0.010	0.039	0.039
Tampa, FL	56%	0.134	0.007	0.032	0.042
Detroit, MI	85%	0.146	0.006	0.066	0.066
Chicago, IL	67%	0.112	0.006	0.031	0.036
Madison, WI	48%	0.132	0.008	0.022	0.032
Austin, TX	85%	0.100	0.016	0.035	0.040
St. Louis, MO	71%	0.109	0.015	0.036	0.041
Bountiful, UT	100%	0.079	0.004	0.027	0.030
Grand Junction, CO	68%	0.095	0.002	0.027	0.030
Seattle, WA	86%	0.224	0.010	0.042	0.053
La Grande, OR	100%	0.256	0.005	0.017	0.034
Kenner, LA	55%	0.040	0.001	0.022	0.021
Gulf Port, MS	65%	0.083	0.003	0.020	0.025
Stennis Airport, MS	33%	0.034	0.002	0.014	0.015
Average	67%	2.970	0.001	0.032	0.044

A total of 1,466 Cr^{6+} measurements were detected at the 22 NMP sites from January 2005 to December 2005. Two hundred and thirty of these were taken at three sites during the clean up after Hurricane Katrina. Of the 1,466 Cr^{6+} measurements, 67% of these results were detects and 9% of these concentrations were below the MDL. The average Cr^{6+} concentration was 0.044 ng/m^3.

Data from the NMP sites is presented in Figure 2. The highest concentration was taken at

Washington, DC, at 2.97 ng/m^3. The samples taken for Katrina were collected on a 1-in-1 schedule starting October 10, 2005. Hexavalent chromium results at Katrina monitoring sites were similar or slightly lower than other sites in the program.

Figure 2: Analytical Cr^{6+} Results for samples collected between January 2005 and December 2005.



DATA QUALITY CONTROL AND ASSURANCE

Precision of the analytical and sampling technique was determined using the analysis of collocated sampling episodes. A collocated sample (i.e., a sample collected simultaneously with the primary and collocated sample using separate sampling systems) provides information on the potential for sampling variability. ERG was not able to perform replicate analyses because the final sample instrument injection volume did not allow the replicate analyses. Method spikes were analyzed, however, and give an acceptable range of 80-120% recovery. The collocated results were compiled from sites sampling in the NMP from January 2005 through December 2005.

The collocated data is presented in Relative Percent Difference (RPD). The RPD expresses average concentration differences relative to the average concentrations detected during collocated analyses. The RPD is calculated as follows:

$$RPD = \frac{|X_1 - X_2|}{\overline{X}} \times 100$$

Where:

X_1 is the ambient air concentration of a given compound measured in one sample;
X_2 is the concentration of the same compound measured during collocated analysis; and
$\overline{X}$ is the arithmetic mean of X_1 and X_2.

As this equation shows analyses with low variability have lower RPDs (and better precision), and analyses with high variability have higher RPDs (and poorer precision). The RPD method quality objective for all data from the NMP is 25 percent. The overall data average RPD result for 2005 was 17%, which is within the 25% target. Table 9 presents the collocated data results.

Table 9: Collocate Statistical Data Results (January 2005 to December 2005).

Site ID	# of Collocates	Median (RPD)	Average (RPD)	Percent Standard Deviation
Roxbury, MA	6	10%	14%	12%
Burlington, VA	11	6%	18%	35%
Providence, RI	6	21%	**35%**	47%
Underhill, VT	6	0%	5%	6%
Washington, DC	4	1%	9%	16%
Chesterfield, SC	6	0%	12%	0%
Hazard, KY	5	0%	6%	0%
North Birmingham, AL	1	0%	0%	0%
Providence, AL	1	0%	0%	0%
Birmingham, AL (site 2)	1	0%	0%	0%
S. Dekalb Co., GA	2	**41%**	**41%**	0%
Tampa, FL	5	0%	18%	29%
Detroit, MI	5	16%	14%	13%
Chicago, IL	3	18%	14%	12%
Madison, WI	4	16%	16%	17%
Austin, TX	1	**33%**	**33%**	0%
St. Louis, MO	4	4%	8%	11%
Grand Junction, CO	5	0%	10%	22%
Seattle, WA	6	10%	**32%**	55%
Gulf Port, MS	7	**27%**	**27%**	25%
Stennis Airport, MS	1	19%	19%	0%
Kenner, LA	4	17%	**35%**	43%
Average	4	8%	17%	16%

CONCLUSIONS

Based on the results of this study, ERG concludes Teflon filters do not collect the Cr^{6+} more efficiently then cellulose. Reducing agents in the ambient air seem to be converting the Cr^{6+} to Cr^{3+} and the filter media must stabilize and protect the Cr^{6+} from these reducing agents. The Teflon filters do not have the buffer coating (sodium bicarbonate) to stabilize the Cr^{6+} on the filter when reducing agents are present (such as acid gases).

ERG laboratory's detection limit for acrolein is 0.012 ng/m^3 (experimentally determined using 40 CFR, Part 136 procedures) which is lower than the cancer and noncancer health risk threshold concentration. Based on the results of this study, sample collection using the sodium bicarbonate coated cellulose filters is recommended. There are certain preservation procedures that must be followed before acceptable sample results should be reported, including:

- The filters must be acid washed and rinsed before coating them with the sodium bicarbonate to prevent Cr^{6+} background. Using this method however, does not lengthen the collection or storage hold time.
- All samples must be retrieved from the field one day after the sample has been collected to prevent Cr^{6+} negative bias (loss) (up to 20% on the first day).
- All samples must be frozen after collection to reduce the risk of Cr^{6+} loss.

Analysis of sodium bicarbonate coated cellulose filters containing known concentrations of Cr^{6+} demonstrated acceptable recoveries, if the samples are recovered as soon as possible after sampling ends.

ERG has determined that this modified method shows consistent recovery for Cr^{6+} over time throughout the country. The collocated sample recoveries meet the method quality objectives set by the EPA for the NATTS program, however there does seem to be limitations on sample recovery for loading filters outside of the controlled laboratory conditions.

ACKNOWLEDGMENTS

The authors would like to express their appreciation for the hard work and dedication shown by the U.S. EPA, OAQPS staff and Eastern Research Group's laboratory.

REFERENCES

1. California Air Resources Board, Standard Operating Procedure for the Analysis of Hexavalent Chromium at Ambient Atmospheric Levels by Ion Chromatography, MLD039, Revision 3. March 2002.

2. Swift, J.; Merrill, R.; Tedder, D. Hexavalent Chromium Method Development. J. Homolya, Work Assignment Manager, U.S. Environmental Protection Agency, Research Triangle Park, NC.

3. Swift, J.; Merrill, R. Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air Analyzed By Ion Chromatography (IC). J. Homolya, Work Assignment Manager, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Appendix E

Region 7 Standard Operating Procedure No. 2314.06A, "Measurement of Hexavalent Chromium Using the BGI PQ167R Low Volume Sampler," (U. S. EPA, 2011)

STANDARD OPERATING PROCEDURE

NO. 2314.06A

Measurement of Hexavalent Chromium Using the BGI PQ167R Low Volume Sampler

November 7, 2011

Leland P. Grooms
ENSV/CARB/ASRS

Approved

Peer Reviewer	Date
Chemical Analysis and Response Brach Manager	Date
Independent Quality Assurance Reviewer	Date

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Attachments
None

A. Purpose

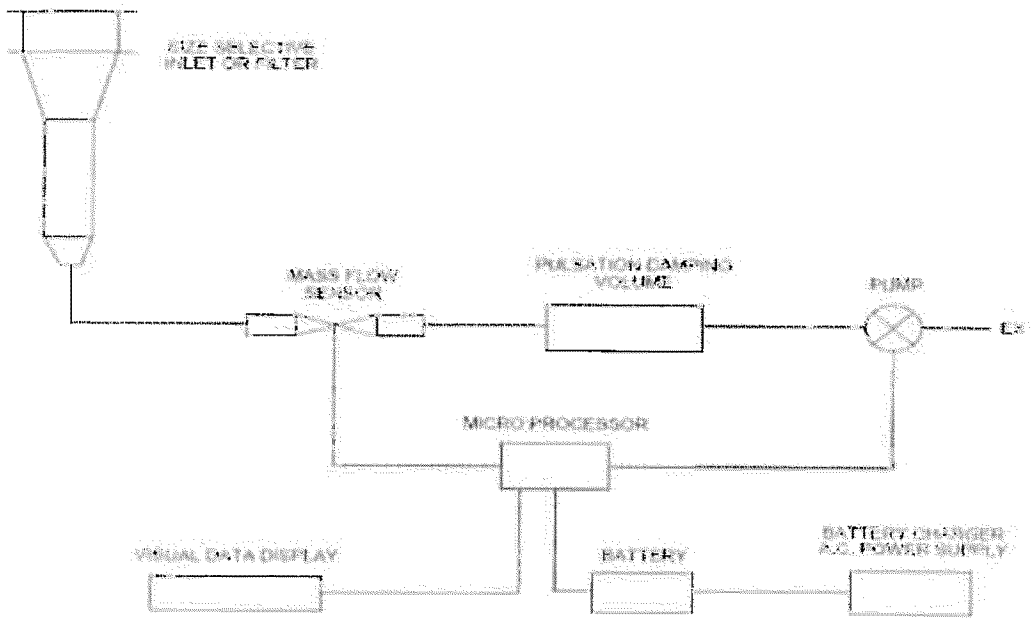
This procedure is designed to provide instruction on collecting hexavalent chromium (Cr+6) in air using the BGI PQ167R ambient air sampler for metals analysis. These procedures are not intended to replace the manufacturer's operations or technical manuals. This SOP is designed to be a step by step method for operating the sampler to be used in conjunction with the manufacturer's operator's manual. Maintenance and troubleshooting should be conducted using the BGI167R operator's manual.

B. Applicability

This SOP is intended to be used during the 2011-2012 CertainTeed ambient air sampling project.

C. Summary of Procedure

The operating principle of the BGI PQ167R can be appreciated by referring to the block diagram in Figure 1 below. The BGI PQ167R is an "Intelligent Air Pump" that can monitor its own airflow rate and thereby adjust the pump speed to compensate for changes in load pressure and/or other forces which would otherwise hamper the flow of air through a filter (or sample collector). The PQ100 unit can be programmed to begin its sampling job at a specific date, time, and stop sampling after the user defined run time is depleted. Air is drawn by the pump through a size selective inlet device and/or filter. It then passes inside the instrument housing to a Mass Flow Sensor. The signal generated by the sensor is then routed to a microprocessor which determines if the flow is at the set value and adjusts the pump speed to maintain the correct flow rate. Because the flow sensor is extremely sensitive and all pumps produce pulsation to some degree, a pulsation damping volume has been introduced to control this effect. The microprocessor not only controls the flow rate accurately and precisely to the set point but also performs several other functions. These include turning the instrument on at a preselected time and running it for a selected interval. The flow is maintained by the processor to a designated pressure and temperature value. A pulse width modulated signal is configured and sent to the pump motor in a constantly updated manner based on signal information received from the Mass Flow Sensor. The microprocessor also stores all parametric information generated during the run period and configures it for presentation on the visual display and downloading to the software provided with the instrument. The system is completed by its 12 volt battery and external battery charger/A.C. power supply. The power supply function permits operation if desired with no battery whatsoever.



(Figure 1)

D. Definitions/Acronyms

1. ERG: Eastern Research Group
2. SOP: Standard Operating Procedure

E. Personnel Qualifications

Only persons familiar with procedures described in the SOP should use the BGI PQ167R.

F. Health and Safety Warnings

1. The BGI PQ167R instrument is not intrinsically safe and should not be used in explosive environments.

2. Whenever the BGI PQ167R is to be installed at a height greater than 3 meters it must be securely bolted in place or anchored in some way.

G. Cautions

Siting instructions should be followed carefully in order to obtain useful data. When determining appropriate sites to place this instrument, both project objectives (how will the data be used and what information is needed?) and site conditions (where are obstructions relative to the monitor?) need to be considered.

H. Interference

The instrument's electronic and mechanical parts should be protected against heavy rain, snow and inclement weather.

I. Equipment and Supplies

1. BGI PQ167R
2. ERG Cr+6 filter holder apparatus
3. Flow calibrator
4. Logbook
5. ERG filter assembly with glass funnel
6. Cooler with ice substitute
7. Powder-free gloves
8. Sample processing paperwork

J. Procedures

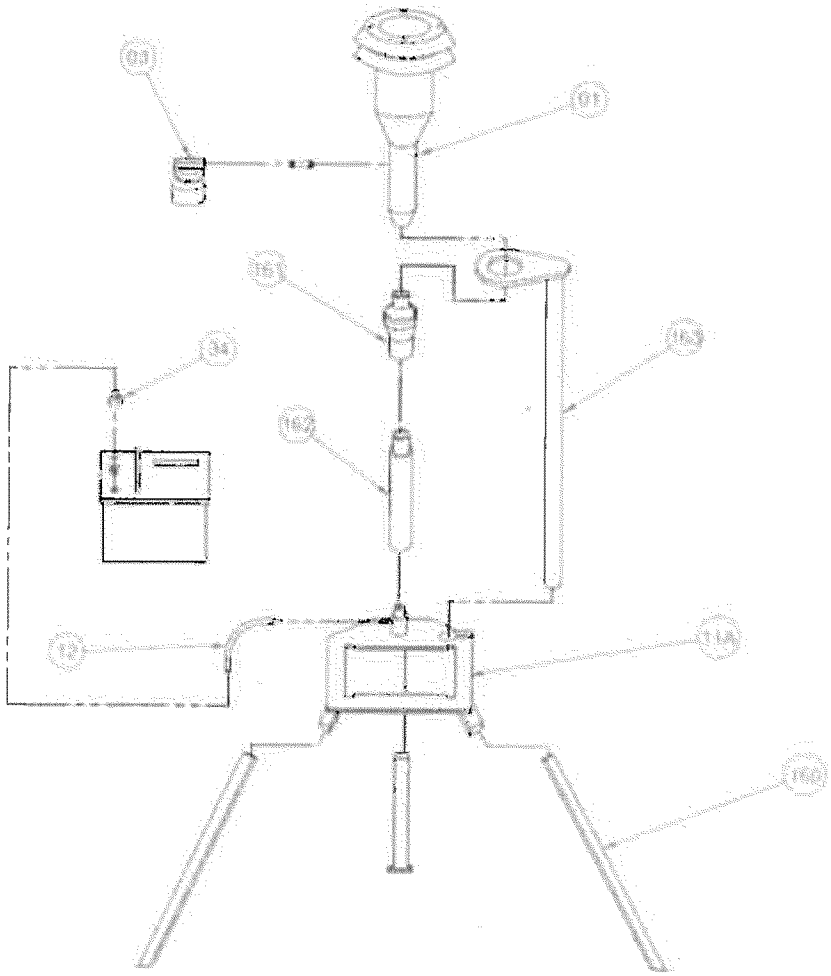
1. Siting the Monitor – The optimal site for ambient air monitoring is in a location where the BGI PQ167R instrument is near the breathing zone. If the BGI PQ167R is placed on a roof or other structure there must be a minimum of 2 meters of separation from walls, parapets, penthouses, etc. If the BGI PQ167R is placed near trees it should be placed at least 20 meters from the drip line of the tree. In general, the BGI PQ167R must be located in an area free from obstructions. The distance between obstructions and the sampler must be at least twice the height of the obstruction. If possible, the BGI PQ167R should not be placed near busy roads (more than 3,000 vehicles per day), if placing the BGI PQ167R near a lower traffic road is unavoidable then it should be placed at least 5 meters from the edge of the nearest traffic lane.

2. Setup

   a. Assemble the sampler according to Figure 2 below omitting the installation of the PM10 inlet head, filter cassette holder assembly, and downtube assembly brace. For detail and illustration, refer to the BGI PQ167 Quick Start document, pages 2 through 8.

   b. Place and level the sampler on site. To secure the sampler and protect membrane roofs, 2 x 4 wooden studs may be cut into one foot sections and fastened to the feet of the legs using lag bolts. Place sand bags on these skids to prevent tipping of the sampler.

   c. Connect the sampler to a grounded electrical outlet with 115 volts, and at least 5 amp service. Protect the connector from precipitation by fastening beneath the sampler or wrapping it with plastic tape.



(Figure 2)

d. If operating using a deep cycle marine battery for power, install the external power cord by screwing the round harness into the "utility adapter" port on top of the sampler. Attach the positive and negative contacts to the deep cycle marine battery and secure. A fully charged battery should provide power for at least 2 sampling runs. Depending on the battery available, more consecutive runs may be possible. Store the battery in a plastic container near the sampler to conceal and protect it from the weather.

e. If collocated samplers will be located at the site, the two samplers must be within four (4) meters of each other, but outside of two (2) meters. The inlet heights must be within one (1) meter vertically.

f. The sampling unit, at this point, should have legs mounted on the stand, and the pump and power components should be secured in the stand

according to the PQ167 Quick Start document. The downtube, PM10 inlet head, and filter cassette holder assembly should NOT be installed.

g. Install the downtube on the top of the cylindrical mount on the stand. The mount should have tubing leading from the port on its side to the inlet on the pump module.

h. The total ERG Cr+6 filter holder apparatus consists of a BGI flow adapter with shut-off valve, stainless steel connector fitting, a length of "U" shaped stainless steel ¼ inch tubing, ERG filter assembly, and a glass funnel. The filter assembly and glass funnel will be provided for each sampling run and should not be installed until a sampling run is setup. Place this apparatus (without ERG filter assembly) on the top of the down-tube, and ensure that the shut-off valve is in the open position.

i. The open end of the stainless steel tubing should be capped when sampling is not in progress to prevent contamination.

3. Operation

a. Plug sampler into AC power and charge the internal battery for at least 24 hours.

b. Check parts and components against the packing list.

c. After charging, ensure sampler will power up and that the main screen is operational

d. The sampler may arrive with a default flow rate of 16.7 Lpm. If during the initial verification, the sampler's target flow rate is displayed as 16.7 Lpm, it must be changed to 15 Lpm. Proceed directly to the calibration section of the SOP for direction in making the change.

e. The ERG Cr+6 Filter Holder Modules will arrive to the field office in a cooler with frozen ice substitutes. The modules will have paperwork designating them for a specific site and run day. The modules must be kept in a freezer prior to sampling. During transport to the monitoring site for run preparation, the filters must be kept cold as well. Samples must be returned to ERG cold using ice substitutes.

4. Verification (Note: The PQ167 does not require a leak test. Cutting off the flow of air by covering or restricting the air flow to the inlet will cause damage to the internal pump and will void the warranty).

a. Install a test ERG Cr+6 filter holder module if available. If a test module is not available, the module to be used for the next sample day is acceptable; however, the module must be used immediately following the verification/calibration.

b. Attach a NIST traceable flow standard to the inlet of the filter module. Ensure the flow standard is on and has equilibrated to ambient conditions.

c. Turn on the PQ167R by pushing the "ON/OFF" button. If a message is blinking on the display, press "ENTER" to proceed to the "MAIN IDLE DISPLAY".

The screen display should read:

ET0000Min TS00.00M (Date)

Q(Flow)Lpm T(Time) Bty(Capacity)%

(Date) – today's date in military notation; e.g., 01JAN= January 1st

(Flow) - the current flow rate selected to be regulated.

(Time) - military time; e.g., 13:08= 13 Hours 8 Minutes or 1:08 PM

(Capacity) - remaining charge in the internal battery.

d. Press SETUP three times until the Set START DATE and TIME screen appears: The screen should appear as below:

Set START DATE and TIME

(Date) (Time) Off

e. The word, "Off", should be displayed in the lower right corner of the screen. The bottom line of the display should be flashing. If "On" is displayed, press the "ENTER" button until "On" stops flashing. Then toggle to "Off" by pressing the + or – buttons.

f. Press the "SETUP" button twice to get to the "MAIN IDLE DISPLAY"

g. Press the "RUN/STOP" button to activate the pump.

h. Allow the pump to stabilize for at least 2 minutes.

i. If the measured flow and the flow indicated on the flow standard are within 4%, the sampler's calibration is acceptable. If the flow is outside 4%, the unit must be recalibrated.

j. Press the "RUN/STOP" button to turn off the pump.

5. Calibration (Note: The PQ167 does not require a leak test. Cutting off the flow of air by covering or restricting the air flow to the inlet will cause damage to the internal pump and will void the warranty).

a. Install a test ERG Cr+6 filter holder module if available. If a test module is not available, the module to be used for the next sample day is acceptable; however, the module must be used immediately following the verification/calibration.

b. Press "SETUP". The screen will read; "Select FLOW RATE"

c. From the "MAIN IDLE DISPLAY" press the "Setup" key once until the message below appears;

Select FLOW RATE

The Target Q should read 15.0 Lpm. If it does not read 15.0 Lpm, set TARGET FLOW RATE to 15.0 Lpm by pressing ENTER.

The whole number value will remain on constant while the tenths still blink); use "+" or "-" to increase or decrease until 15 is displayed.

Press ENTER (Tenths value will now remain constant while whole number blinks); use "+" or "-" to increase or decrease until .0 is displayed.

d. From the "Select FLOW RATE" message screen, press both the "Reset" key and the "Run/Stop" key simultaneously to enter the calibration mode and the message below will appear;

CALIBRATE Target=15.0 Lpm

e. Press the "RUN/STOP" button to activate the pump and the message below will appear:

CALIBRATE Target = 15.0 Lpm

Reference Q.. XX.X

The Reference Q is an approximate flow rate used only as a visual aid in finding the corrected flow on the calibration device. This value may indicate 5 to 15% error. This is for reference only!

f. Use the "+/-" keys to move the pump speed up or down until the calibration device indicates the desired flow rate.

g. When a stable reading has been achieved, press the "ENTER" key to store the flow rate.

h. Exit the Setup menu and return to the "MAIN IDLE DISPLAY".

CALIBRATIONS ARE NOT AFFECTED UNTIL THE ENTER KEY IS PRESSED AND THE PUMP IS RUNNING.

i. Record pre- and post- flow measurements and adjustments in the logbook.

6. Conducting the Sampling Event

a. Visually inspect and ensure all O-rings are in place and secure. Replace if necessary.

b. Always ensure that samples and unused ERG Cr+6 Filter Holder Modules are transported to and from the site cold.

c. Confirm all cables (electrical connections) are secure, and that exterior connections are protected from the elements.

d. Record activities, site observations, and maintenance activities in logbook.

e. Turn on the PQ167R by pushing the "ON/OFF" button. If a message is blinking on the display, press "ENTER" to proceed to the "MAIN IDLE DISPLAY". Then press "RESET" to clear prior run data.

f. Conduct an initial flow check (verification) by following the instructions in *Section 4. Verification*. Record the measurement from the flow standard on the *Ambient Hexavalent Chromium Data Sheet* under the "Field Setup" section on the "Initial Rotameter Setting".

g. Following the flow check, the screen display should read:

ET0000Min TS00.00M (Date)

Q(Flow)Lpm T(Time) Bty(Capacity)%

(Date) – today's date in military notation; e.g., 01JAN= January 1st

(Flow) - the current flow rate selected to be regulated.

(Time) - military time; e.g., 13:08= 13 Hours 8 Minutes or 1:08 PM

(Capacity) - remaining charge in the internal battery.

h. Press "SETUP". The screen will read; "Select FLOW RATE"

The flow rate value will be blinking.

i. The flow rate should read 15.0 Lpm. If it does not read 15.0 Lpm, the unit must be calibrated to 15.0 Lpm. See calibration section for adjusting target flow rate and calibration.

j. Press "SETUP". This is the date and time screen.

The screen should read;

Set DATE and TIME

(dd) (mmm) (yyyy) (time)

k. DAY: Press ENTER and change by pressing the + or - key. When the day is correct, press ENTER.

MONTH: To change, press + or - key. When correct, press ENTER.

YEAR: To change, press + or - key. When correct, press ENTER.

TIME (hrs): To change, press + or - key. When correct, press ENTER.

TIME (min): To change, press + or - key. When correct, press ENTER.

When date and time are correct press "SETUP"

l. This is the sample start screen which reads;

Set START DATE and TIME

(dd) (mmm) 00:00 Off

This screen allows you to set a start date and time for a sampling run. The default is set to midnight the next day. To designate your own start date and time:

DAY: Press ENTER and change by pressing the + or - key. When the day is correct, press ENTER.

MONTH: To change, press + or - key. When correct, press ENTER.

YEAR: To change, press + or - key. When correct, press ENTER.

TIME (hrs): To change, press + or - key. When correct, press ENTER.

TIME (min): To change, press + or - key. When correct, press ENTER

m. Enable the run by setting the "On/Off" function on the screen to "On". WARNING: The sampler will not automatically activate if this option is set to "Off".

n. Press "SETUP"

The screen will read;

Set RUN TIME

Hours: 24 Min: 00 On

Set to 24 hours 0 minutes. The default is always 24 hrs 0 min, the required sample duration. If the sample time needs to be modified, adjust as instructed in step 6 and 8.

o. Press "SETUP". The screen will return to the "MAIN IDLE DISPLAY". WARNING: DO NOT PRESS THE RESET BUTTON AT THIS TIME AS THE START TIME AND RUN TIME WILL DEFAULT.

p. Press "RUN/STOP"

If the START TIME ENABLE is set to "On" then the message "Alarm Triggered Run..." followed by "PQ100 Powering Down" will appear briefly. The PQ100 is now waiting for the internal real time clock to achieve the designated start time and will then power itself on and begin the sampling run. If the START TIME ENABLE is set to "Off" then the pump will begin to run immediately. If this occurs, press RUN/STOP and begin back at step 2 ensuring START TIME ENABLE is set to "On".

7. Installing the ERG Cr+6 Filter Holder Module (NOTE: Gloves must be changed for each sample, i.e. between retrieving a sample and preparing a new run gloves MUST be changed to prevent cross contamination).

a. Remove the sample inlet cover on the stainless steel probe and make sure there is no contamination on the probe.

b. Put on a clean pair of powder-free gloves.

c. Take the ERG Cr+6 Filter Holder Module storage container from the cooler and carefully remove the module. The module may be in a plastic bag. Return the bag to the container for use in the collection procedure.

d. Make sure the glass funnel is securely attached to the filter holder. Loosen the small top nut on the filter container. Arrows will be present on the

filter holder showing air flow direction and they should always point to the end of the sample probe line.

e. Holding the module with the glass funnel facing down, slide the probe into the top fitting of the filter module and tighten the nut. Tighten the nut until the ERG Cr+6 Filter Holder Module is securely fastened to the probe. Do not overtighten the plastic nut.

(Note: If running a field blank, repeat steps 1 through 5, count to 10, and then remove the field blank filter holder module and place it back into the antistatic bag. Label the bag to designate the filter module as a field blank. Log the filter ID as field blank in the comments section of the ERG Hexavalent Chromium Sample Data Sheet. The field blank must be run before the sample filter module is fastened to the probe).

8. Sample Recovery and Data Collection-NOTE: Gloves must be changed for each sample, i.e. between retrieving a sample and preparing a new run, gloves MUST be changed to prevent cross contamination.

a. Record pertinent data on sample sheets. This information will be on the "MAIN STATUS SCREEN".

b. Conduct a final flow check (verification) by following the instructions in section 4-Verification. Record the measurement from the flow standard on the *Ambient Hexavalent Chromium Data Sheet* under the "Field Setup" section, "Final Rotameter Reading".

c. Put on a clean pair of powder free gloves

d. Take the module storage container from the cooler, open, and set aside

e. While holding the ERG Cr+6 Filter Holder Module, loosen the top nut holding the module to the sample inlet and slide the module off the stainless steel probe.

f. Place the ERG Cr+6 Filter Holder Module including glass funnel in the plastic bag and place back into the storage container. Place the storage container into a cooler with ice substitutes.

g. Place cover back on end of probe line.

h. Data may be downloaded to a laptop using the PQ100/200 DOWNLOAD SOFTWARE. ERG does not require this data, but direction can be found in the BGI PQ167 Quick Start document, pages 16 and 17.

9. Sample Shipping - The Cr+6 Filter Holder Module container must be packed in a cooler with ice substitutes and shipped overnight cold to ERG. The sample paperwork must be included in the shipment. Use the pre-filled out FedEx label provided by ERG, and fill out the "Sender" section with the sampling agency's address and phone number. Send priority overnight to ERG.

K. Records Management

The BGI PQ167R instrument may be used as a part of a broad range of project types, and the management of records and data from the operation of the PQ100 instrument are dependent upon the type of project for which it is used. Therefore, operation records and data from the PQ167R will be supplied to the Project Manager for inclusion in the project file. In this way Cr+6 information and data will be managed in accordance with other records and data from the same project.

L. Quality Assurance/Quality Control

1. Flow Calibration - A flow verification must be completed at the beginning of the study period. If the verification does not compare within 4%, the flow must be calibrated. Document all quality assurance activities in the logbook.

2. Flow Verifications - The flow must be verified or checked at the beginning and end of the sampling event to determine an average sample flow, document all quality assurance activities and observations in the logbook.

3. Independent Audits - If possible, it is recommended that an independent flow check of the sampler be conducted at some point during the study. This check may be conducted by a state or local agency's quality assurance team or independent audit program.

M. References

1. BGI Inc. PQ167 Quick Start Guide (Using the PQ100 Immediately) Revision "G"

2. BGI Inc. PQ100 Air Sampler Instruction Manual PM10 Reference Sampler

To: Fairchild, Susan[Fairchild.Susan@epa.gov]
From: McClintock, Katie
Sent: Sun 2/7/2016 9:31:09 PM
Subject: FW: chromium

Susan -

I will be travelling Monday morning, but can you please forward the document you sent to me about chromium to sarah. I wasn't sure if it was okay to release outside of epa.

Katie

-----Original Message-----
From: ARMITAGE Sarah [mailto:ARMITAGE.Sarah@deq.state.or.us]
Sent: Saturday, February 06, 2016 10:29 AM
To: McClintock, Katie <McClintock.Katie@epa.gov>
Cc: Gable, Debra <Gable.Debra@epa.gov>
Subject: RE: chromium

Hi Katie,
We are working on a monitoring plan right now and need to evaluate the need and feasibility of chrome 6 analysis. Can you send me links or other information about the data you were citing last night on refractory breakdown/chrome 6 emissions? There have also been concerns about silica and we would like to learn more about how to monitor that.

Debra, I copied you because I hear you are a monitoring expert and know about silica.

Thanks
Sarah 503-229-5186

From: McClintock, Katie [McClintock.Katie@epa.gov]
Sent: Friday, February 05, 2016 8:59 AM
To: ARMITAGE Sarah
Subject: chromium

Sarah –

I have some info that might be helpful to you regarding chromium from bullseye. I know you are busy but give a call when you can. I left you a voicemail too, but if you are like me I read email before I have time to check voicemail.

Katie McClintock
Air Enforcement Officer
EPA Region 10
1200 Sixth Avenue, Suite 900, OCE-101
Seattle, WA 98101
Phone: 206-553-2143
Fax: 206-553-4743
Mcclintock.katie@epa.gov

To: McClintock, Katie[McClintock.Katie@epa.gov]
From: Fairchild, Susan
Sent: Tue 2/16/2016 7:41:02 PM
Subject: FW: do you know a hexavalent chromium expert in OAQPS?

Katie, Steff says that the Cr+6 will revert back to the Cr+3 unless kept in the hexavalent form using an alkaline reagent. WE used NaOH as that reagent in the Certainteed testing.

Susan Fairchild

Senior Environmental Scientist

(919) 541-5167

USPS Address:

OAQPS/SPPD/MMG

Mail Code D 243-04

Research Triangle Park, NC 27711

From: Johnson, Steffan
Sent: Tuesday, February 16, 2016 2:36 PM
To: Narvaez, Madonna <Narvaez.Madonna@epa.gov>; Pope, Anne <Pope.Anne@epa.gov>

Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Dewees, Jason <Dewees.Jason@epa.gov>; Merrill, Raymond <Merrill.Raymond@epa.gov>
Subject: RE: do you know a hexavalent chromium expert in OAQPS?

Madonna,

In my experience hexavalent forms of chromium are not stable when they are emitted from a source. In fact, EPA has put a good bit of effort into developing a test method designed specifically to capture hex-chrome compounds and keep them in hex form until analysis, as other chromium emissions test methods tend to let the chromium convert to trivalent forms. It is also my understanding (though certainly not the final word on the topic at all) that hex chrome emissions are likely to change state to trivalent chrome post-emission. I believe Jason DeWees and Ray Merrill of my group may also have information to add here, and so I am copying them on this e-mail.

The only reliable test approach that I know to quantify in-stack emissions of hex-chrome is to use a test method known as SW-846-0061. This method uses an alkaline reagent to trap hex-chrome and retain it in hexavalent form until the alkaline solution can be analyzed at a lab. The test method is a bit tricky, but if you need to know in-stack emissions we're certainly available to help you walk through development of a test protocol.

As to ambient sampling for hex chrome, I'll let Hugh in R7 tell you what he knows, my experience stops at the stack.

Please let us know if we can be of further assistance.

Stef

From: Narvaez, Madonna
Sent: Tuesday, February 16, 2016 12:26 PM
To: Pope, Anne <Pope.Anne@epa.gov>
Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Johnson, Steffan <johnson.steffan@epa.gov>
Subject: do you know a hexavalent chromium expert in OAQPS?
Importance: High

Hi, Anne, Susan and Stef. Hope all is well. I don't know if you have heard about the colored glass manufacturer in Portland that DEQ discovered a cadmium hotspot around the facility. In the course of investigations, we discovered that the facility uses Cr+6 as a dry colorant for the glass. Ambient monitoring showed an average of 71.5 ng/m3 of total chromium. I don't know if Katie McClintock, the R10 enforcement contact has asked you for this information yet. If you can point us towards someone, we would really appreciate it. The company uses both Cr+3 and Cr+6, as well as cadmium and arsenic. In the next round of monitoring, the ODEQ will be monitoring for Cr+6 at the day care center, which is 220 meters from the facility. A cadmium hotspot was also detected close to the Harriet Tubman School. A much smaller colored glass mfg facility is close by.

•□□□□□□□ Katie McClintock did a cursory search for information on the conversion of trivalent chromium to hexavalent chromium and found little information, all of which was talking about smelting and coating. The research confirmed that the use of trivalent chromium alone can still produce hexavalent chromium, but found little data on the conversion rate under various circumstances. We need to develop or find an expert who can read more literature and help interpret the data we find in stack tests and ambient monitoring.

Thanks!

==========

Madonna Narvaez

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To: Narvaez, Madonna[Narvaez.Madonna@epa.gov]; Pope, Anne[Pope.Anne@epa.gov]; McClintock, Katie[McClintock.Katie@epa.gov]
Cc: Johnson, Steffan[johnson.steffan@epa.gov]
From: Fairchild, Susan
Sent: Tue 2/16/2016 6:55:48 PM
Subject: RE: do you know a hexavalent chromium expert in OAQPS?

Also, bear in mind that colored glass recipes are not the only ones that may have toxics: lead is used to add brilliance, radiation shielding (TVs, microwave ovens, technical glass, etc.), and expansion/contraction without shattering. Arsenic is a fining agent. Neither of these add color to the glass

Susan Fairchild

Senior Environmental Scientist

(919) 541-5167

USPS Address:

OAQPS/SPPD/MMG

Mail Code D 243-04

Research Triangle Park, NC 27711

From: Narvaez, Madonna
Sent: Tuesday, February 16, 2016 12:26 PM
To: Pope, Anne <Pope.Anne@epa.gov>
Cc: Fairchild, Susan <Fairchild.Susan@epa.gov>; Johnson, Steffan <johnson.steffan@epa.gov>
Subject: do you know a hexavalent chromium expert in OAQPS?
Importance: High

Hi, Anne, Susan and Stef. Hope all is well. I don't know if you have heard about the colored glass manufacturer in Portland that DEQ discovered a cadmium hotspot around the facility. In the course of investigations, we discovered that the facility uses Cr+6 as a dry colorant for the glass. Ambient monitoring showed an average of 71.5 ng/m3 of total chromium. I don't know if Katie McClintock, the R10 enforcement contact has asked you for this information yet. If you can point us towards someone, we would really appreciate it. The company uses both Cr+3 and Cr+6, as well as cadmium and arsenic. In the next round of monitoring, the ODEQ will be monitoring for Cr+6 at the day care center, which is 220 meters from the facility. A cadmium hotspot was also detected close to the Harriet Tubman School. A much smaller colored glass mfg facility is close by.

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Federal Register

Wednesday,
December 26, 2007

Part IV

Environmental Protection Agency

40 CFR Part 63

National Emission Standards for Hazardous Air Pollutants for Area Sources: Clay Ceramics Manufacturing, Glass Manufacturing, and Secondary Nonferrous Metals Processing; Final Rule

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 63

[EPA–HQ–OAR–2006–0424; EPA–HQ–OAR–2006–0360; EPA–HQ–OAR–2006–0940; FRL–8508–5]

National Emission Standards for Hazardous Air Pollutants for Area Sources: Clay Ceramics Manufacturing, Glass Manufacturing, and Secondary Nonferrous Metals Processing

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: EPA is issuing national emission standards for the Clay Ceramics Manufacturing, Glass Manufacturing, and Secondary Nonferrous Metals Processing area source categories. Each of these three final emissions standards reflects the generally available control technology or management practices used by sources within the respective area source category.

DATES: This final rule is effective on December 26, 2007. The incorporation by reference of certain publications listed in this rule are approved by the Director of the Federal Register as of December 26, 2007.

ADDRESSES: EPA has established dockets for this action under Docket ID No. EPA–HQ–OAR–2006–0424 (for Clay Ceramics Manufacturing), Docket ID No. EPA–HQ–OAR–2006–0360 (for Glass Manufacturing), and Docket ID No. EPA–HQ–OAR–2006–0940 (for Secondary Nonferrous Metals Processing). All documents in the docket are listed in the *http://www.regulations.gov* index. Although listed in the index, some information is not publicly available, e.g., confidential business information or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, will be publicly available only in hard copy form. Publicly available docket materials are available either electronically through *http://www.regulations.gov* or in hard copy at the EPA Docket Center, Public Reading Room, EPA West, Room 3334, 1301 Constitution Ave., NW., Washington, DC. The Public Reading Room is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is (202) 566–1744, and the telephone number for the Air Docket is (202) 566–1742.

FOR FURTHER INFORMATION CONTACT: For questions about the final rule for Clay Ceramics Manufacturing, contact Mr. Bill Neuffer, Office of Air Quality Planning and Standards, Sector Policies and Programs Division, Metals and Minerals Group (D243–02), Environmental Protection Agency, Research Triangle Park, NC 27711; *telephone number:* (919) 541–5435; *fax number:* (919) 541–3207; *e-mail address: Neuffer.Bill@epa.gov.* For questions about the final rule for Glass Manufacturing or Secondary Nonferrous Metals Processing, contact Ms. Susan Fairchild, Office of Air Quality Planning and Standards, Sector Policies and Programs Division, Metals and Minerals Group (D243–02), Research Triangle Park, NC 27711, *telephone number:* (919) 541–5167, *fax number:* (919) 541–3207, *e-mail address: Fairchild.Susan@epa.gov.*

SUPPLEMENTARY INFORMATION: The supplementary information presented in this preamble is organized as follows:

I. General Information
A. Does this action apply to me?
B. Where can I get a copy of this document?
C. Judicial Review
II. Background Information for Final Area Source Standards
III. Summary of Final Rules and Changes Since Proposal
A. Area Source NESHAP for Clay Ceramics Manufacturing
B. Area Source NESHAP for Glass Manufacturing
C. Area Source NESHAP for Secondary Nonferrous Metals Processing
IV. Exemption of Certain Area Source Categories From Title V Permitting Requirements
V. Summary of Comments and Responses
A. Area Source NESHAP for Clay Ceramics Manufacturing
B. Area Source NESHAP for Glass Manufacturing
C. Area Source NESHAP for Secondary Nonferrous Metals Processing
D. Area Source NESHAP—General
VI. Impacts of the Final Area Source Standards
A. Glass Manufacturing
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VII. Statutory and Executive Order Reviews
A. Executive Order 12866: Regulatory Planning and Review
B. Paperwork Reduction Act
C. Regulatory Flexibility Act
D. Unfunded Mandates Reform Act
E. Executive Order 13132: Federalism
F. Executive Order 13175: Consultation and Coordination With Indian Tribal Governments
G. Executive Order 13045: Protection of Children From Environmental Health and Safety Risks
H. Executive Order 13211: Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use
I. National Technology Transfer Advancement Act
J. Executive Order 12898: Federal Actions To Address Environmental Justice in Minority Populations and Low-Income Populations
K. Congressional Review Act

I. General Information

A. Does this action apply to me?

The regulated categories and entities potentially affected by these final standards include:

Category (Industry)	NAICS code [1]	Examples of regulated entities
Clay Ceramics Manufacturing	327122 327111 327112	Area source facilities that manufacture ceramic wall and floor tile, vitreous plumbing fixtures, sanitaryware, vitreous china tableware and kitchenware, and/or pottery.
Glass Manufacturing	327211 327212 327213	Area source facilities that manufacture flat glass, glass containers, and other pressed and blown glass and glassware.
Secondary Nonferrous Metals Processing	331492 331423	Area source brass and bronze ingot making, secondary magnesium processing, or secondary zinc processing plants that melt post-consumer nonferrous metal scrap to make products, including bars, ingots, and blocks, or metal powders.[2]

[1] North American Industry Classification System.
[2] The Secondary Nonferrous Metals Processing area source category was originally established under SIC code 3341, a broader classification which included brass and bronze ingot makers. The corresponding NAICS code for brass and bronze ingot makers is 331423.

This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be affected by this action. To determine whether your facility is regulated by this action, you should examine the applicability criteria in 40 CFR 63.11435 of subpart RRRRRR (national emissions standards for hazardous air pollutants (NESHAP) for Clay Ceramics Manufacturing Area Sources), 40 CFR 63.11448 of subpart SSSSSS (NESHAP for Glass Manufacturing Area Sources), and 40 CFR 63.11462 of subpart TTTTTT (NESHAP for Secondary Nonferrous Metals Processing). If you have any questions regarding the applicability of this action to a particular entity, consult either the air permit authority for the entity or your EPA Regional representative as listed in 40 CFR 63.13 of subpart A (General Provisions).

B. Where can I get a copy of this document?

In addition to being available in the docket, an electronic copy of this final action will also be available on the Worldwide Web (WWW) through the Technology Transfer Network (TTN). Following signature, a copy of the final action will be posted on the TTN's policy and guidance page for newly proposed or promulgated rules at the following address: *www.epa.gov/ttn/oarpg/*. The TTN provides information and technology exchange in various areas of air pollution control.

C. Judicial Review

Under section 307(b)(1) of the Clean Air Act (CAA), judicial review of these final rules is available only by filing a petition for review in the U.S. Court of Appeals for the District of Columbia Circuit by February 25, 2008. Under section 307(d)(7)(B) of the CAA, only an objection to these final rules that was raised with reasonable specificity during the period for public comment can be raised during judicial review. This section also provides a mechanism for us to convene a proceeding for reconsideration, ''[i]f the person raising an objection can demonstrate to EPA that it was impracticable to raise such objection within [the period for public comment] or if the grounds for such objection arose after the period for public comment (but within the time specified for judicial review) and if such objection is of central relevance to the outcome of the rule.'' Any person seeking to make such a demonstration to us should submit a Petition for Reconsideration to the Office of the Administrator, Environmental Protection Agency, Room 3000, Ariel Rios Building, 1200 Pennsylvania Ave., NW., Washington, DC 20460, with a copy to the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section, and the Associate General Counsel for the Air and Radiation Law Office, Office of General Counsel (Mail Code 2344A), Environmental Protection Agency, 1200 Pennsylvania Ave., NW., Washington, DC 20004. Moreover, under section 307(d)(7)(B) of the CAA, only an objection to these final rules that was raised with reasonable specificity during the period for public comment can be raised during judicial review. Moreover, under section 307(b)(2) of the CAA, the requirements established by these final rules may not be challenged separately in any civil or criminal proceedings brought by EPA to enforce these requirements.

II. Background Information for Final Area Source Standards

Section 112(k)(3)(B) of the CAA requires EPA to identify at least 30 hazardous air pollutants (HAP) which, as the result of emissions from area sources,[a] pose the greatest threat to public health in urban areas. Consistent with this provision, in 1999, in the Integrated Urban Air Toxics Strategy, EPA identified the 30 HAP that pose the greatest potential health threat in urban areas, and these HAP are referred to as the ''urban HAP.'' *See* 64 FR 38706, 38715–716, July 19, 1999. Section 112(c)(3) requires EPA to list sufficient categories or subcategories of area sources to ensure that area sources representing 90 percent of the emissions of the 30 urban HAP are subject to regulation. EPA listed the source categories that account for 90 percent of the urban HAP emissions in the Integrated Urban Air Toxics Strategy.[b] Sierra Club sued EPA, alleging a failure to complete standards for the source categories listed pursuant to CAA section 112(c)(3) and 112(k)(3)(B) within the timeframe specified by the statute. *See Sierra Club* v. *Johnson,* No. 01–1537, (D.D.C.). On March 31, 2006, the court issued an order requiring EPA to promulgate standards under CAA section 112(d) for those area source categories listed pursuant to CAA section 112(c)(3) and 112(k)(3)(B).

Among other things, the court order, as amended on October 15, 2007, requires that EPA complete standards for 9 area source categories by December 15, 2007. On September 20, 2007 (72 FR 53838), we proposed NESHAP for the following three listed area source categories: (1) Clay Ceramics Manufacturing; (2) Glass Manufacturing; and (3) Secondary Nonferrous Metals Processing as part of our effort to meet the December 15, 2007 deadline. The standards for the other categories are being issued in separate actions.

Under CAA section 112(d)(5), the Administrator may, in lieu of standards requiring maximum achievable control technology (MACT) under section 112(d)(2), elect to promulgate standards or requirements for area sources ''which provide for the use of generally available control technologies or management practices by such sources to reduce emissions of hazardous air pollutants.'' Under section 112(d)(5), the Administrator has the discretion to use generally available control technology or management practices (GACT) in lieu of MACT. As explained in the proposed NESHAP, we are setting standards for these three source categories pursuant to section 112(d)(5). *See* 72 FR 53840, September 20, 2007.

III. Summary of Final Rules and Changes Since Proposal

This section summarizes the final rules and identifies changes since proposal. For changes that were made as a result of public comments, we have provided detailed explanations of the changes and the rationale for the changes in the responses to comments in section V of this preamble.

A. Area Source NESHAP for Clay Ceramics Manufacturing

1. Applicability and Compliance Dates

The only substantive changes to the Clay Ceramics rule made since proposal are clarifications of applicability. There was an error in the wording of the applicable compliance dates, and we have revised the rule since proposal to clarify that an affected source is existing if construction or reconstruction was commenced on or before September 20, 2007, and an affected source is new if construction or reconstruction was commenced after September 20, 2007. These clarifications of existing and new source are consistent with the definitions specified in § 63.2.

The final standards apply to any new or existing affected source at a clay ceramics manufacturing facility that is an area source and uses more than 45 megagrams per year (Mg/yr) (50 tons per year (tpy)) of clay. The affected source are all kilns that fire glazed ceramic

[a] An area source is a stationary source of HAP emissions that is not a major source. A major source is a stationary source that emits or has the potential to emit 10 tons per year (tpy) or more of any HAP or 25 tpy or more of any combination of HAP.

[b] Since its publication in the Integrated Urban Air Toxics Strategy in 1999, the area source category list has undergone several amendments.

ware and all atomized spray glaze operations located at such a facility.

The owner or operator of an existing affected source must comply with the standards by December 26, 2007. The owner or operator of a new affected source is required to comply with the standards by December 26, 2007 or upon startup, whichever is later.

2. Standards

The Clay Products Manufacturing area source category (which included clay ceramics manufacturing) was listed for regulation under section 112(c)(3) for its contribution of the following urban HAP: chromium, lead, manganese, and nickel. No changes have been made since proposal to the standards for clay ceramics manufacturing facilities.

For each kiln firing glazed ceramic ware, the final standards require the facility owner or operator to maintain the kiln peak temperature below 1540°C (2800°F) and either use natural gas, or an equivalent clean-burning fuel, as the kiln fuel. The facility owner or operator has the option of using an electric-powered kiln.

The requirements for atomized spray glaze operations at clay ceramic manufacturing area source facilities differ depending on whether a facility has annual wet glaze usage above or below 227 Mg/yr (250 tpy). Consequently, we are requiring that the facility owner or operator maintain annual wet glaze usage records in order to document whether they are above or below 227 Mg/yr (250 tpy) wet glaze usage.

For each atomized spray glaze operation located at a clay ceramics manufacturing facility that uses more than 227 Mg/yr (250 tpy) of wet glaze(s), the final standards require the facility owner or operator to have an air pollution control device (APCD) on their glazing operations and operate and maintain the control device according to the equipment manufacturer's specifications. As a pollution prevention alternative to this requirement, we are also providing the option to use glazes containing less than 0.1 (weight) percent clay ceramics metal HAP for those facilities above the threshold, which is expected to provide emissions reductions equivalent or greater than those obtained using particulate matter (PM) controls.

For each atomized spray glaze operation located at a clay ceramics manufacturing facility that uses 227 Mg/yr (250 tpy) or less of wet glaze(s), the final standards require the facility owner or operator to employ waste minimization practices in their glazing operations. In the preamble to the proposed rule, we acknowledged that some of these smaller facilities operate their atomized spray glaze operations with APCDs or use glazes containing less than 0.1 (weight) percent clay ceramics metal HAP. These alternative compliance options achieve reductions in metal HAP emissions that are at least equivalent to the metal HAP reductions from the waste minimization practices. Therefore, the final rule includes the use of glazes containing less than 0.1 (weight) percent clay ceramics metal HAP or an APCD as alternative compliance options for the waste minimization practices.

3. Compliance Requirements

No changes have been made since proposal to the compliance requirements for clay ceramics manufacturing facilities.

Initial compliance demonstration requirements. The owner or operator is required to include a compliance certification for the standards in their Notification of Compliance Status. For any wet spray glaze operations controlled with an APCD, an initial inspection of the control equipment must be conducted within 60 days of the compliance date and the results of the inspection included in the Notification of Compliance Status.

Monitoring requirements. For each kiln firing glazed ceramic ware, the final standards require the owner or operator to conduct a check of the kiln peak firing temperature on a daily basis. If the peak firing temperature exceeds 1540°C (2800°F), the owner or operator must take corrective action according to the facility's standard operating procedures.

For all sources that operate an APCD for their atomized spray glaze operations, we are requiring daily and weekly visual APCD inspections, daily EPA Method 22 visible emissions (VE) tests (40 CFR part 60, appendix A–7), or an EPA-approved alternative monitoring program to ensure that the APCD is kept in a satisfactory state of maintenance and repair and continues to operate effectively.

The owner or operator is allowed to use existing operating permit documentation to meet the monitoring requirements, provided it includes the necessary monitoring records (*e.g.*, the date, place, and time of the monitoring; the person conducting the monitoring; the monitoring technique or method; the operating conditions during monitoring; and the monitoring results).

Notification and recordkeeping requirements. We are requiring that affected sources submit Initial Notifications and Notifications of Compliance Status according to the part 63 General Provisions. Facilities must submit the notifications by April 24, 2008.

B. Area Source NESHAP for Glass Manufacturing

1. Summary of Changes Since Proposal

Applicability

We have revised the applicability criteria of the rule in § 63.11448 to clarify that periodic or pot furnaces are not part of the source category. The final rule applies only to glass manufacturing plants that operate continuous furnaces and use one or more of the glass manufacturing metal HAP as raw materials.

In light of the changes made to the applicability criteria in § 63.11448, we added a new paragraph to § 63.11449(a)(1), which states that, to be an affected source, the furnace must be a continuous furnace. We added a definition of ''continuous furnace'' to § 63.11459 to further clarify how affected furnace is defined. We made an additional revision to § 63.11449(a) to clarify that, consistent with the proposed rule, to be an affected source, a furnace must produce least 45 Mg/yr (50 tpy) of glass that contains one or more of the glass manufacturing metal HAP as raw materials. In the proposed rule, it was unclear whether a furnace that is used to produce more than 45 Mg/yr (50 tpy) of glass, but less than 45 Mg/yr (50 tpy) of glass containing metal HAP as raw materials, would be an affected source. The revision clarifies that such a furnace would not be an affected furnace. Finally, we inserted a new paragraph § 63.11449(b) to clarify that furnaces that are used exclusively for research and development (R&D) are not part of the source category and are therefore not subject to regulation under this final rule. We also added a definition for ''research and development process unit'' to § 63.11459.

In addition, we identified an error in the wording of the applicable compliance dates, and we have revised § 63.11449 since proposal to clarify that an affected source is existing if construction or reconstruction was commenced on or before September 20, 2007, and an affected source is new if construction or reconstruction was commenced after September 20, 2007. These clarifications of existing and new source are consistent with the definitions specified in § 63.2. Finally, we added a paragraph to the regulation to clarify that affected facilities must obtain a title V permit.

Performance Test Requirements

We revised § 63.11452(a) by adding paragraph (a)(3), which addresses the situation in which a facility operates affected furnaces that are identical. The new paragraph allows the owner or operator to demonstrate compliance for all such identical furnaces by testing only one of the furnaces. The additional paragraph specifies the criteria for determining if one furnace is identical to another and the conditions under which the furnace must be tested.

Under § 63.11452(b), we deleted paragraph (b)(2), which was redundant and renumbered the remaining paragraphs accordingly. We revised § 63.11452(b)(8), which formerly was paragraph (b)(9), to state that sampling ports for performance testing are to be located at the outlet to the furnace control device or in the furnace stack. The proposed rule was unclear regarding the exact location for emission testing. We added an alternative test method to Methods 3, 3A, and 3B for gas molecular weight analysis. We reorganized the paragraphs that address testing for PM or metal HAP to clarify which procedures to follow to determine compliance with the PM emission limit and which procedures to follow to determine compliance with the metal HAP emission limit. We also revised the definition of the metal HAP mass emission rate in Equation 2, which is signified as the variable ''ERM''. This variable specifies which metals are to be included in the analysis of the emission samples that are collected during testing. The revised text clarifies that ERM represents the combined mass emission rates for only those glass manufacturing metal HAP that are added as raw materials in the batch formulation.

Monitoring and Continuous Compliance Requirements

We revised the monitoring requirements by adding paragraph § 63.11454(a)(7), which specifies that the required monitoring must be performed any time the affected furnace is producing glass that is charged with one or more of the glass manufacturing metal HAP. Monitoring also must be performed during all transition phases from glass containing metal HAP to glass that does not contain metal HAP (i.e., until all HAP-containing glass has left the furnace melter). These transition phases encompass the period that begins when the plant stops charging the metal HAP as raw materials and ends when the furnace is producing a saleable product that does not contain the glass manufacturing metal HAP as raw materials.

We revised § 63.11455(c) to clarify that the continuous compliance requirements apply whenever the affected furnace is producing glass that contains one or more of the glass manufacturing metal HAP, including any transition phases from metal HAP-containing glass to glass that does not contain the metal HAP. We also revised paragraph § 63.11455(c) to clarify the monitoring requirements for existing furnaces versus the monitoring requirements for new furnaces. We further revised § 63.11455 by adding paragraph (e) to clarify the continuous compliance requirements for affected furnaces that can meet the emission limits without the use of a control device. In such cases, the only requirements for demonstrating continuous compliance is to meet the applicable recordkeeping requirements specified in § 63.11457.

Notifications

We have revised § 63.11456 to simplify the section and clarify that the deadline for submitting the Initial Notification is 120 days after the furnace becomes subject to the rule, regardless of whether the furnace is existing or new.

Definitions

We have revised several of the definitions specified in § 63.11459 and added a number of new definitions to the section. We revised the definition of cullet to clarify that cullet is not considered a raw material when determining if a furnace is an affected source. We revised the definition of a glass melting furnace, which is defined in the final rule as the process unit in which raw materials are charged and melted at high temperature to produce molten glass. The previous definition included the raw material charging system and other appendages to the furnace. However, the revised definition is consistent with the procedures for testing furnaces to demonstrate compliance. We revised the definition of particulate matter by replacing the modifier ''total'' with ''filterable.'' This revision makes the definition consistent with the test methods specified for demonstrating compliance with the PM emission limit. Finally, we revised the definition of raw material to clarify that it excludes cullet and material that is recycled from the furnace control device.

To clarify the applicability requirements in §§ 63.11448 and 63.11449, we added the definition of continuous furnace. To clarify the performance testing requirements, we have added a definition for furnace stack. We also added a definition for identical furnaces, which pertains to the performance testing requirements for a facility that operates more than one identical furnace. Finally, we added a definition for research and development process unit. This definition was needed to clarify in § 63.11449(b) that furnaces used strictly for R&D are not subject to regulation under this final rule. Glass manufacturing furnaces used only for R&D were not part of the 1990 inventory and are not part of the listed source category.

Implementation and Enforcement Authority

We deleted paragraph § 63.11460(c), which was redundant. We also added a new paragraph (b)(2) to clarify that EPA retains the authority for approving alternative test methods.

2. Summary of Final Rule

Applicability and Compliance Dates

This NESHAP applies to any glass manufacturing plant that is an area source of HAP emissions and operates one or more continuous furnaces which produce at least 45 Mg/yr (50 tpy) of glass per furnace by melting a mixture of raw materials that includes compounds of one or more of the glass manufacturing metal HAP. The rule does not apply to periodic furnaces or furnaces that are used strictly for research and development.

The compliance date for existing sources is December 28, 2009. However, owners or operators of affected sources may request an extension of one additional year to comply with the rule, as allowed under section 112(i)(3)(B) of the CAA and under § 63.6(i)(4)(A), if the additional time is needed to install emission controls. The compliance date for new sources is December 26, 2007 or the startup date for the source, whichever is later. The compliance date for facilities with no affected sources as of December 26, 2007 and which later change processes or increase production and trigger applicability of the rule, is 2 years following the date on which the facility made the process changes or increased production and thereby became subject to the NESHAP.

Standards

The Glass Manufacturing area source category was listed for regulation under section 112(c)(3) for its contribution of the following urban HAP: arsenic, cadmium, chromium, lead, manganese, and nickel. The glass manufacturing final rule requires each new or existing affected furnace to comply with a PM

emission limit of 0.1 gram per kilogram (g/kg) (0.2 pound per ton (lb/ton)) of glass produced or an equivalent metal HAP emission limit of 0.01 g/kg (0.02 lb/ton) of glass produced.

Performance Testing

This final rule requires an initial one-time performance test on each affected furnace unless the furnace had been tested during the previous 5 years, and the previous test demonstrated compliance with the emission limits in this rule using the same test methods and procedures specified in this rule. This final rule requires testing using EPA Methods 5 or 17 (for PM emissions) or EPA Method 29 (for metal HAP emissions) in 40 CFR part 60, appendix A. This final rule also allows the owner or operator of affected identical furnaces to test only one of the furnaces if certain conditions are met.

Monitoring

The owner or operator of an existing affected glass furnace that is controlled with an electrostatic precipitator (ESP) must monitor the secondary voltage and secondary electrical current to each field of the ESP continuously and record the results at least once every 8 hours. The owner or operator of a new affected furnace equipped with an ESP must install and operate one or more continuous parameter monitoring systems to continuously measure and record the secondary voltage and secondary electrical current to each field of the ESP. Either of these parameters dropping below established levels provides an indication that the electrical power to the ESP field in question has decreased, and collection efficiency may have decreased accordingly.

Owners or operators of an existing affected glass furnace that is controlled with a fabric filter must monitor the fabric filter inlet temperature continuously and record the results at least once every 8 hours. The owner or operator of a new affected furnace that is equipped with a fabric filter must install and operate a bag leak detector.

As an alternative to monitoring ESP secondary voltage and electrical current or fabric filter inlet temperature, owners or operators of affected furnaces equipped with either of these control devices have the option of requesting alternative monitoring, as allowed under § 63.8(f). The alternative monitoring request must include a description of the monitoring device or monitoring method to be used; instrument location; inspection procedures; quality assurance and quality control measures; the parameters to be monitored; and the frequency with which the operating parameter values would be measured and recorded. The owner or operator of an affected furnace that is equipped with a control device other than an ESP or fabric filter, or that uses other methods to reduce emissions, must submit a request for alternative monitoring, as described in § 63.8(f).

Control Device Inspections

The owner or operator of an affected furnace must conduct initial and periodic inspections of the furnace control device. For fabric filters, the final rule requires annual inspections of the ductwork, housing, and fabric filter interior. For electrostatic precipitators, this final rule requires annual inspections of the ductwork, hopper, and housing, and inspections of the ESP interior every 2 years.

Notification and Recordkeeping

Owners and operators of all affected glass manufacturing plants that operate at least one continuous furnace that produces at least 45 Mg/yr (50 tpy) of glass using any of the glass manufacturing metal HAP as raw materials must submit an Initial Notification, as required under § 63.9(b). Any facility with an affected source also must submit a Notification of Compliance Status, as specified in § 63.9(h).

Owners and operators of glass manufacturing facilities are required to keep records of all notifications, as well as supporting documentation for the notifications. In addition, they must keep records of performance tests; parameter monitoring data; monitoring system audits and evaluations; operation and maintenance of control devices and monitoring systems; control device inspections; and glass manufacturing batch formulation and production.

C. Area Source NESHAP for Secondary Nonferrous Metals Processing

1. Applicability and Compliance Dates

There was an error in the wording of the applicable compliance dates, and we have revised the rule since proposal to clarify that an affected source is existing if construction or reconstruction was commenced on or before September 20, 2007, and an affected source is new if construction or reconstruction was commenced after September 20, 2007. These clarifications of existing and new sources are consistent with the definitions specified in § 63.2.

The final standards apply to any new or existing affected source at an area source secondary nonferrous metals processing facility. The affected source includes all crushing or screening operations at a secondary zinc processing facility and all furnace melting operations located at a secondary nonferrous metals processing facility.

The owner or operator of an existing affected source must comply with the standards by December 26, 2007. The owner or operator of a new affected source is required to comply with the standards by December 26, 2007, or upon initial startup, whichever is later.

2. Standards

The Secondary Nonferrous Metals Processing area source category was listed for regulation under section 112(c)(3) for its contribution of the following urban HAP: arsenic, chromium, lead, manganese, and nickel. We proposed to require the use of a fabric filter or baghouse that achieves a PM control efficiency of 99 percent for existing sources and 99.5 percent for new sources. Since our proposal, we learned that a facility had insufficient inlet ductwork to conduct a performance test for determining collection efficiency. The facility requested that we add an alternate emission limit expressed as an outlet concentration limit to the final standards.

As we noted in the proposed rule, the 10 existing facilities reported using baghouses on crushing or screening operations at secondary zinc facilities and on furnace melting operations at all facilities and that such baghouses performed at a PM collection efficiency of at least 99 percent or achieved an outlet PM concentration not exceeding 0.050 grams per dry standard cubic meter (g/dscm) (0.022 grains per dry standard cubic foot (gr/dscf)) where collection efficiency was not reported. Based on available outlet concentration data from ICR responses in the proposal docket and consideration of baghouse performance at similar sources, we have determined that limiting outlet PM concentrations to 0.034 g/dscm (0.015 gr/dscf) and 0.023 g/dscm (0.010 gr/dscf) would control PM and metal HAP emissions at levels that are equivalent to the levels of control from using a baghouse with a control efficiency of 99 and 99.5 percent, respectively. Because both the proposed control efficiency standards and the equivalent outlet concentration limits reflect the GACT levels of control, we have revised the proposed standards to include the outlet concentration limits as alternatives to the control efficiency standards.

The final standards require the owner or operator of an existing affected source

to route the emissions from the affected source through a fabric filter or baghouse that achieves a control efficiency of at least 99.0 percent or an outlet PM concentration limit of 0.034 g/dscm (0.015 gr/dscf). The owner or operator of a new affected source must route the emissions from the affected source through a fabric filter or baghouse that achieves a control efficiency of at least 99.5 percent or an outlet PM concentration limit of 0.023 g/dscm (0.010 gr/dscf).

3. Compliance Requirements

Performance test requirements. The owner or operator of any existing or new affected source must conduct a one-time initial performance test on the affected source. However, a new performance test is not required for existing affected sources that were tested within the past 5 years of the compliance date if the test was conducted using the same procedures specified in the standards and either no process changes had been made since the test, or the owner or operator demonstrates that the results of the performance test, with or without adjustments, reliably demonstrated compliance despite process changes. The tests for new and existing affected sources are to be conducted using EPA Method 5 in 40 CFR part 60, appendix A–3 or EPA Method 17 in 40 CFR part 60, appendix A–6.

Initial control device inspection. The owner or operator of each existing and new affected source is required to conduct an initial inspection of each baghouse. The owner or operator must visually inspect the system ductwork and baghouse unit for leaks and inspect the inside of each baghouse for structural integrity and fabric filter condition. The owner or operator must record the results of the inspection and any maintenance action taken.

For each installed baghouse which is in operation during the 60 days after the compliance date, the owner or operator must conduct the initial inspection no later than 60 days after the applicable compliance date. For an installed baghouse which is not in operation during the 60 days after the compliance date, the owner or operator is required to conduct an initial inspection prior to startup of the baghouse. An initial inspection of the internal components of a baghouse is not required if an inspection has been performed within the past 12 months.

Monitoring requirements. For existing affected sources, the owner or operator must conduct either daily visible emission (VE) tests using EPA Method 22 (40 CFR part 60, appendix A–7) or weekly visual inspections of the baghouse system ductwork for leaks, as well as annual inspections of the interior of the baghouse to determine its structural integrity and to determine the condition of the fabric filter. For new affected sources, the owner or operator must operate and maintain a bag leak detection system for each baghouse used to comply with the standards. The final standards require the owner or operator to keep records of the date, place, and time of the monitoring; the person conducting the monitoring; the monitoring technique or method; the operating conditions during monitoring; and the monitoring results.

Notification and recordkeeping requirements. The owner or operator of an affected source must submit an Initial Notification and Notification of Compliance Status. The Notification of Compliance status must include, among other information, the results from the one-time initial performance test and certifications of compliance for the standards. We proposed to require facilities to submit both notifications no later than 120 days after the applicable compliance date regardless of whether they were required to conduct a performance test. Since our proposal, we discovered that, although we had intended to allow sources 180 days from the compliance date to conduct the initial performance test and an additional 60 days to submit the results of the performance test, the proposed rule implicitly shortened that time frame by 120 days because it required that the Notification of Compliance status include the performance test results and be submitted within 120 days of the compliance date. Therefore, to afford sources the full time to conduct the performance test and submit the results of the testing, we have revised our proposal in this final rule to require that sources required to do performance testing submit the Notification of Compliance Status before the close of business of the 60th day following the completion of a performance test.

IV. Exemption of Certain Area Source Categories From Title V Permitting Requirements

We did not receive any comments on our proposal to exempt facilities in the Clay Ceramics and Secondary Nonferrous Metals Processing area source categories from title V permitting requirements. Therefore, this final rule does not require facilities in these source categories to obtain an operating permit under 40 CFR part 70 or part 71.

The proposed Glass Manufacturing Area Source NESHAP would have required affected facilities to obtain title V permits. Although we received public comments requesting that we exempt the Glass Manufacturing Area Source Category from title V, we are finalizing the approach in the proposed rule and are not exempting the source category from title V. The reasons for this decision are summarized in this notice in the Summary of Comments and Responses section for the Area Source NESHAP for Glass Manufacturing.

V. Summary of Comments and Responses

A. Area Source NESHAP for Clay Ceramics Manufacturing

Comment: One commenter noted that the intent of the CAA, as it relates to the Area Source Program, was to bring about reductions in HAP emissions from area sources. The commenter expressed disappointment that some of the rules proposed under the Area Source Program (e.g., Clay Ceramics Manufacturing) will not result in emissions reductions and recommended that future area source rules incorporate provisions that will provide additional public health protection from the effects of HAP emissions from area sources.

Response: As previously explained, we have determined that GACT for the Clay Ceramics Manufacturing area source category is (1) maintaining the peak firing temperatures of kilns firing glaze ceramic ware below 1540 °C (2800 °F), (2) implementing the equipment requirement (wet control systems for PM emissions) for glaze spray booths at facilities with wet glaze usage above 227 Mg/yr (250 tpy), and (3) implementing the waste minimization practices for glaze spray booths at facilities with wet glaze usage at or below 227 Mg/yr (250 tpy). The use of PM controls and waste minimization practices has been shown to be very effective in controlling PM and metal HAP emissions from this area source category. Keeping kiln peak firing temperatures below the volatilization temperatures of the clay ceramics metal HAP in the spray glazes would also be effective in preventing volatilization of the clay ceramics metal HAP.

The commenter does not challenge any aspect of EPA's proposed GACT determination for this area source category. Instead, the commenter makes a blanket assertion that EPA is not acting consistently with the purposes of the area source provisions in the CAA (i.e., sections 112(c)(3) and 112(k)(3)(B)), because it is not requiring emission reductions beyond the level that is currently being achieved from this well-controlled source category. In support of this assertion, the commenter compares the requirements in the proposed rule to

the area source category's current emission and control status. Such a comparison is flawed and irrelevant.

Congress promulgated the relevant CAA area source provisions in 1990 in light of the level of area source HAP emissions at that time. Congress directed EPA to identify not less than 30 HAP which, as a result of emissions from area sources, present the greatest threat to public health in the largest number of urban areas, and to list sufficient area source categories to ensure that sources representing 90 percent of the 30 listed HAP are subject to regulation. As explained in the Integrated Urban Air Toxics Strategy, EPA based its listing decisions on the baseline National Toxics Inventory (NTI) that the Agency compiled for purposes of implementing its air toxics program after the 1990 CAA Amendments (64 FR 38706, 38711, n.10). The baseline NTI reflected HAP emissions from clay manufacturing area sources in 1990. Thus, contrary to the commenter's suggestion, the relevant emission level for comparison is the emission level reflected in our baseline NTI, not the current emission level.

Furthermore, in promulgating the area source provisions in the CAA, Congress did not require EPA to issue area source standards that must achieve a specific level of emission reduction. Rather, Congress authorized EPA to issue standards under section 112(d)(5) for area sources that reflect GACT for the source category. To qualify as being generally available, a GACT standard would most likely be an existing control technology or management practice. Thus, it is not surprising that the GACT standard being finalized today codifies the existing effective HAP control approach being used by sources in the category. For the reasons stated above, this final rule is consistent with sections 112(c)(3), 112(k)(3)(B), and 112(d)(5).

B. Area Source NESHAP for Glass Manufacturing

1. Definition of Source Category

Comment: Three commenters from companies that make stained glass commented that they own small facilities that operate, with one exception, small periodic furnaces (pot furnaces) that are charged with small amounts of the glass manufacturing metal HAP. They claim that their furnaces would be subject to the emission standards because they use the metal HAP and exceed the 45 Mg/yr (50 tpy) threshold. However, these companies allege that the costs of installing controls on their furnaces could put them out of business. One commenter stated that some artisans and schools also would be subject to the proposed rule based on the applicability criteria. Two of the commenters suggested that the rule exempt small businesses due to the burden that would result from complying with the proposed requirements. One commenter stated that the rule was based on an analysis of the glass manufacturing industry using data on large continuous furnaces that did not account differences in the manufacturing process and emissions associated with stained glass manufacturing. The commenter stated that the rule should exempt periodic furnaces.

Response: After reviewing the emissions inventory in support of the listing decisions made pursuant to sections 112(c)(3) and 112(k) and available information, we have concluded that the glass manufacturing area source category was listed based on emissions from relatively large manufacturing plants that operated continuous glass furnaces. Periodic furnaces were not included in the inventory.

The 45 Mg/yr (50 tpy) threshold that was proposed was meant to define the source category to include only these large manufacturers, but did not properly reflect this criterion. Therefore, we have revised § 63.11448 to specify that periodic or pot furnaces are not subject to the final Glass Manufacturing Area Source NESHAP. We believe this revision will address most of the concerns of the stained glass manufacturing sector as well as other sectors and organizations, such as artisans, schools, studios, and other small facilities that produce glass using periodic furnaces.

Comment: One commenter stated that flat glass should be excluded from the area source category for several reasons. According to the commenter, flat glass was not identified in the Integrated Urban Air Toxics Strategy as a source category for regulation. Therefore, the commenter suggests that EPA cannot regulate the flat glass industry under an area source standard. The commenter added that the administrative record refers only to pressed and blown glass, which has different Standard Industrial Classification (SIC) and North American Industrial Classification System (NAICS) codes than does flat glass manufacturing. The commenter also stated that the administrative record lacks evidence that flat glass manufacturers emit significant quantities of Urban HAP. The commenter pointed out that the Arsenic NESHAP does not apply to flat glass manufacturing for this same reason. Finally, the commenter stated that the proposed rule would not require any flat glass manufacturing plants to install or operate emission control devices.

Response: As explained in the **Federal Register** Notice announcing the Integrated Urban Air Toxics Strategy (64 FR 38707, July 19, 1999), the process of listing area source categories for regulation would be an iterative ongoing approach that would be refined and modified as we obtained better data on emissions. Furthermore, as indicated in section 112(e)(4) of the CAA, the listing of a particular source category is not considered final agency action until we issue emission standards for that source category. Therefore, the source category listing is not necessarily limited only to those sources initially identified by the listing. We considered this authority in light of the legislative history regarding glass manufacturing. The flat glass industry sector has always been part of the glass manufacturing industry, as evidenced by environmental statutes including the glass New Source Performance Standard (NSPS), the Arsenic NESHAP, as well as numerous State rules nationwide. Our study of the glass manufacturing industry includes container glass, pressed and blown glass, and flat glass sectors; these are generally similar with respect to the types of raw materials used and furnaces used to melt those raw materials.

Regarding the comment that the administrative record lacks evidence that flat glass manufacturers emit significant quantities of Urban HAP, we point out that the record does show that some flat glass plants emit some of the glass manufacturing metal HAP. Because several flat glass manufacturers do use the glass manufacturing metal HAP in their formulations, and emit metal HAP as a result, because the raw materials and the melting process are the focal points of the proposed Glass Manufacturing Area Source NESHAP, and because of evidence in the legislative history, we determined that it was appropriate to include flat glass within the area source category.

Based on our knowledge of the flat glass industry, the commenter is correct that no existing flat glass plants would have to install additional controls to comply with this final rule. However, there are existing flat glass plants that use the metal HAP as raw materials and will be subject to the other requirements of this final rule. Our data indicate these plants currently meet the emission limits and keep detailed records. Therefore, their additional burden as a result of this final rule is only related to notifications, which we believe are

justified. The notification requirements apply only if the plant uses one or more of the glass manufacturing metal HAP as raw materials; if the plant does not use any of the glass manufacturing metal HAP, this final rule does not apply. In the event that other flat glass manufacturers decide to change their current glass formulations to include metal HAPs, it is appropriate that those flat glass plants be subject to this final rule. Even in such an instance, an existing facility that changed their formulation such that it became subject to the requirements of the rule would have 2 years following the formulation change to comply with this final rule. For these reasons, we have concluded that inclusion of flat glass manufacturers in the Glass Manufacturing Area Source Category is warranted.

Comment: One commenter requested clarification that the proposed rule applies only to area sources and not major sources of HAP emissions.

Response: As specified in § 63.11448, the Glass Manufacturing Area Source NESHAP applies only to area sources of the glass manufacturing metal HAP.

2. Definition of Affected Source

Comment: Two commenters stated that, although the 45 Mg/yr (50 tpy) furnace threshold was meant to exclude small manufacturers, the proposed threshold is less than the amounts that some stained glass manufacturers, glass studios, and schools produce. The commenters believe that a higher threshold level is warranted to ensure that the small facilities that were meant to be excluded would not be subject to this final rule.

Response: Although we considered revising the definition of affected source in response to the commenters' concerns, we have no data to indicate a specific higher threshold and why that threshold would be more appropriate than the 45 Mg/yr (50 tpy) level specified in the proposed rule. However, based on our review of the comments received on the proposed rule and the available data, we have decided to clarify that this final rule only applies to continuous furnaces and not to periodic furnaces. We believe this clarification ameliorates the commenters' concerns regarding the production threshold. In this final rule, we have revised § 63.11448 to apply only to facilities that use continuous furnaces to produce glass.

Comment: Two commenters expressed concern with the definition of affected source (i.e., furnace). Both commenters stated that the definition in the proposed rule, which was adopted from 40 CFR 60, subpart CC, Standards of Performance for Glass Manufacturing Plants (Glass NSPS), defines furnace to include the ''raw material charging system'' and ''appendages for conditioning and transferring molten glass to forming machines.'' One commenter pointed out that, in the proposed rule, compliance is demonstrated by testing the furnace stack. However, emissions from the ''charging system'' or ''appendages'' are not generally ducted to the furnace stack. The commenter stated that furnace was defined as it was in the NSPS to clarify what constitutes a modification; the definition was not meant to identify emission points or where stack testing should be performed. The other commenter explained that one of the company's plants adds colored frit to the molten glass in the forehearth, which is one of the ''appendages'' referenced in the definition of furnace. The commenter pointed out that emissions from the forehearth are not ducted to the furnace stack. Since the GACT analysis for glass furnaces was based on emissions from furnace stacks, the proposed emission limits should not apply to emissions from forehearths.

Response: In developing the proposed rule, we determined GACT for this source category based on technology used to reduce emissions from glass melting furnace stacks. Glass furnace stacks generally exhaust emissions from the furnace melter, which is the part of the furnace where raw materials are charged and melted. Although furnace stacks may also exhaust emissions from other parts of, or appendages to, the furnace, it was our intent to regulate emissions from the furnace melter. This is consistent with our understanding of the emissions profile of glass manufacturing raw materials; that is, metal HAP are emitted from glass furnaces upon the initial melting step. Later remelting of glass, such as cullet and frit, does not re-emit the metal HAP once the glass has been formed or vitrified.

To clarify this requirement, we have revised § 63.11459 of this final rule to redefine the glass melting furnace as the ''* * * process unit in which raw materials are charged and melted at high temperature to produce molten glass.'' In addition, we have added to § 63.11459 a definition of furnace stack as the conduit or conveyance through which emissions from the furnace melter are released to the atmosphere. We also have revised § 63.11452 in this final rule to clarify that compliance with the emission limits is determined by testing the furnace stack.

Comment: One commenter requested that the rule exempt furnaces that are used strictly for R&D.

Response: We agree with the commenter that this final rule should clarify that sources that are used exclusively for R&D purposes are not regulated by this rule because these sources were not part of the inventory. Therefore, we have added a provision to § 63.11449 that clarifies that such furnaces are not covered by this final rule. We also have added to § 63.11459 of this final rule a definition for research and development process units.

Comment: Three commenters stated that the rule should specify a *de minimis* level for metal HAP usage, below which plants would have no requirements. Two of the commenters suggested setting annual *de minimis* levels for each regulated HAP, below which the rule limit would not apply.

Response: With respect to the use of the glass manufacturing metal HAP in relatively small amounts, the proposed 0.01 g/kg (0.02 lb/ton) metal HAP emission limit should address the commenters' concerns. If metal HAP are added to the batch in very small amounts, compliance with the HAP emission limit could be achieved without having to install a control device on the affected furnace.

It is appropriate under the area source program that glass manufacturers using large amounts of metal HAP in their furnaces install controls to reduce those emissions. Therefore, we have concluded that if would not be appropriate to develop de minimis levels for metal HAP usage.

Comment: One commenter stated that the rule does not define reconstruction as it pertains to reconstructed sources. The commenter suggested that the NSPS definition of reconstruction be adopted or incorporated by reference.

Response: Although the proposed rule did not define reconstruction, § 63.11472 states that the definitions specified in the CAA and § 63.2 of the General Provisions to part 63 also apply to the proposed rule. This is the definition of reconstruction that applies to all part 63 standards. Therefore, we believe it is the appropriate definition for the Glass Manufacturing Area Source NESHAP.

Comment: One commenter addressed the applicability of the proposed rule for furnaces that are used both for making glass that does not contain metal HAP and glass that contains metal HAP. The commenter asked if the 45 Mg/yr (50 tpy) threshold that defines an affected source is based only on the amount of HAP-containing glass produced or on the total amount of glass produced, even

if the amount of HAP-containing glass was less than 45 Mg/yr (50 tpy).

Response: It was our intent for the rule to apply to furnaces that produce at least 45 Mg/yr (50 tpy) of glass that contains one or more of the glass manufacturing metal HAP as raw materials. Therefore, a furnace that produces more than 45 Mg/yr (50 tpy) of glass would not be subject to this final rule if the amount of HAP-containing glass produced in the furnace were less than 45 Mg/yr (50 tpy). We have revised the definition of affected source in § 63.11449 to clarify that a source is an affected source only if it produces at least 45 Mg/yr (50 tpy) of glass that contains one or more of the metal HAP as raw materials.

3. Regulated Pollutants

Comment: One commenter stated that the rule should not regulate arsenic because arsenic emissions are already regulated under the Glass Arsenic NESHAP. The commenter believes that the requirements for both rules will create overlapping and sometimes conflicting requirements. The commenter added that the reporting and recordkeeping burden for a second rule to regulate the same pollutant would be excessive.

Response: The listing of glass manufacturing as an area source category was based in part on arsenic, which was identified in the section 112(k) inventory as one of the HAP emitted by glass manufacturing facilities. Therefore, we are required under sections 112(c)(3) and (d) of the CAA to regulate emissions of arsenic from glass manufacturing plants that are area sources of HAP based on GACT for the glass manufacturing industry.

With respect to the burden associated with complying with both rules, we have tried to minimize the burden associated with the Glass Manufacturing Area Source NESHAP. This final rule will require affected plants to submit an Initial Notification and a Notification of Compliance Status, but will require no additional reporting. Furthermore, the recordkeeping requirements are similar for both the proposed rule and the Glass Arsenic NESHAP. Therefore, we disagree that the reporting and recordkeeping burden associated with complying with both rules will be excessive. With respect to monitoring, the Glass Area Source NESHAP allows affected sources to request approval of alternative monitoring, which likely would result in no changes to the monitoring that is currently performed to comply with the Glass Arsenic NESHAP. In terms of testing, the Glass Area Source NESHAP requires only a one-time test and includes a provision for using data from a previous emission test conducted within the last 5 years, if the test demonstrates compliance with the emission limits specified in the Glass Area Source NESHAP.

4. Title V Permitting

Comment: Two commenters addressed EPA's decision to not exempt the Glass Manufacturing Area Source Category from title V permitting. Both commenters disagreed with the statement in the preamble to the proposed rule that all of the facilities that would be affected by the proposed rule are already subject to title V. One commenter stated that at least one of the company's facilities, which is not subject to title V, would be subject to the proposed rule. The commenter also stated that EPA's reasons for exempting the Clay Ceramics Manufacturing and Secondary Nonferrous Metals Processing Source Categories from title V permitting also apply to the Glass Manufacturing Source Category. The other commenter stated that the company operates two plants that are not currently subject to title V, each with a furnace that would be subject to the proposed rule. Although both furnaces are scheduled for shutdown, the company may reconsider this decision to shut them down if market conditions change. The same commenter stated that it is possible that there are other non-title V facilities that would be subject to the proposed rule, and that it appears it was EPA's intent for the proposed rule to not cause additional facilities to become subject to title V. Both commenters requested that the proposed rule provide title V exemptions for facilities that are not currently subject to title V permitting.

Response: Section 502(a) of the CAA requires sources subject to regulation under section 112 of the CAA to obtain a permit to operate. However, Section 502(a) authorizes the Administrator, in his discretion, to "promulgate regulations to exempt one or more source categories (in whole or in part) from the requirement of (title V) if the Administrator finds that compliance with such requirements is impracticable, infeasible, or unnecessarily burdensome on such categories * * *." EPA promulgated a rule interpreting section 502(a) and therein stated that EPA may only exempt a category from title V permitting if we find compliance to be "impracticable, infeasible, or unnecessarily burdensome" and we determine that exempting the category would not adversely affect public health, welfare, or the environment (see 70 FR 75,320, 75,323 (Dec. 19, 2005)). Nowhere in the rule did we establish a presumption in favor of exempting sources from title V permitting, and the statute leaves such determinations to the discretion of the Administrator.

The commenters have identified three glass manufacturer area source plants that are currently not subject to the operating permit requirements of CAA title V, which renders incorrect our assertion at proposal that all glass manufacturers that would be subject to this final rule were already subject to title V requirements. Notwithstanding this error, comments and other information in the record for this rulemaking do not demonstrate that compliance with title V permitting would be impracticable, infeasible, or unnecessarily burdensome for the sources in this category. Other than these two comments, we did not receive information during the comment period indicating that there are other sources that will be subject to this rule that do not have title V permits already. In this case, more than 80 percent of the sources in the category have title V permits, and of the 3 facilities that do not have such permits, the affected furnaces at two of those facilities are currently scheduled for shutdown. Based on these facts, it is not readily apparent why it would be impracticable, infeasible, or unnecessarily burdensome for sources in this category to comply with the title V requirements.

The two commenters that opposed our decision to not exempt the Glass Manufacturing Area Source Category from title V permitting did not identify their plants in question, did not explain how those plants differed in any way from other plants in this category that currently hold a title V permit, and did not explain how those differences would be relevant to the criteria for an exemption from title V.

For example, one commenter supported its request for exempting its two plants from title V by stating a desire for flexibility in the event that one or more of the affected furnaces at the plants actually do not shut down. (As noted above, the commenter's current plan is to shut down the affected furnaces at these two facilities.) Source flexibility, while important, is not a factor EPA considers in determining whether to exempt a source from title V permitting requirements.

The second commenter seeking a title V exemption for the glass manufacturing source category asserted that the reasons for exempting the other two source categories addressed in today's notice (Clay Ceramics Manufacturing and Secondary Non-ferrous Metals

Processing area sources) applied equally to this category. The commenter, however, offered no information substantiating this assertion, and we cannot dismiss obvious differences between the glass manufacturing source category and the source categories which received a title V exemption. These differences include whether most of the category already has a title V permit and whether most of the category is composed of small businesses that would incur economic hardship were title V requirements imposed on them.

The decision to exempt a source category is made on a case-by-case basis according to the facts of the industry. According to information we have collected on the glass manufacturing area source category, we conclude, in the absence of contrary information, that a title V exemption for this area source category is not warranted. Therefore, in light of the lack of information supporting an exemption of this source category from the title V requirements, we have not exempted the Glass Manufacturing Area Source Category from title V under today's rule.

5. Emission Limits

Comment: One commenter stated that, although emissions from glass furnaces vary by the type of glass produced, the proposed emission limits do not account for the relationship between PM emissions and glass type. The commenter noted that the Glass NSPS accounts for these differences by specifying different PM emission limits depending on the glass formulation and fuel type. The commenter explained that the differences in PM emissions result from differences in the volatilization rate of the constituents of the glass recipe. The commenter suggested that the proposed rule adopt the NSPS emission limits to account for these differences and to avoid confusion.

Response: While the Glass NSPS does regulate glass manufacturing furnaces for emissions of PM, the purpose of the proposed area source NESHAP is to address metal HAP emissions from continuous glass manufacturing furnaces.

Section 112(d)(5) of the CAA requires us to develop emission limits to reduce HAP emissions from area sources based on GACT. For the Glass Manufacturing Area Source Category, we determined GACT to be the level of control achieved by an ESP. In developing the PM emission limit for the proposed rule, our approach was to consider all of the available data on ESP-controlled PM emissions from glass manufacturing furnaces. Those data do not indicate that the variations in PM emissions due to glass formulation that are reflected in the emission limits of the Glass NSPS are appropriate for this rule. For example, the NSPS emission limits (in the format of PM emission factors) are higher for pressed and blown glass formulations than for container or flat glass formulations. However, the data used in developing the proposed PM emission limit do not indicate that controlled PM emissions from pressed and blown glass furnaces are higher than PM emissions from container or flat glass furnaces. In fact, the data with the lowest emission factors are from controlled pressed and blown glass furnaces. Although there are several possible explanations for this discrepancy, we point out that the NSPS emission limits are based on data from the 1970s and may not be representative of current glass manufacturing furnace PM emissions and control device performance. In conclusion, we developed the proposed PM emission limit based on the best available data, and because those data do not indicate variations in controlled PM levels due to glass formulation, we are not adopting the NSPS emission limits or differentiating by glass formulation, as suggested by the commenter.

Comment: One commenter pointed out that many existing glass furnaces comply with the Glass NSPS using modified processes without having to install emission controls. The commenter urged EPA to consider incorporating in this final rule the alternate emission limits for modified processes established in the NSPS. The commenter explained that the cost to retrofit a glass furnace with a control device is prohibitive, particularly in view of the amount of metal HAP reduced by such controls.

Response: The Glass NSPS defines modified process as "* * * any technique designed to minimize emissions without the use of add-on pollution controls." Thus, even though the regulated pollutant for the Glass NSPS is PM, the term "modified process" can apply to emissions of any pollutant. Several glass manufacturing furnaces subject to the NSPS have used this provision for meeting the less stringent PM emission limits for modified processes by installing controls or process modifications to reduce emissions of other pollutants, such as nitrogen oxides (NO_X). However, under Section 112(d) of the CAA, we are required to establish area source standards specifically for emissions of the Urban HAP. Furthermore, we are required to base those emission standards on GACT. As noted above, we determined GACT for this source category based on the level of control achieved by an ESP in controlling metal HAP emissions, and for controlling PM emissions as a surrogate for metal HAP emissions.

We understand that the costs of installing an ESP or equivalent control device on a glass furnace can be high. For example, we estimate the capital costs for installing a control device on a typical container furnace to be $800,000. However, our economic analysis of the industry indicates that the compliance costs for this final rule would be no more than 1 percent of sales, which we do not consider to be prohibitive. Although the metal HAP emissions reductions from an affected facility may be relatively low in terms of control costs, we note that, for facilities that use very small amounts of metal HAP in their glass formulations, the 0.01 g/kg (0.02 lb/ton) metal HAP emission limit can be met without having to install a control device. Finally, in addition to reductions in HAP emissions, the Glass Manufacturing Area Source NESHAP also will achieve significant reductions in fine PM emissions and will result in significant health benefits as a result of those reductions.

Comment: One commenter stated that the proposed rule should incorporate factors to account for emissions during periods of low production, similar to the "zero production rate" factors specified in the Glass NSPS. The commenter reasoned that, without these factors, there will be confusion. Although the PM emission limit in the proposed rule (0.1 g/kg (0.2 lb/ton)) is the same as the NSPS limit for container glass furnaces and for soda lime and lead pressed and blown glass furnaces, the NSPS includes the zero production rate factor, whereas the proposed rule does not incorporate such a factor.

Response: We appreciate the need to avoid confusion and to promote clarity in rulemaking, and we are sensitive to the need to implement the rule with easily understood materials and clear instruction. To that end, EPA currently plans to provide implementation guidance to minimize confusion that may be caused by the applicability of three Federal air pollution regulations that apply to this industry sector: the Arsenic NESHAP, the Glass NSPS, and this Area Source NESHAP. However, we have concluded that it would not be appropriate to incorporate one or more zero production rate factors in the final rule as suggested by the commenter. As specified in § 63.11452(b)(4), compliance with the emission limits in the proposed rule must be determined

through emission testing when the furnace is operating at maximum production rate. Therefore, emission levels when the furnace is operating at low production rates are not relevant with respect to compliance with the emission limits. If the rule were to require demonstrating compliance with the emission limits on a continuous basis, such as by using a continuous emissions monitoring system, it could be argued that there is reason to incorporate a zero production rate factor. In such a case, the emission factor would likely increase as production approached zero, and at zero production, the emission factor would be undefined. However, that is not the case for the proposed rule, which requires parameter monitoring and recordkeeping to demonstrate continuous compliance. Finally, it should be noted that the proposed emission limits were developed from data that did not account for zero production rate emissions. Furthermore, specifying an emission limit without zero production rate factors is consistent with other NESHAP.

Comment: One commenter questioned whether the proposed emission limits were based on data exclusively from large furnaces. The commenter explained that, when emissions are normalized for production, as is the case for the proposed emission factor format, they may not be representative of emissions from small furnaces if the limits are based on data from large furnaces. The commenter stated that, since the rule is likely to apply to small furnaces, the proposed limits should account for the higher emission factors characteristic of smaller furnaces. The commenter's company operates a small furnace that would be subject to the rule, as proposed, but would not be able to meet the proposed emission limit, even though the furnace is exhausted to a fabric filter. The commenter stated that a control efficiency of 99.91 percent would be needed for the furnace to meet the proposed limit. The commenter suggested including a correction factor for small furnaces, such as the zero production rate factors specified in the Glass NSPS, to account for this difference in emission levels between large and small furnaces.

Response: In developing the emission limits for the proposed rule, we reviewed all available emission test data on controlled furnaces, which included the results of tests on a wide range of furnace sizes or production rates. Because the production data for many of the furnaces were claimed as confidential business information, we cannot release the actual production rates to the public. However, we can provide information on the range of the data. The production data for the furnaces used to develop for the PM emission limit ranged from less than 0.9 megagram per hour (Mg/hr) (1 ton per hour (tph)) to just under 27 Mg/hr (30 tph). Of the 19 data points used, 3 data points were for furnaces with production rates of less than 0.9 Mg/hr (1 tph) and 9 data points were for furnaces with production rates less than 4.5 Mg/hr (5 tph). To develop the metal HAP emission limit, the furnace production rates ranged from less than 0.9 Mg/hr (1 tph) to just under 23 Mg/hr (25 tph). Of the 15 data points used, the production rates for 2 furnaces were less than 0.9 Mg/hr (1 tph), and the rates for 9 furnaces were less than 4.5 Mg/hr (5 tph). Although the commenter did not specify the actual production rate for the furnace in question, furnaces with production rates less than 4.5 Mg/hr (5 tph) would most likely be considered small and furnaces with production rates less than 0.9 Mg/hr (1 tph) would certainly be considered small. Therefore, we disagree with the commenter's assumption that only data from large furnaces were used to develop the proposed emission limits.

Although the commenter's suggestion about including a zero production rate factor would reduce the stringency of the standard for small furnaces, we do not believe such a factor is needed for the reasons described in the previous paragraph. Furthermore, as discussed in our response to the previous comment, we do not believe a zero production rate factor is relevant for an emission limit that must be demonstrated by testing when the source is operating at the maximum production rate.

Comment: One commenter stated that the process of manufacturing glass tableware is significantly different from container glass due to the need for higher quality requirements. The raw material formulations differ, and tableware furnaces operate at higher temperatures with longer residence times. Tableware furnaces also are smaller. The commenter stated that the South Coast Air Quality Management District uses an emission factor for tableware furnaces that is nearly five times the factor used for container glass furnaces.

Response: We acknowledge that PM emissions from glass furnaces can vary as a function of the type of glass produced. We also recognize that glass tableware manufacturing is generally classified as a type of pressed and blown glass rather than container glass, and PM emission factors for pressed and blown glass furnaces typically are greater than PM emission factors for container glass furnaces. When determining GACT for the proposed rule, we used all the available data on emissions of PM and metal HAP from furnaces controlled with ESP. Most of the data used in developing the proposed emission factors were from emission tests on pressed and blown glass furnaces. Therefore, we believe those emission limits are generally representative of the emission levels that can be achieved by an ESP-controlled furnace manufacturing pressed and blown glass. We also point out that the NESHAP specifies a metal HAP emission limit which may be more appropriate for specific furnaces that have unusually high PM emissions.

Commenter: One commenter noted that the proposed GACT does not take into consideration the unique nature of the stained glass industry, which generally uses small periodic furnaces rather than large continuous furnaces to produce glass. The commenter believes stained glass manufacturing should be a separate subcategory with GACT defined in terms of the practices and emission reduction methods followed by stained glass manufacturers.

Response: Although we conducted an extensive information gathering effort to compile data for developing the proposed NESHAP, we had little data on the stained glass sector and no basis for identifying stained glass as a separate subcategory of the glass manufacturing industry. We agree with the commenter that GACT for stained glass, if identified as a subcategory, should be based on methods and practices used by that sector to reduce metal HAP emissions. Although we still do not have the data to warrant creating a separate subcategory for stained glass, we have revised § 63.11448 of the rule to clarify that the rule applies to continuous furnaces and not to periodic furnaces. In doing so, we believe we have addressed the commenter's concerns.

6. Compliance Dates

Comment: One commenter stated that most glass manufacturing furnaces are rebuilt every 10 to 15 years. The commenter suggested that the compliance date for an existing furnace should coincide with the next rebuild planned for that furnace. Otherwise, affected facilities would have to install controls "on the fly," and doing so would interrupt glass production by forcing the facility to shut down affected furnaces for long periods. These shutdowns would result in significant costs to the affected facilities. The commenter pointed out that these costs

were not accounted for in the estimated cost effectiveness and impacts for the proposed rule.

Response: Section 112(i) of the CAA specifies that NESHAP require compliance ''* * * as expeditiously as practicable, but in no event later than three years after the effective date* * *'' of the standard. Since we had no information indicating this would be the case for the glass manufacturing industry, we proposed a compliance date of 2 years after promulgation of this final rule, which is consistent with the compliance date for other NESHAP. We believe this provision should allow adequate time for affected sources to install the controls needed to comply with this final rule. However, in the event that 2 years in not adequate, § 63.6(i)(3) of the General Provisions to part 63 allows owners or operators of affected facilities to request a 1-year extension of the compliance date if they can demonstrate that they need the additional time to install controls.

Comment: One commenter noted that additional time is needed for reconstructed furnaces to install controls. The company is rebuilding several furnaces in 2008, which would make them reconstructed furnaces. The compliance date for reconstructed sources would be the startup date (sometime in 2008), but it will take additional time to design, receive, and install a control device on the reconstructed furnaces.

Response: The General Provisions to 40 CFR part 63 define ''new source'' to include reconstructed sources, and for sources subject to 40 CFR part 63 standards, the compliance date for new sources is dictated by § 63.6(b) of the General Provisions to part 63. That is, new sources must be in compliance on the effective date of the rule or upon startup, whichever is later. Based on the limited facts submitted by the commenter, it is unclear if the subject furnaces would be considered existing furnaces or new furnaces. The General Provisions to part 63 define ''commenced'' as it relates to reconstruction as entering ''* * * into a contractual obligation to undertake and complete, within a reasonable time, a continuous program of construction or reconstruction.'' The commenter should evaluate the facts of its particular situations in light of the definitions incorporated into this final rule.

7. Other Compliance Requirements

Comment: One commenter identified an issue concerning furnaces that are used both for making glass that does not contain metal HAP and for making glass that contains metal HAP. The commenter requested clarification of the compliance requirements when the affected furnace is not producing glass that contains metal HAP.

Response: We agree with the commenter that additional clarification is needed on furnaces that are used to produce HAP-containing glass and non-HAP glass. Our intent was that the emission limits and other compliance requirements would apply when the affected furnace is producing glass that contains one or more of the glass manufacturing metal HAP. We have revised § 63.11454 to clarify that the monitoring requirements apply only during times when any of the glass manufacturing metal HAP are used in the glass being produced. We also have revised § 63.11455 to clarify that the continuous compliance requirements apply under the same conditions. However, owners and operators must still keep the applicable records specified in § 63.11457, including records of production data, during any period when an affected furnace is operated, regardless of the batch formulation used.

Comment: One commenter stated that the rule is unclear on the continuous compliance requirements for existing sources, particularly for sources that meet the metal HAP emission limit without having to install a control device.

Response: We agree with the commenter that additional clarification is needed regarding continuous compliance requirements for affected furnaces that meet the emission limit without the use of an emission control device. We have revised § 63.11455 of this final rule to clarify how owners or operators of affected sources must demonstrate continuous compliance. For the specific case cited by the commenter, the only continuous compliance requirement would be the recordkeeping requirements specified in § 63.11457.

Comment: One commenter stated that, even if a plant could meet the emission limit without installing a control device, the reporting and recordkeeping requirements of the rule are unnecessarily burdensome.

Response: We disagree that the reporting and recordkeeping requirements of the proposed rule are overly burdensome. This final rule will require affected plants to submit an Initial Notification and a Notification of Compliance Status, but will require no reporting. As for the recordkeeping requirements, the proposed rule incorporates the basic requirements specified in the General Provisions to part 63, and our understanding is that most facilities routinely maintain these records.

8. Emission Testing

Comment: Two commenters requested clarification of how emissions are tested and analyzed to show compliance with the proposed metal HAP emission limit. Both pointed out that the test method (Method 29) quantifies a wide range of metals, including metals that are not urban HAP and urban HAP metals that may not have been charged to the furnace as raw materials but could be present as contaminants in charge materials or fuels. The commenters stated that the rule should specify that emissions should be analyzed only for the metal HAP that are intentionally added to the batch as raw materials.

Response: We agree with the commenters that the testing requirements specified in the proposed rule need further clarification regarding how the sampled emissions are analyzed. We have revised § 63.11452 in this final rule to clarify Equation 2, which is used to determine compliance with the metal HAP emission limit. We have defined the variable ''ERM'' in this final rule as the sum of the mass emission rates for the glass manufacturing metal HAP that are charged to the furnace as raw materials. We believe this revision addresses the commenters' concern.

Comment: One commenter noted the definition of PM in the rule is ambiguous and could be interpreted to include filterable PM and condensible PM. Because the rule requires testing by Methods 5 or 17, and both of those methods measure filterable PM, the rule needs to clarify that the proposed PM emission limit refers to filterable PM. The commenter suggested that removing the word ''total'' from the definition would eliminate this ambiguity.

Response: We agree with the commenter and have revised the definition of PM in § 63.11458 by replacing the phrase ''total particulate emissions'' with ''filterable particulate emissions.'' This revised definition is consistent with the test methods (Methods 5 and 17) that are specified for determining compliance.

Comment: One commenter operates several identical furnaces that would be subject to the proposed rule. The commenter requested that the rule require testing on only one such furnace rather than on all of them.

Response: We agree with the commenter that it should not be necessary to test multiple identical furnaces to demonstrate that all of the furnaces meet the emission limit. To

address this issue, we revised § 63.11452(a) by adding paragraph (a)(3), which specifies conditions under which testing of a single furnace would be allowed as the compliance demonstration for other identical furnaces. Specifically, the owner or operator must certify that the furnaces that are not tested are identical in design to the furnace that is tested, including manufacturer, dimensions, production capacity, charging method, operating temperature, fuel type, burner configuration, and exhaust system configuration and design. Furthermore, the compliance test must be performed while the furnace is producing the glass formulation with the greatest potential to emit the glass manufacturing metal HAP, and the owner or operator must provide documentation that demonstrates why the tested glass formulation has the greatest potential to emit metal HAP.

9. Other Issues

Comment: Two commenters requested clarification of the definition of raw material. The commenters stated it was not clear if cullet is considered a raw material, and they suggested revising the definition to exclude cullet. One of the commenters suggested adding the phrase ''excluding glass manufacturing metal HAP that are introduced as cullet, trace constituents, or contaminants of other substances'' to §§ 63.11448 and 63.11449(a)(1) to clarify what is considered a raw material. The other commenter suggested revising the definition of raw material to exclude material captured by control devices and recycled into the process.

Response: We agree with the commenters that the proposed rule is not clear on whether or not cullet is considered a raw material. We also agree that material that is captured in a furnace control device and recycled should not be considered a raw material. We have revised the definition of raw material to state that cullet and material captured by the furnace control device are excluded. However, this definition does not exclude material collected from other sources, such as from fabric filters that are used to control emissions from raw material handling or transporting, because, while pre-vitrified materials do not re-emit metal HAP when remelted, baghouse fines from raw material handling and transporting have not been previously vitrified.

Comment: One commenter stated that the rule is unclear as to the notification requirements for furnaces that, at the time of promulgation, were not subject, but later became subject due to increased production or changes in glass formulation.

Response: To address the commenter's concern, we have revised § 63.11456(a) to indicate that the Initial Notification is due 120 days after the furnace becomes subject to this final rule due to increased production or changes in glass formulation. We also have revised § 63.11456(a) to specify deadlines for submitting the Notification of Compliance Status.

C. Area Source NESHAP for Secondary Nonferrous Metals Processing

Comment: One commenter noted that the intent of the CAA, as it relates to the Area Source Program, was to bring about reductions in HAP emissions from area sources. The commenter expressed disappointment that some of the rules proposed under the Area Source Program (*e.g.*, Secondary Nonferrous Metals Processing) will not result in emissions reductions and recommended that future area source rules incorporate provisions that will provide additional public health protection from the effects of HAP emissions from area sources.

Response: As previously explained, we have determined that GACT for the Secondary Nonferrous Metals Processing area source category is the use of a baghouse or fabric filter that achieves a control efficiency of 99 percent for existing sources and 99.5 percent for new sources.[c] The use of baghouses and fabric filters has been shown to be very effective in controlling PM and metal HAP emissions from this area source category. The commenter does not challenge any aspect of EPA's proposed GACT determination for this area source category. Instead, the commenter makes a blanket assertion that EPA is not acting consistently with the purposes of the area source provisions in the CAA (*i.e.*, sections 112(c)(3) and 112(k)(3)(B)), because it is not requiring emission reductions beyond the level that is currently being achieved from this well-controlled source category. In support of this assertion, the commenter compares the requirements in the proposed rule to the area source category's current emission and control status. Such a comparison is flawed and irrelevant.

Congress promulgated the relevant CAA area source provisions in 1990 in light of the level of area source HAP emissions at that time. Congress directed EPA to identify not less than 30 HAP which, as a result of emissions from area sources, present the greatest threat to public health in the largest number of urban areas, and to list sufficient area source categories to ensure that sources representing 90 percent of the 30 listed HAP are subject to regulation. As explained in the *Integrated Urban Air Toxics Strategy,* EPA based its listing decisions on the baseline NTI that the Agency compiled for purposes of implementing its air toxics program after the 1990 CAA Amendments. 64 FR 38706, 38711, n. 10. The baseline NTI reflected HAP emissions from glass manufacturing area sources in 1990. Thus, contrary to the commenter's suggestion, the relevant emission level for comparison is the emission level reflected in our baseline NTI, not the current emission level.

Based on EPA's baseline NTI, emissions of urban metal HAP from this area source category have been reduced from approximately 25 Mg/yr (28 tpy) to less than 0.9 Mg/yr (1 tpy) since 1990. Furthermore, in promulgating the area source provisions in the CAA, Congress did not require EPA to issue area source standards that must achieve a specific level of emission reduction. Rather, Congress authorized EPA to issue standards under section 112(d)(5) for area sources, and those standards are to reflect GACT for the source category. To qualify as being generally available, a GACT standard would most likely be an existing control technology or management practice. Thus, it is not surprising that the GACT standard being finalized today codifies the existing effective HAP control approach being used by sources in the category. For the reasons stated above, this final rule is consistent with sections 112(c)(3), 112(k)(3)(B), and 112(d)(5).

D. Area Source NESHAP—General

Comment: A commenter expressed his ''understanding that Congress only gave EPA [the authority] to establish requirements for new * * * [sic] major sources under the MACT and NSPS standards, and not new area sources.'' The commenter further claimed that new area sources are the ''jurisdiction'' of State and local authorities. The commenter also expressed the policy objection ''that to allow EPA to establish new and modified source requirements is tantamount to overriding the authority given the States and locals for establishing Best Available Control Technology (BACT) through their new source review programs.'' The commenter further questioned which standard would apply to a new area source if EPA established GACT requirements on a new source, and

[c] As previously explained, we have determined that outlet concentration limits of 0.034 g/dscm (0.015 gr/dscf) and 0.023 g/dscm (0.010 gr/dscf) reflect the GACT levels of control for existing and new secondary nonferrous processing area sources, respectively.

these requirements were to differ from BACT requirements in the NSR permit for the source.

Response: The comment above raises issues of EPA's authority for establishing GACT for new area sources and the appropriateness of potentially ''overriding'' locally-made BACT determinations for such sources. As generally discussed in the background section of this final rule, section 112 explicitly requires that EPA list categories of major sources, 42 U.S.C. 7412(c)(1), and area sources if those area sources meet the listing criteria in 42 U.S.C. 7412(c)(3). Furthermore, the statute requires EPA to promulgate emission standards for all listed categories whether the category is composed of major sources of HAP or area sources and directs that these standards address new as well as existing sources (42 U.S.C. 7412(d) & 7412(f)(2)). For area sources, Congress has provided EPA the option to promulgate GACT in lieu of MACT standards (42 U.S.C. 7412(d)(5)). In establishing timeframes for compliance for ''any emission standard, limitation or regulation promulgated under this section [*i.e.*, section 112],'' Congress allowed for different compliance dates for new and existing sources (42 U.S.C. 112(i)(3). This provision reinforces Congress's intent that standards under section 112, including the required area source standards, address both new and existing sources. Therefore, the commenter's understanding of EPA's authority does not reflect these express provisions of the statute. Based on these statutory provisions, EPA disagrees with the commenter's position that EPA lacks authority to establish GACT for new area sources.

Regarding the appropriateness of what the commenter calls ''overriding'' the authority to set BACT and BACT limits, we agree that there is a theoretical possibility inherent in the statute to have a GACT standard differ in stringency with a BACT limit in a permit. Initially, we note that BACT is triggered by the emission of different pollutants than those regulated under section 112 (see 42 U.S.C. 7412(b)(6)). The applicability provisions differ, and a major source under one program may or may not be a minor or area source under the other. Nevertheless, in many circumstances, a BACT limit targeting one pollutant may also, in effect, limit HAP emissions, and a HAP limit may incidentally limit a pollutant to which BACT would apply. It is a requirement for the owner or operator of a stationary source to comply with all air pollution control obligations that apply to the source under the CAA. To the extent that these obligations conflict and cannot be met simultaneously, the statute and EPA's regulations provide several mechanisms for resolving conflicts (*e.g.*, provisions for developing alternate control and monitoring requirements, delegation mechanisms that allow States and local agencies to develop approvable alternate standards, etc.).

Comment: One commenter recommended that EPA provide State and local agencies with sufficient additional grants so that they may participate in the implementation of additional area source rules. According to the commenter, Federal grants currently fall far short of what is needed to support State and local agencies in carrying out their existing responsibilities, and budget requests for the last two years have called for additional cuts. The commenter claimed that, without additional funding, some State and local air agencies may not be able to adopt and enforce additional area source rules. The commenter further stated that, even for permitting authorities that do not adopt these area source rules, it is possible that these rules will increase their work loads and resource needs. The commenter stated that, for example, synthetic minor permits (or Federally Enforceable State Operating Permits) will need to incorporate all applicable requirements, including area source standards. Noting that the title V permit fee funds are not available for these efforts, the commenter asserted that many State and local air agencies do not have sufficient resources for these responsibilities.

Response: State and local air programs are an important and integral part of the regulatory scheme under the CAA. As always, EPA recognizes the efforts of State and local agencies in taking delegations to implement and enforce CAA requirements, including the area source standards under section 112. We understand the importance of adequate resources for State and local agencies to run these programs; however, we do not believe that this issue can be addressed through this rulemaking.

EPA today is promulgating standards for the Secondary Nonferrous Metals Processing, Glass Manufacturing, and Clay Ceramics Manufacturing area source categories that reflect the practices currently in use by sources in these area source categories, and these standards represent what constitutes GACT for these categories under section 112(d)(5). GACT standards are technology-based standards. The level of State and local resources needed to implement these rules is not a factor that we consider in determining what constitutes GACT under section 112(d)(5). Moreover, we note that the commenter did not challenge our proposed determination to exempt from title V the Secondary Nonferrous Metals Processing or Clay Ceramics Manufacturing area source categories.

Although the resource issue cannot be resolved through this rulemaking for the reason stated above, EPA remains committed to working with State and local agencies to implement this final rule. State and local agencies that receive grants for continuing air programs under CAA section 105 should work with their project officer to determine what resources are necessary to implement and enforce the area source standards. EPA will continue to provide the resources appropriated for section 105 grants consistent with the statute and the allotment formula developed pursuant to the statute.

VI. Impacts of the Final Area Source Standards

A. Glass Manufacturing

1. Air Quality Impacts

For the three sources that will be required to install emission controls to meet the emission limits specified in this final rule, we estimate nationwide emissions of the glass manufacturing metal HAP to be 26.2 Mg/yr (28.9 tpy). We estimate that this final rule will reduce nationwide emissions of the glass manufacturing metal HAP by about 25.6 Mg/yr (28.2 tpy). This final rule will also reduce emissions of PM by 377 Mg/yr (415 tpy). These estimates are based on the assumption that an ESP will be installed on one pressed and blown glass furnace, and that fabric filters will be installed on two pressed and blown glass furnaces.

We project that, during the first three years of the standard, nine new furnaces will be constructed and that all nine furnaces will be in the container glass sector. Because none of these new furnaces are expected to use any of the glass manufacturing metal HAP as raw materials, we project that none of the nine new furnaces will be affected by this final rule. Therefore, we estimate that this final rule will have no air quality impacts on new sources.

Indirect or secondary air impacts of this final rule will result from the increased electricity usage associated with the operation of control devices. Assuming that plants will purchase electricity from a power plant, we estimate that the final standards will increase secondary emissions of criteria pollutants, including PM, sulfur dioxide (SO_2), NO_X, and carbon monoxide (CO)

from power plants. For the three existing sources that will be required to install emission controls, this final rule will increase secondary PM emissions by 0.28 Mg/yr (0.31 tpy); secondary SO_2 emissions by about 11.1 Mg/yr (12.2 tpy); secondary NO_X emissions by about 5.5 Mg/yr (6.1 tpy); and secondary CO emissions by about 0.18 Mg/yr (0.20 tpy).

For the estimated nine new sources within the Glass Manufacturing industry over the next three years, we estimate no secondary air impacts because we project that none of the new sources will be affected sources under this rule.

2. Water and Solid Waste Impacts

To comply with this final rule, we expect that affected facilities will control emissions by installing and operating ESP or fabric filters, neither of which generates wastewater. Therefore, we project that this final rule will have no water impacts. Glass manufacturers typically purchase highly refined and purified raw materials, and they usually recycle internal captured baghouse and ESP fines into the raw material to be fed back into the furnace. Therefore, we expect the solid waste impacts to be far less than if facilities were to dispose of their ESP and baghouse fines. We estimate that this final rule will generate 37.7 Mg/yr (41.6 tpy) of solid waste from existing sources. These estimates are based on the assumption that an ESP will be installed on one pressed and blown glass furnace, and that fabric filters will be installed on two pressed and blown glass furnaces. For new sources, we estimate that this final rule will have no impacts on solid waste generation.

3. Energy Impacts

Energy impacts consist of the electricity and fuel needed to operate control devices and other equipment that are required under this final rule. We assume that affected facilities will comply with this final rule by installing and operating either ESP or fabric filters, which require electricity to operate. Specifically, we assumed that an ESP will be installed on one pressed and blown glass furnace, and that fabric filters will be installed on two pressed and blown glass furnaces. Under this scenario, we project that this final rule will increase overall energy demand (i.e., electricity demand) for existing sources by about 1,970 megawatt-hours per year, or 7.1 thousand gigajoules per year (6.7 billion British thermal units per year). We estimate that none of the nine new sources projected to go into operation during the first three years of the standard will be affected by this final rule. Therefore, we are not expecting any energy impacts for new sources.

4. Cost Impacts

The estimated total capital costs of this final rule for existing sources are $1.42 million. These capital costs include the costs to purchase and install ESP or fabric filters on the three affected furnaces that are not currently controlled. The estimated annualized cost of this final rule for existing sources is $491,000 per year. The annualized costs account for the annualized capital costs of the control and monitoring equipment, operation and maintenance expenses, performance testing, and recordkeeping costs for the three existing facilities within the source category that will be required to install new emission controls. The other affected facilities will incur costs only for submitting the notifications and for annual control device inspections because those facilities already meet the testing, monitoring, and recordkeeping requirements that are required under this final rule.

We estimate that none of the nine new sources projected to go into operation during the first three years of the standard will be affected sources under this final rule. Therefore, we estimate no cost impacts for new sources.

5. Economic Impacts

Both the magnitude of control costs needed to comply with this final rule and the distribution of these costs among affected facilities can have an impact in determining how the market will change in response to the rule. Total annualized costs for this final rule are estimated to be approximately $0.48 million. Only three facilities are estimated to require additional capital costs because of this final rule.

We obtained revenue data for two of the three companies that operate facilities that will be required to install emission controls under this final rule. Based on those data, cost-to-sales estimates for those two affected facilities are 0.66 percent and 1.0 percent, respectively. Revenue data were not available for the other facility that will be affected by this final rule, so the national average value of shipments per worker from the 2002 Census of Manufacturers was used along with the average number of workers per facility to estimate revenues. The resulting costs for this and the other two facilities are relatively small and are not expected to result in a significant market impact whether they are passed on to the purchaser or absorbed by the company.

B. Clay Ceramics Manufacturing

Unlike the glass manufacturing industry, which still has some uncontrolled sources of urban HAP, sources in the clay ceramics manufacturing source category have made significant emission reductions through process changes and installation of control equipment. Affected sources are well-controlled, and our GACT determination reflects such controls. We estimate that the only impact to affected sources is the labor burden associated with the reporting and recordkeeping requirements. The cost associated with recordkeeping and the one-time reporting requirements is estimated to be $974 per facility.

C. Secondary Nonferrous Metals Processing

Similar to the clay ceramics manufacturing industry, all of the affected sources in the secondary nonferrous metal processing category have installed control equipment on their furnace melting operations. Affected sources are well-controlled, and our GACT determination reflects such controls. We estimate that the only impact associated with this final rule is the reporting and recordkeeping requirements. The cost associated with recordkeeping and the one-time reporting requirements is estimated to be $390 per facility.

VII. Statutory and Executive Order Reviews

A. Executive Order 12866: Regulatory Planning and Review

Under Executive Order 12866 (58 FR 51735, October 4, 1993), this action is a ''significant regulatory action'' because it may raise novel legal or policy issues. Accordingly, EPA submitted this action to the Office of Management and Budget (OMB) for review under Executive Order 12866, and any changes made in response to OMB recommendations have been documented in the docket for this action.

B. Paperwork Reduction Act

The information collection requirements in these NESHAP for Clay Ceramics Manufacturing Area Sources, Glass Manufacturing Area Sources, and Secondary Nonferrous Metals Processing Area Sources have been submitted for approval to OMB under the *Paperwork Reduction Act*, 44 U.S.C. 3501 *et seq.* The information collection requirements are not enforceable until OMB approves them.

The recordkeeping and reporting requirements in these final rules are based on the information collection

requirements in the part 63 General Provisions (40 CFR part 63, subpart A). These recordkeeping and reporting requirements are mandatory pursuant to section 114 of the CAA (42 U.S.C. 7414). All information submitted to EPA pursuant to the information collection requirements for which a claim of confidentiality is made is safeguarded according to EPA's implementing regulations at 40 CFR part 2, subpart B.

The NESHAP for Clay Ceramics Manufacturing area sources requires applicable one-time notifications required by the General Provisions. Plant owners or operators are required to include compliance certifications for the management practices in their Notifications of Compliance Status. The affected sources are expected to already have the required control and monitoring equipment in place and already conduct the required monitoring and recordkeeping activities.

The annual burden for this information collection averaged over the first three years of this ICR is estimated to total 196 labor hours per year at a cost of approximately $16,600 for 17 existing clay ceramics manufacturing area sources (51 existing sources averaged over three years). No capital/startup costs or operation and maintenance costs are associated with the information collection requirements. No costs or burden hours are estimated for new clay ceramics manufacturing area sources because no new area sources are projected for the next three years.

The NESHAP for Glass Manufacturing also requires applicable one-time notifications required by the General Provisions, monitoring of control device parameters, and recordkeeping. The annual burden for this collection of information averaged over the first three years of this ICR is estimated to total 190 labor hours per year at a cost of $16,130 for the 21 glass manufacturing area source facilities that will be subject to this final rule. This burden estimate includes time for acquisition, installation, and use of monitoring technology and systems, one-time notifications, and recordkeeping. Total capital/startup costs associated with the monitoring requirements (e.g., costs for hiring performance test contractors and purchase of monitoring and file storage equipment) over the three-year period of the ICR are estimated at $15,990, with operation and maintenance costs of $9,850/yr. No costs or burden estimates are estimated for new sources because no new sources are project for the next three years.

The NESHAP for Secondary Nonferrous Metals Processing area sources requires one-time notifications required by the General Provisions. Plant owners or operators are required to conduct performance tests and include compliance certifications for the percent PM reduction achieved by the required control device in their Notifications of Compliance Status. The affected sources are expected to already have the required control and monitoring equipment in place and already conduct the required monitoring and recordkeeping activities.

The annual burden for this information collection averaged over the first three years of this ICR is estimated to total 15 labor hours per year at a cost of approximately $1,300 for three existing secondary nonferrous metals processing area sources (10 existing sources averaged over three years). No capital/startup costs or operation and maintenance costs are associated with the information collection requirements. No costs or burden hours are estimated for new secondary nonferrous metals processing area sources because no new area sources are projected for the next three years.

Burden means the total time, effort, or financial resources expended by persons to generate, maintain, retain, or disclose or provide information to or for a Federal agency. This includes the time needed to review instructions; develop, acquire, install, and utilize technology and systems for the purposes of collecting, validating, and verifying information, processing and maintaining information, and disclosing and providing information; adjust the existing ways to comply with any previously applicable instructions and requirements; train personnel to be able to respond to a collection of information; search data sources; complete and review the collection of information; and transmit or otherwise disclose the information.

An agency may not conduct or sponsor, and a person is not required to, respond to a collection of information unless it displays a currently valid OMB control number. The OMB control numbers for EPA's regulations in 40 CFR part 63 are listed in 40 CFR part 9. When this ICR is approved by OMB, the Agency will publish a technical amendment to 40 CFR part 9 in the **Federal Register** to display the OMB control number for the approved information collection requirements contained in these final rules.

C. Regulatory Flexibility Act

The Regulatory Flexibility Act generally requires an agency to prepare a regulatory flexibility analysis of any rule subject to notice and comment rulemaking requirements under the Administrative Procedure Act or any other statute unless the agency certifies that the rule would not have a significant economic impact on a substantial number of small entities. Small entities include small businesses, small not-for-profit enterprises, and small governmental jurisdictions.

For the purposes of assessing the impacts of the area source NESHAP on small entities, a small entity is defined as: (1) A small business whose parent company meets the Small Business Administration size standards for small businesses found at 13 CFR 121.201 (less than 500 to 750 employees for Clay Ceramics Manufacturing, less than 750 to 1,000 employees for Glass Manufacturing, and less than 750 employees for Secondary Nonferrous Metals Processing, depending on the size definition for the affected NAICS code); (2) a small governmental jurisdiction that is a government of a city, county, town, school district, or special district with a population of less than 50,000; and (3) a small organization that is any not-for-profit enterprise, which is independently owned and operated and is not dominant in its field.

After considering the economic impacts of these final rules on small entities, I certify that this action will not have a significant economic impact on a substantial number of small entities. Based on our estimates, EPA does not expect any new clay ceramic or secondary nonferrous metal processing sources to be constructed in the foreseeable future and so, therefore, did not estimate the impacts for new clay ceramics manufacturing or secondary nonferrous metal processing sources. There would be no significant impacts on new or existing clay ceramics manufacturing facilities or secondary nonferrous metals processing facilities because these final rules do not create any new requirements or burdens other than minimal notification requirements. The minimal notification requirements consist of reading this final rule and providing two initial notifications to EPA: one notifying EPA that the facility is subject to this final rule and one notifying EPA that the facility is in compliance with this final rule. These notifications may be submitted together. We estimate the cost of these one-time notification requirements to be $974 for each clay ceramics manufacturing facility and $390 for each secondary nonferrous metals processing facility. These costs were estimated based on the costs of technical, management, and clerical support salaries. We also estimate that 34 clay ceramics facilities and 6 secondary nonferrous metals

processing facilities are owned and operated by small businesses. These notification costs would be less than 0.25 percent for any of these small businesses.

Twenty-one glass manufacturing facilities are estimated to require additional costs because of this final rule. Only one of these facilities is a small business.

Although these final rules will not have a significant economic impact on a substantial number of small entities, EPA nonetheless has tried to reduce the impact of this final rule on small entities. These final rules are designed to harmonize with existing State and local requirements.

D. Unfunded Mandates Reform Act

Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), Public Law 104–4, establishes requirements for Federal agencies to assess the effects of their regulatory actions on State, local, and tribal governments and the private sector. Under section 202 of the UMRA, EPA generally must prepare a written statement, including a cost-benefit analysis, for proposed and final rules with ''Federal mandates'' that may result in expenditures by State, local, and tribal governments, in the aggregate, or to the private sector, of $100 million or more in any one year. Before promulgating an EPA rule for which a written statement is needed, section 205 of the UMRA generally requires EPA to identify and consider a reasonable number of regulatory alternatives and adopt the least costly, most cost-effective, or least burdensome alternative that achieves the objectives of the rule. The provisions of section 205 do not apply when they are inconsistent with applicable law. Moreover, section 205 allows EPA to adopt an alternative other than the least costly, most cost-effective, or least burdensome alternative if the Administrator publishes with the final rule an explanation why that alternative was not adopted. Before EPA establishes any regulatory requirements that may significantly or uniquely affect small governments, including tribal governments, it must have developed under section 203 of the UMRA a small government agency plan. The plan must provide for notifying potentially affected small governments, enabling officials of affected small governments to have meaningful and timely input in the development of EPA regulatory proposals with significant Federal intergovernmental mandates, and informing, educating, and advising small governments on compliance with the regulatory requirements.

EPA has determined that these final rules do not contain a Federal mandate that may result in expenditures of $100 million or more for State, local, and tribal governments, in the aggregate, or to the private sector in any one year. Thus, these final rules are not subject to the requirements of sections 202 and 205 of the UMRA. EPA has determined that these final rules contain no regulatory requirement that might significantly or uniquely affect small governments. These final rules contain no requirements that apply to such governments, impose no obligations upon them, and will not result in expenditures by them of $100 million or more in any one year or any disproportionate impacts on them.

E. Executive Order 13132: Federalism

Executive Order 13132 (64 FR 43255, August 10, 1999) requires EPA to develop an accountable process to assure ''meaningful and timely input by State and local officials in the development of regulatory policies that have federalism implications.'' ''Policies that have federalism implications'' are defined in the Executive Order to include regulations that have ''substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government.''

These final rules do not have federalism implications. They will not have substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132. These final rules impose requirements on owners and operators of specified area sources and not State and local governments. Thus, Executive Order 13132 does not apply to these final rules.

F. Executive Order 13175: Consultation and Coordination With Indian Tribal Governments

Executive Order 13175 (65 FR 67249, November 6, 2000), requires EPA to develop an accountable process to assure ''meaningful and timely input by tribal officials in the development of regulatory policies that have tribal implications.'' These final rules do not have tribal implications, as specified in Executive Order 13175. They will not have substantial direct effects on tribal governments, on the relationship between the Federal government and Indian tribes, or on the distribution of power and responsibilities between the Federal government and Indian tribes, as specified in Executive Order 13175. These final rules impose requirements on owners and operators of specified area sources and not tribal governments. Thus, Executive Order 13175 does not apply to these final rules.

G. Executive Order 13045: Protection of Children From Environmental Health and Safety Risks

Executive Order 13045: ''Protection of Children from Environmental Health Risks and Safety Risks'' (62 FR 19885, April 23, 1997) applies to any rule that: (1) Is determined to be ''economically significant'' as defined under Executive Order 12866, and (2) concerns an environmental health or safety risk that EPA has reason to believe may have a disproportionate effect on children. If the regulatory action meets both criteria, EPA must evaluate the environmental health or safety effects of the planned rule on children, and explain why the planned regulation is preferable to other potentially effective and reasonably feasible alternatives considered by EPA.

EPA interprets Executive Order 13045 as applying only to those regulatory actions that are based on health or safety risks, such that the analysis required under section 5–501 of the Executive Order has the potential to influence the regulation. These final rules are not subject to Executive Order 13045 because they are based on technology performance and not on health or safety risks.

H. Executive Order 13211: Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use

The glass manufacturing final rule is not a ''significant energy action'' as defined in Executive Order 13211, ''Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use'' (66 FR 28355, May 22, 2001) because it is not likely to have a significant adverse effect on the supply, distribution, or use of energy. Existing energy requirements for this industry will not be significantly impacted by the additional pollution controls or other equipment that may be required by this final rule. Further, we have concluded that this final rule is not likely to have any significant adverse energy effects.

The clay ceramics manufacturing and the secondary nonferrous metals processing final rules are not ''significant energy actions'' as defined in Executive Order 13211 (66 FR 28355, May 22, 2001) because they are not likely to have a significant adverse effect on the supply, distribution, or use of

energy. The energy requirements for these industries will remain at existing levels. No additional pollution controls or other equipment that would consume energy are required by these final rules. Further, we have concluded that these final rules are not likely to have any adverse energy effects.

I. National Technology Transfer Advancement Act

Section 12(d) of the National Technology Transfer and Advancement Act (NTTAA) of 1995 (Public Law No. 104–113, Section 12(d), 15 U.S.C. 272 note) directs EPA to use voluntary consensus standards (VCS) in its regulatory activities, unless to do so would be inconsistent with applicable law or otherwise impractical. The VCS are technical standards (e.g., materials specifications, test methods, sampling procedures, and business practices) that are developed or adopted by VCS bodies. The NTTAA directs EPA to provide Congress, through OMB, explanations when the Agency does not use available and applicable VCS.

These rules involve technical standards. EPA cites the following standards: EPA Methods 1, 1A, 2, 2A, 2C, 2F, 2G, 3, 3A, 3B, 4, 5, 17, 22, and 29 (40 CFR part 60, appendix A).

Consistent with the NTTAA, EPA conducted searches to identify voluntary consensus standards in addition to these EPA methods. No applicable voluntary consensus standards were identified for EPA Methods 1A, 2A, 2F, 2G, 22, and 29. The search and review results are in the dockets for these final rules.

The search identified one voluntary consensus standard as acceptable alternatives to an EPA Method. The standard ASME PTC 19.10–1981, ''Flue and Exhaust Gas Analyses,'' is cited in this rule for its manual method for measuring the oxygen, carbon dioxide, and carbon monoxide content of the exhaust gas. This part of ASME PTC 19.10–1981 is an acceptable alternative to EPA Method 3B.

The search for emissions measurement procedures identified 12 other voluntary consensus standards. EPA determined that these 12 standards identified for measuring emissions of the HAP or surrogates subject to emission standards in these final rules were impractical alternatives to EPA test methods for the purposes of the rules. Therefore, EPA does not intend to adopt these standards for these purposes. The reasons for the determinations for the 12 methods are discussed in the dockets to these final rules.

Under § 63.7(f) and § 63.8(f) of Subpart A of the General Provisions, a source may apply to EPA for permission to use alternative test methods or alternative monitoring requirements in place of any required testing methods, performance specifications, or procedures.

J. Executive Order 12898: Federal Actions To Address Environmental Justice in Minority Populations and Low-Income Populations

Executive Order 12898 (59 FR 7629, February 16, 1994) establishes Federal executive policy on environmental justice. Its main provision directs Federal agencies, to the greatest extent practicable and permitted by law, to make environmental justice part of their mission by identifying and addressing, as appropriate, disproportionately high and adverse human health or environmental effects of their programs, policies, and activities on minority populations and low-income populations in the United States.

EPA has determined that these final rules will not have disproportionately high and adverse human health or environmental effects on minority or low-income populations because they increase the level of environmental protection for all affected populations without having any disproportionately high and adverse human health or environmental effects on any population, including any minority or low-income population. These final rules establish national standards for each area source category.

K. Congressional Review Act

The Congressional Review Act, 5 U.S.C. 801, *et seq.*, as added by the Small Business Regulatory Enforcement Fairness Act of 1996, generally provides that before a rule may take effect the agency promulgating the rule must submit a rule report, which includes a copy of the rule, to each House of Congress and to the Comptroller General of the United States. EPA will submit a report containing these final rules and other required information to the U.S. Senate, the U.S. House of Representatives, and the Comptroller General of the United States prior to publication of these final rules in the **Federal Register**. A major rule cannot take effect until 60 days after it is published in the **Federal Register**. This action is not a ''major rule'' as defined by 5 U.S.C. 804(2). These final rules will be effective on December 26, 2007.

List of Subjects in 40 CFR Part 63

Environmental protection, Air pollution control, Hazardous substances, Incorporations by reference, Reporting and recordkeeping requirements.

Dated: December 14, 2007.

Stephen L. Johnson,

Administrator.

For the reasons stated in the preamble, title 40, chapter I, part 63 of the Code of Federal Regulations is amended as follows:

PART 63—[AMENDED]

1. The authority citation for part 63 continues to read as follows:

Authority: 42 U.S.C. 7401 *et seq.*

Subpart A—[Amended]

2. Section 63.14 is amended by revising paragraph (i)(1) to read as follows:

§ 63.14 Incorporations by reference.

* * * * *

(i) * * *

(1) ANSI/ASME PTC 19.10–1981, ''Flue and Exhaust Gas Analyses [Part 10, Instruments and Apparatus],'' IBR approved for §§ 63.309(k)(1)(iii), 63.865(b), 63.3166(a)(3), 63.3360(e)(1)(iii), 63.3545(a)(3), 63.3555(a)(3), 63.4166(a)(3), 63.4362(a)(3), 63.4766(a)(3), 63.4965(a)(3), 63.5160(d)(1)(iii), 63.9307(c)(2), 63.9323(a)(3), 63.11148(e)(3)(iii), 63.11155(e)(3), 63.11162(f)(3)(iii) and (f)(4), 63.11163(g)(1)(iii) and (g)(2), 63.11410(j)(1)(iii), Table 5 of subpart DDDDD of this part, 63.11452(b)(11), and 63.11466(c)(1)(iii).

* * * * *

3. Part 63 is amended by adding subpart RRRRRR to read as follows:

Subpart RRRRRR—National Emission Standards for Hazardous Air Pollutants for Clay Ceramics Manufacturing Area Sources

Applicability and Compliance Dates

Sec.
63.11435 Am I subject to this subpart?
63.11436 What parts of my plant does this subpart cover?
63.11437 What are my compliance dates?

Standards, Compliance, and Monitoring Requirements

63.11438 What are the standards for new and existing sources?
63.11439 What are the initial compliance demonstration requirements for new and existing sources?
63.11440 What are the monitoring requirements for new and existing sources?
63.11441 What are the notification requirements?
63.11442 What are the recordkeeping requirements?

Other Requirements and Information

63.11443 What General Provisions apply to this subpart?
63.11444 What definitions apply to this subpart?
63.11445 Who implements and enforces this subpart?
63.11446 [Reserved]
63.11447 [Reserved]

Tables to Subpart RRRRRR of Part 63

Table 1 to Subpart RRRRRR of Part 63—Applicability of General Provisions to Subpart RRRRRR

Applicability and Compliance Dates

§ 63.11435 Am I subject to this subpart?

(a) You are subject to this subpart if you own or operate a clay ceramics manufacturing facility (as defined in § 63.11444), with an atomized glaze spray booth or kiln that fires glazed ceramic ware, that processes more than 45 megagrams per year (Mg/yr) (50 tons per year (tpy)) of wet clay and is an area source of hazardous air pollutant (HAP) emissions.

(b) If you are an owner or operator of an area source subject to this subpart, you are exempt from the obligation to obtain a permit under 40 CFR part 70 or 71, provided you are not required to obtain a permit under 40 CFR 70.3(a) or 71.3(a) for a reason other than your status as an area source under this subpart. You must continue to comply with the provisions of this subpart applicable to area sources.

§ 63.11436 What parts of my plant does this subpart cover?

(a) This subpart applies to any existing or new affected source located at a clay ceramics manufacturing facility.

(b) The affected source includes all atomized glaze spray booths and kilns that fire glazed ceramic ware located at a clay ceramics manufacturing facility.

(c) An affected source is existing if you commenced construction or reconstruction of the affected source on or before September 20, 2007.

(d) An affected source is new if you commenced construction or reconstruction of the affected source after September 20, 2007.

§ 63.11437 What are my compliance dates?

(a) If you have an existing affected source, you must comply with the standards no later than December 26, 2007.

(b) If you have a new affected source, you must comply with this subpart according to paragraphs (b)(1) and (2) of this section.

(1) If you start up your affected source on or before December 26, 2007, you must comply with this subpart no later than December 26, 2007.

(2) If you start up your affected source after December 26, 2007, you must comply with this subpart upon initial startup of your affected source.

Standards, Compliance, and Monitoring Requirements

§ 63.11438 What are the standards for new and existing sources?

(a) For each kiln that fires glazed ceramic ware, you must maintain the peak temperature below 1540 °C (2800 °F) and comply with one of the management practices in paragraphs (a)(1) and (2) of this section:

(1) Use natural gas, or equivalent clean-burning fuel, as the kiln fuel; or

(2) Use an electric-powered kiln.

(b) You must maintain annual wet glaze usage records for your facility.

(c) For each atomized glaze spray booth located at a clay ceramics manufacturing facility that uses more than 227 Mg/yr (250 tpy) of wet glaze(s), you must comply with the equipment standard requirements in paragraph (c)(1) of this section or the management practice in paragraph (c)(2) of this section.

(1) Control the emissions from the atomized glaze spray booth with an air pollution control device (APCD), as defined in § 63.11444.

(i) Operate and maintain the APCD in accordance with the equipment manufacturer's specifications; and

(ii) Monitor the APCD according to the applicable requirements in § 63.11440.

(2) Alternatively, use wet glazes containing less than 0.1 (weight) percent clay ceramics metal HAP.

(d) For each atomized glaze spray booth located at a clay ceramics manufacturing facility that uses 227 Mg/yr (250 tpy) or less of wet glaze(s), you must comply with one of the management practices or equipment standards in paragraphs (d)(1) and (2) of this section.

(1) Employ waste minimization practices, as defined in § 63.11444; or

(2) Alternatively, comply with the equipment standard requirements described in paragraph (c)(1) of this section or the management practice described in paragraph (c)(2) of this section.

(e) Surface applications (*e.g.*, wet glazes) containing less than 0.1 (weight) percent clay ceramics metal HAP do not have to be considered in determination of the 227 Mg/yr (250 tpy) threshold for wet glaze usage.

§ 63.11439 What are the initial compliance demonstration requirements for new and existing sources?

(a) You must demonstrate initial compliance with the applicable management practices and equipment standards in § 63.11438 by submitting a Notification of Compliance Status. For any wet spray glaze operation controlled with an APCD, you must conduct an initial inspection of the control equipment as described in § 63.11440(b)(1) within 60 days of the compliance date and include the results of the inspection in the Notification of Compliance Status.

(b) You must demonstrate initial compliance with the applicable management practices or equipment standards in § 63.11438 by submitting the Notification of Compliance Status within 120 days after the applicable compliance date specified in § 63.11437.

§ 63.11440 What are the monitoring requirements for new and existing sources?

(a) For each kiln firing glazed ceramic ware, you must conduct a daily check of the peak firing temperature. If the peak temperature exceeds 1540 °C (2800 °F), you must take corrective action according to your standard operating procedures.

(b) For each existing or new atomized glaze spray booth equipped with an APCD, you must demonstrate compliance by conducting the monitoring activities in paragraph (b)(1) and either paragraph (b)(2) or (3) of this section:

(1) *Initial control device inspection.* You must conduct an initial inspection of each particulate matter (PM) control device according to the requirements in paragraphs (b)(1)(i) or (ii) of this section. You must conduct each inspection no later than 60 days after your applicable compliance date for each installed control device which has been operated within 60 days of the compliance date. For an installed control device which has not been operated within 60 days of the compliance date, you must conduct an initial inspection prior to startup of the control device.

(i) For each wet control system, you must verify the presence of water flow to the control equipment. You must also visually inspect the system ductwork and control equipment for leaks and inspect the interior of the control equipment (if applicable) for structural integrity and the condition of the control system. An initial inspection of the internal components of a wet control system is not required if an inspection has been performed within the past 12 months.

(ii) For each baghouse, you must visually inspect the system ductwork and baghouse unit for leaks. You must also inspect the inside of each baghouse for structural integrity and fabric filter condition. You must record the results of the inspection and any maintenance action as required in paragraph (d) of this section. An initial inspection of the internal components of a baghouse is not required if an inspection has been performed within the past 12 months.

(2) *Periodic inspections/maintenance.* Except as provided in paragraph (b)(3) of this section, you must perform periodic inspections and maintenance of each PM control device following the initial inspection according to the requirements in paragraphs (b)(2)(i) or (ii) of this section.

(i) You must inspect and maintain each wet control system according to the requirements in paragraphs (b)(2)(i)(A) through (C) of this section.

(A) You must conduct a daily inspection to verify the presence of water flow to the wet control system.

(B) You must conduct weekly visual inspections of the system ductwork and control equipment for leaks.

(C) You must conduct inspections of the interior of the wet control system (if applicable) to determine the structural integrity and condition of the control equipment every 12 months.

(ii) You must inspect and maintain each baghouse according to the requirements in paragraphs (b)(2)(ii)(A) and (B) of this section.

(A) You must conduct weekly visual inspections of the system ductwork for leaks.

(B) You must conduct inspections of the interior of the baghouse for structural integrity and to determine the condition of the fabric filter every 12 months.

(3) As an alternative to the monitoring activities in paragraph (b)(2) of this section, you may demonstrate compliance by:

(i) Conducting a daily 30-minute visible emissions (VE) test (i.e., no visible emissions) using EPA Method 22 (40 CFR part 60, appendix A–7); or

(ii) Using an approved alternative monitoring technique under § 63.8(f).

(c) If the results of the visual inspection, VE test, or alternative monitoring technique conducted under paragraph (b) of this section indicate an exceedance, you must take corrective action according to the equipment manufacturer's specifications or instructions.

(d) You must maintain records of your monitoring activities described in paragraphs (a) through (c) of this section. You may use your existing operating permit documentation to meet the monitoring requirements if it includes, but is not limited to, the monitoring records listed in paragraphs (d)(1) through (5) of this section related to any kiln peak temperature checks, visual inspections, VE tests, or alternative monitoring:

(1) The date, place, and time;

(2) Person conducting the activity;

(3) Technique or method used;

(4) Operating conditions during the activity; and

(5) Results.

§ 63.11441 What are the notification requirements?

(a) You must submit an Initial Notification required by § 63.9(b)(2) no later than 120 days after the applicable compliance date specified in § 63.11437. The Initial Notification must include the information specified in § 63.9(b)(2)(i) through (iv) and may be combined with the Notification of Compliance Status required in paragraph (b) of this section.

(b) You must submit a Notification of Compliance Status required by § 63.9(h) no later than 120 days after the applicable compliance date specified in § 63.11437. In addition to the information required in § 63.9(h)(2), your notification(s) must include each compliance certification in paragraphs (b)(1) through (3) of this section that applies to you and may be combined with the Initial Notification required in paragraph (a) of this section.

(1) For each kiln firing glazed ceramic ware, you must certify that you are maintaining the peak temperature below 1540 °C (2800 °F) according to § 63.11438(a) and complying with one of the management practices in § 63.11438(a)(1) or (2).

(2) For atomized glaze spray booths, you must certify that your facility's annual wet glaze usage is above or below 227 Mg/yr (250 tpy).

(3) For atomized glaze spray booths located at a clay ceramics manufacturing facility that uses more than 227 Mg/yr (250 tpy) of wet glaze(s), you must certify that:

(i) You are operating and maintaining an APCD in accordance with § 63.11438(c)(1), and you have conducted an initial control device inspection for each wet control system and baghouse associated with an atomized glaze spray booth; or

(ii) Alternatively, you are using wet glazes containing less than 0.1 (weight) percent clay ceramics metal HAP according to § 63.11438(c)(2).

(4) For atomized glaze spray booths located at a clay ceramics manufacturing facility that uses 227 Mg/yr (250 tpy) or less of wet glaze(s), you must certify that:

(i) You are employing waste minimization practices according to § 63.11438(d)(1); or

(ii) You are complying with the requirements in § 63.11438(c)(1) or (2).

§ 63.11442 What are the recordkeeping requirements?

(a) You must keep the records specified in paragraphs (a)(1) and (2) of this section.

(1) A copy of each notification that you submitted to comply with this subpart, including all documentation supporting any Initial Notification or Notification of Compliance Status that you submitted, according to the requirements in § 63.10(b)(2)(xiv).

(2) Records of all required measurements needed to document compliance with management practices as required in § 63.10(b)(2)(vii), including records of monitoring and inspection data required by § 63.11440.

(b) Your records must be in a form suitable and readily available for expeditious review, according to § 63.10(b)(1).

(c) As specified in § 63.10(b)(1), you must keep each record for 5 years following the date of each occurrence, measurement, maintenance, corrective action, report, or record.

(d) You must keep each record onsite for at least 2 years after the date of each occurrence, measurement, maintenance, corrective action, report, or record, according to § 63.10(b)(1). You may keep the records offsite for the remaining three years.

Other Requirements and Information

§ 63.11443 What General Provisions apply to this subpart?

Table 1 to this subpart shows which parts of the General Provisions in §§ 63.1 through 63.16 apply to you.

§ 63.11444 What definitions apply to this subpart?

Terms used in this subpart are defined in the Clean Air Act, in § 63.2, and in this section as follows:

Air pollution control device (APCD) means any equipment that reduces the quantity of a pollutant that is emitted to the air. Examples of APCD currently used on glaze spray booths include, but are not limited to, wet scrubbers, fabric filters, water curtains, and water-wash systems.

Atomization means the conversion of a liquid into a spray or mist (i.e., collection of drops), often by passing the liquid through a nozzle.

Clay ceramics manufacturing facility means a plant site that manufactures pressed tile, sanitaryware, dinnerware, or pottery. For the purposes of this area

source rule, the following types of facilities are not part of the regulated category: artisan potters, art studios, school and university ceramic arts programs, and any facility that uses less than 45 Mg/yr (50 tpy) of wet clay.

Clay ceramics metal HAP means an oxide or other compound of chromium, lead, manganese, or nickel, which were listed for Clay Ceramics Manufacturing in the Revised Area Source Category List (67 FR 70428, November 22, 2002).

Glaze means a coating of colored, opaque, or transparent material applied to ceramic products before firing.

Glaze spray booth means a type of equipment used for spraying glaze on ceramic products.

High-volume, low-pressure (HVLP) spray equipment means a type of air atomized spray equipment that operates at low atomizing air pressure (0.1 to 10 pounds per square inch (psi) at the air nozzle) and uses 15 to 30 cubic feet per minute (cfm) of air to minimize the amount of overspray and bounce back.

Kiln means equipment used for the initial curing or firing of glaze on ceramic ware. A kiln may operate continuously or by batch process.

Nonatomizing glaze application technique means the application of glaze in the form of a liquid stream without atomization. Such techniques include, but are not limited to, dipping, centrifugal disc, waterfall, flow coaters, curtain coaters, silk-screening, and any direct application by roller, brush, pad, or other means facilitating direct transfer of glaze.

Plant site means all contiguous or adjoining property that is under common control, including properties that are separated only by a road or other public right-of-way. Common control includes properties that are owned, leased, or operated by the same entity, parent entity, subsidiary, or any combination thereof.

Waste minimization practices mean those procedures employed to minimize material losses and prevent unnecessary waste generation, for example, minimizing glaze overspray emissions using HVLP spray equipment (defined in this section) or similar spray equipment; minimizing HAP emissions during cleanup of spray glazing equipment; operating and maintaining spray glazing equipment according to manufacturer's instructions; and minimizing spills through careful handling of HAP-containing glaze materials.

Water curtain means an APCD that draws the exhaust stream through a continuous curtain of moving water to remove suspended particulate. A water curtain may also be called a drip curtain or waterfall.

Water-wash system means an APCD that uses a series of baffles to redirect the upward exhaust stream through a water wash chamber with downward water flow to remove suspended particulate.

§ 63.11445 Who implements and enforces this subpart?

(a) This subpart can be implemented and enforced by the U.S. EPA or a delegated authority such as your State, local, or tribal agency. If the U.S. EPA Administrator has delegated authority to your State, local, or tribal agency, then that agency has the authority to implement and enforce this subpart. You should contact your U.S. EPA Regional Office to find out if this subpart is delegated to your State, local, or tribal agency.

(b) In delegating implementation and enforcement authority of this subpart to a State, local, or tribal agency under 40 CFR part 63, subpart E, the authorities contained in paragraph (c) of this section are retained by the Administrator of the U.S. EPA and are not transferred to the State, local, or tribal agency.

(c) The authorities that will not be delegated to State, local, or tribal agencies are listed in paragraphs (c)(1) through (4) of this section.

(1) Approval of alternatives to the applicability requirements in §§ 63.11435 and 63.11436, the compliance date requirements in § 63.11437, and the management practices and equipment standards in § 63.11438.

(2) Approval of a major change to a test method under § 63.7(e)(2)(ii) and (f). A ''major change to test method'' is defined in § 63.90.

(3) Approval of a major change to monitoring under § 63.8(f). A ''major change to monitoring'' is defined in § 63.90.

(4) Approval of a major change to recordkeeping/reporting under § 63.10(f). A ''major change to recordkeeping/reporting'' is defined in § 63.90.

§ 63.11446 [Reserved]

§ 63.11447 [Reserved]

Tables to Subpart RRRRRR of Part 63

As stated in § 63.11443, you must comply with the requirements of the NESHAP General Provisions (40 CFR part 63, subpart A) shown in the following table:

TABLE 1 TO SUBPART RRRRRR OF PART 63—APPLICABILITY OF GENERAL PROVISIONS TO SUBPART RRRRRR

Citation	Subject
63.1(a)(1)–(a)(4), (a)(6), (a)(10)–(a)(12), (b)(1), (b)(3), (c)(1), (c)(2),[1] (c)(5), (e)	Applicability.
63.2	Definitions.
63.3	Units and Abbreviations.
63.4	Prohibited Activities and Circumvention.
63.6(a), (b)(1)–(b)(5), (b)(7), (c)(1), (c)(2), (c)(5), (e)(1), (f), (g), (i), (j)	Compliance with Standards and Maintenance Requirements.
63.8(a)(1), (a)(2), (b), (c)(1)(i)–(c)(1)(ii), (c)(2), (c)(3), (f)	Monitoring Requirements.
63.9(a), (b)(1), (b)(2), (b)(5), (c), (d), (h)(1)–(h)(3), (h)(5), (h)(6), (i), (j)	Notification Requirements.
63.10(a), (b)(1), (b)(2)(vii), (b)(2)(xiv), (b)(3), (c), (c)(1), (f)	Recordkeeping and Reporting Requirements.
63.12	State Authority and Delegations.
63.13	Addresses.
63.14	Incorporations by Reference.
63.15	Availability of Information and Confidentiality.
63.16	Performance Track Provisions.

[1] Section 63.11435(b) of this subpart exempts area sources from the obligation to obtain title V operating permits.

4. Part 63 is amended by adding subpart SSSSSS to read as follows:

Subpart SSSSSS—National Emission Standards for Hazardous Air Pollutants for Glass Manufacturing Area Sources

Applicability and Compliance Dates

Sec.
63.11448 Am I subject to this subpart?
63.11449 What parts of my plant does this subpart cover?
63.11450 What are my compliance dates?

Standards, Compliance, and Monitoring Requirements

63.11451 What are the standards for new and existing sources?
63.11452 What are the performance test requirements for new and existing sources?
63.11453 What are the initial compliance demonstration requirements for new and existing sources?
63.11454 What are the monitoring requirements for new and existing sources?
63.11455 What are the continuous compliance requirements for new and existing sources?

Notifications and Records

63.11456 What are the notification requirements?
63.11457 What are the recordkeeping requirements?

Other Requirements and Information

63.11458 What General Provisions apply to this subpart?
63.11459 What definitions apply to this subpart?
63.11460 Who implements and enforces this subpart?
63.11461 [Reserved]

Tables to Subpart SSSSSS of Part 63

Table 1 to Subpart SSSSSS of Part 63—Emission Limits
Table 2 to Subpart SSSSSS of Part 63—Applicability of General Provisions to Subpart SSSSSS

Applicability and Compliance Dates

§ 63.11448 Am I subject to this subpart?

You are subject to this subpart if you own or operate a glass manufacturing facility that is an area source of hazardous air pollutant (HAP) emissions and meets all of the criteria specified in paragraphs (a) through (c) of this section.

(a) A glass manufacturing facility is a plant site that manufactures flat glass, glass containers, or pressed and blown glass by melting a mixture of raw materials, as defined in § 63.11459, to produce molten glass and form the molten glass into sheets, containers, or other shapes.

(b) An area source of HAP emissions is any stationary source or group of stationary sources within a contiguous area under common control that does not have the potential to emit any single HAP at a rate of 9.07 megagrams per year (Mg/yr) (10 tons per year (tpy)) or more and any combination of HAP at a rate of 22.68 Mg/yr (25 tpy) or more.

(c) Your glass manufacturing facility uses one or more continuous furnaces to produce glass that contains compounds of one or more glass manufacturing metal HAP, as defined in § 63.11459, as raw materials in a glass manufacturing batch formulation.

§ 63.11449 What parts of my plant does this subpart cover?

(a) This subpart applies to each existing or new affected glass melting furnace that is located at a glass manufacturing facility and satisfies the requirements specified in paragraphs (a)(1) through (3) of this section.

(1) The furnace is a continuous furnace, as defined in § 63.11459.

(2) The furnace is charged with compounds of one or more glass manufacturing metal HAP as raw materials.

(3) The furnace is used to produce glass, which contains one or more of the glass manufacturing metal HAP as raw materials, at a rate of at least 45 Mg/yr (50 tpy).

(b) A furnace that is a research and development process unit, as defined in § 63.11459, is not an affected furnace under this subpart.

(c) An affected source is an existing source if you commenced construction or reconstruction of the affected source on or before September 20, 2007.

(d) An affected source is a new source if you commenced construction or reconstruction of the affected source after September 20, 2007.

(e) If you own or operate an area source subject to this subpart, you must obtain a permit under 40 CFR part 70 or 40 CFR part 71.

§ 63.11450 What are my compliance dates?

(a) If you have an existing affected source, you must comply with the applicable emission limits specified in § 63.11451 of this subpart no later than December 28, 2009. As specified in section 112(i)(3)(B) of the Clean Air Act and in § 63.6(i)(4)(A), you may request that the Administrator or delegated authority grant an extension allowing up to 1 additional year to comply with the applicable emission limits if such additional period is necessary for the installation of emission controls.

(b) If you have a new affected source, you must comply with this subpart according to paragraphs (b)(1) and (2) of this section.

(1) If you start up your affected source on or before December 26, 2007, you must comply with the applicable emission limit specified in § 63.11451 no later than December 26, 2007.

(2) If you start up your affected source after December 26, 2007, you must comply with the applicable emission limit specified in § 63.11451 upon initial startup of your affected source.

(c) If you own or operate a furnace that produces glass containing one or more glass manufacturing metal HAP as raw materials at an annual rate of less than 45 Mg/yr (50 tpy), and you increase glass production for that furnace to an annual rate of at least 45 Mg/yr (50 tpy), you must comply with the applicable emission limit specified in § 63.11451 within 2 years of the date on which you increased the glass production rate for the furnace to at least 45 Mg/yr (50 tpy).

(d) If you own or operate a furnace that produces glass at an annual rate of at least 45 Mg/yr (50 tpy) and is not charged with glass manufacturing metal HAP, and you begin production of a glass product that includes one or more glass manufacturing metal HAP as raw materials, and you produce at least 45 Mg/yr (50 tpy) of this glass product, you must comply with the applicable emission limit specified in § 63.11451 within 2 years of the date on which you introduced production of the glass product that contains glass manufacturing metal HAP.

(e) You must meet the notification requirements in § 63.11456 according to the schedule in § 63.11456 and in 40 CFR part 63, subpart A. Some of the notifications must be submitted before you are required to comply with emission limits specified in this subpart.

Standards, Compliance, and Monitoring Requirements

§ 63.11451 What are the standards for new and existing sources?

If you are an owner or operator of an affected furnace, as defined in § 63.11449(a), you must meet the applicable emission limit specified in Table 1 to this subpart.

§ 63.11452 What are the performance test requirements for new and existing sources?

(a) If you own or operate an affected furnace that is subject to an emission limit specified in Table 1 to this subpart, you must conduct a performance test according to paragraphs (a)(1) through (3) and paragraph (b) of this section.

(1) For each affected furnace, you must conduct a performance test within 180 days after your compliance date and report the results in your Notification of Compliance Status, except as specified in paragraph (a)(2) of this section.

(2) You are not required to conduct a performance test on the affected furnace if you satisfy the conditions described in paragraphs (a)(2)(i) through (iii) of this section.

(i) You conducted a performance test on the affected furnace within the past 5 years of the compliance date using the same test methods and procedures specified in paragraph (b) of this section.

(ii) The performance test demonstrated that the affected furnace met the applicable emission limit specified in Table 1 to this subpart.

(iii) Either no process changes have been made since the test, or you can demonstrate that the results of the performance test, with or without adjustments, reliably demonstrate compliance with the applicable emission limit.

(3) If you operate multiple identical furnaces, as defined in § 63.11459, that are affected furnaces, you are required to test only one of the identical furnaces if you meet the conditions specified in paragraphs (a)(3)(i) through (iii) of this section.

(i) You must conduct the performance test while the furnace is producing glass that has the greatest potential to emit the glass manufacturing metal HAP from among the glass formulations that are used in any of the identical furnaces.

(ii) You certify in your Notification of Compliance Status that the identical furnaces meet the definition of identical furnaces specified in § 63.11459.

(iii) You provide in your Notification of Compliance Status documentation that demonstrates why the tested glass formulation has the greatest potential to emit the glass manufacturing metal HAP.

(b) You must conduct each performance test according to the requirements in § 63.7 and paragraphs (b)(1) through (12) and either paragraph (b)(13) or (b)(14) of this section.

(1) Install and validate all monitoring equipment required by this subpart before conducting the performance test.

(2) You may not conduct performance tests during periods of startup, shutdown, or malfunction, as specified in § 63.7(e)(1).

(3) Conduct the test while the source is operating at the maximum production rate.

(4) Conduct at least three separate test runs with a minimum duration of 1 hour for each test run, as specified in § 63.7(e)(3).

(5) Record the test date.

(6) Identify the emission source tested.

(7) Collect and record the emission test data listed in this section for each run of the performance test.

(8) Locate all sampling sites at the outlet of the furnace control device or at the furnace stack prior to any releases to the atmosphere.

(9) Select the locations of sampling ports and the number of traverse points using Method 1 or 1A of 40 CFR part 60, appendix A–1.

(10) Measure the gas velocity and volumetric flow rate using Method 2, 2A, 2C, 2F, or 2G of 40 CFR part 60, appendices A–1 and A–2, during each test run.

(11) Conduct gas molecular weight analysis using Methods 3, 3A, or 3B of 40 CFR part 60, appendix A–2, during each test run. You may use ANSI/ASME PTC 19.10–1981, Flue and Exhaust Gas Analyses (incorporated by reference—see § 63.14) as an alternative to EPA Method 3B.

(12) Measure gas moisture content using Method 4 of 40 CFR part 60, appendix A–3, during each test run.

(13) To meet the particulate matter (PM) emission limit specified in Table 1 to this subpart, you must conduct the procedures specified in paragraphs (b)(13)(i) through (v) of this section.

(i) Measure the PM mass emission rate at the outlet of the control device or at the stack using Method 5 or 17 of 40 CFR part 60, appendices A–3 or A–6, for each test run.

(ii) Calculate the PM mass emission rate in the exhaust stream for each test run.

(iii) Measure and record the glass production rate (kilograms (tons) per hour of product) for each test run.

(iv) Calculate the production-based PM mass emission rate (g/kg (lb/ton)) for each test run using Equation 1 of this section.

$$MP = \frac{ER}{P} \qquad \text{(Equation 1)}$$

Where:

MP = Production-based PM mass emission rate, grams of PM per kilogram (pounds of PM per ton) of glass produced.

ER = PM mass emission rate measured using Methods 5 or 17 during each performance test run, grams (pounds) per hour.

P = Average glass production rate for the performance test, kilograms (tons) of glass produced per hour.

(v) Calculate the 3-hour block average production-based PM mass emission rate as the average of the production-based PM mass emission rates for each test run.

(14) To meet the metal HAP emission limit specified in Table 1 to this subpart, you must conduct the procedures specified in paragraphs (b)(14)(i) through (v) of this section.

(i) Measure the metal HAP mass emission rate at the outlet of the control device or at the stack using Method 29 of 40 CFR part 60, appendix A–8, for each test run.

(ii) Calculate the metal HAP mass emission rate in the exhaust stream for the glass manufacturing metal HAP that are added as raw materials to the glass manufacturing formulation for each test run.

(iii) Measure and record the glass production rate (kilograms (tons) per hour of product) for each test run.

(iv) Calculate the production-based metal HAP mass emission rate (g/kg (lb/ton)) for each test run using Equation 2 of this section.

$$MPM = \frac{ERM}{P} \qquad \text{(Equation 2)}$$

Where:

MPM = Production-based metal HAP mass emission rate, grams of metal HAP per kilogram (pounds of metal HAP per ton) of glass produced.

ERM = Sum of the metal HAP mass emission rates for the glass manufacturing metal HAP that are added as raw materials to the glass manufacturing formulation and are measured using Method 29 during each performance test run, grams (pounds) per hour.

P = Average glass production rate for the performance test, kilograms (tons) of glass produced per hour.

(v) Calculate the 3-hour block average production-based metal HAP mass emission rate as the average of the production-based metal HAP mass emission rates for each test run.

§ 63.11453 What are the initial compliance demonstration requirements for new and existing sources?

(a) If you own or operate an affected source, you must submit a Notification of Compliance Status in accordance with §§ 63.9(h) and 63.11456(b).

(b) For each existing affected furnace that is subject to the emission limits specified in Table 1 to this subpart, you must demonstrate initial compliance according to the requirements in paragraphs (b)(1) through (4) of this section.

(1) For each fabric filter that is used to meet the emission limit specified in Table 1 to this subpart, you must visually inspect the system ductwork and fabric filter unit for leaks. You must also inspect the inside of each fabric filter for structural integrity and fabric filter condition. You must record the results of the inspection and any maintenance action as required in § 63.11457(a)(6).

(2) For each electrostatic precipitator (ESP) that is used to meet the emission limit specified in Table 1 to this subpart, you must verify the proper functioning of the electronic controls for corona power and rapper operation, that the corona wires are energized, and that adequate air pressure is present on the rapper manifold. You must also visually inspect the system ductwork and ESP housing unit and hopper for leaks and inspect the interior of the ESP to determine the condition and integrity of corona wires, collection plates, hopper, and air diffuser plates. You must record the results of the inspection and any maintenance action as required in § 63.11457(a)(6).

(3) You must conduct each inspection specified in paragraphs (b)(1) and (2) of this section no later than 60 days after your applicable compliance date specified in § 63.11450, except as specified in paragraphs (b)(3)(i) and (ii) of this section.

(i) An initial inspection of the internal components of a fabric filter is not required if an inspection has been performed within the past 12 months.

(ii) An initial inspection of the internal components of an ESP is not required if an inspection has been performed within the past 24 months.

(4) You must satisfy the applicable requirements for performance tests specified in § 63.11452.

(c) For each new affected furnace that is subject to the emission limit specified in Table 1 to this subpart and is controlled with a fabric filter, you must install, operate, and maintain a bag leak detection system according to paragraphs (c)(1) through (3) of this section.

(1) Each bag leak detection system must meet the specifications and requirements in paragraphs (c)(1)(i) through (viii) of this section.

(i) The bag leak detection system must be certified by the manufacturer to be capable of detecting PM emissions at concentrations of 1 milligram per dry standard cubic meter (0.00044 grains per actual cubic foot) or less.

(ii) The bag leak detection system sensor must provide output of relative PM loadings. The owner or operator shall continuously record the output from the bag leak detection system using electronic or other means (e.g., using a strip chart recorder or a data logger).

(iii) The bag leak detection system must be equipped with an alarm system that will sound when the system detects an increase in relative particulate loading over the alarm set point established according to paragraph (c)(1)(iv) of this section, and the alarm must be located such that it can be heard by the appropriate plant personnel.

(iv) In the initial adjustment of the bag leak detection system, you must establish, at a minimum, the baseline output by adjusting the sensitivity (range) and the averaging period of the device, the alarm set points, and the alarm delay time.

(v) Following initial adjustment, you shall not adjust the averaging period, alarm set point, or alarm delay time without approval from the Administrator or delegated authority except as provided in paragraph (c)(1)(vi) of this section.

(vi) Once per quarter, you may adjust the sensitivity of the bag leak detection system to account for seasonal effects, including temperature and humidity, according to the procedures identified in the site-specific monitoring plan required by paragraph (c)(2) of this section.

(vii) You must install the bag leak detection sensor downstream of the fabric filter.

(viii) Where multiple detectors are required, the system's instrumentation and alarm may be shared among detectors.

(2) You must develop and submit to the Administrator or delegated authority for approval a site-specific monitoring plan for each bag leak detection system. You must operate and maintain the bag leak detection system according to the site-specific monitoring plan at all times. Each monitoring plan must describe the items in paragraphs (c)(2)(i) through (vi) of this section.

(i) Installation of the bag leak detection system;

(ii) Initial and periodic adjustment of the bag leak detection system, including how the alarm set-point will be established;

(iii) Operation of the bag leak detection system, including quality assurance procedures;

(iv) How the bag leak detection system will be maintained, including a routine maintenance schedule and spare parts inventory list;

(v) How the bag leak detection system output will be recorded and stored; and

(vi) Corrective action procedures as specified in paragraph (c)(3) of this section. In approving the site-specific monitoring plan, the Administrator or delegated authority may allow owners and operators more than 3 hours to alleviate a specific condition that causes an alarm if the owner or operator identifies in the monitoring plan this specific condition as one that could lead to an alarm, adequately explains why it is not feasible to alleviate this condition within 3 hours of the time the alarm occurs, and demonstrates that the requested time will ensure alleviation of this condition as expeditiously as practicable.

(3) For each bag leak detection system, you must initiate procedures to determine the cause of every alarm within 1 hour of the alarm. Except as provided in paragraph (c)(2)(vi) of this section, you must alleviate the cause of the alarm within 3 hours of the alarm by taking whatever corrective action(s) are necessary. Corrective actions may include, but are not limited to the following:

(i) Inspecting the fabric filter for air leaks, torn or broken bags or filter media, or any other condition that may cause an increase in PM emissions;

(ii) Sealing off defective bags or filter media;

(iii) Replacing defective bags or filter media or otherwise repairing the control device;

(iv) Sealing off a defective fabric filter compartment;

(v) Cleaning the bag leak detection system probe or otherwise repairing the bag leak detection system; or

(vi) Shutting down the process producing the PM emissions.

(d) For each new affected furnace that is subject to the emission limit specified in Table 1 to this subpart and is controlled with an ESP, you must install, operate, and maintain according to the manufacturer's specifications, one or more continuous parameter monitoring systems (CPMS) for measuring and recording the secondary voltage and secondary electrical current to each field of the ESP according to paragraphs (d)(1) through (13) of this section.

(1) The CPMS must have an accuracy of 1 percent of the secondary voltage and secondary electrical current, or better.

(2) Your CPMS must be capable of measuring the secondary voltage and secondary electrical current over a range that extends from a value that is at least 20 percent less than the lowest value that you expect your CPMS to measure, to a value that is at least 20 percent greater than the highest value that you expect your CPMS to measure.

(3) The signal conditioner, wiring, power supply, and data acquisition and recording system of your CPMS must be compatible with the output signal of the sensors used in your CPMS.

(4) The data acquisition and recording system of your CPMS must be able to record values over the entire range specified in paragraph (d)(2) of this section.

(5) The data recording system associated with your CPMS must have

a resolution of one-half of the required overall accuracy of your CPMS, as specified in paragraph (d)(1) of this section, or better.

(6) Your CPMS must be equipped with an alarm system that will sound when the system detects a decrease in secondary voltage or secondary electrical current below the alarm set point established according to paragraph (d)(7) of this section, and the alarm must be located such that it can be heard by the appropriate plant personnel.

(7) In the initial adjustment of the CPMS, you must establish, at a minimum, the baseline output by adjusting the sensitivity (range) and the averaging period of the device, the alarm set points, and the alarm delay time.

(8) You must install each sensor of the CPMS in a location that provides representative measurement of the appropriate parameter over all operating conditions, taking into account the manufacturer's guidelines.

(9) You must perform an initial calibration of your CPMS based on the procedures specified in the manufacturer's owner's manual.

(10) Your CPMS must be designed to complete a minimum of one cycle of operation for each successive 15-minute period. To have a valid hour of data, you must have at least three of four equally-spaced data values (or at least 75 percent of the total number of values if you collect more than four data values per hour) for that hour (not including startup, shutdown, malfunction, or out of control periods).

(11) You must record valid data from at least 90 percent of the hours during which the affected source or process operates.

(12) You must record the results of each inspection, calibration, initial validation, and accuracy audit.

(13) At all times, you must maintain your CPMS including, but not limited to, maintaining necessary parts for routine repairs of the CPMS.

(e) For each new affected furnace that is subject to the emission limit specified in Table 1 to this subpart and is controlled by a device other than a fabric filter or an ESP, you must prepare and submit a monitoring plan to EPA or the delegated authority for approval. Each plan must contain the information in paragraphs (e)(1) through (5) of this section.

(1) A description of the device;

(2) Test results collected in accordance with § 63.11452 verifying the performance of the device for reducing PM or metal HAP to the levels required by this subpart;

(3) Operation and maintenance plan for the control device (including a preventative maintenance schedule consistent with the manufacturer's instructions for routine and long-term maintenance) and continuous monitoring system;

(4) A list of operating parameters that will be monitored to maintain continuous compliance with the applicable emission limits; and

(5) Operating parameter limits based on monitoring data collected during the performance test.

§ 63.11454 What are the monitoring requirements for new and existing sources?

(a) For each monitoring system required by this subpart, you must install, calibrate, operate, and maintain the monitoring system according to the manufacturer's specifications and the requirements specified in paragraphs (a)(1) through (7) of this section.

(1) You must install each sensor of your monitoring system in a location that provides representative measurement of the appropriate parameter over all operating conditions, taking into account the manufacturer's guidelines.

(2) You must perform an initial calibration of your monitoring system based on the manufacturer's recommendations.

(3) You must use a monitoring system that is designed to complete a minimum of one cycle of operation for each successive 15-minute period.

(4) For each existing affected furnace, you must record the value of the monitored parameter at least every 8 hours. The value can be recorded electronically or manually.

(5) You must record the results of each inspection, calibration, monitoring system maintenance, and corrective action taken to return the monitoring system to normal operation.

(6) At all times, you must maintain your monitoring system including, but not limited to, maintaining necessary parts for routine repairs of the system.

(7) You must perform the required monitoring whenever the affected furnace meets the conditions specified in paragraph (a)(7)(i) or (ii) of this section.

(i) The furnace is being charged with one or more of the glass manufacturing metal HAP as raw materials.

(ii) The furnace is in transition between producing glass that contains one or more of the glass metal HAP as raw materials and glass that does not contain any of the glass manufacturing metal HAP as raw materials. The transition period begins when the furnace is charged with raw materials that do not contain any of the glass manufacturing metal HAP as raw materials and ends when the furnace begins producing a saleable glass product that does not contain any of the glass manufacturing metal HAP as raw materials.

(b) For each existing furnace that is subject to the emission limit specified in Table 1 to this subpart and is controlled with an ESP, you must meet the requirements specified in paragraphs (b)(1) or (2) of this section.

(1) You must monitor the secondary voltage and secondary electrical current to each field of the ESP according to the requirements of paragraph (a) of this section, or

(2) You must submit a request for alternative monitoring, as described in paragraph (g) of this section.

(c) For each existing furnace that is subject to the emission limit specified in Table 1 to this subpart and is controlled with a fabric filter, you must meet the requirements specified in paragraphs (c)(1) or (2) of this section.

(1) You must monitor the inlet temperature to the fabric filter according to the requirements of paragraph (a) of this section, or

(2) You must submit a request for alternative monitoring, as described in paragraph (g) of this section.

(d) For each new furnace that is subject to the emission limit specified in Table 1 to this subpart and is controlled with an ESP, you must monitor the voltage and electrical current to each field of the ESP on a continuous basis using one or more CPMS according to the requirements for CPMS specified in § 63.11453(d).

(e) For each new furnace that is subject to the emission limit specified in Table 1 to this subpart and is controlled with a fabric filter, you must install and operate a bag leak detection system according to the requirements specified in § 63.11453(c).

(f) For each new or existing furnace that is subject to the emission limit specified in Table 1 to this subpart and is equipped with a control device other than an ESP or fabric filter, you must meet the requirements in § 63.8(f) and submit a request for approval of alternative monitoring methods to the Administrator no later than the submittal date for the Notification of Compliance Status, as specified in § 63.11456(b). The request must contain the information specified in paragraphs (f)(1) through (5) of this section.

(1) Description of the alternative add-on air pollution control device (APCD).

(2) Type of monitoring device or method that will be used, including the sensor type, location, inspection

procedures, quality assurance and quality control (QA/QC) measures, and data recording device.

(3) Operating parameters that will be monitored.

(4) Frequency that the operating parameter values will be measured and recorded.

(5) Procedures for inspecting the condition and operation of the control device and monitoring system.

(g) If you wish to use a monitoring method other than those specified in paragraph (b)(1) or (c)(1) of this section, you must meet the requirements in § 63.8(f) and submit a request for approval of alternative monitoring methods to the Administrator no later than the submittal date for the Notification of Compliance Status, as specified in § 63.11456(b). The request must contain the information specified in paragraphs (g)(1) through (5) of this section.

(1) Type of monitoring device or method that will be used, including the sensor type, location, inspection procedures, QA/QC measures, and data recording device.

(2) Operating parameters that will be monitored.

(3) Frequency that the operating parameter values will be measured and recorded.

(4) Procedures for inspecting the condition and operation of the monitoring system.

(5) Explanation for how the alternative monitoring method will provide assurance that the emission control device is operating properly.

§ 63.11455 What are the continuous compliance requirements for new and existing sources?

(a) You must be in compliance with the applicable emission limits in this subpart at all times, except during periods of startup, shutdown, and malfunction.

(b) You must always operate and maintain your affected source, including air pollution control and monitoring equipment, according to the provisions in § 63.6(e)(1)(i).

(c) For each affected furnace that is subject to the emission limit specified in Table 1 to this subpart, you must monitor the performance of the furnace emission control device under the conditions specified in § 63.11454(a)(7) and according to the requirements in §§ 63.6(e)(1) and 63.8(c) and paragraphs (c)(1) through (6) of this section.

(1) For each existing affected furnace that is controlled with an ESP, you must monitor the parameters specified in § 63.11454(b) in accordance with the requirements of § 63.11454(a) or as specified in your approved alternative monitoring plan.

(2) For each new affected furnace that is controlled with an ESP, you must comply with the monitoring requirements specified in § 63.11454(d) in accordance with the requirements of § 63.11454(a) or as specified in your approved alternative monitoring plan.

(3) For each existing affected furnace that is controlled with a fabric filter, you must monitor the parameter specified in § 63.11454(c) in accordance with the requirements of § 63.11454(a) or as specified in your approved alternative monitoring plan.

(4) For each new affected furnace that is controlled with a fabric filter, you must comply with the monitoring requirements specified in § 63.11454(e) in accordance with the requirements of § 63.11454(a) or as specified in your approved alternative monitoring plan.

(5) For each affected furnace that is controlled with a device other than a fabric filter or ESP, you must comply with the requirements of your approved alternative monitoring plan, as required in § 63.11454(g).

(6) For each monitoring system that is required under this subpart, you must keep the records specified in § 63.11457.

(d) Following the initial inspections, you must perform periodic inspections and maintenance of each affected furnace control device according to the requirements in paragraphs (d)(1) through (4) of this section.

(1) For each fabric filter, you must conduct inspections at least every 12 months according to paragraphs (d)(1)(i) through (iii) of this section.

(i) You must inspect the ductwork and fabric filter unit for leakage.

(ii) You must inspect the interior of the fabric filter for structural integrity and to determine the condition of the fabric filter.

(iii) If an initial inspection is not required, as specified in § 63.11453(b)(3)(i), the first inspection must not be more than 12 months from the last inspection.

(2) For each ESP, you must conduct inspections according to the requirements in paragraphs (d)(2)(i) through (iii) of this section.

(i) You must conduct visual inspections of the system ductwork, housing unit, and hopper for leaks at least every 12 months.

(ii) You must conduct inspections of the interior of the ESP to determine the condition and integrity of corona wires, collection plates, plate rappers, hopper, and air diffuser plates every 24 months.

(iii) If an initial inspection is not required, as specified in § 63.11453(b)(3)(ii), the first inspection must not be more than 24 months from the last inspection.

(3) You must record the results of each periodic inspection specified in this section in a logbook (written or electronic format), as specified in § 63.11457(c).

(4) If the results of a required inspection indicate a problem with the operation of the emission control system, you must take immediate corrective action to return the control device to normal operation according to the equipment manufacturer's specifications or instructions.

(e) For each affected furnace that is subject to the emission limit specified in Table 1 to this subpart and can meet the applicable emission limit without the use of a control device, you must demonstrate continuous compliance by satisfying the applicable recordkeeping requirements specified in § 63.11457.

Notifications and Records

§ 63.11456 What are the notification requirements?

(a) If you own or operate an affected furnace, as defined in § 63.11449(a), you must submit an Initial Notification in accordance with § 63.9(b) and paragraphs (a)(1) and (2) of this section by the dates specified.

(1) As specified in § 63.9(b)(2), if you start up your affected source before December 26, 2007, you must submit an Initial Notification not later than April 24, 2008 or within 120 days after your affected source becomes subject to the standard.

(2) The Initial Notification must include the information specified in § 63.9(b)(2)(i) through (iv).

(b) You must submit a Notification of Compliance Status in accordance with § 63.9(h) and the requirements in paragraphs (b)(1) and (2) of this section.

(1) If you own or operate an affected furnace and are required to conduct a performance test, you must submit a Notification of Compliance Status, including the performance test results, before the close of business on the 60th day following the completion of the performance test, according to § 60.8 or § 63.10(d)(2).

(2) If you own or operate an affected furnace and satisfy the conditions specified in § 63.11452(a)(2) and are not required to conduct a performance test, you must submit a Notification of Compliance Status, including the results of the previous performance test, before the close of business on the compliance date specified in § 63.11450.

§ 63.11457 What are the recordkeeping requirements?

(a) You must keep the records specified in paragraphs (a)(1) through (8) of this section.

(1) A copy of any Initial Notification and Notification of Compliance Status that you submitted and all documentation supporting those notifications, according to the requirements in § 63.10(b)(2)(xiv).

(2) The records specified in § 63.10(b)(2) and (c)(1) through (13).

(3) The records required to show continuous compliance with each emission limit that applies to you, as specified in § 63.11455.

(4) For each affected source, records of production rate on a process throughput basis (either feed rate to the process unit or discharge rate from the process unit). The production data must include the amount (weight or weight percent) of each ingredient in the batch formulation, including all glass manufacturing metal HAP compounds.

(5) Records of maintenance activities and inspections performed on control devices as specified in §§ 63.11453(b) and 63.11455(d), according to paragraphs (a)(5)(i) through (v) of this section.

(i) The date, place, and time of inspections of control device ductwork, interior, and operation.

(ii) Person conducting the inspection.

(iii) Technique or method used to conduct the inspection.

(iv) Control device operating conditions during the time of the inspection.

(v) Results of the inspection and description of any corrective action taken.

(6) Records of all required monitoring data and supporting information including all calibration and maintenance records.

(7) For each bag leak detection system, the records specified in paragraphs (a)(7)(i) through (iii) of this section.

(i) Records of the bag leak detection system output;

(ii) Records of bag leak detection system adjustments, including the date and time of the adjustment, the initial bag leak detection system settings, and the final bag leak detection system settings; and

(iii) The date and time of all bag leak detection system alarms, the time that procedures to determine the cause of the alarm were initiated, the cause of the alarm, an explanation of the actions taken, the date and time the cause of the alarm was alleviated, and whether the alarm was alleviated within 3 hours of the alarm.

(8) Records of any approved alternative monitoring method(s) or test procedure(s).

(b) Your records must be in a form suitable and readily available for expeditious review, according to § 63.10(b)(1).

(c) You must record the results of each inspection and maintenance action in a logbook (written or electronic format). You must keep the logbook onsite and make the logbook available to the permitting authority upon request.

(d) As specified in § 63.10(b)(1), you must keep each record for a minimum of 5 years following the date of each occurrence, measurement, maintenance, corrective action, report, or record.

You must keep each record onsite for at least 2 years after the date of each occurrence, measurement, maintenance, corrective action, report, or record, according to § 63.10(b)(1). You may keep the records offsite for the remaining three years.

Other Requirements and Information

§ 63.11458 What General Provisions apply to this subpart?

You must satisfy the requirements of the General Provisions in 40 CFR part 63, subpart A, as specified in Table 2 to this subpart.

§ 63.11459 What definitions apply to this subpart?

Terms used in this subpart are defined in the Clean Air Act, in § 63.2, and in this section as follows:

Air pollution control device (APCD) means any equipment that reduces the quantity of a pollutant that is emitted to the air.

Continuous furnace means a glass manufacturing furnace that operates continuously except during periods of maintenance, malfunction, control device installation, reconstruction, or rebuilding.

Cullet means recycled glass that is mixed with raw materials and charged to a glass melting furnace to produce glass. Cullet is not considered to be a raw material for the purposes of this subpart.

Electrostatic precipitator (ESP) means an APCD that removes PM from an exhaust gas stream by applying an electrical charge to particles in the gas stream and collecting the charged particles on plates carrying the opposite electrical charge.

Fabric filter means an APCD used to capture PM by filtering a gas stream through filter media.

Furnace stack means a conduit or conveyance through which emissions from the furnace melter are released to the atmosphere.

Glass manufacturing metal HAP means an oxide or other compound of any of the following metals included in the list of urban HAP for the Integrated Urban Air Toxics Strategy and for which Glass Manufacturing was listed as an area source category: arsenic, cadmium, chromium, lead, manganese, and nickel.

Glass melting furnace means a unit comprising a refractory-lined vessel in which raw materials are charged and melted at high temperature to produce molten glass.

Identical furnaces means two or more furnaces that are identical in design, including manufacturer, dimensions, production capacity, charging method, operating temperature, fuel type, burner configuration, and exhaust system configuration and design.

Particulate matter (PM) means, for purposes of this subpart, emissions of PM that serve as a measure of filterable particulate emissions, as measured by Methods 5 or 17 (40 CFR part 60, appendices A–3 and A–6), and as a surrogate for glass manufacturing metal HAP compounds contained in the PM including, but not limited to, arsenic, cadmium, chromium, lead, manganese, and nickel.

Plant site means all contiguous or adjoining property that is under common control, including properties that are separated only by a road or other public right-of-way. Common control includes properties that are owned, leased, or operated by the same entity, parent entity, subsidiary, or any combination thereof.

Raw material means minerals, such as silica sand, limestone, and dolomite; inorganic chemical compounds, such as soda ash (sodium carbonate), salt cake (sodium sulfate), and potash (potassium carbonate); metal oxides and other metal-based compounds, such as lead oxide, chromium oxide, and sodium antimonate; metal ores, such as chromite and pyrolusite; and other substances that are intentionally added to a glass manufacturing batch and melted in a glass melting furnace to produce glass. Metals that are naturally-occurring trace constituents or contaminants of other substances are not considered to be raw materials. Cullet and material that is recovered from a furnace control device for recycling into the glass formulation are not considered to be raw materials for the purposes of this subpart.

Research and development process unit means a process unit whose purpose is to conduct research and development for new processes and products and is not engaged in the manufacture of products for commercial sale, except in a de minimis manner.

§ 63.11460 Who implements and enforces this subpart?

(a) This subpart can be implemented and enforced by the U.S. EPA, or a delegated authority such as your State, local, or tribal agency. If the U.S. EPA Administrator has delegated authority to your State, local, or tribal agency, then that agency has the authority to implement and enforce this subpart. You should contact your U.S. EPA Regional Office to find out if this subpart is delegated to your State, local, or tribal agency.

(b) In delegating implementation and enforcement authority of this subpart to a State, local, or tribal agency under 40 CFR part 63, subpart E, the authorities contained in paragraphs (b)(1) through (4) of this section are retained by the Administrator of the U.S. EPA and are not transferred to the State, local, or tribal agency.

(1) Approval of alternatives to the applicability requirements in §§ 63.11448 and 63.11449, the compliance date requirements in § 63.11450, and the emission limits specified in § 63.11451.

(2) Approval of a major change to test methods under § 63.7(e)(2)(ii) and (f) and as defined in § 63.90.

(3) Approval of major alternatives to monitoring under § 63.8(f) and as defined in § 63.90.

(4) Approval of major alternatives to recordkeeping under § 63.10(f) and as defined in § 63.90.

§ 63.11461 [Reserved]

Tables to Subpart SSSSSS of Part 63

As required in § 63.11451, you must comply with each emission limit that applies to you according to the following table:

TABLE 1 TO SUBPART SSSSSS OF PART 63—EMISSION LIMITS

For each. . .	You must meet one of the following emission limits. . .
1. New or existing glass melting furnace that produces glass at an annual rate of at least 45 Mg/yr (50 tpy) AND is charged with compounds of arsenic, cadmium, chromium, manganese, lead, or nickel as raw materials.	a. The 3-hour block average production-based PM mass emission rate must not exceed 0.1 gram per kilogram (g/kg) (0.2 pound per ton (lb/ton)) of glass produced; OR b. The 3-hour block average production-based metal HAP mass emission rate must not exceed 0.01 g/kg (0.02 lb/ton) of glass produced.

As stated in § 63.11458, you must comply with the requirements of the NESHAP General Provisions (40 CFR part 63, subpart A), as shown in the following table:

TABLE 2 TO SUBPART SSSSSS OF PART 63—APPLICABILITY OF GENERAL PROVISIONS TO SUBPART SSSSSS

Citation	Subject
§ 63.1(a), (b), (c)(1), (c)(2), (c)(5), (e)	Applicability.
§ 63.2	Definitions.
§ 63.3	Units and Abbreviations.
§ 63.4	Prohibited Activities.
§ 63.5	Construction/Reconstruction.
§ 63.6(a), (b)(1)–(b)(5), (b)(7), (c)(1), (c)(2), (c)(5), (e)(1), (f), (g), (i), (j)	Compliance with Standards and Maintenance Requirements.
§ 63.7	Performance Testing Requirements.
§ 63.8(a)(1), (a)(2), (b), (c)(1)–(c)(4), (c)(7)(i)(B), (c)(7)(ii), (c)(8), (d), (e)(1), (e)(4), (f).	Monitoring Requirements.
§ 63.9(a), (b)(1)(i)–(b)(2)(v), (b)(5), (c), (d), (h)–(j)	Notification Requirements.
§ 63.10(a), (b)(1), (b)(2)(i)–(b)(2)(xii)	Recordkeeping and Reporting Requirements.
§ 63.10(b)(2)(xiv), (c), (f)	Documentation for Initial Notification and Notification of Compliance Status.
§ 63.12	State Authority and Delegations.
§ 63.13	Addresses.
§ 63.14	Incorporations by Reference.
§ 63.15	Availability of Information.
§ 63.16	Performance Track Provisions.

❊5. Part 63 is amended by adding subpart TTTTTT to read as follows:

Subpart TTTTTT—National Emission Standards for Hazardous Air Pollutants for Secondary Nonferrous Metals Processing Area Sources

Applicability and Compliance Dates

Sec.

63.11462 Am I subject to this subpart?

63.11463 What parts of my plant does this subpart cover?

63.11464 What are my compliance dates?

Standards, Compliance, and Monitoring Requirements

63.11465 What are the standards for new and existing sources?

63.11466 What are the performance test requirements for new and existing sources?

63.11467 What are the initial compliance demonstration requirements for new and existing sources?

63.11468 What are the monitoring requirements for new and existing sources?

63.11469 What are the notification requirements?

63.11470 What are the recordkeeping requirements?

Other Requirements and Information

63.11471 What General Provisions apply to this subpart?

63.11472 What definitions apply to this subpart?

63.11473 Who implements and enforces this subpart?

63.11474 [Reserved]

Tables to Subpart TTTTTT of Part 63

Table 1 to Subpart TTTTTT of Part 63—Applicability of General Provisions to Subpart TTTTTT

Applicability and Compliance Dates

§ 63.11462 Am I subject to this subpart?

(a) You are subject to this subpart if you own or operate a secondary nonferrous metals processing facility (as defined in § 63.11472) that is an area source of hazardous air pollutant (HAP) emissions.

(b) If you are an owner or operator of an area source subject to this subpart, you are exempt from the obligation to obtain a permit under 40 CFR part 70 or 71, provided you are not required to obtain a permit under 40 CFR 70.3(a) or 71.3(a) for a reason other than your status as an area source under this subpart. Notwithstanding the previous sentence, you must continue to comply with the provisions of this subpart applicable to area sources.

§ 63.11463 What parts of my plant does this subpart cover?

(a) This subpart applies to any existing or new affected source located at a secondary nonferrous metals processing facility.

(b) The affected source includes all crushing and screening operations at a secondary zinc processing facility and all furnace melting operations located at any secondary nonferrous metals processing facilities.

(c) An affected source is existing if you commenced construction or reconstruction of the affected source on or before September 20, 2007.

(d) An affected source is new if you commenced construction or reconstruction of the affected source after September 20, 2007.

§ 63.11464 What are my compliance dates?

(a) If you have an existing affected source, you must comply with the standards no later than December 26, 2007.

(b) If you have a new affected source, you must comply with this subpart according to paragraphs (b)(1) and (b)(2) of this section.

(1) If you start up your affected source on or before December 26, 2007, you must comply with this subpart no later than December 26, 2007.

(2) If you start up your affected source after December 26, 2007, you must comply with this subpart upon initial startup of your affected source.

Standards, Compliance, and Monitoring Requirements

§ 63.11465 What are the standards for new and existing sources?

(a) You must route the emissions from each existing affected source through a fabric filter or baghouse that achieves a particulate matter (PM) control efficiency of at least 99.0 percent or an outlet PM concentration limit of 0.034 grams per dry standard cubic meter (g/dscm)(0.015 grains per dry standard cubic feet (gr/dscf)).

(b) You must route the emissions from each new affected source through a fabric filter or baghouse that achieves a PM control efficiency of at least 99.5 percent or an outlet PM concentration limit of 0.023 g/dscm (0.010 gr/dscf).

§ 63.11466 What are the performance test requirements for new and existing sources?

(a) Except as specified in paragraph (b) of this section, if you own or operate an existing or new affected source, you must conduct a performance test for each affected source within 180 days of your compliance date and report the results in your notification of compliance status.

(b) If you own or operate an existing affected source, you are not required to conduct a performance test if a prior performance test was conducted within the past 5 years of the compliance date using the same methods specified in paragraph (c) of this section and you meet either of the following two conditions:

(1) No process changes have been made since the test; or

(2) You demonstrate that the results of the performance test, with or without adjustments, reliably demonstrate compliance despite process changes.

(c) You must conduct each performance test according to the requirements in § 63.7 and paragraphs (c)(1) and (2) of this section.

(1) Determine the concentration of PM according to the following test methods in 40 CFR part 60, appendices:

(i) Method 1 or 1A (Appendix A–1) to select sampling port locations and the number of traverse points in each stack or duct. Sampling sites must be located at the outlet of the control device and prior to any releases to the atmosphere.

(ii) Method 2, 2A, 2C, 2F, or 2G (Appendices A–1 and A–2) to determine the volumetric flow rate of the stack gas.

(iii) Method 3, 3A, or 3B (Appendix A–2) to determine the dry molecular weight of the stack gas. You may use ANSI/ASME PTC 19.10–1981, "Flue and Exhaust Gas Analyses" (incorporated by reference-see § 63.14) as an alternative to EPA Method 3B.

(iv) Method 4 (Appendix A–3) to determine the moisture content of the stack gas.

(v) Method 5 or 17 (Appendix A–3) to determine the concentration of particulate matter (front half filterable catch only). Three valid test runs are needed to comprise a performance test.

(2) During the test, you must operate each emissions source within ±10 percent of its normal process rate. You must monitor and record the process rate during the test.

§ 63.11467 What are the initial compliance demonstration requirements for new and existing sources?

(a) You must demonstrate initial compliance with the applicable standards in § 63.11465 by submitting a Notification of Compliance Status in accordance with § 63.11469(b).

(b) You must conduct the inspection specified in paragraph (c) of this section and include the results of the inspection in the Notification of Compliance Status.

(c) For each existing and new affected source, you must conduct an initial inspection of each baghouse. You must visually inspect the system ductwork and baghouse unit for leaks. Except as specified in paragraph (e) of this section, you must also inspect the inside of each baghouse for structural integrity and fabric filter condition. You must record the results of the inspection and any maintenance action as required in § 63.11470.

(d) For each installed baghouse that is in operation during the 60 days after the applicable compliance date, you must conduct the inspection specified in paragraph (c) of this section no later than 60 days after your applicable compliance date. For an installed baghouse that is not in operation during the 60 days after the applicable compliance date, you must conduct an initial inspection prior to startup of the baghouse.

(e) An initial inspection of the internal components of a baghouse is not required if an inspection has been performed within the past 12 months.

(f) If you own or operate an existing affected source and are not required to conduct a performance test under § 63.11466, you must submit the Notification of Compliance Status within 120 days after the applicable compliance date specified in § 63.11464.

(g) If you own or operate an existing affected source and are required to conduct a performance test under § 63.11466, you must submit the Notification of Compliance Status within 60 days after completing the performance test.

§ 63.11468 What are the monitoring requirements for new and existing sources?

(a) For an existing affected source, you must demonstrate compliance by conducting the monitoring activities in paragraph (a)(1) or (a)(2) of this section:

(1) You must perform periodic inspections and maintenance of each

baghouse according to the requirements in paragraphs (a)(1)(i) and (ii) of this section.

(i) You must conduct weekly visual inspections of the system ductwork for leaks.

(ii) You must conduct inspections of the interior of the baghouse for structural integrity and to determine the condition of the fabric filter every 12 months.

(2) As an alternative to the monitoring requirements in paragraph (a)(1) of this section, you may demonstrate compliance by conducting a daily 30-minute visible emissions (VE) test (i.e., no visible emissions) using EPA Method 22 (40 CFR part 60, appendix A–7).

(b) If the results of the visual inspection or VE test conducted under paragraph (a) of this section indicate a problem with the operation of the baghouse, including but not limited to air leaks, torn or broken bags or filter media, or any other condition that may cause an increase in PM emissions, you must take immediate corrective action to return the baghouse to normal operation according to the equipment manufacturer's specifications or instructions and record the corrective action taken.

(c) For each new affected source, you must install, operate, and maintain a bag leak detection system according to paragraphs (c)(1) through (3) of this section.

(1) Each bag leak detection system must meet the specifications and requirements in paragraphs (c)(1)(i) through (viii) of this section.

(i) The bag leak detection system must be certified by the manufacturer to be capable of detecting PM emissions at concentrations of 1 milligram per dry standard cubic meter (0.00044 grains per actual cubic foot) or less.

(ii) The bag leak detection system sensor must provide output of relative PM loadings. The owner or operator shall continuously record the output from the bag leak detection system using electronic or other means (e.g., using a strip chart recorder or a data logger).

(iii) The bag leak detection system must be equipped with an alarm system that will sound when the system detects an increase in relative particulate loading over the alarm set point established according to paragraph (c)(1)(iv) of this section, and the alarm must be located such that it can be heard by the appropriate plant personnel.

(iv) In the initial adjustment of the bag leak detection system, you must establish, at a minimum, the baseline output by adjusting the sensitivity (range) and the averaging period of the device, the alarm set points, and the alarm delay time.

(v) Following initial adjustment, you shall not adjust the averaging period, alarm set point, or alarm delay time without approval from the Administrator or delegated authority except as provided in paragraph (c)(1)(vi) of this section.

(vi) Once per quarter, you may adjust the sensitivity of the bag leak detection system to account for seasonal effects, including temperature and humidity, according to the procedures identified in the site-specific monitoring plan required by paragraph (c)(2) of this section.

(vii) You must install the bag leak detection sensor downstream of the fabric filter.

(viii) Where multiple detectors are required, the system's instrumentation and alarm may be shared among detectors.

(2) You must develop and submit to the Administrator or delegated authority for approval a site-specific monitoring plan for each bag leak detection system. You must operate and maintain the bag leak detection system according to the site-specific monitoring plan at all times. Each monitoring plan must describe the items in paragraphs (c)(2)(i) through (vi) of this section.

(i) Installation of the bag leak detection system;

(ii) Initial and periodic adjustment of the bag leak detection system, including how the alarm set-point will be established;

(iii) Operation of the bag leak detection system, including quality assurance procedures;

(iv) How the bag leak detection system will be maintained, including a routine maintenance schedule and spare parts inventory list;

(v) How the bag leak detection system output will be recorded and stored; and

(vi) Corrective action procedures as specified in paragraph (c)(3) of this section. In approving the site-specific monitoring plan, the Administrator or delegated authority may allow owners and operators more than 3 hours to alleviate a specific condition that causes an alarm if the owner or operator identifies in the monitoring plan this specific condition as one that could lead to an alarm, adequately explains why it is not feasible to alleviate this condition within 3 hours of the time the alarm occurs, and demonstrates that the requested time will ensure alleviation of this condition as expeditiously as practicable.

(3) For each bag leak detection system, you must initiate procedures to determine the cause of every alarm within 1 hour of the alarm. Except as provided in paragraph (c)(2)(vi) of this section, you must alleviate the cause of the alarm within 3 hours of the alarm by taking whatever corrective action(s) are necessary. Corrective actions may include, but are not limited to the following:

(i) Inspecting the fabric filter for air leaks, torn or broken bags or filter media, or any other condition that may cause an increase in PM emissions;

(ii) Sealing off defective bags or filter media;

(iii) Replacing defective bags or filter media or otherwise repairing the control device;

(iv) Sealing off a defective fabric filter compartment;

(v) Cleaning the bag leak detection system probe or otherwise repairing the bag leak detection system; or

(vi) Shutting down the process producing the PM emissions.

§ 63.11469 What are the notification requirements?

(a) You must submit the Initial Notification required by § 63.9(b)(2) no later than 120 days after the applicable compliance date specified in § 63.11464. The Initial Notification must include the information specified in § 63.9(b)(2)(i) through (iv) and may be combined with the Notification of Compliance Status required in § 63.11467 and paragraph (b) of this section if you choose to submit both notifications within 120 days.

(b) You must submit a Notification of Compliance Status in accordance with § 63.9(h) and the requirements in paragraphs (c) and (d) of this section. In addition to the information required in § 63.9(h)(2), § 63.11466, and § 63.11467, your notification must include the following certification(s) of compliance, as applicable, and signature of a responsible official:

(1) This certification of compliance by the owner or operator of an existing affected source who is relying on a previous performance test: "This facility complies with the control efficiency requirement [or the outlet concentration limit] in § 63.11465 based on a previous performance test in accordance with § 63.11466."

(2) This certification of compliance by the owner or operator of any new or existing affected source: "This facility has conducted an initial inspection of each control device according to the requirements in § 63.11467, will conduct periodic inspections and maintenance of control devices in accordance with § 63.11468, and will maintain records of each inspection and maintenance action required by § 63.11470."

(3) This certification of compliance by the owner or operator of a new affected source: ''This facility has an approved bag leak detection system monitoring plan in accordance with § 63.11468(c)(2).''

(c) If you own or operate an affected source and are required to conduct a performance test under § 63.11466, you must submit a Notification of Compliance Status, including the performance test results, before the close of business on the 60th day following the completion of the performance test.

(d) If you own or operate an affected source and are not required to conduct a performance test under § 63.11466, you must submit a Notification of Compliance Status, including the results of the previous performance test, no later than 120 days after the applicable compliance date specified in § 63.11464.

§ 63.11470 What are the recordkeeping requirements?

(a) You must keep the records specified in paragraphs (a)(1) and (2) of this section.

(1) As required in § 63.10(b)(2)(xiv), you must keep a copy of each notification that you submitted to comply with this subpart and all documentation supporting any Initial Notification or Notification of Compliance Status that you submitted.

(2) You must keep the records of all inspection and monitoring data required by §§ 63.11467 and 63.11468, and the information identified in paragraphs (a)(2)(i) through (a)(2)(v) for each required inspection or monitoring.

(i) The date, place, and time;

(ii) Person conducting the activity;

(iii) Technique or method used;

(iv) Operating conditions during the activity; and

(v) Results.

(b) Your records must be in a form suitable and readily available for expeditious review, according to § 63.10(b)(1).

(c) As specified in § 63.10(b)(1), you must keep each record for 5 years following the date of each recorded action.

(d) You must keep each record onsite for at least 2 years after the date of each recorded action according to § 63.10(b)(1). You may keep the records offsite for the remaining three years.

Other Requirements and Information

§ 63.11471 What General Provisions apply to this subpart?

Table 1 to this subpart shows which parts of the General Provisions in §§ 63.1 through 63.16 apply to you.

§ 63.11472 What definitions apply to this subpart?

Terms used in this subpart are defined in the Clean Air Act, in § 63.2, and in this section as follows:

Bag leak detection system means a system that is capable of continuously monitoring relative particulate matter (dust loadings) in the exhaust of a baghouse to detect bag leaks and other upset conditions. A bag leak detection system includes, but is not limited to, an instrument that operates on triboelectric, light scattering, light transmittance, or other effect to continuously monitor relative particulate matter loadings.

Furnace melting operation means the collection of processes used to charge post-consumer nonferrous scrap material to a furnace, melt the material, and transfer the molten material to a forming medium.

Secondary nonferrous metals processing facility means a brass and bronze ingot making, secondary magnesium processing, or secondary zinc processing plant that uses furnace melting operations to melt post-consumer nonferrous metal scrap to make products including bars, ingots, blocks, or metal powders.

§ 63.11473 Who implements and enforces this subpart?

(a) This subpart can be implemented and enforced by the U.S. EPA or a delegated authority such as your State, local, or tribal agency. If the U.S. EPA Administrator has delegated authority to your State, local, or tribal agency, then that agency has the authority to implement and enforce this subpart. You should contact your U.S. EPA Regional Office to find out if this subpart is delegated to your State, local, or tribal agency.

(b) In delegating implementation and enforcement authority of this subpart to a State, local, or tribal agency under 40 CFR part 63, subpart E, the authorities contained in paragraph (c) of this section are retained by the Administrator of the U.S. EPA and are not transferred to the State, local, or tribal agency.

(c) The authorities that will not be delegated to State, local, or tribal agencies are listed in paragraphs (c)(1) through (4) of this section.

(1) Approval of alternatives to the applicability requirements in § 63.11462 and 63.11463, the compliance date requirements in § 63.11464, and the applicable standards in § 63.11465.

(2) Approval of a major change to a test method under § 63.7(e)(2)(ii) and (f). A ''major change to test method'' is defined in § 63.90.

(3) Approval of a major change to monitoring under § 63.8(f). A ''major change to monitoring'' is defined in § 63.90.

(4) Approval of a major change to recordkeeping/reporting under § 63.10(f). A ''major change to recordkeeping/reporting'' is defined in § 63.90.

§ 63.11474 [Reserved]

Tables to Subpart TTTTTT of Part 63

As stated in § 63.11471, you must comply with the requirements of the NESHAP General Provisions (40 CFR part 63, subpart A) shown in the following table:

TABLE 1 TO SUBPART TTTTTT OF PART 63—APPLICABILITY OF GENERAL PROVISIONS TO SUBPART TTTTTT

Citation	Subject
63.1(a)(1)–(a)(4), (a)(6), (a)(10)–(a)(12), (b)(1), (b)(3), (c)(1),[1] (c)(2), (c)(5), (e)	Applicability.
63.2	Definitions.
63.3	Units and Abbreviations.
63.4	Prohibited Activities and Circumvention.
63.6(a), (b)(1)–(b)(5), (b)(7), (c)(1), (c)(2), (c)(5), (e)(1), (f), (g), (i), (j)	Compliance With Standards and Maintenance Requirements.
63.7	Performance Testing Requirements
63.8(a)(1), (a)(2), (b), (c)(1)(i)–(c)(1)(ii), (c)(2), (c)(3), (f)	Monitoring Requirements.
63.9(a), (b)(1), (b)(2), (b)(5), (c), (d), (h)(1)–(h)(3), (h)(5), (h)(6), (i), (j)	Notification Requirements.
63.10(a), (b)(1), (b)(2)(vii), (b)(2)(xiv), (b)(3), (c), (f)	Recordkeeping and Reporting Requirements.
63.12	State Authority and Delegations.
63.13	Addresses.
63.14	Incorporations by Reference.

TABLE 1 TO SUBPART TTTTTT OF PART 63—APPLICABILITY OF GENERAL PROVISIONS TO SUBPART TTTTTT—Continued

Citation	Subject
63.15	Availability of Information and Confidentiality.
63.16	Performance Track Provisions.

[1] Section 63.11462(b) of this subpart exempts area sources from the obligation to obtain title V operating permits.

[FR Doc. E7–24720 Filed 12–21–07; 8:45 am]
BILLING CODE 6560–50–P

To: Fried, Gregory[Fried.Gregory@epa.gov]; Spina, Providence[Spina.Providence@epa.gov]; McClintock, Katie[McClintock.Katie@epa.gov]
From: Froikin, Sara
Sent: Fri 2/12/2016 8:24:33 PM
Subject: US Forest Service moss map for arsenic
USFS arsenic moss map of Portland OR 2013.png

Found this in a news article.

Sara Froikin, Attorney-Advisor

U.S. Environmental Protection Agency

290 Broadway

New York, NY 10007

Phone: 212-637-3263

To: McClintock, Katie[McClintock.Katie@epa.gov]
Cc: Fried, Gregory[Fried.Gregory@epa.gov]; Spina, Providence[Spina.Providence@epa.gov]
From: Froikin, Sara
Sent: Fri 2/12/2016 8:02:21 PM
Subject: Art glass companies list
List of art glass companies.xlsx

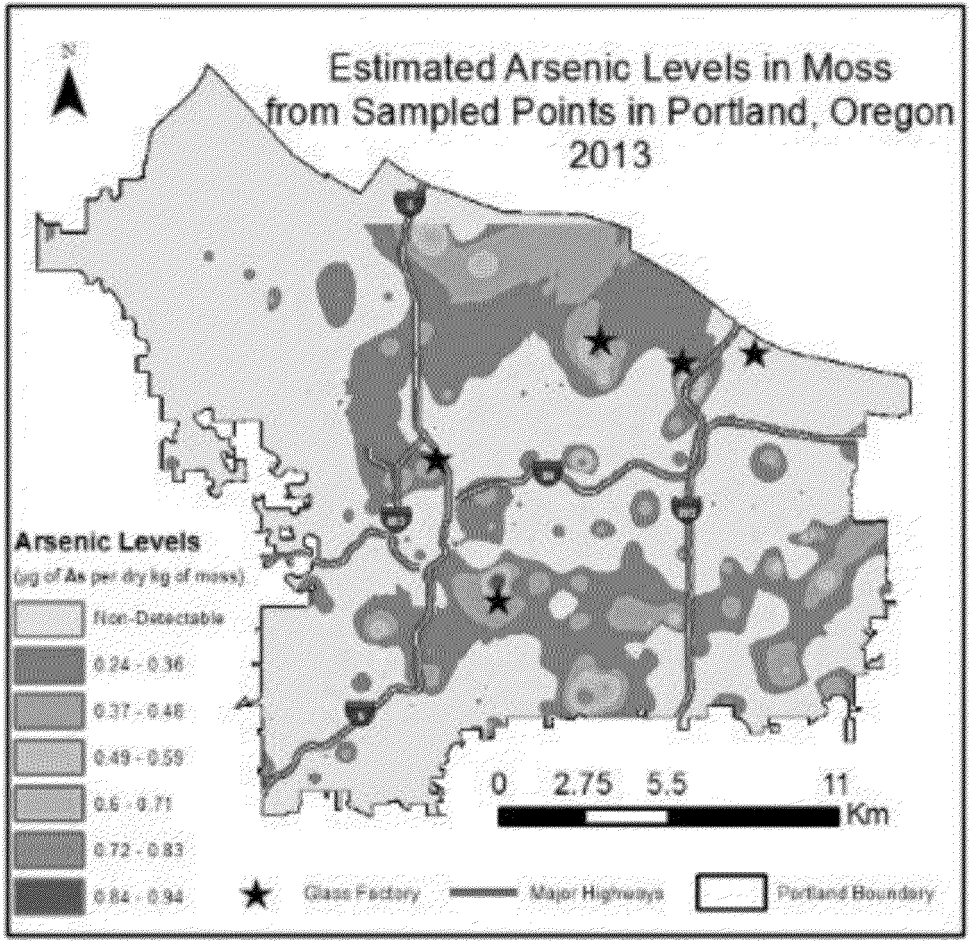
Sara Froikin, Attorney-Advisor

U.S. Environmental Protection Agency

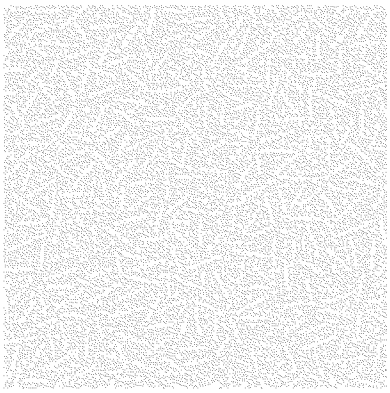
290 Broadway

New York, NY 10007

Phone: 212-637-3263


N
Estimated Arsenic Levels in Moss
from Sampled Points in Portland, Oregon
2013
Arsenic Levels
(µg of As per dry kg of moss)
Non-Detectable
0.24 - 0.36
0.37 - 0.48
0.49 - 0.59
0.6 - 0.71
0.72 - 0.83
0.84 - 0.94
0
2.75
5.5
11
Km
Glass Factory
Major Highways
Portland Boundary

To: Froikin, Sara[Froikin.Sara@epa.gov]
From: McClintock, Katie
Sent: Thur 2/25/2016 3:57:16 PM
Subject: FW: updated list of art glass manufacturers
Known Art Glass Manufacturers in US updated 2 25 2016.xlsx



From: Fairchild, Susan
Sent: Thursday, February 25, 2016 7:47 AM
To: Terry, Sara <Terry.Sara@epa.gov>; Koerber, Mike <Koerber.Mike@epa.gov>; McClintock, Katie <McClintock.Katie@epa.gov>; Narvaez, Madonna <Narvaez.Madonna@epa.gov>
Cc: Rimer, Kelly <Rimer.Kelly@epa.gov>; Barnett, Keith <Barnett.Keith@epa.gov>
Subject: updated list of art glass manufacturers

I've updated this list based on Katie's inspection of the Northstar facility, which identified other similar facilities making colored glass using a borosilicate recipe.

Susan Fairchild

Senior Environmental Scientist

(919) 541-5167

USPS Address:

OAQPS/SPPD/MMG

Mail Code D 243-04

Research Triangle Park, NC 27711

To: McClintock, Katie[McClintock.Katie@epa.gov]; Fried, Gregory[Fried.Gregory@epa.gov]
Sent: Fri 3/4/2016 5:24:23 PM
Subject: FW: Steuben Glass
Steuben Glass Letters.pdf

FYI – Steuben

Sara Froikin, Attorney-Advisor

U.S. Environmental Protection Agency

290 Broadway

New York, NY 10007

Phone: 212-637-3263

From: Patel, Harish
Sent: Friday, March 04, 2016 12:22 PM
To: Carrea, Steve <Carrea.Steve@epa.gov>; Froikin, Sara <Froikin.Sara@epa.gov>; Yee, Katherine <Yee.Katherine@epa.gov>; Lonergan, Ralph <Lonergan.Ralph@epa.gov>
Cc: Buettner, Robert <Buettner.Robert@epa.gov>; LaVigna, Gaetano <LaVigna.Gaetano@epa.gov>; Villatora, Liliana <Villatora.Liliana@epa.gov>
Subject: FW: Steuben Glass

FYI….it appears that the Art Glass facility identified by HQ –Steuben Glass, is no longer operating. They had ceased operations in 2010 and surrendered their Title V permit in 2011.

Harish

From: Zeng, Yuan (DEC) [mailto:yuan.zeng@dec.ny.gov]
Sent: Friday, March 04, 2016 11:12 AM
To: Patel, Harish <Patel.Harish@epa.gov>
Cc: Marriott, Thomas (DEC) <thomas.marriott@dec.ny.gov>; Gentile, Tom (DEC) <tom.gentile@dec.ny.gov>; Flint, Steven (DEC) <steven.flint@dec.ny.gov>
Subject: Steuben Glass

Hello Harish,

As you requested, attached are the letters from Steuben Glass about the permit surrender. Please contact me if you have any further questions.

Yuan Zeng, P.E.

Environmental Engineer II, Division of Air Resources

New York State Department of Environmental Conservation

Region 8, 6274 E Avon-Lima Road, Avon, NY 14414

P: (585) 226-5320 | F: (585) 226-2909 | yuan.zeng@dec.ny.gov

www.dec.ny.gov | | |

Carol Ann Carlson
EHS Coordinator
Workers' Compensation Administrator

One Steuben Way
Corning, NY 14830

t 607.937.8021
www.steuben.com
ccarlson@steuben.com

SteubenGlass LLC

SEP 08 2010

August 25, 2010

Mr. Tom Wickerham
NYS Department of Environmental Conservation
Air Division
6274 E Avon-Lima Road
Avon, NY 14414

Dear Mr. Wickerham:

Per our conversation on June 14, 2010, please consider this letter a request to terminate our Title V Operating Permit ID: 8-4603-00012/02001.

On July 15, 2010, Steuben Glass LLC ceased production from our glass manufacturing tank. The tank was permanently draining and cooled. All batch materials were emptied from our batching system and the system was thorough cleaned. Our Pollution Abatement System was also shutdown. During the week of August 2, 2010, all of the fiber filter bags were removed from our baghouse and the secondary HEPA Type filters were removed from our secondary filter system.

Since Steuben Glass no longer manufactures glass by melting a mixture of raw materials, and will no longer operate a glass manufacturing facility that is an area source of hazardous air pollutant emissions, we will no longer be subject to 40CFR 63 Subpart SSSSSS- NESHAP for Glass Manufacturing Area Sources, therefore we should no longer be subject to Title V requirements.

If you need any additional information or have any questions, please do not hesitate to contact me at 607-346-4255.

Thank you.

Sincerely,

Carol Ann Carlson
EHS Coordinator
Steuben Glass LLC

CC: Y. Zeng – NYSDEC Division of Air Resources
S. Riva – Chief, USEPA Region 2 – Permitting Section, Air Programs Branch

Yvan
make sure AFS
reflects this

O'BRIEN & GERE

RECEIVED

DEC 16 2011

AIR RESOURCES
NYSDEC REGION 8

December 15, 2011

Division of Air Resources
New York State Department of Environmental Conservation
Region 8
6274 E. Avon-Lima Rd. (Rtes. 5 and 20)
Avon, NY 14414-9519

RE: Confirmation of Surrender of Air Facility Registration, Steuben Glass, LLC
(DEC Registration ID #8-4603-00012)

FILE: 1403/48254.001.001

Dear Sir or Madam:

On behalf of Corning, Inc. (Corning), O'Brien & Gere is submitting this letter of confirmation that all active air permits (known DEC Registration/Title V Permit ID #8-4603-00012 and EPA ID #3610100050) have been surrendered for the Steuben Glass, LLC/Schottenstein Stores Corporation facility with the following known addresses:

- One Museum Way, Corning, New York 14830
- One Steuben Way, Corning, New York 14830
- 151 Center Way, Corning, New York 14830

This former Corning facility, as transferred to Steuben Glass, LLC/Schottenstein Stores Corporation, is no longer an active operator; all operations have been permanently discontinued as of October 1, 2011. Corning has assumed control of the building and equipment and is decommissioning the equipment.

We trust the information included in this letter is sufficient to enable the Department to evaluate our request. Please contact me if you have any questions or require additional information.

Very truly yours,
O'BRIEN & GERE ENGINEERS, INC.

Jamie D. Newtown
Senior Managing Scientist

cc: Kenneth Eng – USEPA Region 2
Tracy Hall – Corning, Inc.
Christy Hannan – Corning, Inc.
Joe Dubendorfer – Corning, Inc.
Amber Sweredoski – Corning, Inc.

To: Hedgpeth, Zach[Hedgpeth.Zach@epa.gov]
From: McClintock, Katie
Sent: Tue 2/16/2016 3:39:49 PM
Subject: FW: Uroboros report
removed.txt

From: Eric Lovell [mailto:eric@uroboros.com]
Sent: Monday, February 15, 2016 4:04 PM
To: McClintock, Katie <McClintock.Katie@epa.gov>; monro.david@deq.state.or.us
Subject: Uroboros report

Dear Ms. McClintock and Mr. Monro,

Per Ms. McClintock's request, we are accumulating a packet of documents for you both. I may email a few sample documents to Ms. McClintock for approval of their format Tuesday AM.

Meanwhile, I would like to know what data you are using to support the idea that hexavalent chromium, Cadmium, or any other metal vapors, are being emitted from melts in the Uroboros furnaces. You appear to be relying on some outside information other than physical testing around Uroboros' location for your decision to direct the suspension of use of these chemicals here. Perhaps this information is in the form of studies that specifically examine metal vapor volatilization rates in glass melters. I have never seen such studies, but if they exist and you have access to them, I would like to know what the study parameters were, so I would appreciate copies to help me understand your suspension directives and work toward a rapid solution.

For examples:

•□□□□□□□□ Was peak melt temperature a factor in volatilization rates?

•□□□□□□□□ Was there a correlation between metal oxide source compounds and variations in the vapor emissions?

•□□□□□□□□ What type of furnaces were used during the tests?

These are urgent questions for Uroboros Glass, since despite the fact that no test has determined that we emit any, let alone excessive levels of Hex. Chromium, we have already voluntarily suspended production of over 2/3 of our entire product line. There is not much time before Uroboros Glass will be insolvent if this situation isn't changed. I am laying people off starting today that have been employed here for decades, and have moved to suspend dozens of normally ongoing activities due to the uncertainty.

If your goal is to shut us down without ever determining if we actually emitted or not, feel free not to reply. If you want to participate in a solution for the situation, provide me the data and reports you must have access to so I can study and learn from them, in the hopes of finding a solution quicker.

Sincerely,

Eric Lovell
President

2139 N. Kerby Ave
Portland, OR 97227
503-284-4900 x 201 T
503-284-7584 F

********** ATTACHMENT REMOVED **********

This message contained an attachment which the administrator has caused to be removed.

********** ATTACHMENT REMOVED **********

Attachment name: [image001.jpg]
Attachment type: [image/jpeg]

SOILSOLUTIONS
ENVIRONMENTAL SERVICES

Fact Sheet

Background Levels of Metals in Soils for Cleanups

State of Oregon
Department of Environmental Quality

Land Quality Division
Environmental Cleanup Program
811 SW 6th Avenue
Portland, OR 97204
Phone: (503) 229-6258
(800) 452-4011
Fax: (503) 229-6954
Contact: Annette Dietz
www.oregon.gov/DEQ

Background

To help improve assessment and eventual cleanup of metals-contaminated sites in Oregon, the Oregon Department of Environmental Quality Cleanup Program has prepared a data table specifying regional default background concentrations of various metals in Oregon soils.

DEQ compiled a statewide database for naturally occurring metals in soil and calculated summary statistics for 16 of these metals including lead, arsenic and mercury. It also calculated background metals concentrations, including the 95 percent upper prediction limit, using methods consistent with U.S. Environmental Protection Agency policy and guidance for 10 separate regions in Oregon (see Figure 1). These data and the statistical values derived from them will replace previous background metals concentrations in use by the DEQ Cleanup Program.

Why the new background data is important

DEQ analyzed and compiled the background metals data to:

- Better distinguish the sources of metals contamination on cleanup sites
- Reduce the burden of sampling and analytical costs for sites with metals contamination
- Refine and improve previous guidance on background metals concentrations
- Enable better comparisons of site data to background concentrations for naturally occurring contaminants

How DEQ gathered the data

DEQ compiled roughly 230,000 data points representing about 5,100 individual sampling locations statewide. For the 16 metals statistically analyzed, it calculated data minimums, maximums, means, percentiles, tolerance limits and prediction limits to characterize typical metals concentrations in soils within each individual region. The data came from a compilation of 10 individual databases from state (Department of Geology and Mineral Industries, DEQ), federal (U.S. Geological Survey, U.S. Department of Agriculture, Natural Resources Conservation Service), and academic (Portland State University) sources generated during geochemical, soil and mining exploration investigations and several environmental cleanup sites. DEQ has posted a technical report summarizing the development of the background values at http://www.deq.state.or.us/lq/pubs/docs/cu/DebORbackgroundMetal.pdf

Updated values may now be used

These updated metals background values may now be applied on project-specific decision making for cleanup work in Oregon. The values in Table 1 of this fact sheet replace previous statewide background values contained in a 2002 DEQ memorandum subsequently incorporated into Appendix B of DEQ's Guidance for Assessing Bioaccumulative Chemicals of Concern in Sediment and into Table 1 of DEQ's Human Health Risk Assessment Guidance.

Applicability

DEQ has established background soil concentrations for 16 metals (antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, manganese, mercury, nickel, selenium, silver, thallium, vanadium and zinc) in 10 regions across the state. These data can be used to:

- Determine whether the metals are present in site soil at concentrations exceeding estimates of background
- Identify whether or not these metals should be retained as chemicals of potential concern or chemicals of potential ecological concern in the DEQ cleanup process.

Use of regional default background concentrations

The regional default background concentrations for metals in soils presented in Table 1 represent the 95 percent upper prediction limit for 16 metals in 10 regions of Oregon. The numbers can be used by comparing the maximum detected concentration from a site database with the default background concentration for the appropriate region. If the maximum detected concentration is less than the default value, then that metal is not present in site soil above background levels and that metal is not a chemical of potential concern or potential ecological concern.

Last Updated: 3/20/2013
By: Annette Dietz

DEQ may develop additional guidance describing alternate methods to evaluate background samples such as statistical comparative screening techniques, hypothesis testing or application of geochemical evaluation techniques, in the future.

Alternate sources of background values

DEQ recognizes that at some sites it may be appropriate to use background values other than the regional default background metals concentrations. Any of the following options may be used to define natural background concentrations for metals at cleanup sites:

1) Site-specific background evaluations (i.e., a background evaluation done on un-impacted areas of similar soil type at or in the immediate vicinity of the subject site)
2) Site-specific background evaluations previously completed in the site's vicinity
3) DEQ regional default background concentrations

Transboundary soil transport

As shown in Figure 1 and Table 1, background levels for metals can vary from one region to the next. DEQ project managers need to carefully evaluate site-specific requirements when selecting a cleanup remedy including a "clean" soil cap by specifying background concentrations for the region where the facility is located in the Record of Decision.

DEQ Solid Waste makes determinations regarding soil that qualifies as "clean fill" for other circumstances. Contact Bill Mason, (541) 687-7427, for more information about the definition of clean fill.

Disclaimer

This document provides information and technical assistance to the public and DEQ employees about DEQ's Cleanup Program. This information should be interpreted and used in a manner fully consistent with the state's environmental cleanup laws and implementing rules. This document does not constitute rulemaking by the Oregon Environmental Quality Commission and may not be relied on to create a right or benefit, substantive or procedural, enforceable at law or in equity, by any person, including DEQ employees. DEQ may take action at variance with this guidance.

For more information

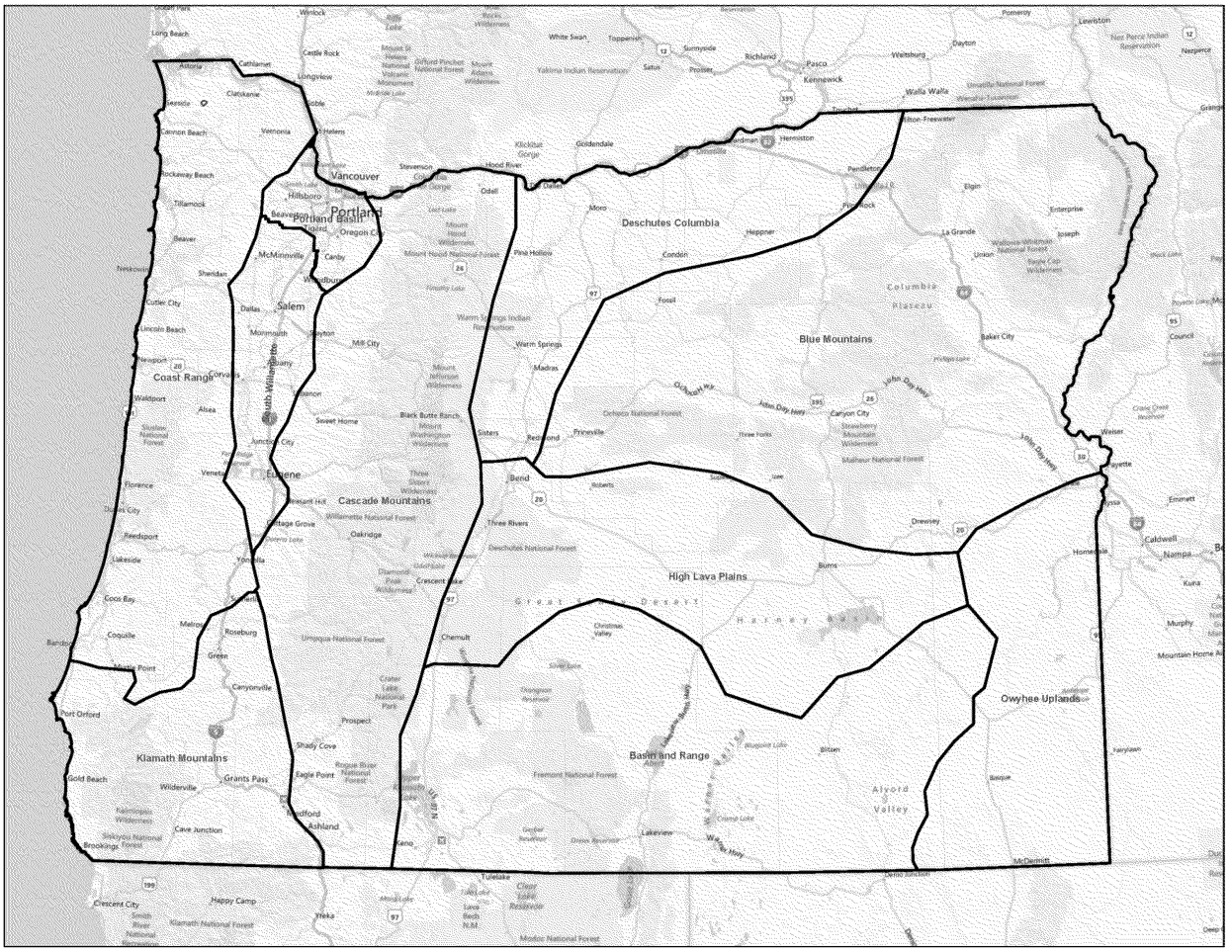
Contact Annette Dietz, DEQ Cleanup Program coordinator, Portland, 503-229-6258, or call toll-free in Oregon at 800-452-4011, ext. 6258.

Alternative formats

Alternative formats of this document can be made available. Contact DEQ's Office of Communications and Outreach, Portland, for more information at 503-229-5696, or call toll-free in Oregon at 800-452-4011, ext. 5696. People with hearing impediments may call 711.

Background Levels of Metals in Soils for Cleanups

Figure 1. Regional Boundaries for Default Background Metals Concentrations in Soil



Background Levels of Metals in Soils for Cleanups

Table 1. Regional Default Background Concentrations for Metals in Soil
State of Oregon

All concentrations in mg/kg

Metal	Basin and Range	Blue Mountains	Cascade Range	Coast Range	Deschutes - Columbia Plateau	High Lava Plains	Klamath Mountains	Owyhee Uplands	South Willamette Valley	Portland Basin
Antimony	0.86 (a)	N/A (c)	0.67 (a)	0.55 (a)	1.3 (a)	0.35 (a)	0.59 (a)	N/A (d)	0.39 (a)	0.56 (b)
Arsenic	12 (a)	14 (a)	19 (a)	12 (b)	6.8 (b)	7.2 (a)	12 (a)	17 (a)	18 (b)	8.8 (b)
Barium	790 (b)	950 (b)	630 (b)	840 (b)	700 (b)	790 (b)	630 (b)	970 (b)	730 (b)	790 (b)
Beryllium	2.4 (a)	2.6 (a)	2.1 (a)	2.8 (a)	2.6 (a)	2.6 (a)	1.4 (a)	2.0 (b)	2.6 (a)	2.0 (b)
Cadmium	0.81 (a)	0.69 (a)	0.54 (a)	0.54 (a)	0.40 (a)	0.78 (a)	0.52 (a)	N/A (c)	1.6 (a)	0.63 (a)
Chromium	100 (b)	190 (b)	200 (b)	240 (b)	170 (b)	140 (b)	890 (b)	120 (b)	100 (b)	76 (b)
Copper	110 (b)	120 (b)	73 (b)	100 (a)	29 (b)	62 (b)	110 (b)	50 (b)	140 (b)	34 (b)
Lead	29 (a)	21 (a)	34 (a)	34 (a)	18 (b)	21 (b)	36 (a)	30 (a)	28 (a)	79 (b)
Manganese	1600 (b)	1800 (b)	2100 (b)	2100 (b)	1300 (b)	1500 (b)	3000 (b)	1200 (b)	2900 (b)	1800 (b)
Mercury	0.28 (a)	1.4 (a)	0.24 (a)	0.11 (a)	0.040 (a)	0.060 (a)	0.17 (a)	0.75 (a)	0.070 (a)	0.23 (b)
Nickel	66 (b)	92 (b)	110 (a)	160 (b)	78 (b)	75 (b)	630 (b)	53 (b)	50 (b)	47 (b)
Selenium	0.41 (a)	0.93 (a)	0.52 (a)	1.5 (a)	0.46 (a)	0.54 (a)	0.80 (a)	0.49 (a)	0.68 (a)	0.71 (a)
Silver	0.42 (a)	0.51 (a)	0.17 (a)	0.41 (a)	0.82 (a)	0.68 (a)	0.16 (a)	2.2 (a)	0.33 (a)	0.82 (a)
Thallium	0.22 (a)	N/A (c)	2.8 (a)	5.4 (a)	4.6 (a)	0.21 (a)	0.31 (a)	N/A (d)	5.7 (a)	5.2 (a)
Vanadium	270 (b)	400 (b)	280 (b)	260 (b)	300 (b)	220 (b)	290 (b)	190 (b)	370 (b)	180 (b)
Zinc	130 (b)	160 (b)	170 (b)	140 (b)	130 (b)	140 (b)	140 (b)	120 (b)	200 (b)	180 (b)

Notes:
Data generated with ProUCL, Version 4.1.00
N/A = Not available
UPL = Upper prediction limit
(a) = 95% Kaplan-Meier UPL (t)
(b) = 95% UPL
(c) = Not Enough Samples
(d) = No Data

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SOILSOLUTIONS
ENVIRONMENTAL SERVICES

3540 SE 28th Avenue Portland, Oregon 97202

Office 503.234.2118
Toll Free 877.234.2118
Fax 503.331.7133

www.soilsolutionsenvironmental.com

Soil Sample Statement – As, Cd, Cr, Cr-VI, Pb, & Hg

February 18, 2016

Client: New Day School
Site address: 1825 SE Clinton St
Portland, OR 97202

- Soil samples were collected by Soil Solutions at the address listed above on February 10, 2016. Samples were collected at ground surface in locations identified by the client. The three composite soil samples were submitted to Friedman and Bruya Laboratory in Seattle, WA to be analyzed for the presence of arsenic, cadmium, chromium, lead, and mercury by EPA Method 6020A. The samples were also analyzed for the presence of hexavalent chromium. The laboratory report number 602174 dated February 16, 2016 showed detections in the soil samples as listed below.

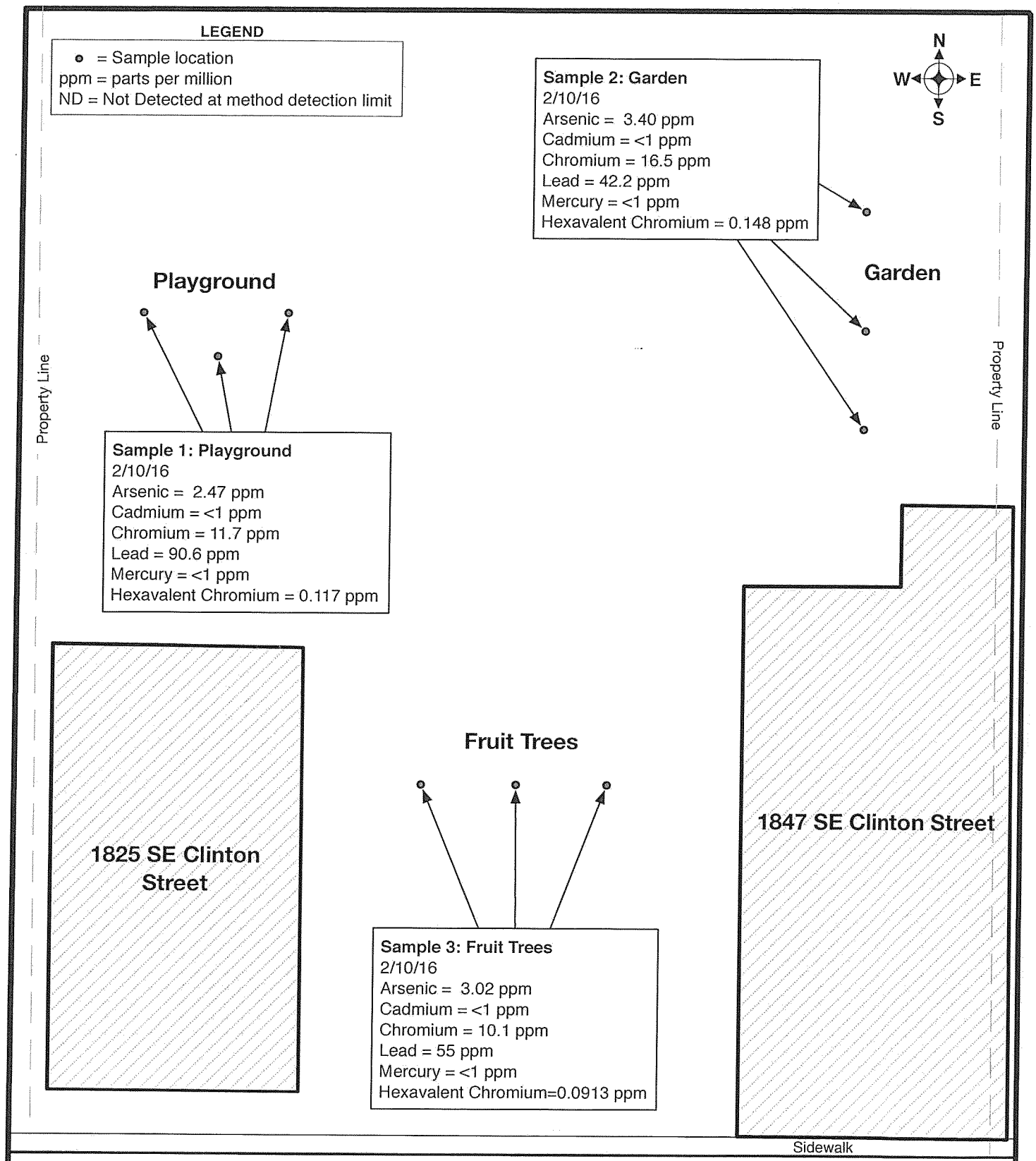
Sample ID	**Arsenic Results**	**Portland Background Level****	**OrDEQ RBC-** *Ingestion, Contact Inhalation****
Playground	**2.47 ppm**	8.8 ppm	0.43 ppm
Garden	**3.4 ppm**	8.8 ppm	0.43 ppm
Fruit Trees	**3.02 ppm**	8.8 ppm	0.43 ppm
Sample ID	**Cadmium Results**	**Portland Background Level****	**OrDEQ RBC-** *Ingestion, Contact Inhalation****
Playground	**<1 ppm**	0.63 ppm	78 ppm
Garden	**<1 ppm**	0.63 ppm	78 ppm
Fruit Trees	**<1 ppm**	0.63 ppm	78 ppm

Sample ID	**Total Chromium Results**	**Portland Background Level****	**OrDEQ RBC-** *Ingestion, Contact Inhalation****
Playground	**11.7 ppm**	76 ppm	120,000.3 ppm
Garden	**16.5 ppm**	76 ppm	120,000.3 ppm
Fruit Trees	**10.1 ppm**	76 ppm	120,000.3 ppm
Sample ID	**Chromium VI Results**	**Portland Background Level****	**OrDEQ RBC-** *Ingestion, Contact Inhalation****
Playground	**0.117 ppm**	-	0.3 ppm
Garden	**0.148 ppm**	-	0.3 ppm
Fruit Trees	**0.0913 ppm**	-	0.3 ppm

Sample ID	Lead Results	Portland Background Level**	OrDEQ RBC- *Ingestion, Contact Inhalation****
Playground	**90.6 ppm**	79 ppm	400 ppm
Garden	**42.2 ppm**	79 ppm	400 ppm
Fruit Trees	**55 ppm**	79 ppm	400 ppm
Sample ID	**Mercury Results**	**Portland Background Level****	**OrDEQ RBC-** *Ingestion, Contact Inhalation****
Playground	**<1 ppm**	0.23 ppm	23 ppm
Garden	**<1 ppm**	0.23 ppm	23 ppm
Fruit Trees	**<1 ppm**	0.23 ppm	23 ppm

**ppm (parts-per-million)*
*** Oregon Department of Environmental Quality (2013) Fact Sheet: Background Levels of Metals in Soils for Cleanups <http://www.deq.state.or.us/lq/pubs/docs/cu/FSbackgroundmetals.pdf>*
**** Oregon Department of Environmental Quality (2015) Risk Based Concentration Table <http://www.deq.state.or.us/lq/pubs/docs/RBDMTable.pdf>*

- As noted above, the measured arsenic concentrations exceed the strictest Oregon Department of Environmental Quality (DEQ) Risk Based Concentrations (RBCs) of metals in soil. The measured concentrations of arsenic, however, are all below the background levels for naturally occurring metals in the Portland area and therefore may not be related to recent concerns about industrial emissions of metals. Additionally, one of the detected lead concentrations exceed background levels of lead in soil in the Portland area, according to the Oregon Department of Environmental Quality (2013). This value is still well below the Oregon DEQ RBC for lead in soils.
- This investigation conducted by Soil Solutions is only a representation of the soil conditions at the surface for the approximate locations indicated on the attached map.



Soil Solutions Environmental Services, Inc.	Site Map with Sample Locations 1825 SE Clinton Street Portland, Oregon 97202	PROJECT: NEW DAY DATE: 2/10/16 SCALE 1" = 20'

To: McClintock, Katie[McClintock.Katie@epa.gov]
From: Doyle, Liz
Sent: Wed 2/24/2016 9:08:55 PM
Subject: FW: Glass mfg in R10
glass.xls

Hi Katie,

While I pursue other sources of data or literature on glass chemistry, I thought you might be interested in this spreadsheet of R10 glass companies in Region 10.

Liz Doyle, MILS

Supervisory Librarian (contractor, ASRC Primus)
U.S. EPA Region 10 Library / OMP-0102 / 1200 6th Ave, Ste 900
Seattle WA 98101-3140

doyle.**liz**@epa.gov

p: 206-553-2134
http://www2.epa.gov/libraries/region-10-library-services

From: Doyle, Liz
Sent: Thursday, February 04, 2016 2:24 PM
To: Lopez-Baird, James <Lopez-Baird.James@epa.gov>
Cc: 'R10-LIBRARY Mail Group (R10LIBRARY_Mail_Group@epa.gov)' <R10LIBRARY_Mail_Group@epa.gov>
Subject: Glass mfg in R10

Dear James,

This is your spreadsheet to save, sort, modify, etc. as you wish. I'll keep in on file for a while in case you need it again. Comments, questions, suggestions? Let me know.

Please don't hesitate to contact us again if you have further questions.

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http://www.surveymonkey.com/s/epalibsurvey

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- test methods
- legal or regulatory research
- company research

Liz Doyle, MILS

Supervisory Librarian (contractor, ASRC Primus)
U.S. EPA Region 10 Library / OMP-0102 / 1200 6th Ave, Ste 900
Seattle WA 98101-3140
http://204.47.216.153:9876/r10/infopage/infopage.nsf/webpage/Region+10+Library

doyle.liz@epa.gov

p: 206-553-2134

The EPA Region 10 Library serves EPA staff and all residents of Alaska, Idaho, Oregon, and Washington. We can help locate technical EPA information, publications, regulations, legislation, guidance, and more. Hours are M-F, 9:00 - 12, and 1 - 4 at our Seattle location, except on Federal Holidays.

To: Vergeront, Julie[Vergeront.Julie@epa.gov]
From: McClintock, Katie
Sent: Thur 2/4/2016 8:10:30 PM
Subject: if you have it, can you send me your old bullseye case?

Katie McClintock

Air Enforcement Officer

EPA Region 10

1200 Sixth Avenue, Suite 900, OCE-101

Seattle, WA 98101

Phone: 206-553-2143

Fax: 206-553-4743

Mcclintock.katie@epa.gov

To: McClintock, Katie[McClintock.Katie@epa.gov]; Narvaez, Madonna[Narvaez.Madonna@epa.gov]
From: Narvaez, Madonna
Sent: Wed 2/24/2016 5:36:03 PM
Subject: Conversation with McClintock, Katie

Narvaez, Madonna 9:19 AM:

I didn't get to ask you about North Star(?) glass you visited. 120k pounds exceeds the 50 tpy threshold. Are the furnaces continuous? Do you know if any hotspots show up around the facility?

McClintock, Katie 9:20 AM:

they have many units (i can't tell you how many in writing since cbi). per unit under the 50 tpy

let's talk more about your questions

Narvaez, Madonna 9:23 AM:

Also, could you please add Katie Owens to the Colored Glass OneDrive. Thanks!

McClintock, Katie 9:24 AM:

yep

To: McClintock, Katie[McClintock.Katie@epa.gov]; Narvaez, Madonna[Narvaez.Madonna@epa.gov]
From: McClintock, Katie
Sent: Fri 2/19/2016 6:12:44 PM
Subject: Conversation with McClintock, Katie

McClintock, Katie 9:46 AM:

they are selling wissmach and bullseye glass

Narvaez, Madonna 9:48 AM:

Okay. Do you know if Bullseye is doing any chrome plating? I didn't do a search of any chrome plating shops in the area. I would hope that DEQ would have mentioned that.

McClintock, Katie 9:49 AM:

i don't know

we did not see coating operations there (but they might just not have been coating that product)

uroboros was coating and it was tin. Spectrum wasn't coating but then can with tin and titanium

Narvaez, Madonna 9:53 AM:

I just got a question from someone in Portland asking we are going to be any monitoring at other schools in southeast Portland.

McClintock, Katie 9:55 AM:

i don't know. good question

are you getting lots of public questions?

Narvaez, Madonna 10:00 AM:

That was the first today. :-)

The schools she mentioned did not show up as troublesome on the 2005 NATA.

From: Wroble, Julie
Location: R10Sea-Room-12Maple/R10-Rooms-Service-Center
Importance: Normal
Subject: Tentative: hold for bullseye conversation if necessary
Start Date/Time: Mon 2/8/2016 10:00:00 PM
End Date/Time: Mon 2/8/2016 11:00:00 PM