Attorney General
1275 WEST WASHINGTON
Phoenix, Arizona 85007
Robert K. Corbin

September 19, 1983

INTERAGENCY
Mr. Donald B. Mathis
Director
Arizona Department of Health Services
1740 West Adams Street
Phoenix, AZ 85007

SEP 2 0 1983

Re: A. G. Rule No. 83-111

Dear Mr. Mathis:

We have reviewed the above-referenced rule approved by the Department of Health Services in January 1983. We have determined that the rules are in proper form and within the Department's authority to adopt.

Accordingly, pursuant to A.R.S. § 41-1002.01, I have affixed my certification to the original Form R102 and have forwarded the same together with the original Order of Rule Adoption and two copies of each to the Secretary of State.

We have enclosed a copy for your reference.

Very truly yours,

Bob Corbin

BOB CORBIN
Attorney General

BC:JKW:cmb

Enclosure

Certified approved Sep. 19, 1983

A.G. RULE NO: 83-111

FOR USE BY SECRETARY OF STATE

Rose Mofford
Secretary of State

State of Arizona
Capitol, West Wing, Suite 706
Phoenix 85007

CERTIFICATION OF RULES AND ORDER OF RULE PROMULGATION

1 **Name of Agency, Board, Commission, Department, Officer**
Arizona Department of Health Services

2 **Name of person to call re document** — Telephone #
Lloyd J. Rowe — 255-1140

3 **Statutory Authority for Promulgating Rules:** A.R.S. §§ 36-1706, 36-1707, 36-1707.01, 36-1707.02, 36-1719

4 **Date Form R101 Filed**
2/8/83

5 **Date Published in Administrative Digest**
3 (Vol.) 4 (Issue) A.A.D. 78-79 (Page) 4/1/83 (Date)

6 **Date Rules Promulgated subject to Certification by Attorney General**

7 **Check and complete applicable items below to show Action taken:**

[X] REPEALED See Attachment I
A.C.R.R. Rule Number(s)

[X] ADOPTED See Attachment I
A.C.R.R. Rule Number(s)

[X] AMENDED See Attachment I
A.C.R.R. Rule Number(s)

[X] Incorporation by Reference to A.C.R.R. R9-3-215 (incl. Air Quality Monitoring Procedures Manual); R9-3-310 (Arizona Testing Manual); R9-3-402 (incl. Open Burning Guidelines for Air Pollution Control) [one (1) copy of document is attached].
Rule Number(s)

8 [ ] **Check if this action was previously promulgated as an emergency. See R1-2-203.01.**

9 **Check the applicable item for effective date:**

[X] Date filed with the Office of the Secretary of State
[ ] Other (pursuant to A.R.S. § 41-1005) (Other date)

10 **Certificate of Authorized Officer**
Donald B. Mathis
Signature of Officer
Director — 255-1024
Title — Telephone
Donald B. Mathis — 8/2/83
Name (typed) of Officer — Date

11 **Certificate of approval and certification by the Attorney General**
A.G. Rule No. 83-111
APPROVED AND CERTIFIED pursuant to A.R.S. § 41-1002.01 this 19th day of Sept., 19 83
BOB CORBIN Bob Corbin
Attorney General

Rev. 4/83 Form R102

A.G. RULE NO: 83-111

ATTACHMENT I

REPEAL Appendix 4

ADOPT R9-3-215 (incl. Air Quality Monitoring Procedures Manual). R9-3-321, R9-3-322, R9-3-323, R9-3-529, R9-3-709, R9-3-835, R9-3-838, R9-3-845.

AMEND R9-3-101, R9-3-201 through R9-3-207, R9-3-218, R9-3-301, R9-3-307, R9-3-310 (Arizona Testing Manual), R9-3-402 (incl. Open Burning Guidelines for Air Pollution Control) R9-3-404, R9-3-502, R9-3-503, R9-3-505, R9-3-508 through R9-3-513, R9-3-515 through R9-3-518, R9-3-520 through R9-3-522, R9-3-524, R9-3-529, R9-3-703, R9-3-705, R9-3-1101, Appendix 1, Appendix 11.

ADM:LJR:7250

A.G. RULE NO: 83-111

ORDER OF ADOPTION

BUREAU OF AIR QUALITY CONTROL HEARING OF APRIL 28, 1983

Submitted By:	Page	Line	Description
Salt River Project	10	8, 9	Add "as a guide to be used in assessing implementation plans to achieve the 24-hour standard" per the Federal Register.
Bureau of Air Quality Control (BAQC)	13	2	Delete R9-3-203 Hydrocarbons and change to reserved. Federal standard was repealed by Federal Register of January 5, 1983 and ARS 36-1707.A prohibits State ambient standard from being more restrictive than Federal standard.
ASARCO	20	10, 11	Add "for each pollutant" and "and the standard for ozone" for clarification.
ASARCO	23	27	Substitute alternate language for clarification.
BAQC	25	14	Add "GEP" to correct typographical omission.
BAQC	27	17 thru 20	Enters document entitled "Open Burning Guidelines for Air Pollution Control" into record and thus regulatory system.
R. R. Donnelley	31	21 thru 24	Withdraw Subsection R9-3-502.K. Following comments from R. R. Donnelley, BAQC recommends more study.
Salt River Project	32	10	Add word "reconstruction" for clarity.

Submitted By:	Page	Line	Description
Salt River Project	38	9	Add and delete ~~58~~; underline 79. Underline 81 of D-439-~~70~~ 81.
Phelps Dodge & Kennecott Magma	44.a 44 b	2 10, 11 13, 14	Rectifies "internal inconsistency" re. the period for determining compliance with cumulative occurance emission limitations under MPR.
BAQC	51	9 thru 14	Delete A.5.b. re. odor masking.
BAQC & Environmental Defense Fund (EDF)	64	7 thru 11	Starting at "finding" add. An application to the Director for a second NSO shall contain a finding by the Administrator of EPA that the means proposed by source have been demonstrated to be reasonably available technology as defined by Section 119 of the CAA.
EDF	64	16	Add "the Federal Clean Air Act" (CAA) for clarification.
EDF	64	19, 20	Add "and the EPA Administrator" and "for incorporation as a condition of the NSO".
BAQC	66 & 67	9, 16	Revised as to form only to standarize.
BAQC	71	All	Withdraw Appendix 4, Fee Schedule For Installation And Operating Permits to comply with newly passed HB 2415, approved by the Governor on April 19, 1983. The new wording relating to permit fees is as follows: ". . . .subject to payment, upon issuance, of a reasonable fee based on the actual cost of processing the permit applications, but not exceeding six thousand six hundred dollars for an installation permit and five thousand five hundred dollars for an initial operating permit."

AIR QUALITY MONITORING PROCEDURES MANUAL

Submitted By:	Page	Paragraph	Subject	Context of Change
Tucson Electric Power and BAQC	4	1.3.1.1	Precision	Substitute 16 and 20 for 25 and 75.
Tucson Electric Power and BAQC	5	1.3.1.2	Accuracy	Amend Concentration Range % of Full Scale.

DIRECTOR OF THE DEPARTMENT OF HEALTH SERVICES

Order of Adoption

Pursuant to A.R.S. § 36-1706, 36-1707, 36-1707.01, 36-1707.02 and 36-3719, as amended Laws 1980, the Director of the Department of Health Services proposes to adopt rules similar in substance, terms and conditions to the wording of the following:

1 Part 1. Section R9-3-101, Definitions, is amended to read as follows:

2 R9-3-101. Definitions

3 In these Rules and Regulations the following definitions in this Section

4 shall govern, unless the context otherwise requires, and unless in conflict

5 with a definition given in Article 8, New Source Performance Standards, or in

6 Article 9, Hazardous Air Pollutant Standards. In such case, the definitions

7 given in Article 8 or 9 shall apply only to sources covered by those Articles,

8 and the definitions given in this Section shall govern elsewhere.

9 1 - 28 No change.

10 29. "Categorical sources" means the following classes of sources:

11 a. Coal cleaning plants (with thermal dryers);

12 b. Kraft pulp mills;

13 c. Portland cement plants;

14 d. Primary zinc smelters;

15 e. Iron and steel mills;

16 f. Primary aluminum ore reduction plants;

17 g. Primary copper smelters;

18 h. Municipal incinerators capable of charging more than 250 tons of

19 refuse per day;

20 i. Hydrofluoric, sulfuric, or nitric acid plants;

21 j. Petroleum refineries;

22 k. Lime plants;

23 l. Phosphate rock processing plants;

24

25

m. Coke oven batteries;

n. Sulfur recovery plants;

o. Carbon black plants (furnace process);

p. Primary lead smelters;

q. Fuel conversion plants;

r. Sintering plants;

s. Secondary metal production plants;

t. Chemical process plants;

u. Fossil-fuel boilers (or combination thereof) totaling more than 250 million Btu's per hour heat input;

v. Petroleum storage and transfer units with a total storage capacity exceeding 300,000 barrels;

w. Taconite preprocessing plants;

x. Glass fiber processing plants;

y. Charcoal production plants;

z. Fossil fuel-fired steam electric plants of more than 250 million Btu's per hour heat input.

aa. Lead-acid battery manufacturing plants.

bb. Asphalt processing and asphalt roofing manufacture.

30 - 50 No Change

51. "Dispersion technique" means any technique which attempts to affect the concentration of a pollutant in the ambient air by using that portion of a stack which exceeds good engineering practice stack height, varying the rate of emission of a pollutant according to atmospheric conditions of ambient concentrations of that pollutant, or by addition of a fan or reheater to obtain a less stringent emission limitation. The preceding sentence does not include:

a. The reheating of a gas stream, following use of a pollution control system, for the purpose of returning the gas to the temperature at which it was originally discharged from the facility generating the gas stream;

b. The use of smoke management in agricultural or silvicultural programs;

c. Combining the exhaust gases from several stacks into one stack.

51 - 53. Renumber as 52 - 54.

55. "Elevated terrain" means terrain which exceeds the top elevation of the good engineering practice stack as calculated under Definition 76 of this Section.

54 - 58. Renumber as 56 - 60.

61. "Excessive concentrations" for the purpose of determining good engineering practice stack height in a fluid model or field study means a maximum concentration due to downwash, wakes, or eddy effects produced by structures or terrain features which is at least 40 percent in excess of the maximum concentration experienced in the absence of such downwash, wakes, or eddy effects.

59 - 60. Renumber as 62 - 63.

64. "Facility" means an identifiable piece of stationary process equipment along with all associated air pollution equipment.

61 - 71. Renumber as 65 - 75.

76. "Good engineering practice (GEP) stack height" means the greater of:

a. 213.25 feet (65 meters);

b. Other stacks:

i. For stacks in existence on January 12, 1979 and for which the owner or operator had obtained all applicable preconstruction permits or approvals required under 40 CFR Parts 51 and 52 and A.C.R.R. R9-3-301, $H_g = 2.5H$,

ii. For all other stacks,

$H_g = H + 1.5L$, where

H_g = good engineering practice stack height, measured from the ground-level elevation at the base of the stack,

H = height of nearby structure(s) measured from the ground-level elevation at the base of the stack,

L = lesser dimension (height or projected width) of nearby structure(s);

c. The height demonstrated by a fluid model or a field study approved by the reviewing agency, which ensures that the emissions from a stack do not result in excessive concentrations of any air pollutant as a result of

atmospheric downwash, wakes, or eddy effects created by the source itself, structures, or terrain obstacles.

72 - 90. Renumber as 77 - 95.

91. Renumber as 96.

96. "Major stationary source" means:

a. No change.

b. No change.

~~c.---Any-physical-change-that-would-occur-at-a-stationary-source not-otherwise-qualifying-under-Subparagraphs-a.-and-b.,-above,-as-a-major stationary-source,-if-the-change-would-constitute-a-major-stationary-source by-itself,-or,~~

c. Any change to a minor source which would increase its emissions to the qualifying levels specified under Subparagraphs a. or b., above.

~~d.---Any-source-with-the-capability-of-generating-more-than-a-total of-seventy-five-(75)-tons-of-air-contaminants-per-day.~~

~~e.~~ d. No change.

~~f.~~ e. No change.

92. Renumber as 97.

98. "Miscellaneous metal parts and products" for purposes of industrial coating mean:

a. Large farm machinery (harvesting, fertilizing and planting machines, tractors, combines, etc.);

b. Small farm machinery (lawn and garden tractors, lawn mowers, roto-tillers, etc.);

c. Small appliances (fans, mixers, blenders, crock pots, dehumidifiers, vacuum cleaners, etc.);

d. Commercial machinery (office equipment, computers and auxiliary equipment, typewriters, calculators, vending machines, etc.);

e. Industrial machinery (pumps, compressors, conveyor components, fans, blowers, transformers, etc.);

f. Fabricated metal products (metal covered doors, frames, etc.); and

g. Any other industrial category which coats metal parts or products under the Standard Industrial Classification Code of Major Group 33 (primary metal industries), Major Group 34 (fabricated metal products), Major Group 35 (non-electric machinery), Major Group 36 (electrical machinery), Major Group 37 (transportation equipment), Major Group 38 (miscellaneous instruments), and Major Group 39 (miscellaneous manufacturing industries), except:

i. automobiles and light-duty trucks;

ii. metal cans;

iii. flat metal sheets and strips in the form of rolls or coils;

iv. magnet wire for use in electrical machinery;

v. metal furniture;

vi. large appliances;

vii. exterior of airplanes;

viii. automobile refinishing;

ix. customized top coating of automobiles and trucks, if production is less than 35 vehicles per day; and,

x. exterior of marine vessels.

93. Renumber as 99.

100. "Mobile or portable sources" mean combustion engines, machinery, and equipment which are capable of being operated in more than one county. The Director shall have original jurisdiction over these sources unless delegated in writing and shall be the sole arbiter in defining mobile or portable sources.

94 - 97. Renumber as 101 - 104.

105. "Nearby" as used in the GEP definition is that distance up to five times the lesser of the height or the width dimension of a structure but not greater than 0.8 km (one-half mile). The height of the structure is measured from the ground-level elevation at the base of the stack.

98 - 115. Renumber as 106 - 123.

124. "Plume impaction" means concentrations measured or predicted to occur when the plume interacts with elevated terrain.

116 - 125 Renumber as 125 - 134

135. "Reconstruction" of sources located in nonattainment areas will be presumed to have taken place where the fixed capital cost of the new components exceeds 50 percent of the fixed capital cost of a comparable entirely new stationary source. Any final decision as to whether reconstruction has occurred shall be made in accordance with the provisions of 40 CFR 60.15(f)(1)-(3). A reconstructed stationary source will be treated as a new stationary source for purposes of nonattainment area source review. In determining lowest achievable emission rate for a reconstructed stationary source, the provisions of 40 CFR 60.15(f)(4) shall be taken into account in assessing whether a new source performance standard is applicable to such stationary source.

126 - 141 Renumber as 136 - 151

152 "Stack" means any point in a source designated to emit solids, liquids, or gases into the air, including a pipe or duct but not including flares.

142 - 145 Renumber as 153 - 156

146 Renumber as 157

157. "Stationary source" means any building, structure, facility or installation which emits or may emit any air pollutant subject to regulation under this Chapter.

a. The following are not considered stationary sources for purposes of these Regulations:

i. Motor vehicles

ii. Fuel burning equipment which, in the aggregate with such other equipment of the applicant at the same location of property, other than a one or two family residence, is rated at less than 500,000 Btu's per hour.

iii. Agricultural vehicles or agricultural equipment used in normal farm operations.

b. "Building," "structure," "facility," or "installation" means, for sources located in attainment areas, all of the pollutant-emitting activities which belong to the same industrial grouping, are located on one or more contiguous or adjacent properties, and are under the control of the same person (or persons under common control). Pollutant-emitting activities shall be considered as part of the same industrial grouping if they belong to the same "Major Group" (i.e., which have the same first two digit code) as described in the "Standard Industrial Classification Manual, 1972," as amended by the 1977 Supplement (U.S. Government Printing Office stock numbers 4101-0066 and 003-005-00176-0, respectively).

c. "Building," "structure," or "facility" means, for sources located in nonattainment areas, all of the pollutant-emitting activities which belong to the same industrial grouping, are located on one or more contiguous or adjacent properties, and are under the control of the same person (or persons under common control). Pollutant-emitting activities shall be considered as part of the same industrial grouping if they belong to the same "Major Group" (i.e., which have the same two digit code) as described in the "Standard Industrial Classification Manual, 1972," as amended by the 1977 Supplement (U.S. Government Printing Office stock numbers 4101-0066 and 003-005-00176-0, respectively).

d. "Installation" means, for sources located in nonattainment areas, an identifiable piece of process equipment.

158. "Statutory major source" means a stationary source which is capable of generating more than seventy-five (75) tons of uncontrolled air contaminants per day or, having less emissions, has been designated as a class by the Director to be a major source. The following classifications have been so designated by the Director:

a. The smelting of copper ore.

b. The refining of crude oil.

147 - 158. Renumber as 159 - 170.

Part 2. Section R9-3-201, Particulate matter, is amended to read as follows:

R9-3-201. Particulate matter

A. The primary ambient air quality standards for particulate matter are:

1. 75 micrograms per cubic meter - annual geometric mean.

2. 260 micrograms per cubic meter - maximum 24-hour concentration not to be exceeded more than once per year.

B. The secondary ambient air quality standards for particulate matter are:

1. 60 micrograms per cubic meter - annual geometric mean, <u>as a guide to be used in assessing implementation plans to achieve the 24-hour standard.</u>

2. 150 micrograms per cubic meter - maximum 24-hour concentration not to be exceeded more than once a year.

~~C.-----Except-as-provided-under-Subsections-D-and-E-below,-particulate concentrations-shall-be-measured-by-the-reference-method-described-in-40-CFR-50, Appendix-B,-or-by-one-of-the-following:~~

~~1.-----A-method-of-measurement-that-has-been-designated-prior-to-June-18, 1980,-as-a-reference-or-equivalent-method-by-the-Administrator-acting-pursuant-to 40-CFR-53.~~

~~2.-----A-method-of-measurement-that,-though-not-designated-as-a-reference-or equivalent-method,-has-been-approved-for-use-prior-to-June-18,-1980,-by-the-Administrator-acting-pursuant-to-40-CFR-51.17-a.--Such-method-shall-be-subject-to-any restrictions-placed-on-its-use-by-the-Administrator.~~

~~D.-----The-director-may-approve-additional-methods-of-measurement-upon-a finding-that:~~

~~1.-----The-method-of-measurement-proposed-for-use-has-been-designated,-subsequent-to-June-18,-1980,-a-reference-or-equivalent-method-by-the-Administrator acting-pursuant-to-40-CFR-53.~~

~~2.-----The-accuracy-and-other-performance-specifications-of-the-method-of~~

~~measurement for which approval is sought make that method substantially equivalent or superior to methods previously approved for use.~~

~~E. The cancellation or supersession of designation of a reference or equivalent method, subsequent to June 13, 1980, by the Administrator acting pursuant to 40 CFR §53.11 and 40 CFR §53.16, shall also amount to a withdrawal of the authorization for use of that method for purposes of this Regulation. However, such withdrawal of the authorization shall not become effective until the Director has determined that such withdrawal was supported by sufficient evidence and has specified a period of not less than nine (9) months in which existing, non approved analyzers may be replaced.~~

Part 3. Section R9-3-202, Sulfur oxides (sulfur dioxide) is amended to read as follows:

R9-3-202. Sulfur oxides (sulfur dioxide)

A. The primary ambient air quality standards for sulfur oxides, measured as sulfur dioxide, are:

1. 80 micrograms per cubic meter (0.03 ppm) - annual arithmetic mean.

2. 365 micrograms per cubic meter (0.14 ppm) - maximum 24-hour concentration not to be exceeded more than once per year.

B. The secondary ambient air quality standard for sulfur oxides measured as sulfur dioxide is 1300 micrograms per cubic meter (0.5 ppm) maximum 3-hour concentration not to be exceeded more than once per year.

~~C. Except as provided under Subsections D. and E. below, sulfur dioxide concentrations shall be measured by the reference method described in 40 CFR 50, Appendix A, or by one of the following:~~

1. A method of measurement that has been designated, prior to June 13, 1980, as a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.

2. A method of measurement that, though not designated as a reference or equivalent method, has been approved for use prior to June 13, 1980, by the Administrator acting pursuant to 40 CFR 51.17 a. Such method shall be subject to any restrictions placed on its use by the Administrator.

B. The Director may approve additional methods of measurement upon a finding that:

1. The method of measurement proposed for use has been designated, subsequent to June 13, 1980, a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.

2. The accuracy and other performance specifications of the method of measurement for which approval is sought make that method substantially equivalent or superior to methods previously approved for use.

C. The cancellation or supersession of designation of a reference or equivalent method, subsequent to June 13, 1980, by the Administrator acting pursuant to 40 CFR 53.11 and 40 CFR 53.16, shall also amount to a withdrawal of authorization for use of that method for purposes of this Regulation. However, such withdrawal of authorization shall not become effective until the Director has determined that such withdrawal was supported by sufficient evidence and has specified a period of not less than nine (9) months in which existing, non-approved analyzers may be replaced.

Part 4. Section R9-3-203, Hydrocarbons, is amended to read as follows:

R9-3-203. ~~Hydrocarbons~~ Reserved

~~A.---For purposes of this Chapter, the hydrocarbons standard is for use only as a guide to assist the State in devising strategies to achieve the ambient air quality standards for ozone contained in R9-3-204.~~

~~B.---The primary and secondary standard for hydrocarbons, measured and corrected for methane, is 160 micrograms per cubic meter (0.24 ppm)---maximum 3-hour concentration (6 to 9 a.m.) not to be exceeded more than once per year.~~

~~C.---Except as provided under Subsections D. and E. below, hydrocarbons concentrations shall be measured by the reference method described in 40 CFR 50, Appendix E, or by one of the following:~~

~~1.---A method of measurement that has been designated, prior to June 18, 1980, as a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.~~

~~2.---A method of measurement that, though not designated as a reference or equivalent method, has been approved for use prior to June 18, 1980, by the Administrator acting pursuant to 40 CFR 51.17.a.--Such method shall be subject to any restrictions placed on its use by the Administrator.~~

~~D.---The Director may approve additional methods of measurement upon a finding that:~~

~~1.---The method of measurement proposed for use has been designated, subsequent to June 18, 1980, a reference or equivalent by the Administrator acting pursuant to 40 CFR 53.~~

~~2.---The accuracy and other performance specifications of the method of measurement for which approval is sought make that method substantially equivalent or superior to methods previously approved for use.~~

~~E.------The cancellation or supersession of designation of a reference or equivalent method, subsequent to June 13, 1980, by the Administrator acting pursuant to 40 CFR 53.11 and 40 CFR 53.16, shall also amount to a withdrawal of authorization for use of that method for purposes of this Regulation. However, such withdrawal of authorization shall not become effective until the Director has determined that such withdrawal was supported by sufficient evidence and has specified a period of not less than nine (9) months in which existing, non-approved analyzers may be replaced.~~

Part 5. Section R9-3-204, Ozone, is amended to read as follows:

R9-3-204. Ozone

A. The primary and secondary ambient air quality standard for ozone is 0.12 ppm (235 micrograms per cubic meter). The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm (235 micrograms per cubic meter) is equal to or less than one (1), as determined by 40 CFR 50, Appendix H.

~~B.------Except as provided under Subsections C. and D. below, ozone concentrations shall be measured by the reference method described in 40 CFR 50, Appendix D, or by one of the following:~~

~~1.------A method of measurement that has been designated, prior to June 13, 1980, as a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.~~

~~2.------A method of measurement that, though not designated as a reference or equivalent method, has been approved for use prior to June 13, 1980, by the Administrator acting pursuant to 40 CFR 51.17 a.--Such method shall be subject to any restrictions placed on its use by the Administrator.~~

~~C. The Director may approve additional methods of measurement upon a finding that:~~

~~1. The method of measurement proposed for use has been designated, subsequent to June 13, 1980, a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.~~

~~2. The accuracy and other performance specifications of the method of measurement for which approval is sought make that method substantially equivalent or superior to methods previously approved for use.~~

~~D. The cancellation or supersession of designation of a reference or equivalent method, subsequent to June 13, 1980, by the Administrator acting pursuant to 40 CFR 53.11 and 40 CFR 53.16, shall also amount to a withdrawal of authorization for use of that method for purposes of this Regulation. However, such withdrawal of authorization shall not become effective until the Director has determined that such withdrawal was supported by sufficient evidence and has specified a period of not less than nine (9) months in which existing, non-approved analyzers may be replaced.~~

Part 6. Section R9-3-205, Carbon monoxide, is amended to read as follows:

R9-3-205. Carbon monoxide

A. The primary and secondary ambient air quality standards for carbon monoxide are:

1. 10 milligrams per cubic meter (9 ppm) - maximum 8-hour concentration not to be exceeded more than once per year.

2. 40 milligrams per cubic meter (35 ppm) - maximum 1-hour concentration not to be exceeded more than once per year.

3.------Except as provided under Subsections C. and D. below, carbon monoxide concentrations shall be measured by the reference method described in 40 CFR 50, Appendix C, or by one of the following:

1.------A method of measurement that has been designated, prior to June 13, 1980, as a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.

2.------A method of measurement that, though not designated as a reference or equivalent method, has been approved for use prior to June 13, 1980, by the Administrator acting pursuant to 40 CFR 51.17 a.---Such method shall be subject to any restrictions placed on its use by the Administrator.

C.------The Director may approve additional methods of measurement upon a finding that:

1.------The method of measurement proposed for use has been designated, subsequent to June 13, 1980, a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.

2.------The accuracy and other performance specifications of the method of measurement for which approval is sought make that method substantially equivalent or superior to methods previously approved for use.

D.------The cancellation or supersession of designation of a reference or equivalent method, subsequent to June 13, 1980, by the Administrator acting pursuant to 40 CFR 53.11 and 40 CFR 53.16, shall also amount to a withdrawal of authorization for use of that method for purposes of this Regulation.---However, such withdrawal of authorization shall not become effective until the Director has determined that such withdrawal was supported by sufficient evidence and has specified a period of not less than nine (9) months in which existing, non-approved analyzers may be replaced.

Part 7. Section R9-3-206, Nitrogen dioxide, is amended to read as follows:

R9-3-206. Nitrogen dioxide

A. The primary and secondary ambient air quality standard for nitrogen dioxide is 100 micrograms per cubic meter (0.05 ppm) - annual arithmetic mean.

~~B. Except as provided under Subsections C. and D. below, nitrogen dioxide concentrations shall be measured by the reference method described in 40 CFR 50, Appendix F, or by one of the following:~~

~~1. A method of measurement that has been designated, prior to June 18, 1980, as a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.~~

~~2. A method of measurement that, though not designated as a reference or equivalent method, has been approved for use prior to June 18, 1980, by the Administrator acting pursuant to 40 CFR 53.17 b. Such method shall be subject to any restrictions placed on its use by the Administrator.~~

~~C. The Director may approve additional methods of measurement upon a finding that:~~

~~1. The method of measurement proposed for use has been designated, subsequent to June 18, 1980, a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.~~

~~2. The accuracy and other performance specifications of the method of measurement for which approval is sought make that method substantially equivalent or superior to methods previously approved for use.~~

~~D. The cancellation or supersession of designation of a reference or equivalent method, subsequent to June 18, 1980, by the Administrator acting pursuant to 40 CFR 53.11 and 40 CFR 53.16, shall also amount to a withdrawal of authorization for use of that method for purposes of this Regulation. However,~~

~~such withdrawal of authorization shall not become effective until the Director has determined that such withdrawal was supported by sufficient evidence and has specified a period of not less than nine (9) months in which existing, non-approved analyzers may be replaced.~~

Part 8. Section R9-3-207, Lead, is amended to read as follows:

R9-3-207. Lead

A. The primary and secondary ambient air quality standard for lead and its compounds, measured as elemental lead, is 1.5 micrograms per cubic meter, maximum arithmetic mean averaged over a calendar quarter.

~~B. Lead concentrations shall be measured by the reference method described in 40 CFR 50, Appendix G, or by one of the following:~~

~~1. A method of measurement that has been designated prior to June 13, 1980, as a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.~~

~~2. A method of measurement that, though not designated as a reference or equivalent method, has been approved for use prior to June 13, 1980, by the Administrator acting pursuant to 40 CFR 51.17 a. Such method shall be subject to any restrictions placed on its use by the Administrator.~~

~~C. The Director may approve additional methods of measurement upon a finding that:~~

~~1. The method of measurement proposed for use has been designated, subsequent to June 13, 1980, a reference or equivalent method by the Administrator acting pursuant to 40 CFR 53.~~

~~2. The accuracy and other performance specifications of the method of~~

~~measurements for which approval is sought make that method substantially equivalent or superior to methods previously approved for use.~~

~~9. The cancellation or supersession of designation of a reference or equivalent method, subsequent to June 18, 1980, by the Administrator acting pursuant to 40 CFR 53.11 and 40 CFR 53.16, shall also amount to a withdrawal of authorization for use of that method for purposes of this Regulation. However, such withdrawal of authorization shall not become effective until the Director has determined that such withdrawal was supported by sufficient evidence and has specified a period of not less than nine (9) months in which existing, non-approved analyzers may be replaced.~~

Part 9. Section R9-3-215, is adopted to read as follows:

R9-3-215. Ambient air quality monitoring methods and procedures

A. Only those methods which have been either designated by the Administrator as reference or equivalent methods or approved by the Director shall be used to monitor ambient air.

B. Quality assurance, monitor siting, and sample probe installation procedures shall be in accordance with procedures described in "Air Quality Monitoring Procedures Manual," Arizona Department of Health Services, September, 1982 (adopted herewith and on file with the Office of the Secretary of State). The Director may approve other procedures upon a finding that the proposed procedures are substantially equivalent or superior to procedures in the Manual. The Manual shall not apply to continuous sulfur dioxide monitoring performed by copper smelters which operate supplementary control systems because such monitoring is subject to the requirements in R9-3-704.

Part 10. Section R9-3-218. Violations, is amended to read as follows:

R9-3-218. Violations

~~A---Any-person-who-causes,-suffers,-allows-or-permits-the-emission-into the-ambient-air-of-any-substance-which-causes-a-measured-concentration-of air-contaminants-in-excess-of-the-ambient-air-quality-standards-set-forth in-this-Article-shall-be-guilty-of-violating-these-Regulations.~~

~~B---Ambient-air-quality-violations-measured-at-different-locations-but during-the-same-time-period-shall-constitute-separate-violations.~~

A. One exceedance per year of the ambient air quality standards in this Article, except for the annual and quarterly standards, and the standard for ozone, shall be allowed for each pollutant at each monitoring site. Each additional exceedance at each site shall constitute a violation of ambient air quality standards.

Part 11. Section R9-3-301, Installation permits: general, is amended to read as follows:

R9-3-301. Installation permits: general

A. No change

B. There shall be three clauses of installation permits:

1. No change.

2. No change.

3. Class C permits shall be issued to persons proposing to commence construction of or make a modification to a minor source. Minor sources which do not emit any pollutant at greater than or equal to an emissions rate defined herein as "significant" shall not require an installation or operating permit, except that, stationary rotating machinery of greater than 325 brake

horsepower and fuel burning equipment or incinerators that are fired at a sustained rate of more than 500,000 Btu per hour for more than an eight-hour period shall require installation and operating permits as herein specified.

C. No Class A installation permit shall be issued to a person proposing to commence construction of a new major source or make a major alteration to a major source unless one of the following conditions is met:

1. A new major source or major alteration to a major source that is classified as a major source ~~solely because it is capable of generating more than a total of seventy-five tons per day of air pollutants regulated~~ under this Chapter and not because the source has ~~potential~~ controlled emissions of 100 or 250 tons per year (as applicable) of any single pollutant regulated under this Chapter, shall meet the following requirements:

a. The source or alteration shall comply with the general Class A installation permit requirements in Subsection D;

b. The source or alteration shall comply with the installation permit application requirements in Subsection E.

c. The source or alteration shall comply with the more stringent of the applicable new source performance standards in Article 8 or the existing source performance standards in Article 5; or,

2. ~~A new major source or major alteration to a major source, or~~ A new stationary source or alteration to a stationary source that emits 5 or more tons of lead per year, and not regulated under Paragraph 1 above shall meet the following requirements:

a. The source or alteration shall comply with all applicable provisions of Sections R9-3-302 through R9-3-305.

b. The source or alteration shall comply with the general Class A installation permit requirements of Subsection D.

c. The source or alteration shall comply with the installation permit application requirements of Subsection E.

D. through Q. No change.

Part 12. R9-3-307, Innovative control technology, is amended to read as follows:

R9-3-307. Innovative control technology.

A. No change.

B. The Director shall approve the installation of a system of innovative control technology if the following conditions are met:

1. No change.

2. No change.

3. No change.

4. Before the date specified in the installation permit, the source or alteration would not:

a. Cause or contribute to any violation of an applicable State ambient air quality standard; or,

b. Impact any portion of any Class I area; ~~where an applicable ambient incremental standard is known to be violated in that portion~~; or

c. Impact any portion of any other area where an applicable ambient incremental standard is known to be violated in that portion.

5. No change.

C. No change.

D. No change.

Part 12 A (R9-3-310, "Arizona Testing Manual for Air Pollutant Emissions" adopted May 14, 1979 and on file with the Office of the Secretary of State is amended herewith by reference.)

Part 13. R9-3-321 is adopted to read as follows:

R9-3-321. Operating permits containing the terms and conditions of primary non-ferrous smelter orders (NSO) or federal delayed compliance orders (DCO).

A. An operating permit containing the terms and conditions of either a DCO or NSO may be issued for a period of greater than one year corresponding to the life of the NSO or DCO. The Director may alter or amend the terms and conditions of an NSO or DCO operating permit as required for consistency with the Federal Clean Air Act, as amended.

B. The owner or operator of such a source shall be required to furnish the Director with a quarterly report of the status of the source and construction progress. Reporting by the owner of a source having an NSO or DCO shall conform as a minimum to Sections R9-3-703, R9-3-704, R9-3-705, and if applicable, R9-3-706. In addition, the Director shall receive copies of any reports to EPA under these orders. Certain additional reporting requirements and conditions may be specified by the Director in operating permits issued under this Section.

C. For the purpose of this Chapter, sources operating under a consent decree issued by a Federal court shall meet the same requirements as these with a DCO.

Part 14. R9-3-322 is adopted to read as follows:

1 R9-3-322. Temporary conditional permits

2 Temporary conditional permits may be issued by the Director in accord-

3 ance with Section 36-1711, Arizona Revised Statutes.

4

5

6 Part 15. R9-3-323 is adopted to read as follows:

7 R9-3-323. Stack height limitation

8 A. The limitations set forth herein shall not apply to stacks or dis-

9 persion techniques used by the owner or operator prior to December 31, 1970,

10 for which the owner or operator had:

11 1. Begun, or caused to begin, a continuous program of physical on-site

12 construction of the stack;

13 2. Entered into binding agreements or contractual obligations, which

14 could not be cancelled or modified without substantial loss to the owner or

15 operator, to undertake a program of construction of the stack to be completed

16 in a reasonable time; or

17 3. Coal fired steam electric generating units, subject to the provisions

18 of Section 118 of the Federal Clean Air Act which commenced operation before

19 July 1, 1975, with stacks constructed under a construction contract awarded

20 before February 8, 1974.

21 B. The degree of emission limitation required of any source after the

22 respective date given in Subsection A above for control of any pollutant

23 must not be affected by so much of any source's stack height that exceeds

24 good engineering practice or by any other dispersion technique.

25 C. The good engineering practice (GEP) stack height for any source

26 seeking credit because of plume impaction which results in concentrations

in violation of national ambient air quality standards or applicable prevention of significant deterioration increments can be adjusted by determining the stack height necessary to predict the same maximum air pollutant concentration on any elevated terrain feature as the maximum concentration associated with the emission limit which results from modelling the source using the GEP stack height as determined herein and assuming the elevated terrain features to be equal in elevation to the GEP stack height. If this adjusted GEP stack height is greater than stack height the source proposes to use, the source's emission limitation and air quality impact shall be determined using the proposed stack height and the actual terrain heights.

D. Before the State issues a permit to a source based on a good engineering practice stack height that exceeds the height allowed by Subparagraphs a. and b. of the GEP definition given herein, the State must notify the public of the availability of the demonstration study and must provide opportunity for public hearing on it.

Part 16. Section R9-3-402, Unlawful open burning, is amended to read as follows:

R9-3-402. Unlawful open burning

A. through C. No change.

1. through 4. No change.

5. Delete.

D. No change.

F. The following fires may be excepted from the provisions of this

Section when permitted in writing by the Director of the Department of Health Services or the control officer of the county, district or region in which such fire is allowed:

1. Fires set for the disposal of dangerous materials where there is no safe alternative method of disposal.

a. "Dangerous material" is any substance or combination of substances which is able or likely to inflict bodily harm or property loss unless neutralized, consumed or otherwise disposed of in a controlled and safe manner.

b. Fires set for the disposal of dangerous materials shall be permitted only when there is no safe alternative method of disposal, and when the burning of such materials does not result in the emission of hazardous or toxic substances either directly or as a product of combustion in amounts which will endanger health or safety.

2. Open outdoor fires for the disposal of ordinary household trash in an approved waste burner in non-urban areas of less than 100 well spread out dwelling units per square mile where no refuse collection and disposal service is available.

a. An "approved waste burner" is an incinerator constructed of fire resistant material with a cover or screen which is closed when in use having openings in the sides or top no greater than one inch in diameter.

b. Open burning of the following materials is forbidden: garbage resulting from the processing, storage, serving or consumption of food; asphalt shingles; tar paper; plastic and rubber products (such as waste crankcase oil, transmission oil and oil filters); transformer oils; and

hazardous material containers including those that contained inorganic pesticides, lead, cadmium, mercury, or arsenic compounds.

F. The Director of the Department of Health Services or the air pollution control officer, if any, of the county, district, or region may delegate the authority for the issuance of allowable open burning permits to responsible local officers. Such permits shall contain conditions limiting the manner and the time of the setting of such fires as specified in the Arizona Guidelines for Open Burning and shall contain a provision that all burning be extinguished at the discretion of the Director or his authorized representative during periods of inadequate atmospheric smoke dispersion, periods of excessive visibility impairment which could adversely affect public safety, or periods when smoke is blown into populated areas so as to create a public nuisance.

Part 16A. Section (R9-3-402,"Open Burning Guidelines for Air Pollution Control" was entered into the public record by the Bureau of Air Quality Control at the Public Hearing of April 28, 1983 and is hereby filed with the Secretary of State for adoption.)

1. Any local officer delegated the authority for issuance of open burning permits shall maintain a copy of all currently effective permits issued including a means of contacting the person authorized by the permit to set an open fire in the event that an order for extinguishing of open burning is issued.

~~F.~~ G No change.

Part 17. Section R9-3-404, Open areas, is amended to read as follows:

R9-3-404. Open areas, dry washes or riverbeds

A. No change.

B. No change.

C. No person shall operate a motor vehicle for recreational purposes in a dry wash, riverbed or open area in such a way as to cause or contribute to visible dust emissions which then cross property lines into a residential, recreational, institutional, educational, retail sales, hotel or business premises. For purposes of this Subsection "motor vehicles" shall include, but not be limited to trucks, cars, cycles, bikes, buggies and three-wheelers. Any person who violates the provisions of this Subsection shall be subject to prosecution under Section 36-1720, Arizona Revised Statutes.

Part 18. Section R9-3-502, Unclassified sources, is amended to read as follows:

R9-3-502. Unclassified sources

A. No existing major source which is not otherwise covered under any other Section of these Regulations shall cause or permit the emission of pollutants at rates greater than the following:

1. No person shall cause, suffer, allow or permit the discharge of

particulate matter into the atmosphere in any one hour from any unclassified process source ~~outside Gila, Maricopa, Pima, Pinal, or Santa Cruz counties~~ in total quantities in excess of the amounts calculated by the equations set forth below.

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight in tons-mass per hour.

b. For process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any unclassified process source located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below.~~

~~a. For process sources having a process rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 3.59P^{0.62}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~b.------For-process-industries-having-a-process-weight-rate-greater-than 60,000-pounds-per-hour-(30-tons-per-hour),-the-maximum-allowable-emissions shall-be-determined-by-the-following-equation:~~

$$\cancel{E = 17.31P^{0.16}}$$

~~where-"E"-and-"P"-are-defined-as-indicated-in-A.1.a.-above.~~

-3- 2. No change.

-4- 3. For reference only, the equations in A.1. ~~and-A.2.~~ above are plotted in Appendix 11, Figure 2. The emission values obtained from the graph are approximately correct for the process weight rates shown. However, the actual values shall be calculated from the applicable equations and rounded off to two decimal places.

-5- 4. No change.

-6- 5. No change.

B. through G. No change.

H. No person shall allow hydrogen cyanide to be emitted from any location in such manner and amount that the concentration of such emissions into the ambient air at any occupied place beyond the premises on which the source is located exceeds 0.3 parts per million by volume for any averaging period of 8 hours.

I. No person shall allow sodium cyanide dust or dust from any other solid cyanide to be emitted from any location in such manner and amount that the concentration of such emissions into the ambient air at any occupied place beyond the premises on which the source is located exceeds 140 micrograms per cubic meter for any averaging period of 8 hours.

J. No owner or operator of a facility engaged in the surface coating of miscellaneous metal parts and products may operate a coating application system subject to this regulation that emits volatile organic compounds in excess of:

1. 4.3 pounds per gallon (0.5 kilograms per liter) of coating, excluding water, delivered to a coating applicator that applies clear coatings:

2. 3.5 pounds per gallon (0.42 kilograms per liter) of coating, excluding water delivered to a coating applicator in a coating application system that is air dried or forced warm air dried at temperatures up to 194°F (90°C);

3. 3.5 pounds per gallon (0.42 kilograms per liter) of coating, excluding water, delivered to a coating applicator that applies extreme performance coatings; and,

4. 3.0 pounds per gallon (0.36 kilograms per liter) of coating, excluding water, delivered to a coating applicator for all other coatings and coating application systems.

5. If more than one emission limitation in this Subsection applies to a specific coating, then the least stringent emission limitation shall be applied.

6. All VOC emissions from solvent washings shall be considered in the emission limitations in this Subsection, unless the solvent is directed into containers that prevent evaporation into the atmosphere.

Part 19. Section R9-3-503. Standards of performance for existing fossil fuel fired steam generators and general fuel burning equipment, is amended to read as follows:

R9-3-503. Standards of performance for existing fossil-fuel fired steam generators and general fuel burning equipment

A. No change

B. No change

C. The provisions of this Section are applicable to fossil-fuel fired steam generating units or general fuel burning equipment which are existing sources or for which construction, reconstruction or major alteration has commenced prior to the effective date of this Section, ~~or~~ which are ~~of less~~ greater than or equal to 73 megawatts capacity.

1. through 6. No change

Part 20. Section R9-3-505. Standards of performance for existing portland cement plants, is amended to read as follows:

R9-3-505. Standards of performance for existing portland cement plants

A. No change

B. The provisions of this Section are applicable to all cement plants under State of Arizona jurisdiction which are existing sources.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter from any identifiable process source within ~~from the kilns of~~ any existing cement plant subject tohe provisions of this Section ~~and located in Gila, Maricopa, Pima, Pinal or Santa Cruz counties~~ which ~~is:~~

~~a. in excess of 0.30 pounds per ton of feed to the kilns.~~

~~b. Greater than 20 percent opacity.~~

~~2. No person shall cause, suffer, allow or permit the discharge of particulate matter from the stacks or other of any existing plant located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties which is:~~

~~a. In excess of 0.10 pound per ton of feed to the kilns.~~

~~b. Ten percent opacity or greater.~~

~~3. Other existing cement plant facilities within Gila, Maricopa, Pima, Pinal, or Santa Cruz counties shall meet the requirements of Subsection A. of Section 20-2-502. Unclassified sources, and shall not exceed 20 percent opacity.~~

~~4. Cement plants subject to the provisions of this Section and outside of Gila, Maricopa, Pima, Pinal or Santa Cruz counties shall not emit from any equipment particulate matter which is greater than 40 percent opacity or~~ exceeds the amounts allowable under the following:

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in ~~B.4.a~~ B.1.a. above.

2. No process source within any existing cement plant shall exceed 20 percent opacity.

~~5.~~ 3. No change.

C. and D., No change.

Part 21. Section R9-3-508. Standards of performance for existing asphalt concrete plants, is amended to read as follows:

R9-3-508. Standards of performance for existing asphalt concrete plants

A. No change.

B. Fixed asphalt plants or portable asphalt plants which are existing sources shall meet the standards set forth in this Section. The owner or operator shall submit proof of prior use to the Director.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any existing asphalt plant ~~located outside of Gila, Maricopa, Pima, Pinal, or Santa Cruz counties~~ in total quantities in excess of the amounts calculated by the equations set forth below:

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emission rate in pounds-mass per hour.

P - the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E - 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in B.1.a. above.

~~2. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any existing asphalt plant located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below.~~

~~a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 3.59P^{0.62}}$$

~~where "E" and "P" are defined as indicated in B.1.a. of this Section.~~

~~b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 17.31P^{0.16}}$$

~~where "E" and "P" are defined as indicated in B.1.a. above.~~

~~3.~~ 2. No change.

~~4.~~ 3. No change.

~~5. Nothing in this Regulation shall be construed to prohibit the Director from issuing an installation or operating permit for an asphalt plant which will not operate in compliance with B.2. above provided that the plant will operate in compliance with B.1. above and the permit contains~~

~~a condition prohibiting the operating of the plant in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties.~~

~~6.~~ 4. No change.

C. No change.

Part 22. Section R9-3-509, Standards of performance for existing petroleum refineries, is amended to read as follows:

R9-3-509. Standards of performance for existing petroleum refineries

A. The provisions of this Section are applicable to the following affected facilities in petroleum refineries: fluid catalytic cracking unit catalyst regenerators, fluid catalytic cracking unit incinerator-waste heat boilers, and fuel gas combustion devices. All petroleum refineries which are existing sources are subject to the provisions of Section R9-3-808.

B. The owner or operator of a petroleum refinery complex subject to this regulation shall develop and conduct a leak monitoring program in accordance with EPA Petroleum Refinery Enforcement Manual (EPA 340/1-80-008), Appendix H as incorporated by reference and on file with the Secretary of State.

1. Upon detection of a leaking component, which has a volatile organic compound concentration exceeding 10,000 ppm when tested in the manner described in the Arizona Testing Manual the owner shall:

a. Include the leaking component on a written list of scheduled repairs within 24 hours; and,

b. Repair and retest the component within 15 days.

2. Except for safety pressure relief valves, no owner or operator of a petroleum refinery shall install a valve at the end of a pipe or line containing volatile organic compounds unless the pipe or line is sealed with a

second valve, a blind flange, a plug, or a cap. The sealing device may be removed only when the line is in use (i.e., when a sample is being taken).

3. No owner or operator of a petroleum refinery shall operate a pipeline valve or pressure relief valve in gaseous volatile organic compound service unless it is marked in some manner that will be readily obvious to both refinery personnel performing monitoring and the Director.

C. Existing petroleum refineries of a capacity of 7,000 barrels per day or less shall be exempt from the emissions monitoring requirements of 40CFR60.105 provided the owner or operator of such a refinery complies with the following:

1. All process gases or fuel gases shall be treated in an afterburner, flare or other combustion device to insure complete combustion of carbon monoxide, hydrogen sulfide, and unburned hydrocarbons.

2. Ambient concentrations of SO_2 in the vicinity of the refinery shall be calculated using a suitable model approved by the Director and shall not exceed the Class II increments given in Section R9-3-217.

3. A continuous SO_2 ambient air monitor approved by the Director shall be placed in a location selected by the Director and shall be maintained in accordance with Section R9-3-215, and SO_2 concentrations shall not exceed Class II increments.

Part 23. Section R9-3-510, Standards of performance for existing storage vessels for petroleum liquids is amended to read as follows:

R9-3-510 Standards of performance for existing storage vessles for petroleum liquids.

A. No change.

B. No change.

C. No change.

D. No change

E. Gasoline volatility testing and control program.

1. No change.

2. No change.

3. The requirements enumerated in this egulation are based upon vapor pressure and shall be determined by ASTM designation: D-323-~~58~~79 Standard method of test vapor pressure of petroleum products (Reid Method). This method of test covers the determination of the absolute vapor pressure of volatile crude oil and volatile non-viscous petroleum products except liquified petroleum gases.

4. The seasonal distribution of the four grades of gasoline (A,B,C and D) shall conform to the schedule in Table 2 of D-439-~~70~~81 as follows:

Table 2. No change.

5. No change.

Part 24. Section R9-3-511, Standards of performance for existing secondary lead smelter, is amended to read as follows:

R9-3-511. Standards of performance for existing secondary lead smelters

A. This Section shall be applicable to all secondary lead smelters which are existing sources.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any existing

secondary lead smelter ~~outside of Gila, Maricopa, Pima, Pinal, or Santa Cruz counties~~ in total quantities in excess of the amounts calculated by the equations set forth below.

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions

shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable emission rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any existing secondary lead smelter located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below.~~

~~a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 3.59P^{0.62}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~b. For process industries having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 17.31P^{0.16}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~3.~~ 2. For reference purposes only, the equations in A.1. ~~and A.2.~~ above

are plotted in Figure 2, Appendix 11. The emission values obtained from the graph are approximately correct for the process weight rates shown. However, the actual values shall be calculated from the applicable equations and rounded off to two decimal places.

~~-4-~~ 3. No change.

~~-5-~~ 4. No change.

B. No change.

Part 25. Section R9-3-512. Standards of performance for existing secondary brass and bronze ingot production plants, is amended to read as follows:

R9-3-512. Standards of performance for existing secondary brass and bronze ingot production plants.

A. The standards set forth in this Section are applicable to all secondary brass and bronze ingot production plants which are existing sources.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any secondary brass or bronze ingot production plant ~~outside of the Phoenix-Tucson Air Quality Control Region~~ in total quantities in excess of the amount calculated by the equations set forth below.

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = maximum allowable particulate emissions rate in pounds-mass per hour.

p = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11}-40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any secondary brass or bronze ingot production plant located in the Phoenix-Tucson Air Quality Control Region in total quantities in excess of the amount calculated by the equations set forth below.~~

$$\cancel{E = 3.59P^{0.62}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~b. For process industries having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 17.31P^{0.16}}$$

~~where E"E and "P" are defined as indicated in A.1.a. above.~~

~~3.~~ 2. For reference purposes only, the equations in A.1. and ~~A.2.~~ above are plotted in Figure 2, Appendix 11. The emissions values obtained from the graph are approximately correct for the process weight rates shown. However, the actual values shall be calculated from the applicable equations and rounded off to two decimal places.

~~4.~~ 3. No change.

~~5.~~ 4. No change.

8. No change.

Part 26. Section R9-3-513. Standards of performance for existing iron and steel plants, is amended to read as follows:

9-3-513. Standards of performance for existing iron and steel plants

A. The standards set forth in this Section are applicable to basic oxygen process furnaces under State of Arizona jurisdiction which are existing sources.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any basic oxygen process furnace ~~outside of Gila, Maricopa, Pima, Pinal, or Santa Cruz counties~~ in total quantities in excess of the amount calculated by the equations set forth below.

a. For process sources having a process weight of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall

be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any (unclassified) process source located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below.~~

~~a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 3.59P^{0.62}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~b. For process industries having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 17.31P^{0.16}}$$

~~where "E" and "P" are defined as indicated in A.1.a. of this Section.~~

~~3.~~ 2. For reference purposes only, the equations in A.a. ~~and A.2.~~ above are plotted in Figure 2, Appendix 11. The emission values obtained from the graph are approximately correct for the process weight rates shown. However, the actual values shall be calculated from the applicable equations and rounded off to two decimal places.

~~4.~~ 3. No change.

~~5.~~ 4. No change.

B. No change.

Part 27. Section R9-3-515, Standards of performance for existing primary copper smelters, is amended as follows:

A. No change.

B. No change.

C. No change.

1. No change.

2. No change.

3. Compliance with the cumulative occurrence and emission limits contained in Paragraph 1. for all compliance periods subsequent to the initial 365-day compliance period specified in Paragraph 2 shall be determined as follows:

a. Annual average emissions shall be calculated at the end of each day by averaging the emissions for all hours measured during the compliance period ending that day.

An annual emissions average in excess of the allowable annual average emission limit will be considered a violation if:

i. The annual average is larger than the annual average computed for the preceding day; or

ii. The annual averages computed for the five (5) preceding days all exceed the allowable annual average emission limit.

b. Three-hour emissions averages shall be calculated at the end of each clock hour by averaging the hourly emissions for the preceding three consecutive hours whenever each such hour was measured in accordance with the requirements contained in Paragraph 4.

c. For the purposes of this Paragraph, a three-hour emissions average in excess of an emission level (E) will be considered to violate the associated cumulative occurrence limit (n) listed in Paragraph 1. if:

i. The number of all three-hour emissions averages measured during the compliance period in excess of that emission level exceeds the cumulative occurrence limit

associated with the emission level; and

ii. The average was measured during the last ~~month~~ operating day of the compliance period being reported.

d. A three-hour emissions average can only violate the cumulative occurrence limit (n) of an emission level (E) in the day containing the last hour in the average.

e. Multiple violations of a cumulative occurrence limit in the same day and violations of different cumulative limits in the same day shall constitute a single violation of the requirements of this Section.

f. The violation of any cumulative occurrence limit and an annual average emission limit in the same day shall constitute only a single violation of the requirements of this Section.

g. Multiple violations of a cumulative occurrence limit by different three-hour emissions averages containing any common hour shall constitute a single violation of the requirements of this Section.

h. For purposes of determining compliance with this Paragraph, the compliance period shall consist of the 365 calendar days immediately preceding the ~~last~~ end of each day of the month being reported unless that period includes less that 300 operating days. In such case the number of days preceding the last day of the compliance period shall be increased until the compliance period contains 300 operating days. Any day in which sulfur containing feed is introduced into the smelting process constitutes an operating day.

C.4. No change.

C.5. The owner of operator of any smelter subject to this Section shall maintain a record of all average hourly emissions measurements required by this Section. The record of such emissions shall be retained for at least two years following the date of measurement. Measurement results shall be expressed as pounds per hour of sulfur

dioxide. The following measurements shall be summarized monthly and submitted to the Director within fifteen (15) days after the end of each month:

a. During the initial 365-day period described in Paragraph 2. the cumulative average hourly emissions as of the last day of the month. For all subsequent periods described in Paragraph 3., the annual average emissions (expressed in pounds per hour) as calculated at the end of each day of the month;

b. The total number of hourly periods during the month in which measurements were not taken and of the reason for loss of measurement for each period;

c. The number of three-hour emissions averages which exceeded each of the applicable emissions levels listed in Paragraph 1. for the compliance periods ending on ~~the last~~ each day of the month being reported;

d. The date(s) on which a cumulative occurrence limit(s) listed in Paragraph 1. was exceeded if such exceedance occurred during the ~~last~~ month ~~of the compliance period~~ being reported.

C.6. through C.6.b.iv. No change.

v. No later than eighteen (18) months prior to the compliance date, the initiation of the demonstrations of stack gas volumetric flow rate and sulfur dioxide concentration measurement systems required by Paragraph 4, Subparagraphs a. and b.

C.6.b.vi. through c.9. No change.

Part 28. Section R9-3-516, Standards of performance for existing coal preparation plants, is amended to read as follows:

R9-3-516. Standards of performance for existing coal preparation plants

A. The provisions of this Section are applicable to any of the following affected facilities in coal preparation plants: thermal dryers, pneumatic coal cleaning equipment (air tables), coal processing and conveying equipment (including breakers and crushers), coal storage systems, and coal transfer and loading systems. This Section is applicable to all coal preparation plants which are existing sources. For purposes of this Section, the definitions contained in 40 CFR 60.251 are adopted by reference and incorporated herein.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any existing coal preparation plant located ~~outside of Gila, Maricopa, Pima, Pinal, or Santa Cruz counties~~ in total quantities in excess of the amounts calculated by the equations set forth below:

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11}-40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any existing coal~~

~~preparation plant located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below:~~

~~a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$E = 3.59P^{0.62}$$

~~where:~~

~~E = maximum allowable particulate emissions rate in pounds mass per hour.~~

~~P = the process rate in tons mass per hour.~~

~~b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:~~

$$E = 17.31P^{0.16}$$

~~where "E" and "P" are defined as indicated in A.2.a. above.~~

~~3.~~ 2. For reference purposes only, the equations in A.1. and ~~A.2.~~ above are plotted in Figure 2, Appendix 11. The emission values obtained from the graph are approximately correct for the process weight rates shown. However, the actual values shall be calculated from the applicable equations and rounded off to two decimal places.

~~4.~~ 3. No change.

~~5.~~ 4. No change.

~~6.~~ 5. No change.

B. No change.

Part 29. Section R9-3-517, Standards of performance for steel plants: existing electric arc furnaces (EAF), is amended to read as follows:

R9-3-517. Standards of performance for steel plants: existing electric arc furnaces (EAF)

A. The provisions of this Section are applicable to the following affected facilities in steel plants which are existing sources: electric arc furnaces and dust-handling equipment.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any steel plant ~~located outside of Gila, Maricopa, Pima, Pinal, or Santa Cruz counties~~ in total quantities in excess of the amount calculated by the equations set forth below:

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any steel plant source~~

~~located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below:~~

~~a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$E = 3.59P^{0.62}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~b. For process industries having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:~~

$$E = 17.31P^{0.16}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~-3-~~ 2. No change.

~~-4-~~ 3. No change.

~~-5-~~ 4. No change.

B. No change.

C. No change.

Part 30. Section R9-3-518, Standards of performance for existing kraft pulp mills, is amended to read as follows:

R9-3-518. Standards of performance for existing kraft pulp mills

A. The provisions of this Section are applicable to the following affected facilities in kraft pulp mills: digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, recovery furnace, smelt dissolving tank, lime kiln, and condensate stripper system. In pulp mills in which kraft pulping is combined with neutral sulfite semichemical pulping, the provisions of this Section are applicable when any portion of the material charged to an affected facility is produced by the kraft pulping operation. The provisions of this Section are applicable only to kraft pulp mills which are existing sources.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any kraft pulp mill process source ~~located outside of Gila, Maricopa, Pima, Pinal, or Santa Cruz counties~~ in total quantities in excess of the amounts calculated by the equations set forth below:

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be

determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2.---No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any kraft pulp mill located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below:~~

~~a.---For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 3.59P^{0.62}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~b.---For process industries having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 17.31P^{0.16}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~-3-~~ 2. No change.

~~-4-~~ 3. No change.

~~-5-~~ 4. No change.

5. The standards for total reduced sulfur measured as hydrogen sulfide (H_2S) utilizing Method II in the Arizona Testing Manual are:

a. No person shall cause, suffer, allow or permit the discharge of H_2S in excess of the following amounts:

i. From any recovery furnace any gases which contain H_2S in excess of 20 ppm by volume corrected to 8 percent oxygen.

ii. From any lime kiln any gases which contain H_2S in excess of 40 ppm by volume corrected to 10 percent oxygen.

B. Monitoring of emissions and operations required by this Section is as follows:

1. Any owner or operator subject to the provisions of this Section shall install, calibrate, maintain, and operate the following continuous monitoring systems:

a. A continuous monitoring system to monitor and record the opacity of the gases discharged into the atmosphere from any recovery furnace. The span of this system shall be set at 70 percent opacity.

b. A continuous monitoring system, to monitor and record the concentration of H_2S emissions discharged into the atmosphere from any recovery furnace or lime kiln. The span shall be set at H_2S concentration of 50 ppm.

c. A continuous monitoring system to monitor and record the percent of oxygen by volume in the gases discharged from any recovery furnace or lime kiln. The continuous monitoring system shall be located downstream of the control device(s) for the recovery furnace or lime kiln, and all measurements shall be made on a dry basis. The span of this system shall be set at 20 percent oxygen.

~~b.~~ d. No change.

C. The test methods and procedures required by this Section are as follows:

1. Reference methods in the Arizona Testing Manual except as provided under Section R9-3-312, shall be used to determine compliance with Subsection A. and B. above as follows:

a. Method 5 for the concentration of particulate matter and the associated moisture content.

b. Method 1 for sample and velocity traverses.

c. Method 3 for gas analysis, and

d. Method 9 for visible emissions.

e. Method 11 for total reduced sulfur as hydrogen sulfide.

2. No change.

Part 31. Section R9-3-520, Standards of performance for existing lime manufacturing plants, is amended to read as follows:

R9-3-520. Standards of performance for existing lime manufacturing plants

A. The provisions of this Section are applicable to the following affected facilities used in the manufacture of lime: rotary lime kilns, vertical lime kilns, lime hydrators, and limestone crushing facilities which are existing sources. This Section is also applicable to limestone crushing equipment which exists apart from other lime manufacturing facilities.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any lime manufacturing or limestone crushing facility ~~located outside of Gila, Maricopa, Pima, Pinal, and Santa Cruz counties~~ in total quantities in excess of the amounts calculated by the equations set forth below:

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2. No person shall cause, suffer, allow or permit the discharge of~~

~~particulate matter into the atmosphere in any one hour from any lime manufacturing or limestone crushing facility located within Gila, Maricopa, Pima, Pinal, and Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below:~~

~~a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$E = 3.59P^{0.62}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~b. For process industries having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:~~

$$E = 17.31P^{0.16}$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~-3-~~ 2. For reference purposes only, the equations in A.1. ~~and A.2.~~ above are plotted in Appendix 11, Figure 2. The emission values obtained from the graph are approximately correct for the process weight rates shown. However, the actual values shall be calculated from the applicable equations and rounded off to two decimal places.

~~-4-~~ 3. No change.

~~-5-~~ 4. No change.

~~-6-~~ 5. No change.

B. No change.

C. No change.

Part 32. Section R9-3-521, Standards of performance for existing non-ferrous metals industry sources, is amended to read as follows:

R9-3-521. Standards of performance for existing nonferrous metals industry sources

A. The provisions of this Section are applicable to the following affected facilities: mines, mills, concentrators, crushers, screens, material handling facilities, fine ore storage, dryers, roasters, and loaders which are existing sources.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any process source subject to the provisions of this Section ~~and outside of Gila, Maricopa, Pima Pinal, and Santa Cruz counties,~~ in total quantities in excess of the amounts calculated by the equations set forth below:

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2.---No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere in any one hour from any mining property process source located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties except smelters, in total quantities in excess of the amount calculated by the equations set forth below:~~

~~a.---For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 3.59P^{0.62}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~b.---For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 17.31P^{0.16}}$$

~~where "E" and "P" are defined as indicated in A.1.a. above.~~

~~-3-~~ 2. For reference purposes only, the equations in A.1. ~~and A.2.~~ above are plotted in Appendix 11, Figure 2. The emissions values obtained from the graph are approximately correct for the process weight rates shown. However, the actual values shall be calculated from the applicable equations and rounded off to two decimal places.

~~-4-~~ 3. No change.

~~-5-~~ 4. No change.

B. No change.

C. No change.

D. No change.

Part 33. Section R9-3-522, Standards of performance for existing gravel or crushed stone processing plants, is amended to read as follows:

R9-3-522. Standards of performance for existing gravel or crushed stone processing plants

A. The provisions of this Section are applicable to the following affected facilities: primary rock crushers, secondary rock crushers, tertiary rock crushers, screens, conveyors and conveyor transfer points, stackers, reclaimers, and all gravel or crushed stone processing plants and rock storage piles which are existing sources.

1. No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere except as fugitive emissions in any one hour from any gravel or crushed stone processing plant ~~outside of Gila, Maricopa, Pima, Pinal, or Santa Cruz counties~~ in total quantities in excess of the amounts calculated by the equations set forth below:

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.1.a. above.

~~2.------No person shall cause, suffer, allow or permit the discharge of particulate matter into the atmosphere except as fugitive emissions in any one hour from any gravel or crushed stone processing plant located in Gila, Maricopa, Pima, Pinal, or Santa Cruz counties in total quantities in excess of the amount calculated by the equations set forth below:~~

~~a.------For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:~~

$$\cancel{E = 3.59P^{0.62}}$$

~~where:~~

~~E = the maximum allowable particulate emissions rate in pounds mass per hour.~~

~~P = the process weight rate in tons mass per hour.~~

~~b.------For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emission shall be determined by the following equation:~~

$$\cancel{E = 17.31P^{0.16}}$$

~~where "E" and "P" are defined as indicated in A.2.a. above.~~

-3- 2. For reference purposes only, the equations in A.1. ~~and A.2.~~ above are plotted in Appendix II, Figure 2. The emission values obtained from the graph are approximately correct for the process weight rates shown. However, the actual values shall be calculated from the applicable equations and rounded off to two decimal places.

-4- 3. Notwithstanding the provisions of Section R9-3-501, no person shall cause, suffer, allow or permit to be emitted into the atmosphere from any gravel or crushed stone processing plants, smoke or dust that exceeds 40 percent opacity.

Spray bar pollution controls shall be utilized in accordance with EPA Control of Air Emissions From Process Operations In The Rock Crushing Industry (EPA 340/1-79-002), Wet Suppression System (p.p. 15-34) as incorporated by reference and on file with the Secretary of State, with placement of spray bars and nozzles as required by the Director to minimize air pollution.

-5- 4. No change.

B. No change.

C. No change.

Part 34. Section R9-3-524, Standards of performance for existing fossil-fuel fired industrial and commercial equipment, is amended to read as follows:

R9-3-524. Standards of performance for ~~existing~~ fossil-fuel fired industrial and commercial equipment.

A. This Section applies to industrial and commercial installations which are less than 73 megawatts capacity (250 million British thermal units per hour) but in the aggregate on any premises are rated at greater than 500,000 British thermal units per hour (0.146 megawatts) and in which fuel is burned for the primary purpose of producing steam, hot water, hot air or other liquids, gases or solids and in the course of doing so the products of combustion do not come into direct contact with process materials. When any products or byproducts of a manufacturing process are burned for the same purpose or in conjunction with any fuel, the same maximum emission limitations shall apply. ~~This Section shall be applicable to all such fossil-fuel fired industrial and commercial equipment which are exting sources.~~

B. No change.

C. No change.

D. No change.

E. No change.

F. No change.

Part 35. Section R9-3-529, is adopted to read as follows:

R9-3-529. Standards of performance for cotton gins

A. The provisions of this Section are applicable to all new or existing cotton gins in the State of Arizona.

1. Fugitive dust, lint, bolls, cotton seed or other material emitted from the gin or lying loose in the yard shall be collected and disposed of in an efficient manner or shall be treated in accordance with Sections R9-3-404 through R9-3-407.

2. Cotton gins shall conform to Section R9-3-501, Visible emissions: general, at all times. An opacity of 40 percent or less shall exempt the source from mass emissions testing. In the event that the cotton gin does not comply with the 40 percent opacity standard, the owner or operator may request the permission of the Director to perform a mass emissions test observed by a representative of the Bureau of Air Quality Control. Successful completion of this test will result in an adjustment to the simultaneous opacity standard in accordance with Section R9-3-501.C.

3. No person shall cause, suffer, allow, or permit the discharge of particulate matter into the atmosphere in any one hour from any cotton gin in total quantities in excess of the amounts calculated by the equations set forth below.

a. For process sources having a process weight rate of 60,000 pounds per hour (30 tons per hour) or less, the maximum allowable emissions shall be determined by the following equation:

$$E = 4.10P^{0.67}$$

where:

E = the maximum allowable particulate emissions rate in pounds-mass per hour.

P = the process weight rate in tons-mass per hour.

b. For process sources having a process weight rate greater than 60,000 pounds per hour (30 tons per hour), the maximum allowable emissions shall be determined by the following equation:

$$E = 55.0P^{0.11} - 40$$

where "E" and "P" are defined as indicated in A.3.a. above.

B. The test methods and procedures required by this Section are as follows:

1. The reference methods in the Arizona Testing Manual shall be used to determine compliance with Subsection A. above as follows:

a. Method A-2 for the measurement of particulate matter,

b. Method 1 for sample and velocity traverses,

c. Method 2 for velocity and volumetric flow rate,

d. Method 3 for gas analysis,

e. Method 9 for visible emissions.

2. For Method A-2, the sampling time for each run shall be at least 60 minutes and the sampling rate shall be at least 0.85 dry standard cubic meters per hour (0.53 dry standard cubic feet per minute), except that shorter sampling times, when necessitated by process variables or other factors, may be approved by the Director.

Part 36. Section R9-3-703, Interim continuous emission reduction technology, is amended to read as follows:

R9-3-703. Interim continuous emission reduction technology

E. For purposes of determining compliance with the sulfur dioxide removal efficiency standard and the bypass limitation provisions in Subsection C., above, the owner or operator of a smelter issued an NSO pursuant to this Article shall install, calibrate, maintain, and operate continuous sulfur dioxide monitoring equipment meeting the following requirements:

1. No change.

2. No change.

1. As expeditiously as practicable, but not later than eighteen (18) months following ~~the effective date of this Section~~ the date of issuance of an initial NSO by the Director or within 90 days of resumption of operations for a smelter which is not operating at this time and at such other times as the Director may specify the stack gas volumetric flow rate measurement system(s) installed and operated pursuant to this Section shall be demonstrated to meet the performance specifications prescribed in Appendix E to Part 52, Title 40 of the Code of Federal Regulations.

4. As expeditiously as practicable, but not later than eighteen (18) months following ~~the effective date of this Section~~ the date of issuance of an initial NSO by the Director or within 90 days of resumption of operations for a smelter which is not operating at this time and at such other times as the Director may specify, the sulfur dioxide concentration measurement system(s) installed and operated pursuant to this Section shall be demonstrated to meet the measurement system performance specifications prescribed in Appendix D to Part 52, Title 40, of the Code of Federal Regulations.

5. No change.

6. No change.

7. No change.

Part 37. Section R9-3-705, Fugitive emissions evaluation and control, is amended to read as follows:

R9-3-705. Fugitive emissions evaluation and control

A. Within one year following the date on which an initial NSO is issued pursuant to this Article or within one year of resumption of operations for a smelter which has been inoperative during the year following issuance of the initial NSO, the owner or operator of the smelter receiving the NSO shall submit to the Director the results of an evaluation of the fugitive emissions from the smelter. The evaluation results shall contain the following information:

1. No change.

2. No change.

3. No change.

B. No change.

C. No change.

D. Within twenty-four (24) months of the issuance of an initial NSO, the Director shall adopt final findings concerning each of the issues described in Subsections B. and C. above. If the Director finds that a smelter's fugitive emissions have the potential to cause or significantly contribute to violations of ambient sulfur dioxide standards in the vicinity of the smelter and the measures necessary to maintain the standards threatened by fugitive emissions will require the installation of control technology or implementation of work practices which are economically reasonable and technologically sound for the smelter, the Director shall amend the NSO to impose such measures. If the amendment to an NSO required by this Subsection requires the installation of fugitive emissions control technology, then such amendment shall include a compliance schedule with increments of progress requiring the installation and start-up of the control technology no later than the date ~~of termination of the initial NSO~~ when compliance with R9-3-515 is required.

1 Part 38. Section R9-3-709 is adopted to read as follows:

2 R9-3-709. Compliance schedule requirements

3 A. The owner or operator of any primary copper smelter within the State

4 of Arizona which has previously been issued an initial primary nonferrous

5 smelter order (NSO) by the Director may apply for and may be granted a second

6 NSO to expire no later than January 1, 1988. An application to the Director

7 for a second NSO shall contain a finding by the Administrator of the United

8 States Environmental Protection Agency (EPA) that the means of emission limita-

9 tion proposed by said owner or operator have been demonstrated to be reasonably

10 available within the meaning of subsection 119 (b) (3) of the Federal Clean

11 Air Act. This application to the Director for a second NSO shall also contain

12 a compliance schedule demonstrating increments as hereinafter specified. The

13 owner or operator of a primary copper smelter which has been granted a waiver

14 of interim continuous emission reduction requirements in accordance with

15 Section R9-3-708 and Subparagraph 119(d)(1)(C)(2) of the Federal Clean Air Act

16 shall be exempt from the provisions of these Rules and Regulations relating

17 to compliance schedules, and requirements for research and development, but

18 shall furnish the Director and the EPA Administrator each with a letter of in-

19 tent, for incorporation as a condition of the NSO, to cease operations on or

20 before January 1, 1988. During the period of these second NSO's these owners

21 or operators shall each operate a Supplementary Control System (SCS) in com-

22 pliance with Section R9-3-704. Compliance with Section R9-3-705 is also

23 required.

24 B. The applicant shall furnish the Director with a statement of the

25 grounds upon which the application is based and shall include all supporting

26 documentation. Such information shall be made available to the public

1 except as provided in A.R.S. § 36-1708.D. for a thirty-day period,
2 following which a hearing shall be conducted. Said application and documen-
3 tation shall be made a part of the record of the hearing.
4 C. A compliance schedule for the second NSO shall comply with the follow-
5 ing requirements. Each NSO shall require the smelter owner to meet all of the
6 requirements of the NSO as expeditiously as practicable. All NSO requirements
7 shall be immediately effective, except to the extent that the owner is able to
8 justify by purchase orders, delivery schedules and other pertinent documents,
9 the necessity for additional time. For requirements not immediately effective,
10 the NSO shall provide increments of progress and schedules for compliance.
11 The compliance schedule shall contain dates and increments for both stack
12 emission and fugitive emission control. In the event that the Director has not
13 issued findings concerning fugitive control measures by the second NSO applica-
14 tion date, the smelter owner shall submit the fugitive compliance schedule within
15 sixty (60) days after such findings are received by certified mail, unless the
16 smelter operator demonstrates that more time is required. These schedules shall
17 include the following increments of progress:
18 1. The date by which contracts will be let or purchase orders issued to
19 accomplish any necessary performance improvements;
20 2. The date for initiating on-site construction or installation of
21 necessary equipment;
22 3. The date by which on-site construction or installation of equipment
23 is to be completed; and,
24 4. The date for achievement of final compliance with emission limitations
25 given in Section R9-3-515.C.1.

5. In no event will the final compliance date for both stack and fugitive emissions be later than January 1, 1988.

D. During the life of the second NSO all interim continuous emission reduction technology shall be operated in accordance with Section R9-3-703.

E. Each second NSO shall require the immediate operation of any existing supplementary control system and the assumption of liability for violations of the National Ambient Air Quality Standards at existing monitor sites. The supplementary control system shall be operated in accordance with Section R9-3-704.

F. Fugitive emissions evaluation and control for the second NSO shall comply with Section R9-3-705.

G. The owner or operator shall certify to the Director, within fifteen (15) days after the deadline for completion of each increment, whether the required increment of progress has been met.

Part 39.A. Section R9-3-835 is adopted to read as follows:

R9-3-835. Standards of performance for lead-acid battery manufacturing plants Subpart KK of Part 60, Title 40 of the Code of Federal Regulations along with all duly promulgated revisions as of April 16, 1982 is herewith adopted by reference.

Part 39.B. Section R9-3-838 is adopted to read as follows:

R9-3-838. Standards of performance for phosphate rock plants

Subpart NN of Part 60, Title 40 of the Code of Federal Regulations along with all duly promulgated revisions as of April 16, 1982 is herewith adopted by reference.

R9-3-839 to R9-3-840. No change.

R9-3-841. Reserved.

R9-3-842. Reserved.

R9-3-843. Reserved.

R9-3-844. Reserved.

Part 39.C. Section R9-3-845 is adopted to read as follows:

R9-3-845. Standards of performance for asphalt processing and asphalt roofing manufacture.

40 CFR 60, Subpart UU (§ 60.470 et.seq.) along with all duly promulgated revisions as of August 5, 1982 is herewith adopted by reference.

Part 40. Section R9-3-1101, Jurisdiction, is amended to read as follows:

R9-3-1101. Jurisdiction

A. The Department and Hearing Board shall have original jurisdiction and control over such air pollution matters, air pollution sources, installation permits, operating permits and violations that pertain to any major source, the construction or major alteration of which commenced after May 14, 1979. If the Director determines that a county or multi-county air quality control district has adopted regulations for the issuance and enforcement of installation and operating permits to any major source, the construction or a major alteration of which commenced after May 14, 1979, and the regulations contain standards at least equal to or more restrictive than those contained in this Chapter, then the Director shall relinquish to such county or multi-county air quality control district the authority to issue and enforce installation and operating permits to such major sources (except for sources of lead) provided that their maximum potential to emit is less than 75 tons of air contaminants per day or are portable sources deemed by the Director to be stationary. In the case of lead sources, the State will maintain jurisdiction and control of all stationary sources that have the potential to emit 5 or more tons of lead per year.

B. The Department and Hearing Board shall have exclusive jurisdiction and control over such air pollution matters, air pollution sources, installation permits, operating permits and violations that pertain to:

1. Any existing source which has the potential to emit 75 tons of air contaminants per day or is otherwise designated as a statutory major source.

2. The smelting of copper ore.

3. The refining of crude oil.

4. Air pollution generated by operations and activities of all agencies and departments of the State and its political subdivisions.

5. Air pollution generated by mobile or portable combustion engines, machinery and equipment which are capable, without major alteration, of being operated in more than one county, except those sources deemed by the Director to be stationary.

6. Air pollution by motor vehicles.

C. No change.

D. No change.

Part 41. A1. Appendix 1 is amended to read as follows:

A1. APPENDIX 1

FILING INSTRUCTIONS FOR INSTALLATION PERMIT APPLICATION

A1.1. No change.

A1.2. No change.

A1.3. No change.

A1.4.1. No change.

A1.4.2. No change.

A1.4.3. Renumber as A1.4.4

A1.4.3. Class C. installation permits are issued to persons proposing to commence construction of a minor source.

A1.5 General application. Applicants for either a Class A, or Class B, or Class C installation permit shall complete an application on a form to be supplied by the Bureau of Air Quality Control. The application form

shall require, at a minimum, that the applicant supply the following information:

A1.5.1. No change

A1.5.2. No change

A1.5.3. No change

A1.5.4. No change

A1.5.5. No change

A1.5.6. The basis for the application (new major source, major alteration of existing source, air pollution control equipment, minor source etc.).

A1.5.7. No change

A1.5.8 No change

A1.5.9. No change

A1.5.10. No change

A1.6. Through A1.8.6. No change

A1.9. Class C Installation Permit-Source or facility description.

A1.9.1. In addition to the information required to be submitted by A1.5. above, an applicant for an installation permit for a new minor source shall submit the following information:

A1.9.1.1. An operating schedule stating the percent of annual production by season, the days of the week normally in operation, the shifts or hours of the day normally in operation, and the number of days per year in operation.

A1.9.1.2. A brief sketch of equipment layout showing relationship to buildings, property lines, adjacent streets or roads and directional arrow.

A1.9.1.3. A description of all basic operating and control equipment for which permits are required. Include the name, make, size and type of equipment.

A1.9.1.4. Flow diagrams for air pollution control processes and production processes.

A1.9.1.5. The rated and operating efficiency of air pollution control equipment. The

total quantity of gases exhausted to the atmosphere and the emissions of air pollutants to the atmosphere. The temperature, and the barometric pressure shall be given for all gas flow. Where spray nozzles are used as control devices, pressure drop, water requirements in gallons per minute per nozzle, location and direction of spray shall be shown. All process materials entering the equipment must be stated and the maximum hourly quantities given. A sieve analysis of all particulate solids must be given.

A1.9.1.6. Fuel type and consumption must be given.

A1.9.1.7. The manufacturers catalog designating specific standard commercial equipment may be submitted in lieu of item A1.9.1.3. this item. Structural details are not required.

Part 42. Appendix 4, is herewith repealed.

FEE SCHEDULE FOR INSTALLATION AND OPERATING PERMITS which appeared on Pages 71 thru 74 of proposed regulations as filed with the Secretary of State is withdrawn to comply with newly passed HB-2415, approved by the Governor on April 19, 1983. The new wording relating to permit permit fees is as follows:

". . . .subject to payment, upon issuance, of a reasonable fee based on the actual cost of processing the permit applications, but not exceeding six thousand six hundred dollars for an installation permit and five thousand five hundred dollars for an initial operating permit."

Part 43, A 11.

A11. APPENDIX 11, is amended to read as follows:

ALLOWABLE PARTICULATE EMISSIONS COMPUTATIONS

A11.1 Figure 1, hereto, plots the formulae for determining allowable particulate emissions from fuel burning equipment, based on the heat input to the equipment.

A11.2 Figure 2, hereto, plots the formulae for determining allowable particulate emissions from process industries, based on the process weight rate of the industry. ~~Plots-are-shown-for-industries-located-both-within-and-outside of-the-boundaries-of-the-Phoenix/Tucson-Air-Quality-Control-Region-(PTAQCR).~~

FIGURE 1 - NO CHANGE

FIGURE 2 IS REDRAWN TO SHOW ONLY ONE CURVE DELINEATING:

$$E = 4.10^{0.67} \quad \text{AND} \quad E = 55.0P^{0.11} - 40$$

(Graph Figure 2 is submitted for certification).

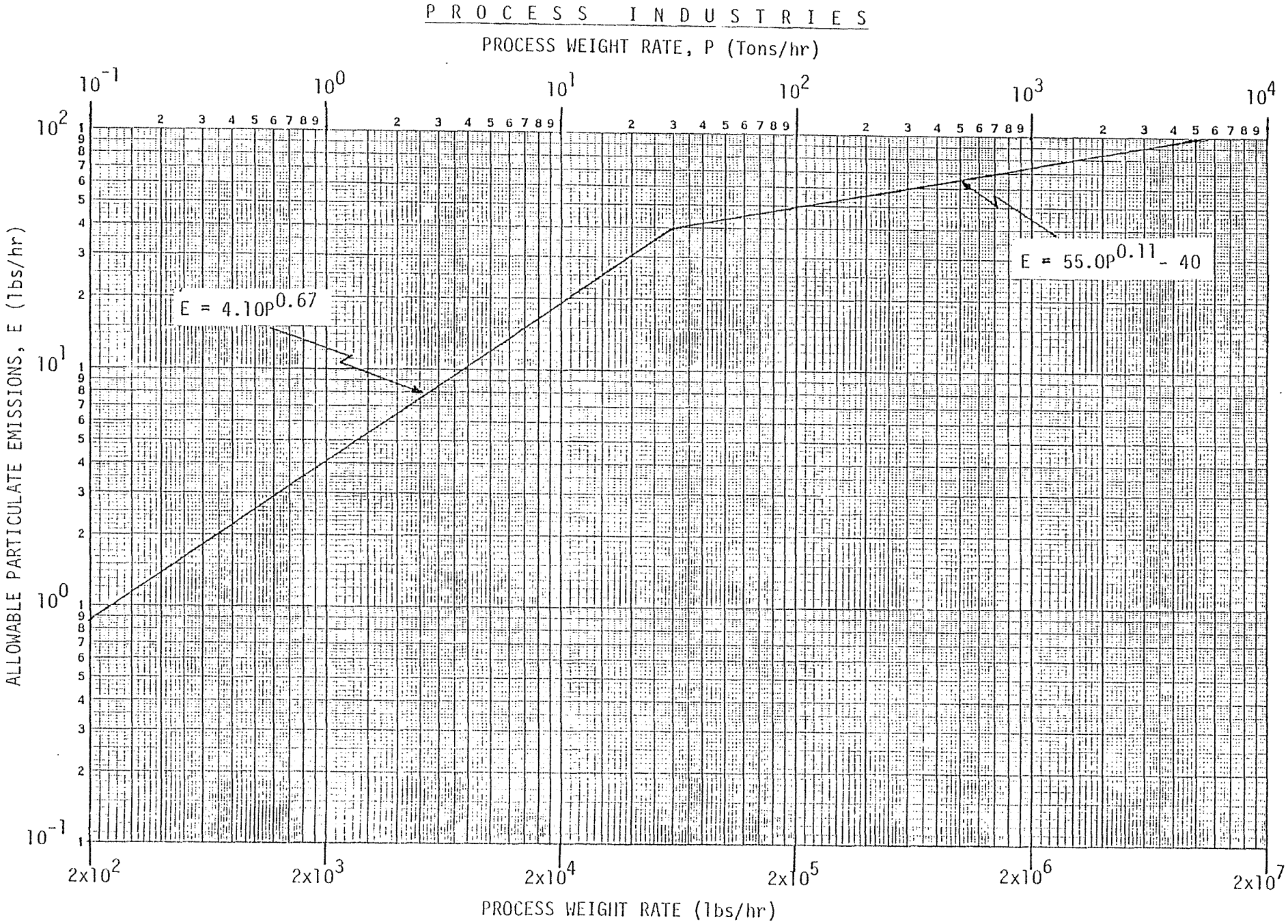
PROCESS INDUSTRIES
PROCESS WEIGHT RATE, P (Tons/hr)
ALLOWABLE PARTICULATE EMISSIONS, E (lbs/hr)
E = 4.10P^0.67
E = 55.0P^0.11 - 40
PROCESS WEIGHT RATE (lbs/hr)

FIGURE 2

A.G. RULE NO: 83-111

AIR QUALITY MONITORING PROCEDURES MANUAL

Arizona Department of Health Services

Division of Environmental Health Services

Bureau of Air Quality Control

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AIR QUALITY MONITORING PROCEDURES

1. QUALITY ASSURANCE

This section contains the minimum quality assurance requirements for air monitoring networks. These requirements are regarded as the minimum necessary for the control and assessment of the quality of ambient air monitoring data submitted to the State of Arizona. Operators of monitoring stations are encouraged to develop and implement quality assurance programs more extensive than the minimum required or to continue such programs where they already exist.

Quality assurance consists of two distinct and equally important functions. One function is the assessment of the quality of the monitoring data by estimating their precision and accuracy. The other function is the control, and improvement, of the quality of the monitoring data by implementation of quality control policies, procedures, and corrective actions. These two functions form a control loop: When the assessment function indicates that the data quality is inadequate, the control effort must be increased until the data quality is acceptable.

In order to provide uniformity in the assessment and reporting of data quality among all networks, the assessment procedures are specified explicitly in subsections 1.3 through 1.7 of these procedures.

In contrast, the control and corrective action function encompasses a variety of policies, procedures, specifications, standards, and corrective measures which have varying effects on the resulting data

quality. The selection and degree of specific control measures and corrective actions used depend on a number of factors such as the monitoring methods and equipment used, field and laboratory conditions, the objectives of the monitoring, the level of data quality needed, the expertise of assigned personnel, the cost of control procedures, pollutant concentration levels, etc. Accordingly, quality control requirements are specified in general terms below, to allow each operator to develop a quality control system which is most effective for its own circumstances.

1.1 Quality Control Program

Each operator must develop and implement a quality control program consisting of policies, procedures, specifications, standards, and documentation necessary to:

(1) Provide data of adequate quality to meet monitoring objectives

(2) Minimize loss of air quality data due to malfunctions or out-of-control conditions.

The quality control program must be described in detail, suitably documented, and approved by the Director.

Primary guidance for developing the quality control programs is contained in references 1 and 2, which also contain many suggested procedures, checks, and control specifications. Many specific quality control checks and specifications for manual methods are included in the respective reference methods described in 40 CFR 50 or in the respective equivalent method descriptions available from the U. S. Environmental Protection Agency (see reference 5). Similarly, quality control procedures related to specifically designated reference and equivalent analyzers are contained in their respective operation and

instruction manuals. This guidance, and any other pertinent information from appropriate sources, should be used by operators in developing their quality control programs.

As a minimum, each quality control program must have operational procedures for each of the following activities:

(1) Selection of methods, analyzers, or samplers

(2) Installation of equipment

(3) Calibration

(4) Zero/span checks and adjustments of automated analyzers

(5) Control checks and their frequency

(6) Control limits for zero, span and other control checks, and respective corrective actions when such limits are surpassed.

(7) Use of multiple ranges with automated analyzers

(8) Preventive and remedial maintenance

(9) Air pollution episode monitoring

(10) Recording and validating data

(11) Documentation of quality control information

1.2 Pollutant Standards

Gaseous standards (permeation tubes, permeation devices or cylinders of compressed gas) used to obtain test concentrations for CO, SO_2, and NO_2 must be working standards certified by comparison to a National Bureau of Standards (NBS) gaseous Standard Reference Material (SRM). A traceability protocol for certifying a working standard by direct comparison to an NBS SRM is given in reference 3. Direct use of an NBS SRM as a working standard is not prohibited but is discouraged because of their limited supply and expense.

Test concentrations for ozone must be obtained in accordance with the UV photometric calibration procedure specified in Appendix D of 40 CFR Part 50, or by means of an ozone transfer standard which has been certified. Consult reference 4 for guidance on ozone transfer standards. Flow measurements must be made by a flow measuring instrument which is traceable to an authoritative volume or other standard.

1.3 Data Quality Assessment

1.3.1 Automated Methods

1.3.1.1 Precision

A one-point precision check must be carried out at least once every two weeks on each automated analyzer used to measure SO_2, NO_2, O_3 and CO. The precision check is made by challenging the analyzer with a precision check gas of known concentration between 16 and 20 percent of full scale. The standards from which precision checks test concentrations are obtained must be traceable to NBS SRM's as specified in subsection 1.2. Except for certain CO analyzers described below, analyzers must operate in their normal sampling mode during the precision check, and the test atmosphere must pass through all filters, scrubbers, conditioners and other components used during normal ambient sampling and as much of the ambient air inlet system as is practicable. If permitted by the associated operation or instruction manual, a CO analyzer may be temporarily modified during the precision check to reduce vent or purge flows, or the test atmosphere may enter the analyzer at a point other than the normal sample inlet, provided that the analyzer's response is not likely to be altered by these

deviations from the normal operational mode. If a precision check is made in conjunction with a zero/span adjustment, it must be made prior to such zero and span adjustments.

The difference between the actual concentration of the precision check gas and the concentration indicated by the analyzer is used to assess the precision of the monitoring data as described in 1.4.1.1.

1.3.1.2 Accuracy

Each calendar quarter audit at least 25 percent of all analyzers that monitor for SO_2, NO_2, O_3 or CO such that each analyzer is audited at least once per year. If there are fewer than four analyzers for a pollutant within a network, randomly reaudit one or more analyzers so that at least one analyzer for that pollutant is audited each calendar quarter.

The audit is made by challenging the analyzer with at least one audit gas of known concentration from each of the following ranges which fall within the measurement range of the analyzer being audited:

Audit Point	Concentration Range % of Full-Scale
1	3 to 8 or .03 to .08 ppm, whichever is greater
2	15 to 20 or .15 to .20 ppm, whichever is greater
3	40 to 45 or .40 to .45 ppm, whichever is greater
4	80 to 90 or .80 to .90 ppm, whichever is greater

The standards from which audit gas test concentrations are obtained must be traceable to NBS SRM's as specified in subsection 1.2. Except for NBS gaseous SRM's, standards and equipment used must be different from the standards and equipment used for calibration and spanning. The

auditor should not be the operator/analyst who conducts the routine monitoring, calibration, and analysis.

The audit shall be carried out by allowing the analyzer to analyze an audit test atmosphere in the same manner as described for precision checks. The exception given in 1.3.1.1 for certain CO analyzers does not apply for audits.

The difference between the actual concentration of the audit test gas and the concentration indicated by the analyzer is used to assess the accuracy of the monitoring data as described in section 1.4.1.2.

1.3.2 Manual Methods

1.3.2.1 Precision

For networks with one to nine sites, select at least one TSP, NO_2, and SO_2 monitoring site for duplicate sampling and collocate two samplers at the selected site. For networks with ten or more sites, select at least two sites for duplicate sampling. Although only one or two pairs of collocated samplers are required to estimate the precision of a reporting organization, additional collocated sampling is encouraged. Sites with the highest expected annual mean concentration must be selected, or if such sites are impractical, alternate sites approved by the Director may be selected. The collocated samplers must be within four meters of each other, but high volume samplers must be at least two meters apart to preclude airflow interference. Calibration, sampling and analysis must be the same for both collocated samplers as well as for all samplers in the network. The collocated samplers must be operated whenever routine sampling is scheduled. For each pair of collocated samplers, designate one as the sampler which will be used to report air quality for

the site and designate the other as the duplicate sampler. The differences in measured concentration (ug/m^3) between the two collocated samplers are used to calculate precision as described in 1.4.2.1.

For Pb, precision will be estimated from duplicate filter strip analyses performed on samples from the expected highest concentration lead site. The precision of an equivalent method may be assessed by analyzing identical aliquots of the samples collected at the highest concentration lead site.

For each day lead samples are collected, cut two identical strips from the filter or take two identical aliquots. Designate the first strip/aliquot as the sample which will be used to report air quality for the site and designate the other as the duplicate sample. The difference in measured concentration (ug/m^3) between the two samples is used to calculate precision as described in 1.4.2.

1.3.2.2 Accuracy

The accuracy of manual sampling methods is assessed by auditing a portion of the measurement process. For TSP, flow rate measurement is audited. For the Pb, SO_2, and NO_2 methods, analytical measurement is audited.

For the TSP method, audit the flow rate of at least 25 percent of the high volume samplers such that each sampler is audited at least once per year. If there are fewer than four high volume samplers within a reporting organization, randomly reaudit one or more samplers so that one sampler is audited each calendar quarter.

Audit the flow rate at one flow rate, between 40 and 60 cfm, using a reference flow device described in section 2.2.8, pages 3-5, of reference 2, or a similar transfer flow standard. The audit device must be calibrated against a flow standard different from the one used to calibrate the flow of the high volume sampler being audited. With the audit device and a normal glass fiber filter in place, operate the high volume sampler at its normal flow rate. The difference in flow rate (in m^3/min) between the audit flow measurement and the flow indicated by the sampler's normal flow indicator are used to calculate accuracy as described in 1.4.2.2.

Great care must be used in auditing high volume samplers having flow regulators because the introduction of resistance plates in the audit device can cause abnormal flow patterns at the point of flow sensing. For this reason the orifice of the flow audit device should be used without resistance plates in auditing flow regulated high volume samplers, or other steps should be taken to assure that flow patterns are not perturbed at the point of flow sensing.

For the SO_2 method, prepare audit solutions from a working sulfite-TCM solution as described in section 6.2.9 of the SO_2 Reference Method (40 CFR 50, Appendix A). These audit samples must be prepared independently from the standardized sulfite solutions used in the routine analysis procedure. New sulfite-TCM audit samples must be prepared every 30 days and must be stored between 0 and 5°C.

Prepare audit samples in each of the concentration ranges of 0.2-0.3, 0.5-0.6, and 0.8-0.9 ug SO_2/ml. Analyze an audit sample in each of the

three ranges at least once each day that samples are analyzed and at least twice per calendar quarter. The differences between the audit concentrations and the indicated concentrations (in ug/SO_2 ml) are used to calculate accuracy as described in section 1.4.2.2.

For the NO_2 method, prepare audit solutions from a working sodium nitrite solution as described in the appropriate equivalent method (see reference 5). These audit samples must be prepared independently from the standardized nitrite solution used in the routine analysis procedure. New aqueous sodium nitrite audit samples must be prepared every three months. Prepare audit samples in each of the concentration ranges of 0.2-0.3, 0.5-0.6, and 0.8-0.9 ug NO_2/ml. Analyze an audit sample in each of the three ranges at least once each day that samples are analyzed and at least twice per calendar quarter. The differences between the audit concentrations (in ug NO_2/ml) and the indicated concentrations (in ug NO_2/ml) are used to calculate accuracy as described in 1.4.2.2.

For the Pb method, for each calendar quarter, audit the Pb analysis using glass fiber filter strips containing a known quantity of lead. Audit samples are prepared by depositing a Pb solution on 1.9 cm by 20.3 cm (3/4 inch by 8 inch) unexposed glass fiber filter strips and allowing to dry thoroughly. The audit samples must be prepared by using reagents different from those used to calibrate the Pb analytical equipment being audited. Prepare audit samples in the following concentration ranges:

Pb Concentration ug/strip	Equivalent Ambient Pb Concentration, ug/m^3
100- 300	.5-1.5
600-1000	3.0-5.0

The above equivalent ambient Pb concentrations are based on sampling at 1.7 m^3/min. for 24 hours on 20.3 x 25.4 cm (8 inch x 10 inch) glass fiber filters.

Audit samples must be extracted using the same extraction procedures used for exposed filters. Analyze three audit samples in each of the two ranges each quarter that samples are analyzed. The audit sample analyses are to be spread out as much as possible over the entire calendar quarter. The percent difference between the audit concentration and the analyst's measured concentrations (in ug Pb/strip) is used to calculate accuracy as described in 1.4.2.2.

1.4 Calculations for Data Quality Assessment

1.4.1 Automated Methods

1.4.1.1 Precision

Estimates of the precision are calculated from the results of biweekly precision checks as specified in section 1.3.1.1. At the end of each calendar quarter calculate a combined precision probability interval for all analyzers in the network for each pollutant. Directions for calculations are given below and directions for reporting are given in section 1.5. If monitoring data are invalidated during the entire period represented by a given precision check, the results of that precision check shall be excluded from the calculations.

For single analyzer precision, calculate the percentage difference (d_i) for each precision check using equation 1.

$$d_i = \frac{Y_i - X_i \times 100}{X_i} \qquad (1)$$

where: Y_i = analyzer's indicated concentration from the i-th precision check.

X_i = known concentration of test gas used for the i-th precision check.

For each analyzer calculate the quarterly average (d_j), equation 2, and the standard deviation (S_j), equation 3.

$$\bar{d}_j = \frac{1}{n} \sum_{i=1}^{n} d_i \tag{2}$$

$$S_j = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left[d_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} d_i \right)^2 \right]} \tag{3}$$

In the equations, n is the number of precision checks on the instrument made during the calendar quarter. For example, n should be 6 or 7 if precision checks are made biweekly during a quarter.

To compute network precision for each pollutant, calculate the average of averages (D) and pooled standard deviation (S_a) for all analyzers monitoring the pollutant using either equations 4 and 5 or 4a and 5a.

$$\bar{D} = \frac{1}{k} \sum_{j=1}^{k} \bar{d}_i \tag{4}$$

$$S_a = \frac{1}{k} \sum_{j=1}^{k} S_j^2 \tag{5}$$

In these equations, k is the number of analyzers within the reporting organization for a single pollutant. Use equations 4 and 5 when the same number of precision checks are made for each instrument. Otherwise, use equations 4a and 5a to obtain a weighted average and a weighted standard deviation.

$$\bar{D} = \frac{n_1\bar{d}_1 + n_2\bar{d}_2 + \ldots + n_j\bar{d}_j + n_k\bar{d}_k}{n_1 + n_2 + \ldots + n_j + \ldots + n_k} \tag{4a}$$

$$S_a = \sqrt{\frac{(n_1 - 1)\ S^2 + (n_2 - 1)\ S_2^2 + \ldots + (n_{-1})\ S_j^2 + \ldots + (n_k - 1)\ S_k^2}{n_1 + n_2 + \ldots\ n_j + \ldots + n_k - k}} \qquad (5a)$$

For each pollutant, calculate the 95 percent probability limits for the precision of a reporting network using equations 6 and 7 and record these limits on the front of Form 1 under columns 11-18. (See section 1.5 for explanation of Form 1).

$$\text{Upper 95 Percent Probability Limit} = \overline{D} + 1.96\ S_a \qquad (6)$$

$$\text{Lower 95 Percent Probability Limit} = \overline{D} - 1.96\ S_a \qquad (7)$$

1.4.1.2 Accuracy

Estimates of the accuracy are calculated from the results of independent audits as described in section 1.3.1.2. At the end of each calendar quarter, calculate a combined accuracy probability interval for all analyzers in the network for each pollutant. Separate probability limits are calculated for each audit concentration level listed in 1.3.1.2. Directions for calculations are given below (directions for reporting are given in section 1.5).

For single analyzer accuracy, calculate the percentage difference (d_i) for each audit concentration using equation 1 where Y_i is the analyzer's indicated concentration from the i-th audit check and X_i is the known concentration of the audit gas used for the i-th audit check.

For network accuracy, using equation 8, calculate, for each audit concentration level, the average ($\overline{D}$) of the individual percentage differences (d_i) for all k analyzers measuring a given pollutant audited during the quarter.

$$D = \frac{1}{k} \sum_{i=1}^{k} \overline{d_i} \qquad (8)$$

For each concentration level, calculate the standard deviation (S_a) of all the individual percentage differences for all analyzers audited during the quarter, using equation 9. Repeat for each pollutant.

$$S_a = \sqrt{\frac{1}{k-1}\left[\sum_{i=1}^{k} d_i^2 - \frac{1}{k}\left(\sum_{i=1}^{k} d_i\right)^2\right]} \qquad (9)$$

For networks having four or fewer analyzers for a particular pollutant, only one audit is required each quarter. Therefore, the average and the standard deviation cannot be calculated. For such reporting units, the audit results of two consecutive quarters are required to calculate an average and a standard deviation using equations 8 and 9, and the reporting or probability limits are therefore required on a semi-annual (instead of a quarterly) basis. For each pollutant, calculate the 95 percent probability limits for the accuracy of a reporting network at each audit concentration level using equations 6 and 7 and record these limits on Form 2. (See section 1.5 for explanation of Form 2).

1.4.2 Manual Methods

1.4.2.1 Precision

Estimates of precision are calculated from the results obtained from collocation of TSP, NO_2, and SO_2 samplers or by duplicate Pb analyses as described in section 1.3.2.1. At the end of each calendar quarter, calculate a combined precision probability interval for each

pollutant. Directions for calculation are given below and directions for reporting are given in section 1.5.

To compute single site precision, calculate the percentage difference (d_i) for each of the paired measurements obtained in accordance with 1.3.2.1, using equation 1 where Y_i is the concentration of pollutant measured by the duplicate sampler and X_i is the concentration of pollutant measured by the sampler reporting air quality for the site. For each site, calculate the quarterly average percentage difference (d_j), using equation 2, and the standard deviation (S_j), using equation 3.

At low concentrations, agreement between the measurements of collocated samplers, expressed as 95 percent probability limits, may be poor. For this reason a separate count is made of the occurrence of pollutant measurements below specified levels. Count the number of samples which indicate a measurement from a sampler reporting air quality for the site below the following limits:

TSP - less than 20 ug/m^3

SO_2 - less than 40 ug/m^3

NO_2 - less than 30 ug/m^3

Pb - less than .15 ug/m^3

Report the counts on Form 2.

To compute network precision for each pollutant, calculate the average percentage difference ($\overline{D}$) and pooled standard deviation (S_a) using equations 4 and 5, or using equations 4a and 5a if different numbers

of paired measurements are made at the collocated sites. Results from all collocated sampling sites shall be reported.

Calculate the 95 percent probability limits for the precision of a reporting unit, using equations 10 and 11, and record them on Form 1. (See section 1.5 for explanation of Form 2).

$$\text{Upper 95 Percent Probability Limit} = \overline{D} + 1.96\ S_a/\sqrt{2} \qquad (10)$$

$$\text{Lower 95 Percent Probability Limit} = \overline{D} - 1.96\ S_a/\sqrt{2} \qquad (11)$$

1.4.2.2 Accuracy

To compute TSP single sampler accuracy, calculate the percentage difference (d_i) for each audit performed in accordance with 1.3.2.2, using equation 1. Let X_i represent the known flow rate and Y_i represent the indicated flow rate in equation 1.

To compute TSP network accuracy, calculate the average ($\overline{D}$) of the individual percent differences for all high volume samplers audited during the calendar quarter, using equation 8. Compute the standard deviation (S_a) of all the percentage differences for all the samplers audited during the calendar quarter, using equation 9.

Calculate the 95 percent probability limits for the accuracy of a reporting network using equations 6 and 7, and record these limits on Form 2 under the middle level column. Note that since the audit is conducted at only one level, the low level and high levels columns are note used. For reporting networks having four or fewer high volume samplers for TSP, only one audit is required each quarter. For such

reporting networks, the audit results of two consecutive quarters are required to calculate an average and a standard deviation using equations 8 and 9. Therefore, semi-annual reporting (instead of quarterly) of probability limits is required.

To compute single-analysis-day accuracy for SO_2, NO_2, and Pb, calculate the percentage difference (d_i) for each audit at each concentration level using equation 1. Let X_i represent the known value of the audit sample and Y_i the indicated value of SO_2, NO_2, or Pb in equation 1. Audits of the analysis for SO_2, NO_2, and Pb are performed in accordance with 1.3.2.2.

To compute network accuracy for SO_2, NO_2, and Pb, calculate the average ($\overline{D}$) of the percent differences at each concentration level for all analysis days during the quarter using equation 8. Compute the standard deviation (S_a) of the individual percentage differences using equation 9. Calculate the 95 percent probability limits for the accuracy of the network using equations 6 and 7 and record these limits on Form 2 for each concentration level.

1.5 Reporting Requirements

1.5.1 Quarterly Reports

For each network fill out Form 1 and Form 2 according to the directions given below, and submit the forms within 90 days of the end of the quarter to the Department.

1.5.2 Annual Reports

Compute the annual mean and standard deviation of the percent differences for all precision checks and audits performed during the year. Using these values, calculate the annual probability limits for precision and for

accuracy at each audit level. Record these data on Forms 1 and 2 and submit the forms to the Department within 90 days after the end of the year.

1.5.3 Instructions for Form 1 - Automated Analyzers

Line	Entry
Name of Reporting Organization:	Name of company
Network:	Geographical location, referring to city or town.
Block No.	
1-2	Year: Last two digits of the calendar year.
3	Quarter: Enter 1, 2, 3 or 4 to refer to calendar quarter the monitoring data and quality assessment represent. Enter 0 to indicate annual report.
4-6	Number of Analyzers: Count the number of analyzers in the network that report monitoring data for each pollutant.
7-10	Number of Precision Checks: Count the total number of precision checks included in the calculations reported.
11-14	Lower Probability Limit, Precision: Block 11 is either "+" or "-". Blocks 12-14 contain the percentage (round off to a whole number) obtained from equation 11.
15-18	Upper Probability Limit, Precision: Block 15 is either "+" or "-". Blocks 16-18 contain the percentage obtained from equation 10. Note: If precision limits exceed three digits, report as 999.
19	Source of Audit Gas: For accuracy determination, refer to code table, note 1, on the form.
20-21	Number of Audits: Report the total number of multipoint audits performed on the analyzers reported in blocks 20-21.
22-53	Probability Limits, Accuracy: The lower and upper probability limits for each pollutant concentration level of the accuracy audits are entered in blocks 22-53.

22-25 Lower Probability Limits, Accuracy: Blocks 22, 30, 38, and 46
30-33 are either "+" or "-". Blocks 23-25, 31-33, 39-41, and 47-49
38-41 contain the percentages obtained from equation 7.
46-49

26-29 Upper Probability Limit, Accuracy: Blocks 26, 34, 42, and 50
34-37 are either "+" or "-". Blocks 27-29, 35-37, 43-45, and 51-53
42-45 contain the percentages obtained from equation 6. Note: If
50-53 only one audit is performed during a given quarter for a given pollutant, it is not possible to calculate probability limits for that quarter. In that case, blocks 22-53 are left blank for the first such quarter and the number 01 is reported in blocks 20-21. Probability limits are then computed and reported on a semi-annual basis (i.e., after the next quarter) from the audit data obtained during the two consecutive quarters.

1.5.4 Instructions for Form 2 - Manual Methods

Line	Entry

Name of Reporting Organization: Name of Company

Network: Geographical location, referring to city or town.

Block No.

1-2 Year: Last two digits of the calendar year.

3 Quarter: Enter 1, 2, 3 or 4 to refer to calendar quarter for which the monitoring data and quality assessments were obtained. Enter 0 to indicate annual report.

4-5 Number of Samplers: Count the number of samplers for each pollutant for which monitoring data are reported.

6-7 Number of Collocated Sites: Number of sites having collocated samplers.

8-10 Number of Collocated Samples Below the Limit: Count the number of samples from the collocated sites where the measurements from the sampler reporting air quality for the site are below the indicated limits.

11-14 Lower Probability Limit, Precision: Block 11 is either "+" or "-". Blocks 12-14 contain the percentage obtained from equation 11. Round off to a whole number.

15-18 Upper Probability Limit, Precision: Block 15 is either "+" or "-". Blocks 16-18 contain the percentage obtained from equation 10. Note: If precision limits exceed three digits, report as 999.

19 Type Sampler: Enter A, B, or C, depending on type of flow control.

20-21 Number Audits: Number of audits performed.

22-25 Lower Probability Limits, Accuracy: Blocks 22, 30, and 38 are
30-33 either "+" or "-". Blocks 23-25, 31-33, and 39-41 contain the
38-41 percentages obtained from equation 7.

26-29 Upper Probability Limit, Accuracy: Blocks 26, 34, and 42 are
34-37 either "+" or "-". Blocks 27-29, 35-37, and 43-45 contain
42-45 the percentages obtained from equation 6. Note: If accuracy limits exceed three digits, report as 999. Report, as required, all pollutants (TSP, SO_2, NO_2, Pb) as determined by manual sampling methods. Note that only blocks 30-37 are used for TSP. Note: If only one audit is performed during a given quarter for a given pollutant, it is not possible to calculate probability limits for that quarter. In that case, blocks 22-45 are left blank for the first such quarter and the number

01 is reported in blocks 20-21. Probability limits are then computed and reported on a semi-annual basis (i.e., after the next quarter) from the audit data obtained during the two consecutive quarters.

ARIZONA DEPARTMENT OF HEALTH SERVICES • DIVISION OF ENVIRONMENTAL HEALTH SERVICES

FORM 1

AIR QUALITY DATA ASSESSMENT REPORT

YEAR (1 2) QUARTER (3)

NAME OF REPORTING ORGANIZATION _____ NETWORK _____

PRECISION—AUTOMATED ANALYZERS

POLLUTANT	NUMBER ANALYZERS	NUMBER PRECISION CHECKS	Lower	Upper
CO	4-6	7-10	+/- 11-18	+/-
NO_2	4-6	7-10	+/- 11-18	+/-
O_3	4-6	7-10	+/- 11-18	+/-
SO_2	4-6	7-10	+/- 11-18	+/-

ACCURACY—AUTOMATED ANALYZERS

POLLUTANT	AUDIT GAS SOURCE[1]	NUMBER AUDITS	PROBABLITY LIMITS LEVEL 1 Lower	LEVEL 1 Upper	LEVEL 2 Lower	LEVEL 2 Upper	LEVEL 3 Lower	LEVEL 3 Upper	LEVEL 4 Lower	LEVEL 4 Upper
CO	19	20-21	+/- 22-29	+/-	+/- 30-37	+/-	+/- 38-45	+/-	+/- 46-53	+/-
NO_2	19	20-21	+/- 22-29	+/-	+/- 30-37	+/-	+/- 38-45	+/-	+/- 46-53	+/-
O_3	19	20-21	+/- 22-29	+/-	+/- 30-37	+/-	+/- 38-45	+/-	+/- 46-53	+/-
SO_2	19	20-21	+/- 22-29	+/-	+/- 30-37	+/-	+/- 38-45	+/-	+/- 46-53	+/-

[1] A - [illegible]S Supplied SRM
B - [illegible]MSL Reference Gas
C - Other (Identify Vendor) CO
D - Other (Identify Vendor) NO_2
E - Other (Identify Vendor) O_3
F - Other (Identify Vendor SO_2

ADHS/EHS/Air Quality Control/Monitoring Section-030 (7-82)

ARIZONA DEPARTMENT OF HEALTH SERVICES • DIVISION OF ENVIRONMENTAL HEALTH SERVICES

FORM 2

AIR QUALITY DATA ASSESSMENT REPORT

YEAR (1 2) QUARTER (3)

NAME OF REPORTING ORGANIZATION _____ NETWORK _____

PRECISION—MANUAL METHODS

POLLUTANT	NUMBER SAMPLERS (4-5)	NUMBER COLOCATED SITES (6-7)	NUMBER COLOCATED SAMPLES LIMIT (8-10)	LIMIT (ug/m³)	PROBABILITY LIMITS Lower (11-18)	PROBABILITY LIMITS Upper (11-18)
TSP				20		
SO_2				40		
NO_2				30		
Pb				.15		

ACCURACY—MANUAL METHODS

POLLUTANT	TYPE SAMPLER[1] (19)	NUMBER AUDITS (20-21)	LEVEL 1 Lower (22-29)	LEVEL 1 Upper (22-29)	LEVEL 2 Lower (30-37)	LEVEL 2 Upper (30-37)	LEVEL 3 Lower (38-45)	LEVEL 3 Upper (38-45)
TSP								
SO_2								
NO_2								
Pb								

[1]A - With Automatic Flow Control B - Without Automatic Flow Control C - With Critical Orifice Flow Control

ADHS/EHS/Air Quality Control/Monitoring Section 031 (7 82)

References

1. "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I - Principles." EPA-600/9-76-500. March 1976, available from U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, NC 27711.

2. "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - Ambient Air Specific Methods." EPA-600/4-77-027a, May, 1977. Available from U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, NC 27711

3. "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Air Pollution Analyzers," (Protocol No. 2), June, 1978. Available from U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch, (MD-77), Research Triangle Park, NC 27711.

4. "Transfer Standards for Calibration of Ambient Air Monitoring Analyzers for Ozone," June, 1978. Available from U. S. Environmental Protection Agency, Department E (MD-77), Research Triangle Park, NC 27711.

5. List of Reference and Equivalent Methods." Available from U. S. Environmental Protection Agency, Department E (MD-77), Research Triangle Park, NC 27711.

1.6 Data Quality Assessment Requirements for PSD (Prevention of Significant Deterioration) Monitoring

Section 1.1 Quality Control Program, section 1.2 Pollutant Standards, and section 1.5 Reporting Requirements, shall apply to PSD monitoring as well as to other types of monitoring. However, section 1.3 Data Quality Assessment and section 1.4 Calculations for Data Quality Assessment, are modified as noted below in 1.6.1 and 1.7.1.

1.6.1 Automated Methods

1.6.1.1 Precision

Refer to 1.3.1.1 for test procedures and to 1.7.1.1 for calculation procedures.

1.6.1.2 Accuracy

Refer to 1.3.1.2 for test procedures with the following exception. Each sampling quarter audit each analyzer that monitors for SO_2, NO_2, O_3, or CO at least once. Calculation procedures are specified in 1.7.1.2.

1.6.2 Manual Methods

1.6.2.1 Precision

For a PSD monitoring network, one sampling site must have collocated samplers. The site with the highest expected 24-hour pollutant concentration must be selected. The two samplers must be within four meters of each other but at least two meters apart to preclude airflow interference. Calibration, sampling and analysis must be the same for both collocated samplers as well as for all other samplers in the network. The collocated samplers must be operated as a minimum every third day when continuous sampling is used. When a less frequent sample schedule

is used, the collocated samplers must be operated at least once each week. For each pair of collocated samplers, designate one sampler as the sampler which will be used to report air quality for the site and designate the other as the duplicate sampler. The differences in measured concentration between the two collocated samplers are used to calculate precision as described in 1.7.2.1.

1.6.2.2 Accuracy

Refer to 1.3.2.2 for test procedures except for TSP and Pb. For TSP during each sampling quarter, audit the flow rate of each high volume sampler at least once. For Pb during each sampling quarter, analyze at least one audit sample in each of the two ranges each day that samples are analyzed.

1.7 Calculation for Data Quality Assessment for PSD Monitoring

1.7.1 Automated Methods

1.7.1.1 Precision

Each organization, at the end of each sampling quarter, shall calculate and report a precision probability interval for each analyzer. Directions for calculations are given below and directions for reporting are given in section 1.5. If monitoring data are invalidated during the period represented by a given precision check, the results of that precision check shall be excluded from the calculations. Calculate the percentage difference (d_i) for each precision check using equation 1.

$$d_i = \frac{Y_i - X_i}{X_i} \times 100 \qquad (1)$$

where: Y_i = analyzer's indicated concentration from the i-th precision check.

X_i = known concentration of the test gas used for the i-th precision check.

For each instrument, calculate the quarterly average ($\overline{d}_j$), using equation 2, and the standard deviation (S_j), using equation 3.

$$\overline{d}_j = \frac{1}{n} \sum_{i=1}^{n} d_i \qquad (2)$$

$$S_j = \sqrt{\frac{1}{n-1}\left[\sum_{i=1}^{n} d_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} d_i\right)^2\right]} \qquad (3)$$

where n is the number of precision checks on the instrument made during the sampling quarter. For example, n should be 6 or 7 if span checks are made biweekly during a quarter.

Calculate the 95 percent probability limits for precision using equations 4 and 5.

$$\text{Upper 95 Percent Probability Limit} = \overline{d}_j + 1.96\ S_j \qquad (4)$$

$$\text{Lower 95 Percent Probability Limit} = \overline{d}_j - 1.96\ S_j \qquad (5)$$

Report the results in accordance with section 1.5.

1.7.1.2 Accuracy

Each organization, at the end of each sampling quarter, shall calculate and report accuracy for each audit concentration for each analyzer audited during the quarter. Directions for calculations are given below (directions for reporting are given in section 1.5.

Calculate the percentage difference d_i for each audit concentration using equation 1 where Y_i is the analyzer's indicated concentration

from the i-th audit check and X_i is the known concentration of the audit gas used for the i-th audit check.

For each instrument, calculate the quarterly average $\overline{d}_j$ and the standard deviation S_j, using equations 2 and 3, where n is the number of audit checks.

Calculate the 95 percent probability limits for accuracy using equations 4 and 5. Report the results in accordance with section 1.5.

1.7.2 Manual Methods

1.7.2.1 Precision

Estimates of precision for TSP, SO_2, NO_2 and Pb are calculated quarterly from results obtained from the collocation of two samplers at one site as described in section 1.6.2.1. For the paired measurements, calculate the percentage difference d_i for each pollutant, using equation 1 where Y_i is the pollutant concentration measured by the duplicate sampler and X_i is the pollutant concentration measured by the sampler reporting air quality for the site. Calculate the quarterly average percentage difference $\overline{d}_j$, the standard deviation S_j, and the upper and lower 95 percent probability limits for precision, using equations 2, 3, 6 and 7.

Upper 95 Percent Probability

$$\text{Limit} = \overline{d}_j + 1.96\ S_j/\sqrt{2} \qquad (6)$$

Lower 95 Percent Probability

$$\text{Limit} = \overline{d}_j - 1.96\ S_j/\sqrt{2} \qquad (7)$$

Report the results in accordance with section 1.5.

1.7.2.2 Accuracy

At the end of each sampling quarter, each organization shall calculate and report the accuracy for each high volume sampler and for SO_2, NO_2, and Pb analyses. Calculate the percentage difference d_j for each high volume sampler and for SO_2, NO_2, and Pb analysis using equation 1 where Y_i is the indicated flow rate or indicated SO_2, NO_2, or Pb concentration and X_i is the known flow rate or known SO_2, NO_2, or Pb concentration from the i-th audit check.

Calculate the quarterly average d_j for each high volume sampler and SO_2, NO_2, or Pb analyses and the standard deviation S_j, using equations 2 and 3, where n is the number of audit checks.

Calculate the 95 percent probability limits for accuracy using equations 4 and 5. Report the results in accordance with section 1.5.

2. SITING OF AIR MONITORING STATIONS

2.1 Monitoring Objectives

Air monitoring stations shall be sited to meet two basic monitoring objectives. One objective is to determine maximum pollutant concentrations for each of the averaging times for which ambient air quality standards have been established. A second objective is to determine representative concentrations in populated areas. The total number of monitoring stations required to meet these objectives will vary, depending on the source, meteorology, topography, location of the source relative to populated areas, etc.

2.2 Approval

The siting of all air monitoring stations must be approved by the Bureau of Air Quality Control prior to installation.

3. Sampling Probe Installation

3.1 Probe Siting

This section contains probe siting criteria to be applied to ambient air quality monitors or monitor sample probes. These criteria must be followed as closely as possible to ensure the collection of valid and useful data.

The height above ground shall be 3-15 meters for all pollutants, except for particulates, carbon monoxide (microscale) and lead in which cases it shall be 2-15, 2.5-3.5, and 2-7 meters, respectively.

The distance from the vertical and horizontal supporting structures shall be greater than 1 meter, except when probe is located on rooftop, in which case it shall be greater than 2 meters from walls, parapets, or penthouses.

The distance from trees shall be greater than 20 meters.
The distance from obstacles, such as buildings, must be at least twice the height the obstacle protrudes above the particulate or lead sampler or the inlet probe for other pollutants.

Airflow must be unrestricted for at least 270° around particulate and lead samplers and inlet probes for other pollutants, or at least 180° if the probe is on the side of a building.

Particulate samplers and inlet probes for other pollutants shall not be located near localized sources such as furnace or incinerator flues and unpaved roads or unpaved parking lots.

3.2 Probe Material

Sampling probes and the lines connecting them to the analyzers must be constructed of teflon or pyrex glass when sampling for sulfur dioxide, nitrogen dioxide, and ozone.

3.3 Sample Residence Time

The sample residence time, from the inlet of the probe to the inlet of the analyzer, must be less than 20 seconds.

A.G. RULE NO: 83-111

Revision B

Arizona Testing Manual for Air Pollutant Emission

February 7, 1983

The Testing Manual is revised to incorporate changes to existing test methods and new test methods which have been promulgated by the Federal Environmental Protection Agency since the last revision on May 19, 1980. Arizona Test Methods A2 and A3 are added to provide a simplified particulate test method for certain sources having low stack humidity, and to provide a test method for determination of gaseous emissions from bulk gasoline loading terminals, respectively. The latter is applicable in counties which adopt Phase One gasoline vapor recovery programs.

The test limits for certification of visible emissions observers by the Bureau of Air Quality Control have also been revised. The maximum allowable deviation of 15% from the smoke generator transmissometer reading at the random 25 opacity settings for either black or white smoke has been deleted, and the maximum allowable average deviation of 7.5 percent has been reduced to 6.0 percent. Experience has demonstrated that candidates for certification may exceed the maximum allowable deviation under highly variable field testing conditions while achieving fully acceptable average deviations. Since compliance with the specified visible emissions limitations in the regulations is based on the average of 24 consecutive observations during any visible emissions test, the limit on individual observations is not applicable.

ARIZONA TESTING MANUAL FOR
AIR POLLUTANT EMISSIONS

Revision Control Record

Revision No.	Date	Section	Description of Revision
N/C	09-30-78	All	Issued
A	05-19-80	2	Revised P 2.1-1 of 8
		3	1. Update Method 11 to revisions of January 10, 1978 2. Update Method 16 to revisions of January 12, 1979 3. Add Reference Method 19 4. Add Reference Method 20
B	02-07-83	1	Revised Section 1.1.3 Updated Exhibit 1.1.3-1 Updated Exhibit 1.2-2 Revised Exhibit 1.2-2 Revised Exhibit 1.4.1-1
		2	Added Method A2 Added Method A3
		3	Added Methods 5A, 12, 22, 24, & 25 Added Alternate to Method 9 Updated Methods 13A, 13B, & 14
		5	Updated Methods 101, 102, 106, & 107 Added Method 101A
		6	Added 40 CFR Part 61 Appendix C

ARIZONA TESTING MANUAL FOR AIR POLLUTANT EMISSIONS

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1.0	ARIZONA SOURCE TESTING POLICY	1	0	06-23-78
1.1	SOURCE TEST QUALIFICATION	14	1	02-07-83
1.1.1	Agency Observer Requirements			
1.1.2	Mass Emissions Test Training			
1.1.3	Visible Emissions Evaluator Training and Certification			
1.2	SOURCE TEST PLANNING AND APPROVAL	7	1	02-07-83
1.3	QUALITY ASSURANCE PROVISIONS	1	0	06-23-78
1.3.1	Equipment Maintenance and Calibration			
1.3.2	Interlaboratory Control Audits			
1.4	DATA COLLECTION AND EVALUATION	6	0	02-07-83
1.4.1	Agency Observer Activities			
1.4.2	Compliance Test Review			
1.4.3	Test Documentation			
2.0	ARIZONA EMISSION TEST METHODS	18	A	05-19-80
2.1	METHOD A1: Method for Determination of Particulate Emissions from Stationary Sources in the Presence of Sulfuric Acid Mist and Sulfur Oxides			
2.2	METHOD A2: Arizona Emission Test Method for Determination of Dry Particulate Matter from Stationary Sources	16	0	02-07-83
2.3	METHOD A3: Emission Test Procedure for Bulk Gasoline Loading Terminals	20	0	02-07-83

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3.0	ENVIRONMENTAL PROTECTION AGENCY REFERENCE METHODS (40 CFR Part 60, Appendix A)	
3.1	METHOD 1: "Sample and Velocity Traverses for Stationary Sources:	03-23-78
3.2	METHOD 2: "Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)"	03-23-78
3.3	METHOD 3: "Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight"	03-23-78
3.4	METHOD 4: "Determination of Moisture in Stack Gases:	03-23-78
3.5	METHOD 5: "Determination of Particulate Emissions from Stationary Sources"	03-23-78
	METHOD 5A: "Determination of Particulate Emissions from the Asphalt Processing and Asphalt Roofing Industry:	08-06-82
3.6	METHOD 6: "Determination of Sulfur Dioxide Emissions from Stationary Sources"	03-23-78
3.7	METHOD 7: "Determination of Nitrogen Oxide Emissions from Stationary Sources"	03-23-78
3.8	METHOD 8: "Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources"	03-23-78
3.9	METHOD 9: "Visual Determination of the Opacity of Emissions from Stationary Sources"	11-12-74
3.10	METHOD 10: "Determination of Carbon Monoxide Emissions from Stationary Sources"	03-08-78
3.11	METHOD 11: "Determination of Hydrogen Sulfide Emissions from Stationary Sources"	01-10-78
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3.15	METHOD 15: "Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide Emissions from Stationary Sources"	03-15-80

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3.16	METHOD 16: "Semicontinuous Determination of Sulfur Emissions from Stationary Sources"	01-12-79
3.17	METHOD 17: "Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration Method)	02-23-78
3.19	METHOD 19: "Determination of Sulfur Dioxide Removal Efficiency and Particulate, Sulfur Dioxide, and Nitrogen Oxides Emission Rates from Electric Utility Steam Generators"	06-11-79
3.20	METHOD 20: "Determination of Nitrogen Oxides, Sulfur Dioxide, and Oxygen Emissions from Stationary Gas Turbines"	09-10-79
3.22	METHOD 22: "Visible Determination of Fugitive Emissions from Material Processing Sources"	08-06-82
3.24	METHOD 24: "Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings"	10-03-80
3.25	METHOD 25: "Determination of Total Gaseous Nonmethane Organic Emissions as Carbon"	10-03-80

Section	Subject	Pages	Revision	Date
4.0	ENVIRONMENTAL PROTECTION AGENCY PERFORMANCE SPECIFICATIONS (40 CFR Part 60, Appendix B)	Applicable Revision of Performance Specification will be defined and recorded at date of continuous monitoring equipment performance evaluation planning approval.		
4.1	PERFORMANCE SPECIFICATION 1: "Performance Specifications and Specification test procedures for transmissometer systems for continuous measurement of the opacity of stack emissions"			
4.2	PERFORMANCE SPECIFICATION 2: "Performance Specifications and Specification Test Procedures for Monitors of SO_2 and NO_x from Stationary Sources"			
4.3	PERFORMANCE SPECIFICATION 3: "Performance Specifications and Specification Test Procedures for Monitors of CO_2 and O_2 from Stationary Sources"			

Section	Subject	Latest Revision Date
5.0	ENVIRONMENTAL PROTECTION AGENCY TEST METHODS (40 CFR Part 61, Appendix B)	
5.1	METHOD 101: "Reference Method for Determination of Particulate and Gaseous Mercury Emissions from Stationary Sources (Air Streams)"	06-08-82
5.1A	METHOD 101A: "Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators"	06-08-82
5.2	METHOD 102: "Reference Method for Determination of Particulate and Gaseous Mercury Emissions from Stationary Sources (Hydrogen Streams)"	06-08-82
5.3	METHOD 103: "Beryllium Screening Method"	04-06-73
5.4	METHOD 104: "Reference Method for Determination of Beryllium Emissions from Stationary Sources"	04-06-73
5.5	METHOD 105: "Method for Determination of Mercury in Wastewater Treatment Plant Sewage Sludges"	10-14-75
5.6	METHOD 106: "Determination of Vinyl Chloride from Stationary Sources"	09-07-82
5.7	METHOD 107: "Determination of Vinyl Chloride of Inprocess Wastewater Samples, and Vinyl Chloride Content of Polyvinyl Chloride Resin, Slurry, Wet Cake, and Latex Samples"	09-07-82

Section	Subject	Latest Revision Date
6.0	ENVIRONMENTAL PROTECTION AGENCY QUALITY ASSURANCE PROCEDURES (40 CFR Part 61, Appendix C)	
6.1	PROCEDURE 1: "Determination of Adequate Chromatographic Peak Resolution:	09-07-82
6.2	PROCEDURE 2: "Procedure for Field Auditing GC Analysis	09-07-82

1.1.3 VISIBLE EMISSIONS EVALUATOR TRAINING AND CERTIFICATION

The Bureau shall conduct training and certification testing for visible emissions evaluators for use in determination of compliance with applicable visible emissions regulations. At a minimum, detailed training relating to visible emissions observations shall be presented semi-annually, and certification testing shall be conducted quarterly.

Equipment utilized for visible emissions evaluator training shall be calibrated, operated, and maintained in accordance with Exhibit 1.1.3-1.

To receive initial certification as a qualified observer, a candidate must attend the Bureau training school on the theory and practice of visible emissions evaluation, be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an average error not to exceed 6.0 percent opacity in each category. Successful candidates are issued certification indicating qualification as a visible emissions evaluator (Exhibit 1.1.3-2). Certifications must be renewed at least every six months to remain valid.

To recertify as a qualified observer, a candidate must have attended the classroom training school within the last twelve months and successfully pass the certification testing within the tolerance noted above.

CALIBRATION, OPERATION, AND MAINTENANCE OF THE SMOKE EMISSION GENERATOR

A. Introduction

The visible emissions generator used for training and qualification for certification of visible opacity evaluators is designed to produce black and white plumes representing the opacity standards. The black plumes are produced by burning a controlled stream of toluene in a firebox with insufficient oxygen to produce particulate carbon aerosol (soot). The white plume is generated by vaporizing diesel fuel in a propane gas heated chamber and the condensing of the vapor in a cool air stream to form an aerosol of finely divided droplets which appear white in the plume. The opacity is controlled by regulation of the amount of diesel oil while the carrier gas volume is constant. The opacity of the generated plume is accurately measured by a transmissometer located across the diameter of the stack.

B. Smoke Generator Specification Compliance

Any opacity generator used for purposes of visible emissions evaluator certification shall be equipped with an opacity meter installed across the diameter of the generator stack. The meter output shall display in-stack opacity based on a path length equal to the stack exit diameter, on a 0-100% chart recorder scale. The transmissometer installed in the Arizona Smoke Generator complies with the optical design and performance specifications of CFR 40 Part 60 New Source Performance Standards Appendix A Test Method No. 9 "Visual Determination of the Opacity of Emissions from Stationary Sources."

Method 9 Specifications

	Specification	Arizona Opacity Generator
1. Light Source.	Incandescent lamp operated ± 5% nominal voltage.	Incandescent lamp with a constant voltage transformer ± 1% regulation for ± 15 volt line change.
2. Spectral response of photocell.	Photopic spectral response.	Selenium type photocell stable in photopic range.
3. Angle of Projection.	Total angle < 15°.	Total angle 8°.
4. Angle of View.	Total angle < 15°.	Total angle 12°.
5. Response Time.	≤ 5 seconds.	< 2 seconds.
6. Zero and span drift.	± 1% opacity, maximum 30 minutes.	± 1% opacity, 30 minutes.
7. Calibration error.	± 3% opacity maximum.	± 2% maximum.

C. Calibration Procedure

The transmissometer (opacity meter) is calibrated by the following procedure:

1. The meter activated and allowed to stabilize for a minimum thirty minutes warm up.

2. The zero and span of the opacity meter scale are verified by switching on the light source to produce a simulated 0% opacity, and by switching off the light source to produce a simulated 100% opacity. When a stable response at 0 and 100% is produced on the chart recorder indicator, the zero and 100% opacity is set adjusting the calibration potentiometer on the control panel (see Figure 2).

3. The zero and span drift are determined by operating the opacity generator for one hour, and then checking the amount of zero and span deviation. The zero and span should not drift more than 1%.

4. The opacity meter is calibrated with standard neutral density filters at three points on the opacity scale. The calibration is accomplished by inserting each of the filters into the opacity meter light path and recording five non consecutive readings for each filter. The filters are calibrated to a tolerance of ± 2%. The maximum error on any one reading shall be ± 3% opacity. The calibration is done at each use of the smoke generator, and is recorded on a calibration data form which becomes a part of the certification examination records. The "response time" of the meter is checked at each operational period by switching the light source "on" then "off" to simulate 0 and 100% opacity. The procedure is performed five times and time interval to reach a stable response is recorded on the calibration data form (see Figure 3).

D. <u>Operation</u>

1. The generator is positioned so that the opacity observer certification candidates have a clear unobstructed view of the stack inlet, have the sun at a 140° quadrant at their back, and can be located at

least two stack heights distant from the generator.

2. The generator should be charged with sufficient toluene for the day's run before connecting the electrical supply or lighting the LP gas burner. This is for safety in handling the volatile highly inflammable liquid toluene.
3. The unit is connected by extension cord line to a stable 110-120V alternating current supply with at least 20 ampere capacity.
4. The opacity meter-transmissometer system should be connected to the constant voltage power supply. All other electrical connections are direct to the power supply.
5. Connect the recorder readout and switch on light source to allow for a 30 minute warm up of electronics.
6. Ignite the propane burner on the white opacity generator to allow for warm up. The burner is normally allowed to burn at a constant rate for the complete series of runs.
7. Put generator in configuration for black opacity by removing the sheet metal baffle at the firebox outlet, turning on the induction draft fan, and turning on the stack fans.
8. Turn on the firebox ignitor switch which will be left on for the duration of the day's run. Visually check firebox to assure ignitor is operating.
9. Turn on toluene pump and adjust supply valves so that toluene is delivered to the firebox.

10. Regulate flow of toluene to about 40% opacity and allow unit to warm up thirty minutes. Check the plume color and adjust the firebox air inlet for maximum black shade. Adjust toluene feed to produce representative opacities of black smoke. Shut off pump and valve. Allow toluene to burn out of firebox.

11. Install sheet metal baffle to block firebox vent to the exhaust system. Check white smoke system by starting diesel fuel pump and adjusting diesel fuel flow control valve to produce a representative range of opacities. Shut off pump and valve. Allow plume to dissipate.

12. Calibrate the transmissometer in accordance with Section C. When the calibration procedure is completed and the generator is found in compliance with the required performance specifications training may be started.

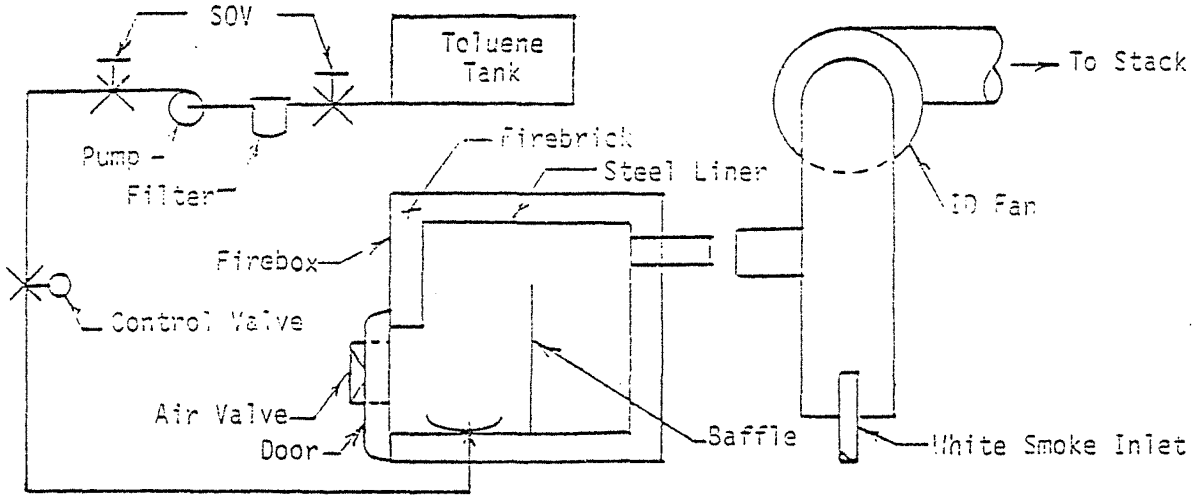
13. The examination for certification is conducted in two segments: one with 25 random black plumes, the second with 25 random white plumes. The person(s) conducting the training sounds the horn each time an observation is to be taken and records the transmissometer reading on a master test record which is identified by run number. The candidate marks the opacity value for each plume to the nearest 5% opacity. The examination is recorded on forms making a duplicate copy of the examination. The examination originals are collected by the examiner. He then reads the recorded transmissometer readings for each plume. The candidate is qualified for certification if his readings of opacity deviate no more than 6% from the arithmetic average of the opacity meter readings in each category.

E. Calibration Schedule

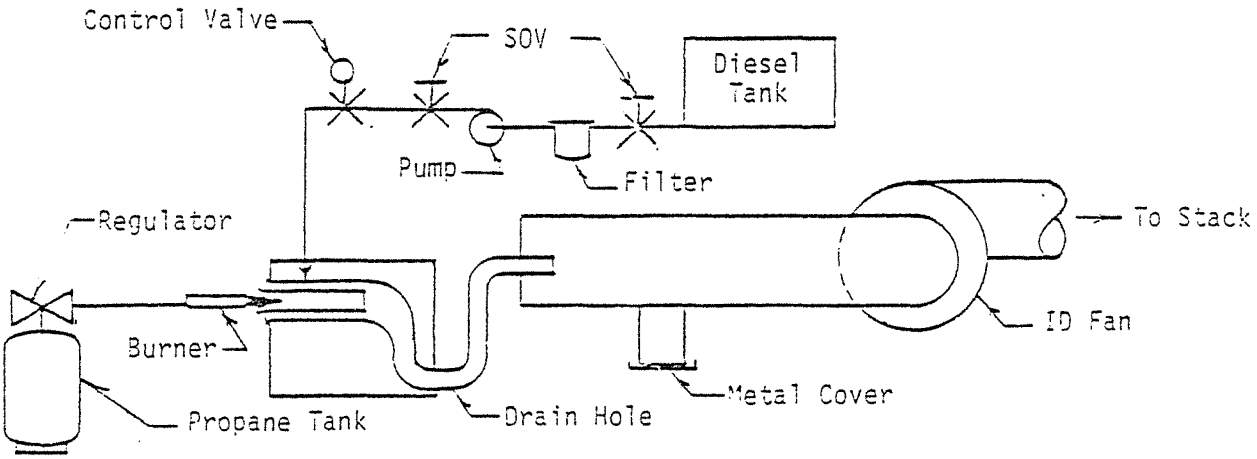
Calibrate at each use which is normally each month.

F. Maintenance Schedule

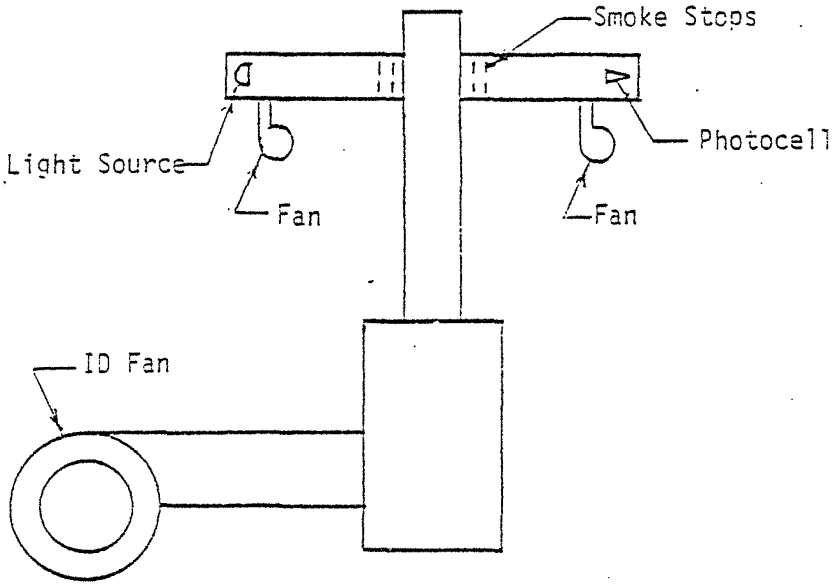
Each 6 months. Check all systems. Since there are no moving parts to be lubricated or adjusted maintenance is confined to obvious deterioration of the equipment.



Black Smoke Generator



White Smoke Generator



Smoke Generator Stack

Figure 1

EXHIBIT 1.1.3-1
REVISION 1
DATE 02-07-83
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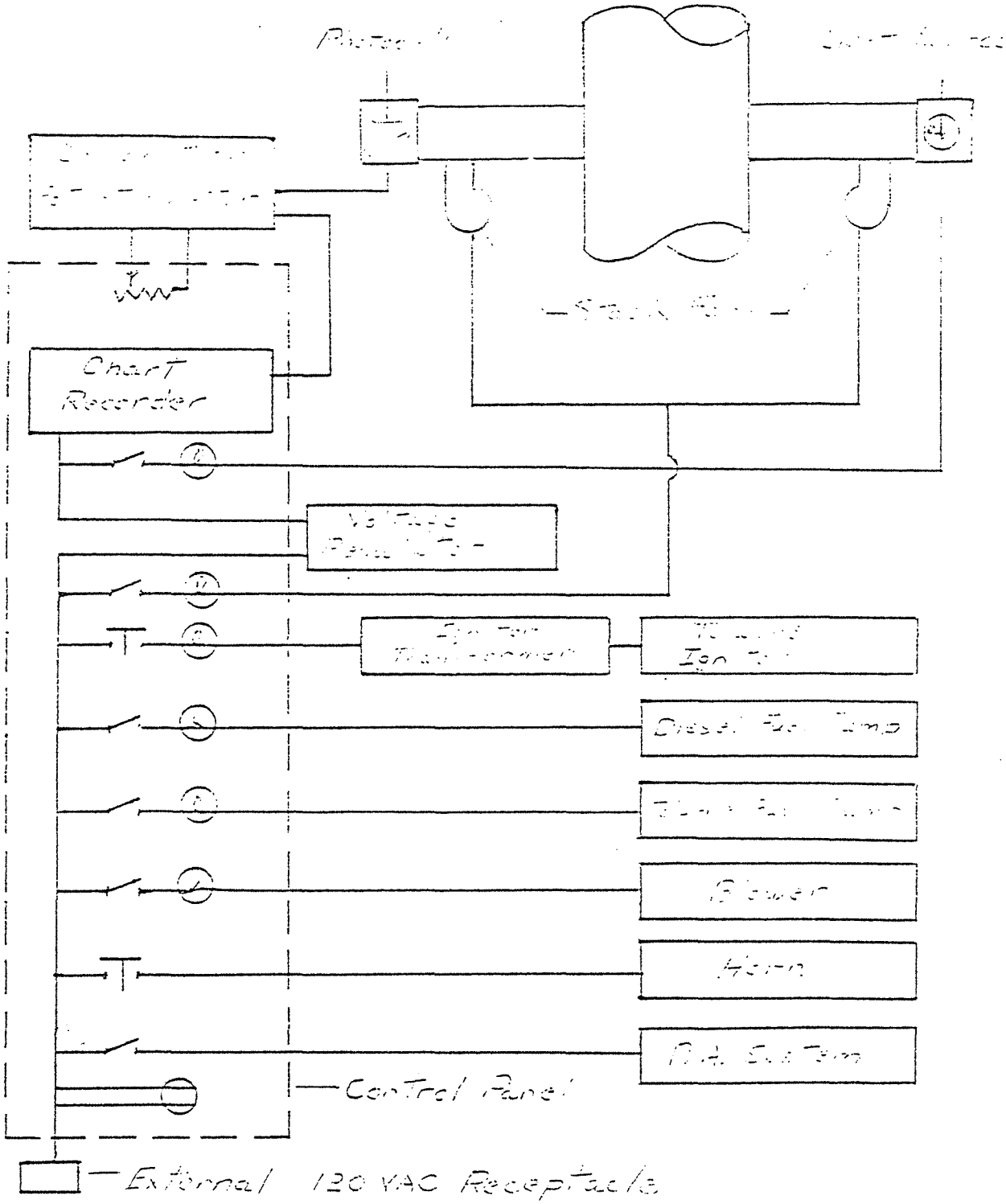

ELECTRICAL BLOCK DIAGRAM
SMOKE EMISSIONS GENERATOR

Figure 2

EXHIBIT 1.1.3-1
REVISION 1
DATE 02-07-83
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VISIBLE OPACITY GENERATOR CALIBRATION

Date _____

Procedure:

The generator electronics are allowed to warm up 30 minutes (transmissometer light on) before calibration.

1. Adjust 0% opacity (light on).
2. Adjust 100% (span) opacity (light off).
3. Repeat above two times and at same time check response time which should be no more than 2 seconds.
4. Position each of the three standard neutral density filters in the transmissometer light path. Repeat three times for each filter.
5. Repeat zero and span checks after each run. Record drift. If the drift is more than 1% the run should be repeated.
6. Repeat complete calibration procedure each 4 hours.

Neutral Density Filter Standardization values _____% _____% _____% _____%

Time	Run	0 Dev.	Span Dev.	Filter 1	Filter 2	Filter 3	Response	Operator

BAQC:CS:8/81

Figure 3

ARIZONA DEPARTMENT OF HEALTH SERVICES

BUREAU OF AIR QUALITY CONTROL

PLANNING REPORT FOR COMPLIANCE TESTING

DATE _____

COMPANY _____

ADDRESS _____

SOURCE(S) _____

_____

CONTACT _____ PHONE _____

ENVIRONMENTAL CONSULTANT (if used) _____

_____

PROPOSED TEST DATE(S) _____

PROPOSED TEST PROCEDURES _____

_____

TEST(S) APPROVED FOR METHODOLOGY AND TIME FOR BAQC _____

BY _____

SAMPLING PLATFORM(S) COMPLY WITH BUREAU MINIMUM STANDARDS? _____

STACK DIAMETERS TO NEAREST FLOW DISTURBANCE. UPSTREAM _____

DOWNSTREAM _____

CYCLONIC FLOW DISTURBANCE NOT PRESENT OR LESS THAN 10 DEGREES? _____

EMISSIONS CONTROL DEVICE(S) _____

_____

PLEASE NOTE ANY PROPOSED DEVIATION FROM TESTING MANUAL PROCEDURES AND/OR ANY POSSIBLE BUT NONPREDICTABLE CONDITIONS WHICH MAY EXTEND OR DELAY TESTING

_____

_____

_____

_____

_____

_____

ADHS/EHS/BAQC:CS/3/82

Exhibit 1.2-2
Revision 1
Date 02-07-83
Page 1 of 1

GUIDELINES FOR COMPLIANCE TESTING

All mass emissions testing required to demonstrate compliance with applicable emission standards shall be performed in accordance with the following guidelines:

1. An item of equipment not covered by an operating permit, but for which an installation permit has been issued, may be operated for purposes of start-up and testing only if written authorization has been obtained from the Bureau of Air Quality Control acting for the Director which designates dates of such operation.

2. The applicant will file a test plan no later than two weeks before the proposed compliance testing detailing the specific methods from the Arizona Testing Manual to be used. The "Planning Report for Compliance Testing," Exhibit 1.2-2, may be used for this purpose. A pretest conference on the proposed compliance test with the Bureau's Compliance Section is recommended for initial testing of new types of emission points process or control equipment or if any difficulty is anticipated obtaining representative samples of the maximum expected emissions from the source. Any deviation from the applicable methods in the Arizona Testing Manual must be approved in writing by the Bureau acting for the Director.

3. The Bureau of Air Quality must be notified of the dates of start-up and emission testing as soon as they are set, but in no event less than two weeks (14 days) prior to testing.

4. It is the applicant's responsibility to have employees qualified by training and experience in source sampling or to retain a qualified professional firm to perform the testing.

5. Stack sampling facilities meeting the requirements of Exhibit 1.2-1 shall be provided, unless written approval of any deviation from those requirements has been obtained from the Bureau's Compliance Section.

6. The Bureau may require that an observer be present at all replicate testing and subsequent laboratory procedures for quality assurance verification of the testing procedures, or may observe the procedures on a sampling basis. The observer will make out a quality assurance check list report which will be available for copying by the source. The source will be informed of any perceived testing deficiencies at the time of testing. The designated observer may approve minor variations in test procedures which are justified by field conditions.

7. All equipment covered by the permit application shall be operated during the test in such a manner and the process feed shall be of such composition and amounts to produce the maximum expected loading of control equipment.

8. Equipment operating conditions shall be monitored and submitted as part of the test report including process feed composition and mass.

9. A copy of "raw data" from the emission tests shall be submitted to the Department's field representative at the time of testing, if requested. Compliance test data and final test report shall be submitted to the Bureau within twenty one (21) days following completion of tests.

10. No less than three (3) tests, unless otherwise specified in the applicable regulations or test procedures, shall be performed at a given sampling site under the same equipment operating conditions of raw material feed rate and raw material quality.

A2. ARIZONA EMISSION TEST METHOD FOR DETERMINATION OF DRY PARTICULATE MATTER FROM STATIONARY SOURCES

A2.1 Principle and applicability.

1.1 Applicability.

This method is applicable to sources where particulate matter can be expected to consist entirely of dust, lint, fibers, sawdust and other dry particulate matter, with no condensable particulates. The amount of moisture in the gas stream should be very low, and in all cases at least 10° F below the moisture dewpoint at minimum sample temperature in the sampling train. Some sources where the method is applicable are: cotton gins (without wet collectors); grain elevators; feed mills; and other sources controlled by inertial separators, baghouses, and other dry particulate collectors, subject to approval by the Director.

1.2 Principle.

The particulate matter is removed from the gas stream under isokinetic conditions by collection on a glass fiber filter. Moisture in the gas stream is determined by wet and dry bulb thermometer readings of the gas stream, or alternately by capturing moisture from sampled gas on a desiccant and weighing.

A2.2 Equipment.

2.1 Sampling Train.

A schematic of the sampling train used is shown in Figure 1.

2.1.1 Probe - Stainless Steel, other inert plastic, glass or fluorocarbon lined. Length sufficient to traverse the stack or duct to be sampled.

2.1.2 Probe Nozzle - The probe nozzle shall have a tapered leading edge. The angle of the taper shall be <30° and shall be on the outside to preserve a

constant inside diameter. The probe nozzle shall be of buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling shall be available.

2.1.3 Pitot Tube - S-type pitot tube attached to the probe to measure gas velocity simultaneous with sample withdrawal.

2.1.4 Filter Holder - Metal or glass sufficient size to support a 10cm or 4-inch circular glass fiber filter. The filter should be attached to the probe.

2.1.5 Meter System - Leak-proof pump capable of moving 3 CFM at 10 inches mercury vacuum. A calibrated orifice with means for measuring pressure drop and determine flow rate. A dry gas meter accurate ± 1%.

2.1.6 Alternate desiccant gas dryer (optional) - Use a leak-tight container made of metal or plastic, which can be filled with approximately 500 gm of desiccant and used as an in line moisture absorber. The container and desiccant should be capable of being sealed and weighed ± 1 gm.

2.1.7 Vacuum Gage - 0 — 20" mercury range.

2.1.8 Temperature Sensor - Can be a thermocouple reading 0 — 300° F accurate to ± 5° F, or a thermometer accurate to ± 5° F.

2.1.9 Wet-Dry Bulb Psychrometer - A psychrometer capable of measuring stack temperature and wet bulb temperature differential to 1° F. Psychrometric chart to read dew point and indicated water content of carrier gas in range of 20 to 300° F.

A2.3 Pretest preparations.

3.1.1 All components shall be maintained and calibrated as required in the Arizona Testing Manual.

3.1.2 If a desiccator container is used to remove moisture from the sampled gas (optional) weigh several portions of 500 gm desiccant to 0.5 gm and store in airtight containers. Alternately the desiccant can be weighed directly in the container used in the sampling train.

3.1.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

3.1.4 The filters may be oven dried at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Director.

A2.4 Preliminary determinations.

4.1.1 Select the sampling site and the minimum number of sampling points according to Method 1. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines according to directions in Method 2 be performed.

4.1.2 Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gage is chosen for the range of velocity heads encountered.

4.1.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

4.1.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min (or some greater time interval as specified by the Director), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Director's approval must first be obtained.

4.2 Preparation of Collection Train.

4.2.1 Leak-Check Procedures.

After the sampling train has been assembled, leak-check the train at the sampling site by plugging the nozzle and applying Hg (15 inc. Hg) vacuum.

NOTE. — A lower vacuum may be used, provided that it is not exceeded during the test.

4.2.2 Post-test Leak-Check.

A leak-check is mandatory at the conclusion of each sampling run. It shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.02 cfm or 4 percent of the average sampling rate (whichever

is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume, or shall void the sampling run.

A2.5 Particulate Train Operation.

5.1 During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic).

For each run, record the data required on a data sheet such as the one shown in Figure 2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling assure that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type 8 pitot tube coefficient is 0.85 ± 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by Method 1 or as specified by the Director, being careful not to bump the probe nozzle into the stack

walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

Take other readings required at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manameter level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check. Also, leak-check the pitot lines as described in Method 2; the lines must pass this leak-check, in order to validate the velocity head data.

5.2 Calculation of Percent Isokinetic.

Calculate percent isokinetic to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining

isokinetic rates due to source conditions, consult with the Director for possible variance on the isokinetic rates.

5.3 Sample Recovery.

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe.

Transfer the probe and filter assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold.

Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Director and shall be used when specified by the Director; in these cases, save a water blank and follow the Director's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the swagelok fitting and acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the

upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surface with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Whenever possible, containers should be shipped in such a way that they remain upright at all times.

5.4 Analysis.

Record the data required on a sheet such as the one shown in Figure 3. Handle each sample container as follows:

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section 5, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Alternatively, the sample may be oven dried at 105° C (220° F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Director. The tester may also opt to oven dry the sample at 105° C (220° F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Director, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE. — At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

A2.6 Calculations.

6.1 Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

6.2 Nomenclature

An - cross sectional area of nozzle (ft^2)

Bws - water vapor in gas stream proportion by volume

Ca - acetone blank residue concentration mg/ml

Cp - pitot tube coefficient

C_s - concentration of particulate matter in stack gas dry basis corrected to standard conditions (g/dscf)

As - Area of stack (ft^2)

I - percent of isokinetic sampling

Ds - stack diameter

m_n - total amount of particulate matter collected mg

M_s - molecular weight of stack gas (air = 29)

m_w - mass of residue of acetone wash after evaporation

P_{Bar} - barometric pressure in Hg

P_s - pressure of stack (absolute)

P_{stp} - standard absolute pressure 29.92 in Hg

Tm - absolute dry gas meter temperature in degrees R

Ts - absolute average stack gas temperature in degrees R

Va - volume of acetone used

Vm - volume of gas sample as measured by dry gas meter (dcf)

V_s - stack gas velocity, calculated by Method 2 using data obtained from Method 5 (ft^3/sec)

Y - dry gas meter calibration factor

ΔH - average pressure differential across the orifice meter

Θ - total sampling time in minutes

Meter Volume

$$Vm(std) = Vm\ Y\ \left(\frac{Tstd}{Tm}\right) \left[\frac{P_{Bar} + \frac{\Delta H\ avg}{13.6}}{P_{std}}\right]$$

NOTE. — If the "optional" desiccant gas dryer for moisture is used in the sampling train, the water collected must be calculated as water vapor at

standard conditions and added to the dry gas meter volume as measured in the test and converted to standard conditions before calculating particulate concentration.

(wt. desiccant after test — wt. desiccant before test) x 0.04707 = SCF water vapor in gas sampled ÷ Vm_{std} = Total gas sampled.

Stack Velocity (V_s)

$$V_s - avg = 85.48\ (cp)\ (\sqrt{\Delta P})avg \sqrt{\frac{Ts\ avg}{P_s\ M_s}}$$

Isokinetic Variation (I)

$$I = \frac{1.667\ (T_s - avg)\ \frac{Vm\ std}{17.65}}{Vs - avg\ (P_s)\ \Theta\ An}$$

Particulate Concentration C_s

$$C_s = 2.205 \times 10^{-6}\ \frac{Mn}{Vm\ std} = lbs/dscf$$

Volumetric Flow Rate

$$Q_{sd} = 3600\ V_s\ As\ (\frac{Tstd}{T_s})\ dscf/hr$$

Pollutant Mass Rate PMR

$$PMR_c = (C_s)\ Q_{sd}$$

$$PMR_c = lbs/hour$$

PLANT _____

LOCATION _____

OPERATOR _____

DATE _____

RUN NO. _____

AMBIENT TEMPERATURE _____

BAROMETRIC PRESSURE _____

PROBE LENGTH m(ft) _____

SCHEMATIC OF STACK CROSS SECTION

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STACK TEMPERATURE °C (°F)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), mm(in.) H_2O	METER READING GAS SAMPLE VOLUME m^3 (ft^3)	ΔV_m m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER	
						INLET ($T_{m(in)}$), °C (°F)	OUTLET ($T_{m(out)}$), °C (°F)
TOTAL						Avg.	Avg.
AVERAGE						Avg.	

Figure 2. Field Data Record

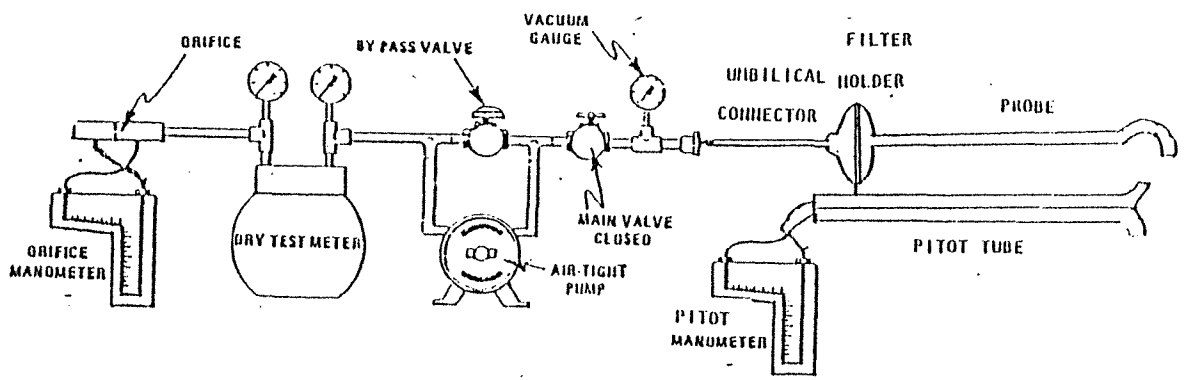

Figure 1. Simplified Particulate Sampling Train

ARIZONA TEST METHOD A2
EMISSIONS TEST ANALYSIS

DATE _____

SOURCE SAMPLED _____

STACK CONDITIONS

Dry Bulb Temp. _____ °F Difference _____ °F

Wet Bulb Temp. _____ °F Water Vapor _____ %

Lowest sampling train temperature _____ °F

	Probe No. _____	Probe No. _____	Probe No. _____
Gross Wt. gm	_____	_____	_____
Tare Wt. gm	_____	_____	_____
Net Wt. gm	_____	_____	_____

	Filter No. _____	Filter No. _____	Filter No. _____
Gross Wt. gm	_____	_____	_____
Tare Wt. gm	_____	_____	_____
Net Wt. gm	_____	_____	_____

P = Process Rate _____ Pounds-Mass Per Hour (PPH)

P = $\leq$ 60,000 PPH:

Allowable Emission Rate, E = $4.10P^{0.67}$ = _____ PPH

P>60,000 PPH:

Allowable Emission Rate, E = $55.0P^{0.11}-40$ = _____ PPH

Figure 3. Emission Test Analysis

ARIZONA TEST METHOD A3

Emission Test Procedure for Bulk Gasoline Loading Terminals

A3.1 PRINCIPLE

Hydrocarbon mass emissions are determined directly using flow meters and hydrocarbon analysis. The volume of liquid gasoline dispensed is determined. Results are expressed in grams of hydrocarbons emitted per gallon of gasoline transferred. Results are also expressed in terms of hydrocarbon control efficiency.

A3.2 APPLICABILITY

This method is applicable to determining hydrocarbon emission rates and control efficiency at bulk gasoline loading terminals employing either balance or vacuum-assist types of vapor collection systems and either continuous or intermittent vapor processing devices. This method is applicable to motor truck tanker and trailer loading only.

A3.3 DEFINITIONS

A3.3.1 Bulk Terminal

A primary distribution point for delivering gasoline to bulk plants, service stations, and other distribution points; where delivery to the terminal is by means other than truck; and where the total throughput is greater than 20,000 gallons/day.

A3.3.2 Loading Rack

An aggregation or combination of gasoline loading equipment arranged so that all loading outlets in the combination can be connected to a truck tanker or trailer parked in a specified loading space.

A3.3.3 Balance Vapor Collection System

A vapor transport system which uses direct displacement by the liquid loaded to force vapors from the tank truck or trailer into the recovery system.

A3.3.4 Vacuum-assist Vapor Collection System

A vapor transport system which uses a pump, blower, or other vacuum-inducing device to aspirate vapors from the tank truck or trailer into the recovery system.

A3.3.5 Continuous Vapor Processing Device

A hydrocarbon vapor control system that treats vapors from tank trucks or trailers on a demand basis without intermediate accumulation.

A3.3.6 Intermittent Vapor Processing Device

A hydrocarbon vapor control system that employs an intermediate vapor holder to accumulate recovered vapors from tank trucks or trailers. The processing unit treats the accumulated vapors only during automatically controlled cycles.

A3.4 SUMMARY OF THE METHOD

This method describes the test conditions and test procedures to be followed in determining the efficiency of the systems installed to control emissions resulting from tank truck loading operations at bulk terminals. Under this procedure, the vapors returned from the tank trucks or trailers during the loading operation are measured from representative loadings, and if necessary, extrapolated to determine the total recovered emissions that are processed by the control device. It is assumed that the monitored loadings are representative of all loadings at controlled product racks at any one facility. Direct measurements are made to calculate the hydrocarbon mass exhausted from

the processing equipment. All possible sources of leaks are checked and estimates are made of their magnitude if possible. The results are expressed in terms of mass hydrocarbons emitted per unit volume of gasoline transferred and control system efficiency. Emissions are determined on a total hydrocarbon basis. If significant methane is present in the vapors returned from the tank trucks or trailers, provisions are included for conversion to a total non-methane hydrocarbons basis.

A3.5 TEST SCOPE AND CONDITIONS APPLICABLE TO TEST

A3.5.1 Test Period

The elapsed time during which the test is performed shall not be less than 4-hour test repetitions.

A3.5.2 Number of Loadings to be Tested

At least ten tanker loadings shall be monitored for each rack under test during each of the three test repetitions. For terminals equipped with up to three controlled racks, only one rack must be tested. For terminals with more than three controlled racks, two racks must be tested.

A3.5.3 Terminal Status During Test Period

The test procedure is designed to measure control system performance under conditions of normal operation. Normal operation will vary from terminal-to-terminal and from day-to-day. Therefore, no specific criteria can be set forth to define normal operation. The following guidelines are provided to assist in determining normal operation.

A3.5.3.1 Closing of Loading Racks

During the test period, all loading racks shall be open for each product line which is controlled by the system under test. Simultaneous use of more than one loading rack shall

occur to the extent that such use would normally occur.

A3.5.3.2 Simultaneous use of more than one dispenser on each loading rack shall occur to the extent that such use would normally occur.

A3.5.3.3 Dispensing rates shall be set at the maximum rate at which the equipment is designed to be operated. Automatic product dispensers are to be used according to normal operating practices.

A3.5.4 Vapor Control System Status During Tests

Applicable operating parameters shall be monitored to demonstrate that the processing unit is operating at design levels. For intermittent vapor processing units employing a vapor holder, each test repetition shall include at least one fully automatic operation cycle of the vapor holder and processing device.

A3.6 BASIC MEASUREMENTS AND EQUIPMENT REQUIRED

A3.6.1 Basic measurements required for evaluation of gasoline bulk loading terminals are described below. Some measurements are noted as optional. These are not necessary in the determination of emission rate, but can be of value in the description and explanation of the operation of the vapor recovery system. The various sampling points are numbered in Figure 1.

Sample Point	Measurements Necessary
1. Gasoline dispenser	- Amount dispensed - Dispensing rate (optional) - Temperature (optional) - Reid vapor pressure of dispensed fuel (optional)

Sample Point	Measurements Necessary
2. Vapor return line	- Temperature of returned vapors - Volume of vapors displaced - Pressure - HC concentration of displaced vapors - Gas chromatograph analysis of HC vapors* (optional) - O_2 and N_2 concentration in vapor (optional) - Leak check all fittings
3. Processing unit exhaust	- Temperature of vapors exhausted - Pressure of vapors exhausted - Volume of vapors exhausted - HC concentration of vapors - Gas chromatograph analysis of HC* (optional) - O_2 and N_2 analysis of exhaust vapors (optional)

A3.6.2. The equipment required for the basic measurements are listed below:

Sample Point	Equipment and Specifications
2**	1 gas volume meter, properly sized for maximum flow assuming all dispensers on one rack operate simultaneously 1 flexible thermocouple, (0-150°F) with recorder 1 inclined manometer (0-10" H_2O), or calibrated pressure transducer with readout/recorder 1 portable combustible gas detector, (0-100% LEL) 1 total hydrocarbon analyzer (FID or NDIR type equipped to read out 1-100% by volume hydrocarbons as propane) with recorder

*Required if methane is present in recovered vapors.

**Equipment indicated is required for each loading rack being tested.

Sample Point	Equipment and Specifications
3	1 flexible thermocouple (0-150°F) with recorder
	1 gas volume meter, appropriately sized for exhaust flow rate and range
	1 total hydrocarbon analyzer with recorder; (FID or NDIR type, equipped to read out 0-10% by volume hydrocarbons as propane for vapor recovery processing devices; or, 0-1000 ppmv HC as propane for incineration processing devices)
Miscellaneous	1 barometer
	1 O_2, N_2 analyzer, GC/w thermal conductivity detector or equivalent (optional)
	1 GC/FID w/column to separate C_1 - C_7 alkanes* (optional)

A3.7 TEST PROCEDURES

A3.7.1 Preparation for testing includes:

A3.7.1.1 Install into the vapor return line of each rack to be tested a gas volume meter. At the meter inlet, install a thermocouple and a tap for connection of a 0-10" manometer or transducer. On the meter outlet, install two taps for 1/4" tubing. Connect one tap to a sample line for a total hydrocarbon (0-100% as propane) analyzer. The sample pump for the THC analyzer should draw no more than 300 cc/min of sample. Provision should be made so that the sample line can be disconnected when no loading is in progress. Connect the remaining tap to a constant volume sample pump/evaluated bag assembly** if a methane determination is required. If not, cap to prevent vapor loss.

*Required if methane is present in recovered vapors or if incineration is the vapor processing technique.

**Described in Method 3, Federal Register V36, pp247, December 23, 1971.

A3.7.1.2 Install an appropriately sized gas meter on the exhaust vent of the vapor processing device. A gas volume meter can be used at the exhaust of most vapor recovery processing devices. For those where size restrictions preclude the use of a volume meter; or when incineration is used for vapor processing, a gas flow rate meter (orifice, annubar) is necessary. At the meter inlet, install a thermocouple with recorder. Install a 1/4" tap at the volume meter outlet. Attach a sample line for a total hydrocarbon analyzer (0-10% as propane) to this tap. If the meter pressure is different than barometric pressure, install a second 1/4" tap at the meter outlet and attach an appropriate manometer for pressure measurement. If methane analysis is required, install a third tap for connection to a constant volume sample pump/evacuated bag assembly.*

A3.7.1.3 Calibrate and span all instruments as outlined in Section 9.

A3.7.2 Measurements and data required for evaluating system efficiency during collection include:

A3.7.2.1 At the beginning and end of each test repetition record the volume readings on each product dispenser on each loading rack served by the system under test.

A3.7.2.2 At the beginning of each test repetition and each hour thereafter, record the ambient temperature and the barometric pressure.

A3.7.2.3 For intermittent processing units employing a vapor holder, the unit shall be manually started and allowed to process vapors in the holder until the lower automatic cut-off is reached. This cycle should be performed immediately prior to the beginning of the test repetition before readings in 7.2.1 are taken. No loading shall be in progress during this manual cycle.

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*Described in Method 3, Federal Register, V36, n247, December 23, 1971

A3.7.2.4 For each cycle of the processing unit during each test repetition, record the processor start and stop time, the initial and final gas meter readings, and the average vapor temperature, pressure and hydrocarbon concentration. If a flow rate meter is used, record flow meter readouts continuously during the cycle. If required, extract a sample continuously during each cycle for chromatographic analysis for hydrocarbons and O_2/N_2.

A3.7.2.5 For each tanker loading:

A3.7.2.5.1 Record the identification number and ownership if required of each tanker or trailer tested. Record compartment numbers, capacity, and product loaded into each.

A3.7.2.5.2 Record the initial meter reading on the volume meter in the vapor return line prior to loading.

A3.7.2.5.3 During loading, monitor the vapor return line temperature, pressure and hydrocarbon concentration.

A3.7.2.5.4 Time the loading operation so as to obtain the total dispensing time into each compartment and dispensing rate of liquid. (optional)

A3.7.2.5.5 During loading, check all fittings and seals on the tanker compartments with the combustible gas detector. Record the maximum combustible gas reading for any incidents of leakage of hydrocarbon vapors. Explore the entire periphery of the potential leak source with the sample hose inlet 1 cm away from the interface.

A3.7.2.5.6 If required, extract a continuous sample of the returned vapors during loading for chromatographic hydrocarbon analysis and O_2/N_2 analysis.

A3.7.2.5.7 After loading, record the final gas meter reading, average temperature, pressure, and hydrocarbon concentration of the returned vapors. If the hydrocarbon concentration varies

significantly with time, integrate the chart record to obtain an average loading concentration.

A3.7.2.6 For intermittent systems, the processing unit shall be manually started and allowed to process vapors in the holder until the lower automatic shut-off is reached at the end of each test repetition. Record the data in 7.2.4 for this manual cycle. No loading shall be in progress during this manual cycle.

A3.8 CALCULATIONS

8.1 Terminology

V_r = Volume of returned air-hydrocarbon mixture from tanker loading (ft^3)

V_{ri} = Initial gas meter reading in vapor return line (ft^3)

V_{vf} = Final gas meter reading in vapor return line (ft^3)

T_r = Temperature of returned air-hydrocarbon mixture (°F)

P_r = Absolute pressure of returned air-hydrocarbon mixture (inches Hg)

V_{rs} = Volume of returned air-hydrocarbon mixture at standard conditions (SCF at 20°C, 760 mmHg)

T_a = Ambient temperature (°F)

P_b = Barometric pressure (inches Hg)

L_d = Volume of liquid fuel dispensed for each tanker loading tested (gallons).

C_r = Volume fraction of hydrocarbons in returned mixture from each tanker (volume % as C_3H_{10}/100), corrected for methane content if required.

M_r = Mass of returned hydrocarbons vapors from each tanker.

$(M/L)_r$ = Volume of air-hydrocarbon mixture returned per volume of liquid dispensed for each tanker (ft^3/ft^3)

L_t = Total volume of liquid dispensed from all controlled racks during the test period (gallons). NOTE: This value is equal to ΣL_d only if <u>all</u> loadings during the test period are tested.

V_e = Volume of air-hydrocarbon mixture exhausted from the processing unit (ft^3).

C_e = Volume fraction of hydrocarbons in exhausted mixture (volume % as C_3H_{10}/100), corrected for methane content if required.

T_e = Temperature at processing unit exhaust (°F).

P_e = Pressure at processing unit exhaust (in Hg. abs.).

$(M/L)_e$ = Mass of hydrocarbons exhausted from the processing unit per volume of liquid loaded, (gm/gallon).

E_p = Average processing unit hydrocarbon recovery efficiency, (%)

$(\frac{V}{L})_{rp}$ = Average potential volumetric recovery factor (ft^3/ft^3).

$(M/L)_p$ = Potential hydrocarbon mass recoverable per volume of liquid dispensed for each tanker, (gm/gallon).

$(M/L)_T$ = Total system average hydrocarbon emission, grams/gallon.

E_s = Average total system hydrocarbon recovery efficiency, %

$(\overline{\ })$ = Denotes weighted average

* = Denotes loading with no leakage

A3.8.2 Individual Loading Results

Calculate the following results for each tanker loading.

A3.8.2.1 Volume of air-hydrocarbon mixture returned:

$$V_r = V_{rf} - V_{ri} \qquad (ft^3)$$

A3.8.2.2 Volume of mixture returned per volume of liquid dispensed:

$$(V/L)_r = \frac{V_r}{L_d} \left(7.481 \frac{\text{gallons}}{ft^3}\right) \quad (ft^3/ft^3)$$

A3.8.2.3 Standard volume of returned mixture:

$$V_{rs} = \frac{(17.65°R/"Hg)\ V_r P_r}{T_r + 460} \quad \text{SCF @ 68°F, 29.92 in. Hg}$$

A3.8.2.4 Mass hydrocarbons returned:

$$M_r = \left(51.80 \frac{\text{grams } C_3H_8}{ft^3 C_3H_8}\right) V_{rs} C_r \text{ (grams)}$$

A3.8.2.5 Mass of hydrocarbons returned per volume of liquid:

$$(M/L) = \frac{M_r}{L_d} \quad \text{(grams/gallon)}$$

A3.8.3 Average Tanker Loading Results

Calculate the following weighted averages from the results obtained in 8.2. (NOTE: All averages are weighted based on the volumes loaded to properly proportion the impact of a disproportionately large or small loading.)

A3.8.3.1 Average volume of mixture returned per volume of liquid dispensed:

$$(\overline{V/L})_r = \left(\frac{\Sigma V_r}{\Sigma L_d}\right)\left(7.481 \frac{\text{gallons}}{ft^3}\right), \ (ft^3/ft^3)$$

A3.8.3.2 Average mass of hydrocarbons returned per volume of liquid dispensed:

$$(\overline{M/L})_r = \frac{\Sigma M_r}{\Sigma L_d} \quad \text{(grams/gallon)}$$

A3.8.4 Processing Unit Emissions

Calculate the following results for each period of processing unit operation:

A3.8.4.1 Volume of air-hydrocarbon mixture exhausted from the processing unit:

$$V_e = V_{ef} - V_{ei}, \text{ or } \quad (ft^3)$$

V_e = totalized volume from flow rate and time records.

A3.8.4.2 Standard volume of exhausted mixture:

$$V_{es} = \frac{(17.65\ °R/"Hg)\ V_e\ P_e}{T_e + 460.0} \quad \text{SCF @68°F, 29.92"Hg}$$

A3.8.4.3 Mass of hydrocarbons exhausted from the processing unit:

$$M_e = \left(51.80\ \frac{\text{grams } C_3H_8}{ft^3\ C_3H_8}\right) \cdot Ves\ C_e \quad \text{(grams)}$$

A3.8.5 Average Processing Unit Emissions

A3.8.5.1 Average mass of hydrocarbons emitted per volume of gasoline loaded:

$$(M/L)_e = \frac{\Sigma M_e}{L_t} \quad \text{(grams/gallon)}$$

A3.8.6 Processing Unit Efficiency

Calculate the hydrocarbon recovery efficiency using the equation below. The system efficiency is calculated on a weighted average basis.

A3.8.6.1 Average processing unit hydrocarbon recovery efficiency:

$$E_p = 1 - \left[\frac{(M/L)_e}{(M/L)_r}\right] \times 100\% \quad (\%)$$

A3.8.7 Potential Hydrocarbons Recoverable During Loading

When air-hydrocarbon mixture leakage is detected around hatch covers or vent valves on the tankers during loading, the actual hydrocarbons recovered are less than those potentially recoverable. Estimates of the hydrocarbon losses can be made as follows.

A3.8.7.1 Potential recovery factors: Separate the loadings during which there were no leakage losses detected by the combustible gas indicator. For these loadings calculate:

The weighted average potential volumetric recovery:

$$\left(\frac{\overline{V}}{L}\right)_p = \frac{(\Sigma V_r^*)(7.481\ \frac{\text{gallons}}{ft^3})}{\Sigma L_d} \qquad \left(\frac{ft^3}{ft^3}\right)$$

A3.8.7.2 For the cases where leakage was detected, calculate the potential hydrocarbon mass per volume of liquid ratio and the hydrocarbon mass lost per volume of liquid ration for each loading by:

A3.8.7.2.1 Potential hydrocarbon mass per volume of liquid ratio for each loading:

$$(M/L)_p = \frac{(V/L)_p}{(V/L)_r}\ (M/L)_r \qquad \text{(grams/gallon)}$$

A3.8.7.2.2 Hydrocarbon mass lost per volume of liquid ratio for each loading:

$$(M/L)_1 = (M/L)_p - (M/L)_r \ \text{(grams/gallon)}$$

A3.8.7.3 Average potential recovery and leakage losses. Calculate the following average factors from the data in 8.7.2.

A3.8.7.3.1 Average potential hydrocarbon recovery ratio:

$$(M/L)_p = \frac{\Sigma(M/L)_p - L_d}{\Sigma L_d} \qquad \text{(grams/gallon)}$$

Note: For cases where there was no leakage $(M/L)_p = (M/L)_r$.

For cases where there was leakage $(M/L)_p$ = results in 8.7.2.1.

A3.8.7.3.2 Average hydrocarbon leakage loss:

$$(\overline{M/L})_l = \frac{\Sigma(M/L)_l \cdot L_d}{\Sigma L_d} \quad \text{(grams/gallon)}$$

Note: For cases where there was no leakage $(M/L)_l = 0$

For cases where there was leakage $(M/L)_l$ = results in 8.7.2.2.

A3.8.8 Total System Average Emissions

Calculate the total emissions for the recovery system by:

$$(\overline{M/L})_t = (\overline{M/L})_e + (\overline{M/L})_l \quad \text{(grams/gallon)}$$

A3.8.9 Total System Average Efficiency:

$$E_s = 1 - \left[\frac{(\overline{M/L})_e + (\overline{M/L})_l}{(\overline{M/L})_p}\right] \times 100\%$$

A3.9 CALIBRATIONS

A3.9.1 Flow Meters

Use standard methods and equipment which have been approved by the Administrator to calibrate the gas meters.

A3.9.2 Temperature Recording Instruments

Calibrate prior to the test period and following the test period using an ice bath (32°F) and a known reference temperature source of about 100°F. Daily during the test period, use an accurate reference to measure the ambient temperature and compare the ambient temperature reading of all other instruments to this value.

A3.9.3 Total Hydocarbon analyzer

Follow the manufacturer's instructions concerning warm-up and adjustments. Prior to and immediately after the emission test, perform a comprehensive laboratory calibration on each analyzer used. Calibration gases should be propane in nitrogen prepared gravimetrically with mass quantities of approximately 100 percent propane. A calibration curve shall be provided using a minimum of five prepared standards in the range of concentrations expected during testing.

For each repetition, zero with zero gas (3 ppm C) and span with 70% propane for instruments used in the vapor return lines and with 10% propane for instruments used at the control device exhaust.

The zero and span procedure shall be performed at least once prior to the first test measurement, once during the middle of the run, and once following the final test measurement for each run.

Conditions in calibration gas cylinders must be kept such that condensation of propane does not occur. A safety factor of 2 for pressure and temperature is recommended.

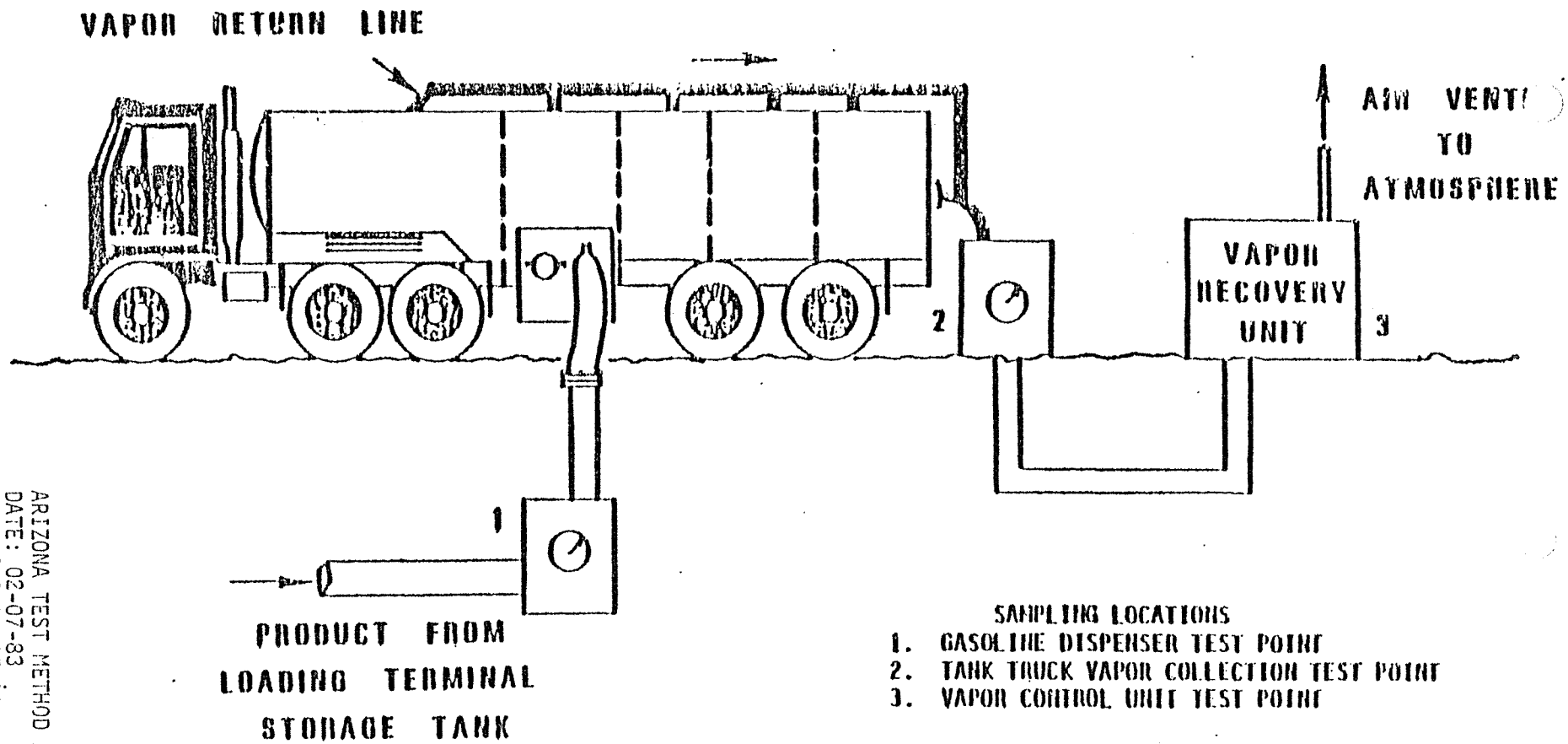


Figure 1. Sampling Locations

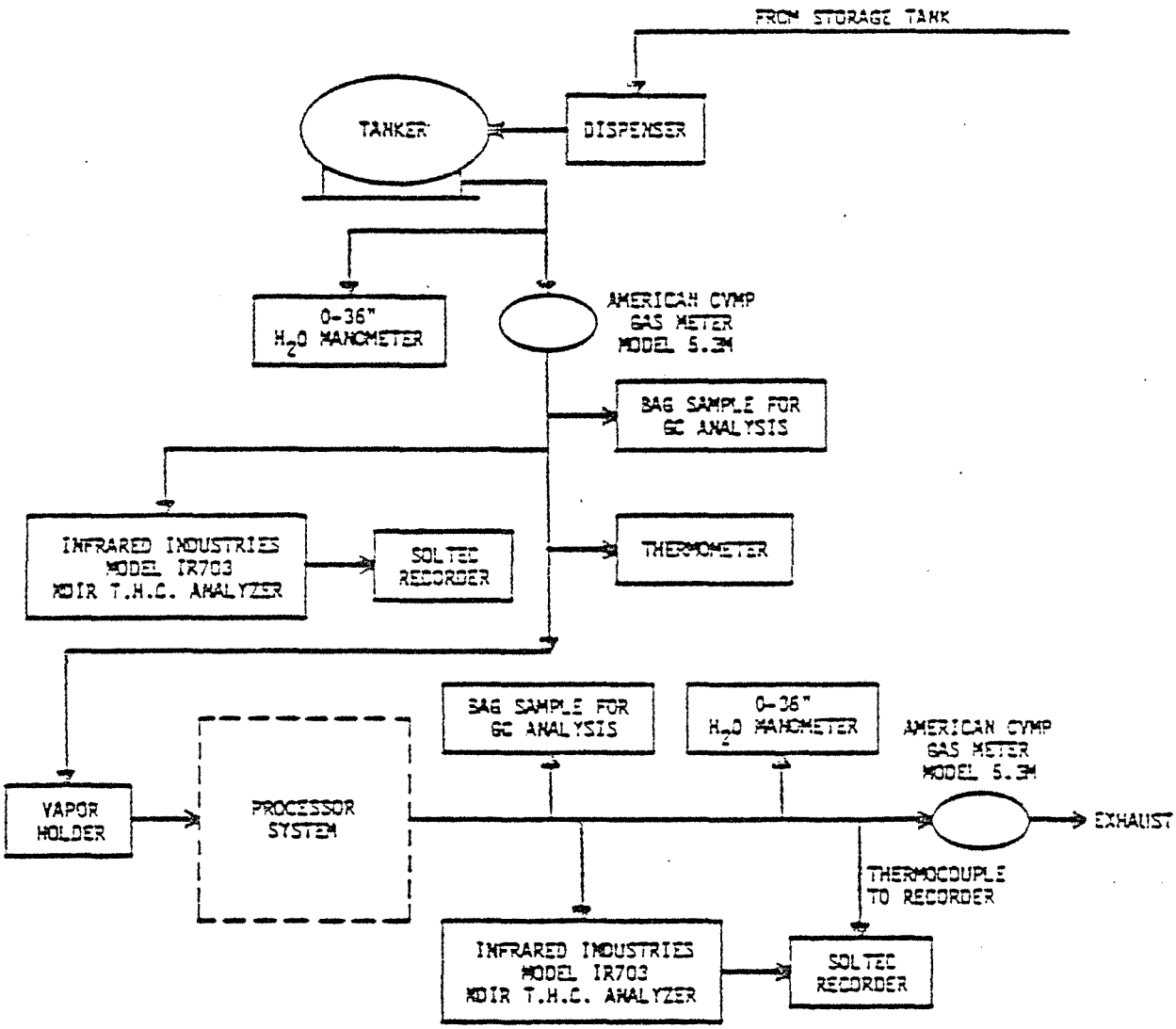


Figure 2. OAQPS Method Sampling Locations and Test Equipment

GASOLINE BULK TRANSFER DATA SHEETS

Terminal Name:_____ Date:_____

Location:_____ Rack No._____ Run No._____

Ambient Temperature ___°F Barometric Pressure_____in Hg.

Tanker Information:

Time of Day:_____

Identification No._____

Capacity (gallons):		Fuel Grade Loaded:
Compartment 1:	_____	_____
Compartment 2:	_____	_____
Compartment 3:	_____	_____
Compartment 4:	_____	_____
Compartment 5:	_____	_____

Measurements:

During Loading:

Recovery System Pressure: _____in H_2O
Dispensed Liquid Temperature: _____°F
Returned Vapor Temperature: _____°F
Average HC Concentration in Returned Vapor (% as_____):_____%
Gasoline Dispensed: _____gal
Dispensing Time: _____min
Final Gas Meter Reading: _____ft^3
Initial Gas Meter Reading: _____ft^3
GC/HC Analysis: Yes_____No _____
O_2/N_2 Analysis: Yes _____No_____

Explosimeter Readings:

Location	Reading
_____	_____
_____	_____
_____	_____

NOTES: _____

_____

Table A-1 GASOLINE BULK TRANSFER TERMINAL DATA SHEET No.

Terminal Name: _____ Date: _____

Location: _____

Daily Ambient Data: (record every 2 hours)

	Time	T_a	P_b
Start:			
End:			

Schematic Diagram of Rack Layout

Dispenser Meter Readings

Time Pump No.	Initial	Final	Time Pump No.	Initial	Final

GASOLINE BULK TRANSFER TERMINAL CONTROL SYSTEM
DATA SHEET NO. 2

Terminal Name: _____ Date: _____

Location: _____

Control Device Outlet

Gas meter readings Initial _____ Final _____

Time Test Start _____ Test End _____

Record the following for each processing unit operating cycle or emission period.

Time		Volume Reading		Average		
Start	Stop	Initial	Final	Temperature	Pressure	HC Concentration % as _____

Method 5A—Determination of Particulate Emissions from the Asphalt Processing and Asphalt Roofing Industry

[Method 5A added by 47 FR 34142, August 6, 1982]

1. *Applicability and Principle.*

1.1 *Applicability.* This method applies to the determination of particulate emissions from asphalt roofing industry process saturators, blowing stills, and other sources as specified in the regulations.

1.2 *Principle.* Particulate matter is withdrawn isokinetically from the source and collected on a glass filter fiber maintained at a temperature of 42°±10°C (108°±18°F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

2. *Apparatus.*

2.1 *Sampling Train.* The sampling train configuration is the same as shown in Figure 5-1 of Method 5. The sampling train consists of the following components:

2.1.1 *Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Holder, Condenser, Metering System, Barometer, and Gas Density Determination Equipment.* Same as Method 5, Sections 2.1.1, 2.1.3 to 2.1.5, and 2.1.7 to 2.1.10, respectively.

2.1.2 *Probe Liner.* Same as in Method 5, Section 2.1.2, with the note that at high stack gas temperatures (greater than 250°C (480°F)), water-cooled probes may be required to control the probe exit temperature to 42°±10°C (108±18°F).

2.1.3 *Precollector Cyclone.* Borosilicate glass following the construction details shown in Air Pollution Technical Document-0581, "Construction Details of Isokinetic Source-Sampling Equipment".

Note.—The tester shall use the cyclone when the stack gas moisture is greater than 10 percent. The tester shall not use the precollector cyclone under other, less severe conditions.

2.1.4 *Filter Heating System.* Any heating (or cooling) system capable of maintaining a sample gas temperature at the exit end of the filter holder during sampling at 42°±10°C (108°±18°F). Install a temperature gauge capable of measuring temperature to within 3°C (5.4°F) at the exit end of the filter holder so that the sample gas temperature can be regulated and monitored during sampling. The tester may use systems other than the one shown in APTD-0581.

2.2 *Sample Recovery.* The equipment required for sample recovery is as follows:

2.2.1 *Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman.* Same as Method 5, Sections 2.2.1, 2.2.5, 2.2.6, and 2.2.7, respectively.

2.2.2 *Wash Bottles.* Glass.

2.2.3 *Sample Storage Containers.* Chemically resistant, borosilicate glass bottles, with rubber-backed Teflon screw cap liners or caps that are constructed so as to be leak-free and resistant to chemical attack by 1,1,1-trichloroethane (TCE), 500-ml or 1000-ml. (Narrow mouth glass bottles have been found to be less prone to leakage.)

2.2.4 *Petri Dishes.* Glass, unless otherwise specified by the Administrator.

2.2.5 *Funnel.* Glass.

2.3 *Analysis.* For analysis, the following equipment is needed:

2.3.1 *Glass Weighing Dishes, Desiccator, Analytical Balance, Balance, Hygrometer, and Temperature Gauge.* Same as Method 5, Sections 2.3.1 to 2.3.4, 2.3.6, and 2.3.7, respectively.

2.3.2 *Beakers.* Glass, 250-ml and 500-ml.

2.3.3 *Separatory Funnel.* 100-ml or greater.

3. *Reagents.*

3.1 *Sampling.* The reagents used in sampling are as follows:

3.1.1 *Filters, Silica Gel, and Crushed Ice.* Same as Method 5, Sections 3.1.1, 3.1.2, and 3.1.4, respectively.

3.1.2 *Stopcock Grease.* TCE-insoluble, heat-stable grease (if needed). This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used.

3.2 *Sample Recovery.* Reagent grade 1,1,1-trichloroethane (TCE), ≤0.001 percent residue and stored in glass bottles, is required. Run TCE blanks prior to field use and use only TCE with low blank values (≤0.001 percent). The tester shall in no case subtract a blank value of greater than 0.001 percent of the weight of TCE used from the sample weight.

3.3 *Analysis.* Two reagents are required for the analysis:

3.3.1 *TCE.* Same as 3.2.

3.3.2 *Desiccant.* Same as Method 5, Section 3.3.2.

4. *Procedure.*

4.1 *Sampling Train Operation.* The complexity of this method is such that in order to obtain reliable results, testers should be trained and experienced with Method 5 test procedures.

4.1.1 *Pretest Preparation.* Unless otherwise specified, maintain and calibrate all components according to the procedure described in Air Pollution Technical Document-0576, "Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment".

Prepare probe liners and sampling nozzles as needed for use. Thoroughly clean each component with soap and water followed by a minimum of three TCE rinses. Use the probe and nozzle brushes during at least one of the TCE rinses (refer to Section 4.2 for rinsing techniques). Cap or seal the open ends of the probe liners and nozzles to prevent contamination during shipping.

Prepare silica gel portions and glass filters as specified in Method 5, Section 4.1.1.

4.1.2 *Preliminary Determinations.* Select the sampling site, probe nozzle, and probe length as specified in Method 5, Section 4.1.2.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures section of the applicable regulation. Follow the guidelines outlined in Method 5, Section 4.1.2 for sampling time per point and total sample volume collected.

4.1.3 *Preparation of Collection Train.* Prepare the collection train as specified in Method 5, Section 4.1.3, with the addition of the following:

Set up the sampling train as shown in Figure 5-1 of Method 5 with the addition of the precollector cyclone, if used, between the probe and filter holder. The temperature of the precollector cyclone, if used, should be about the same as for the filter, i.e., 42° ±10°C (108° ±18°F). Use no stopcock grease on ground glass joints unless the grease is insoluble in TCE.

4.1.4 *Leak Check Procedures.* Follow the procedures given in Method 5, Sections 4.1.4.1 (Pretest Leak Check), 4.1.4.2 (Leak Check During Sample Run), and 4.1.4.3 (Post-Test Leak Check).

4.1.5 *Particulate Train Operation.* Operate the sampling train as described in Method 5, Section 4.1.5, except maintain the gas temperature exiting the filter at 42° ±10°C (108° ±18°F).

4.1.6 *Calculation of Percent Isokinetic.* Same as in Method 5, Section 4.1.6.

4.2 *Sample Recovery.* Using the procedures and techniques described in Method 5, Section 4.2, quantitatively recover any particulate matter into the following containers (additions and deviations to the stated procedures are as noted):

4.2.1 *Container No. 1 (Filter).* Same instructions as Method 5, Section 4.2, "Container No. 1." If it is necessary to fold the filter, do so such that the film of oil is inside the fold.

4.2.2 *Container No. 2 (Probe to Filter Holder).* Taking care to see that material on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, precollector cyclone and collector flask (if used), and front half of the filter holder by washing these components with TCE and placing the wash in a glass container. Carefully measure the total amount of TCE used in the rinses. Perform the TCE rinses as described in Method 5, Section 4.2 "Container No. 2" using TCE instead of acetone.

Brush and rinse the inside of the cyclone, cyclone collection flask, and the front half of the filter holder. Brush and rinse each surface three times or more, if necessary, to remove visible particulate.

4.2.3 *Container No. 3 (Silica Gel).* Same procedure as in Method 5, Section 4.2, "Container No. 3."

4.2.4 *Impinger Water.* Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Follow the same procedure as in Method 5, Section 4.2, "Impinger Water."

4.2.5 *Blank.* Save a portion of the TCE used for cleanup as a blank. Take 200 ml of this TCE directly from the wash bottle being used and place it in a glass sample container labeled "TCE blank."

4.3 *Analysis.* Record the data required on a sheet such as the one shown in Figure 5A-1. Handle each sample container as follows:

4.3.1 *Container No. 1 (Filter).* Transfer the filter from the sample container to a tared glass weighing dish and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Rinse Container No. 1 with a measured amount of TCE and analyze this rinse with the contents of Container No. 2. Weigh the filter to a constant weight. For the purpose of Section 4.3, the term "constant weight" means a difference of no more than 10 percent or 2 mg (whichever is greater) between two consecutive weighings made 24 hours apart. Report the "final weight" to the nearest 0.1 mg as the average of these two values.

4.3.2 *Container No. 2 (Probe to Filter Holder).* Before adding the rinse from Container No. 1 to Container No. 2, note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If noticeable leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to correct the final results.

Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Check to see if there is any appreciable quantity of condensed water present in the TCE rinse (look for a boundary layer or phase separation). If the volume of condensed water appears larger than 5 ml, separate the oil-TCE fraction from the water fraction using a separatory funnel. Measure the volume of the water phase to the nearest ml; adjust the stack gas moisture content, if necessary (see Sections 6.4 and 6.5). Next, extract the water phase with several 25-ml portions of TCE until, by visual observation, the TCE does not remove any additional organic material. Evaporate the remaining water fraction to dryness at 93°C (200°F), desiccate for 24 hours, and weigh to the nearest 0.1 mg.

Treat the total TCE fraction (including TCE from the filter container rinse and water phase extractions) as follows: Transfer the TCE and oil to a tared beaker and evaporate at ambient temperature and pressure. The evaporation of TCE from the solution may take several days. Do not desiccate the sample until the solution reaches an apparent constant volume or until the odor of TCE is not detected. When it appears that the TCE has evaporated, desiccate the sample and weigh it at 24-hour intervals to obtain a "constant weight" (as defined for Container No. 1 above). The "total weight" for Container No. 2 is the sum of the evaporated particulate weight of the TCE-oil and water phase fractions. Report the results to the nearest 0.1 mg.

4.3.3 *Container No. 3 (Silica Gel).* This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

4.3.4 *"TCE Blank" Container.* Measure TCE in this container either volumetrically or gravimetrically. Transfer the TCE to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Note.—In order to facilitate the evaporation of TCE liquid samples, these samples may be dried in a controlled temperature oven at temperatures up to 38°C (100°F) until the liquid is evaporated.

5. *Calibration.*

Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (5.1), Pitot Tube Assembly (5.2), Metering System (5.3), Probe Heater (5.4), Temperature Gauges (5.5), Leak Check of Metering System (5.6), and Barometer (5.7).

6. *Calculations.*

6.1 *Nomenclature.* Same as in Method 5, Section 6.1, with the following additions:

C_a = TCE blank residue concentration, mg/g.
M_a = Mass of residue of TCE after evaporation, mg.
V_{wc} = Volume of water collected in precollector, ml.
V_a = Volume of TCE blank, ml.
V_w = Volume of TCE used in wash, ml.
W_a = Weight of residue in TCE wash, mg.
ρ_a = Density of TCE, mg/ml (see label on bottle).

6.2 *Dry Gas Meter Temperature and Orifice Pressure Drop.* Using the data obtained in this test, calculate the average dry gas meter temperature and average orifice pressure drop (see Figure 5-2 of Method 5).

6.3 *Dry Gas Volume.* Using the data from this test, calculate $V_{m(std)}$ by using Equation 5-1 of Method 5, if necessary, adjust the volume for leakages.

6.4 *Volume of Water Vapor.*

$$V_{w(std)} = K_1(V_{lc} + V_{wc}) \qquad \text{Eq. 5A-1.}$$

Where:

K_1 = 0.00133 m³/ml for metric units.
= 0.04707 ft³/ml for English units.

$$B_{ws} = V_{w(std)} / V_{m(std)} + V_{w(std)} \qquad \text{Eq. 5A-2}$$

Note.—In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger and precollector analysis (Equations 5A-1 and 5A-2) and a second from the assumption of saturated conditions. The lower of the two values of moisture content shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the note of Section 1.2

of Method 4. For the purpose of this method, the average stack gas temperature from Figure 2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is within ±1°C (2°F).

6.6 *TCE Blank Concentration.*

$C_a = M_a / V_a B_{ws}$ Eq. 3A-6.

6.7 *TCE Wash Blank.*

$W_a = (C_a)(V_{ta})(B_{ws})$ Eq. 3A-7.

6.8 *Total Particulate Weight.* Determine the total particulate catch from the sum of the weights obtained from Containers 1, 2 and 3, less the TCE blank.

6.9 *Particulate Concentration.*

$C_s = K_4 M_n / V_{m(std)}$ Eq. 3A-8.

Where:

$K_4 = 0.001$ g/mg.

6.10 *Isokinetic Variation and Acceptable Results.* Method 5, Section 6.11 and 6.12, respectively.

7. *Bibliography.*

The bibliography for Reference Method 5A is the same as for Method 5, Section 7.

Alternate Method 1—Determination of the Opacity of Emissions From Stationary Sources Remotely by Lidar

[Method 9, Alternate Method 1 added by 46 FR 53148, October 28, 1981]

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar: Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser (Reference 5.1).

1. *Principle and Applicability*

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR § 60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field-of-view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line-of-sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range of distance from the lidar to a point of interest along the lidar line-of-sight.

Near region: The region of the atmospheric path along the lidar line-of-sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

$1/R^2$ correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (t_o) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. *Procedures.*

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line-of-sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1-1):

$$D(\text{lidar}) = A + R\phi < 0.75\ D(\text{Plume}) \quad \text{(AM1-1)}$$

where:

D(Plume) = diameter of the plume (cm),

ϕ = laser beam divergence measured in radians

R = range from the lidar to the source (cm)

D(Lidar = diameter of the laser beam at range R (cm).

A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal (Reference 5.1). This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line-of-sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line-of-sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, nonciricular stacks, etc.), the lidar shall be placed in a position so that its line-of-sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an angle of ± 15° (cone angle) of the sun.

This method shall not be used to make opacity measurements if thunderstorms, snowstorms, hail storms, high wind, high-ambient dust levels, fog or other atmospheric conditions cause the reference signals to consistently exceed the limits specified in Section 2.3.

2.3 Reference Signal Requirements. Once placed in its proper position for opacity measurement, the laser is aimed and fired with the line-of-sight near the outlet height and rotated horizontally to a position clear of the source structure and the associated plume. The backscatter signal obtained from this position is called the ambient-air or reference signal. The lidar operator shall inspect this signal (Section V of Reference 5.1) to: (1) determine if the lidar line-of-sight is free from interference from other plumes and from physical obstructions such as cables, power lines, etc., for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, and (2) obtain a qualitative measure of the homogeneity of the ambient air by noting any signal spikes.

Should there be any signal spikes on the reference signal within a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, the laser shall be fired three more times and the operator shall inspect the reference signals on the display. If the spike(s) remains, the azimuth angle shall be changed and the above procedures conducted again. If the spike(s) disappears in all three reference signals, the lidar line-of-sight is acceptable if there is shot-to-shot consistency and there is no interference from other plumes.

Shot-to-shot consistency of a series of reference signals over a period of twenty seconds is verified in either of two ways. (1) The lidar operator shall observe the reference signal amplitudes. For shot-to-shot consistency the ratio of R_n to R_o (amplitudes of the near and far region pick intervals (Section 2.6.1)) shall vary by not more than ± 8% between shots; or (2) the lidar operator shall accept any one of the reference signals and treat the other two as plume signals; then the opacity for each of the subsequent reference signals is calculated (Equation AM1-2). For shot-to-shot consistency, the opacity values shall be within ± 3% of 0% opacity and the associated S_n values less than or equal to 8% (full scale) (Section 2.6).

If a set of reference signals fails to meet the requirements of this section, then all plume signals (Section 2.4) from the last set of acceptable reference signals to the failed set shall be discarded.

2.3.1 Initial and Final Reference Signals. Three reference signals shall be obtained within a 90-second time period prior to any data run. A final set of three reference signals

shall be obtained within three (3) minutes after the completion of the same data run.

2.3.2 Temporal Criterion for Additional Reference Signals. An additional set of reference signals shall be obtained during a data run if there is a change in wind direction or plume drift at 30° or more from the direction that was prevalent when the last set of reference signals were obtained. An additional set of reference signals shall also be obtained if there is a change in amplitude in either the near or the far region of the plume signal, that is greater than 6% of the near signal amplitude and this change in amplitude remains for 30 seconds or more.

2.4 Plume Signal Requirements. Once properly aimed, the lidar is placed in operation with the nominal pulse or firing rate of six pulses/minute (1 pulse/10 seconds). The lidar operator shall observe the plume backscatter signals to determine the need for additional reference signals as required by Section 2.3.2. The plume signals are recorded from lidar start to stop and are called a data run. The length of a data run is determined by operator discretion. Short-term stops of the lidar to record additional reference signals do not constitute the end of a data run if plume signals are resumed within 90 seconds after the reference signals have been recorded, and the total stop or interrupt time does not exceed 3 minutes.

2.4.1 Non-hydrated Plumes. The laser shall be aimed at the region of the plume which displays the greatest opacity. The lidar operator must visually verify that the laser is aimed clearly above the source exit structure.

2.4.2 Hydrated Plumes. The lidar will be used to measure the opacity of hydrated or so-called steam plumes. As listed in the reference method, there are two types, i.e., attached and detached steam plumes.

2.4.2.1 Attached Steam Plumes. When condensed water vapor is present within a plume, lidar opacity measurements shall be made at a point within the residual plume where the condensed water vapor is no longer visible. The laser shall be aimed into the most dense region (region of highest opacity) of the residual plume.

During daylight hours the lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night vision scope, or low light level TV, etc., can be used as an aid to locate the residual plume. If visual determination is ineffective, the lidar may be used to locate the most dense region of the residual plume by repeatedly measuring opacity, along the longitudinal axis or center of the plume from the emissions outlet to a point just beyond the steam plume. The lidar operator should also observe color differences and plume reflectivity to ensure that the lidar is aimed completely within the residual plume. If the operator does not obtain a clear indication of the location of the residual plume, this method shall not be used.

Once the region of highest opacity of the residual plume has been located, aiming adjustments shall be made to the laser line-of-sight to correct for the following: movement to the region of highest opacity out of the lidar line-of-sight (away from the laser beam) for more than 15 seconds, expansion of the steam plume (air temperature lowers and/or relative humidity increases) so that it just begins to encroach on the field-of-view of the lidar's optical telescope receiver, or a decrease in the size of the steam plume (air temperature higher and/or relative humidity decreases) so that regions within the residual plume whose opacity is higher than the one being monitored, are present.

2.4.2.2 Detached Steam Plumes. When the water vapor in a hydrated plume condenses and becomes visible at a finite distance from the stack or source emissions outlet, the opacity of the emissions shall be measured in the region of the plume clearly above the emissions outlet and below condensation of the water vapor.

During daylight hours the lidar operators can visually determine if the steam plume is detached from the stack outlet. During nighttime hours a high-intensity spotlight, night vision scope, low light level TV, etc., can be used as an aid in determining if the steam plume is detached. If visual determination is ineffective, the lidar may be used to determine if the steam plume is detached by repeatedly measuring plume opacity from the outlet to the steam plume along the plume's longitudinal axis or center line. The lidar operator should also observe color differences and plume reflectivity to detect a detached plume. If the operator does not obtain a clear indication of the location of the detached plume, this method shall not be used to make opacity measurements between the outlet and the detached plume.

Once the determination of a detached steam plume has been confirmed, the laser shall be aimed into the region of highest opacity in the plume between the outlet and the formation of the steam plume. Aiming adjustments shall be made to the lidar's line-of-sight within the plume to correct for changes in the location of the most dense region of the plume due to changes in wind direction and speed or if the detached steam plume moves closer to the source outlet encroaching on the most dense region of the plume. If the detached steam plume should move too close to the source outlet for the lidar to make interference-free opacity measurements, this method shall not be used.

2.5 Field Records. In addition to the recording recommendations listed in other sections of this method the following records should be maintained. Each plume measured should be uniquely identified. The name of the facility, type of facility, emission source type, geographic location of the lidar with respect to the plume, and plume characteristics should be recorded. The date of the test, the time period that a source was monitored, the time (to the nearest second) of each opacity measurement, and the sample interval should also be recorded. The wind speed, wind direction, air temperature, relative humidity, visibility (measured at the lidar's position), and cloud cover should be recorded at the beginning and end of each time period for a given source. A small sketch depicting the location of the laser beam within the plume should be recorded.

If a detached or attached steam plume is present at the emissions source, this fact should be recorded. Figures AM1-I and AM1-II are examples of logbook forms that may be used to record this type of data. Magnetic tape or paper tape may also be used to record data.

LIDAR LOG CONTROL NUMBER TABULATION

Log Book Number-_____

(Assign a CONTROL NUMBER to each individual source under test)

CONTROL NUMBER	DATE ASSIGNED	PROJECT	CITY, STATE

continued on next page

LIDAR LOG CONTROL NUMBER TABULATION (cont')

(Assign a CONTROL NUMBER to each individual source under test)

CONTROL NUMBER	DATE ASSIGNED	PROJECT	CITY, STATE

Next Log Book Number-_____

Figure AM1-1 Lidar Log Control Number Tabulation

LIDAR LOG OF OPERATIONS

Control number: OMEGA-_____

Facility name and location:

At the field site on / / from _____ to _____ (local time)

Location of LIDAR:

Direction to source _____ Range to source _____ km

Laser inclination (+ angle is up, horizontal is 0) _____

Source type and official designation:

Plume characteristics (color, shape, steam present, etc.)

Wind speed: begin _____ km hr and _____ km hr Wind direction: begin _____ and _____

Air temperature: begin _____ C and _____ C Relative humidity: begin _____ % and _____ %

Barometer: begin _____ and _____ Visibility: begin _____ km and _____ km

Cloud cover: begin _____ and _____

Data records made in field (tapes, printouts, photos, etc.)

MAGNETIC TAPES

tape# track# files

OPERATOR'S SIGNATURE: _____ DATE: _____

WITNESS SIGNATURE: _____ DATE: _____

LIDAR OPERATOR'S NOTES

(include position of laser beam within plume -- attached plume, etc.)

LIDAR FUNCTION VERIFICATION

Source: optical generator ( ) screens ( )

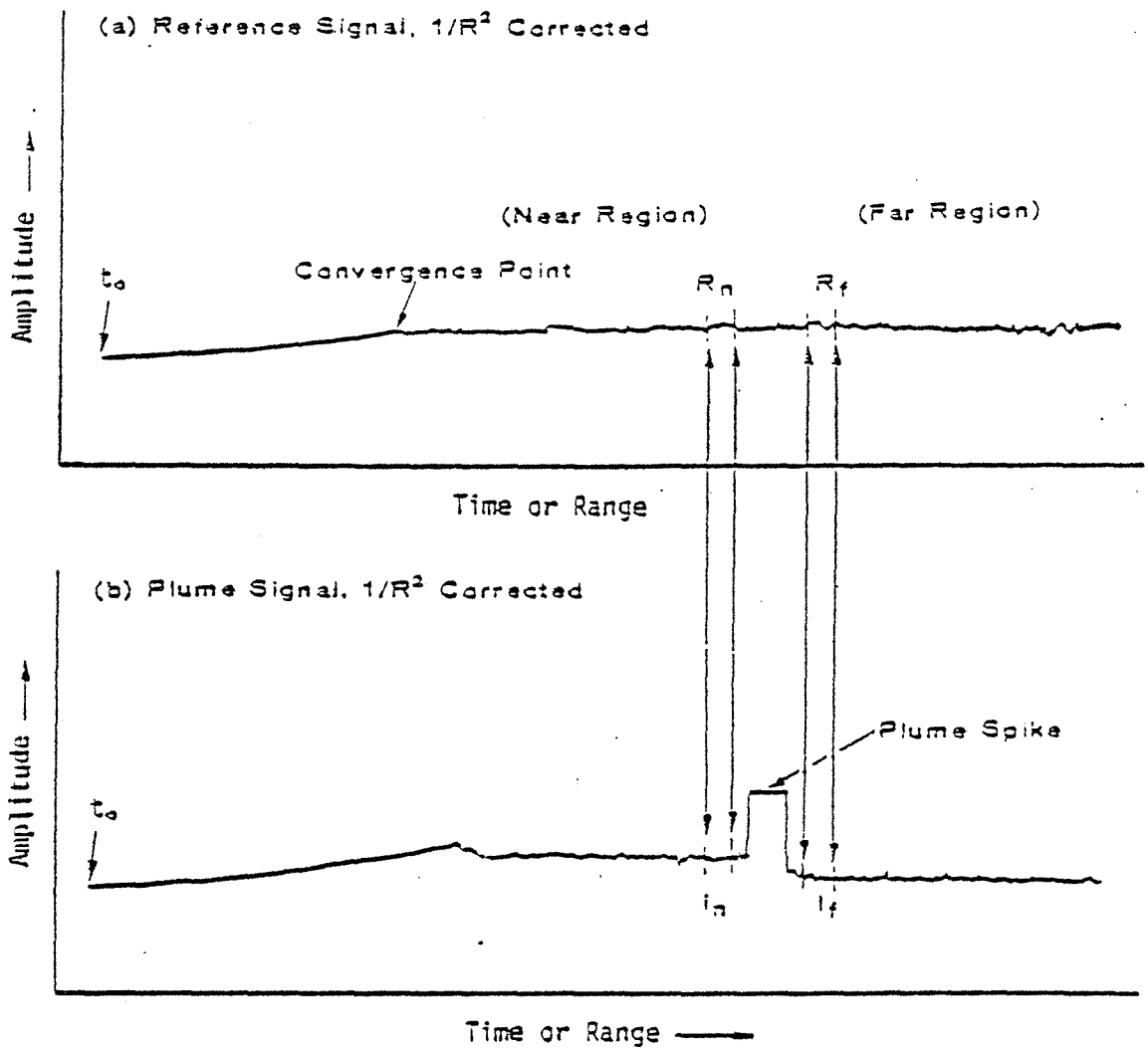
Date of last calibration _____ This test recorded on tape# _____ track# _____

	1	2	3	4	5	6	7	8
Calibrated opacity								
Calculated opacity								
Recorded on flip								

OPERATOR'S SIGNATURE: _____ DATE: _____

WITNESS SIGNATURE: _____ DATE: _____

Figure AM1-II Lidar Log Of Operations



(a) Reference signal, $1/R^2$-corrected. This reference signal is for plume signal (b). R_n, R_f are chosen to coincide with I_n, I_f.

(b) Plume signal, $1/R^2$-corrected. The plume spike and the decrease in the backscatter signal amplitude in the far region are due to the opacity of the plume. I_n, I_f are chosen as indicated in Section 2.6.

Figure AMI-III. Plots of Lidar Backscatter Signals

2.8 Opacity Calculation and Data Analysis. Referring to the reference signal and plume signal in Figure AM1–III, the measured opacity (O_p) in percent for each lidar measurement is calculated using Equation AM1–2. ($O_p = 1 - T_p$; T_p is the plume transmittance.)

$$O_p = (100\%)\left[1 - \left(\frac{I_f}{R_f}\frac{R_n}{I_n}\right)^{1/2}\right], \qquad \text{(AM1-2)}$$

where:

I_n = near-region pick interval signal amplitude, plume signal, $1/R^2$ corrected.

I_f = far-region pick interval signal amplitude, plume signal, $1/R^2$ corrected.

R_n = near-region pick interval signal amplitude, reference signal, $1/R^2$ corrected, and

R_f = far-region pick interval signal amplitude, reference signal, $1/R^2$ corrected.

The $1/R^2$ correction to the plume and reference signal amplitudes is made by multiplying the amplitude for each successive sample interval from the time reference, by the square of the lidar time (or range) associated with that sample interval [Reference 5.1].

The first step in selecting the pick intervals for Equation AM1–2 is to divide the plume signal amplitude by the reference signal amplitude at the same respective ranges to obtain a "normalized" signal. The pick intervals selected using this normalized signal are a minimum of 15 m (100 nanoseconds) in length and consist of at least 5 contiguous sample intervals. In addition, the following criteria, listed in order of importance, govern pick interval selection. (1) The intervals shall be in a region of the normalized signal where the reference signal meets the requirements of Section 2.3 and is everywhere greater than zero. (2) The intervals (near and far) with the minimum average amplitude are chosen. (3) If more than one interval with the same minimum average amplitude is found, the interval closest to the plume is chosen. (4) The standard deviation, S_o, for the calculated opacity shall be 8% or less. (S_o is calculated by Equation AM1–7).

If S_o is greater than 8%, then the far pick interval shall be changed to the next interval of minimal average amplitude. If S_o is still greater than 8%, then this procedure is repeated for the far pick interval. This procedure may be repeated once again for the near pick interval, but if S_o remains greater than 8%, the plume signal shall be discarded.

The reference signal pick intervals, R_n and R_f, must be chosen over the same time interval as the plume signal pick intervals, I_n and I_f, respectively (Figure AM1–III). Other methods of selecting pick intervals may be used if they give equivalent results. Field-oriented examples of pick interval selection are available in Reference 5.1.

The average amplitudes for each of the pick intervals, I_n, I_f, R_n, R_f, shall be calculated by averaging the respective individual amplitudes of the sample intervals from the plume signal and the associated reference signal each corrected for $1/R^2$. The amplitude of I_n shall be calculated according to Equation (AM–3).

$$I_n = \frac{1}{m}\sum_{i=1}^{m} I_{ni}, \qquad \text{(AM1-3)}$$

where:

I_{ni} = the amplitude of the ith sample interval (near-region).

Σ = sum of the individual amplitudes for the sample intervals.

m = number of sample intervals in the pick interval, and

I_n = average amplitude of the near-region pick interval.

Similarly, the amplitudes for I_f, R_n, and R_f are calculated with the three expressions in Equation (AM1–4).

$$I_f = \frac{1}{m}\sum_{i=1}^{m} I_{fi}, \quad R_n = \frac{1}{m}\sum_{i=1}^{m} R_{ni}, \quad R_f = \frac{1}{m}\sum_{i=1}^{m} R_{fi}. \qquad \text{(AM1-4)}$$

The standard deviation, S_{In}, of the set of amplitudes for the near-region pick interval, I_n, shall be calculated using Equation (AM1–5).

$$S_{In} = \left[\sum_{i=1}^{m}\frac{(I_{ni} - I_n)^2}{(m-1)}\right]^{1/2}. \qquad \text{(AM1-5)}$$

Similarly, the standard deviations S_{If}, S_{Rn}, and S_{Rf} are calculated with the three expressions in Equation (AM1–6).

$$S_{If} = \left[\sum_{i=1}^{m}\frac{(I_{fi} - I_f)^2}{(m-1)}\right]^{1/2}, \quad S_{Rn} = \left[\sum_{i=1}^{m}\frac{(R_{ni} - R_n)^2}{(m-1)}\right]^{1/2}, \quad S_{Rf} = \left[\sum_{i=1}^{m}\frac{(R_{fi} - R_f)^2}{(m-1)}\right]^{1/2}. \qquad \text{(AM1-6)}$$

The standard deviation, S_o, for each associated opacity value, O_p, shall be calculated using Equation (AM1–7).

$$S_o = \frac{1}{2}\left(\frac{I_f}{R_f}\frac{R_n}{I_n}\right)^{1/2}\left[\frac{S_{In}^2}{I_n^2} + \frac{S_{If}^2}{I_f^2} + \frac{S_{Rn}^2}{R_n^2} + \frac{S_{Rf}^2}{R_f^2}\right]^{1/2} \qquad \text{(AM1-7)}$$

The calculated values of I_n, I_f, R_n, R_f, S_{In}, S_{If}, S_{Rn}, S_{Rf}, O_p, and S_o should be recorded. Any plume signal with an S_o greater than 8% shall be discarded.

2.8.1 Azimuth Angle Correction. If the azimuth angle correction to opacity specified in this section is performed, then the elevation angle correction specified in Section 2.8.2 shall not be performed. When opacity is measured in the residual region of an attached steam plume, and the lidar line-of-sight is not perpendicular to the plume, it may be necessary to correct the opacity measured by the lidar to obtain the opacity that would be measured on a path perpendicular to the plume. The following method, or any other method which produces equivalent results, shall be used to determine the need for a correction, to calculate the correction, and to document the point within the plume at which the opacity was measured.

Figure AM1–IV(b) shows the geometry of the opacity correction. L' is the path through the plume along which the opacity measurement is made. P' is the path perpendicular to the plume at the same point. The angle ϵ is the angle between L' and the plume center line. The angle $(\pi/2-\epsilon)$, is the angle between the L' and P'. The measured opacity, O_p, measured along the path L' shall be corrected to obtain the corrected opacity, O_{pc}, for the path P', using Equation (AM1–8).

$$O_{pc} = 1 - (1 - O_p)^{\cos(\pi/2-\epsilon)} = 1 - (1 - O_p)^{\sin\epsilon} \qquad \text{(AM1-8)}$$

The correction in Equation (AM1–8) shall be performed if the inequality in Equation (AM1–9) is true.

$$\epsilon \geq \sin^{-1}\left[\frac{\ln(1.01 - O_o)}{\ln(1 - O_p)}\right] \qquad \text{(AM1-9)}$$

Figure AM1–IV(a) shows the geometry used to calculate ϵ and the position in the plume at which the lidar measurement is made. This analysis assumes that for a given lidar measurement, the range from the lidar to the plume, the elevation angle of the lidar from the horizontal plane, and the azimuth angle of the lidar from an arbitrary fixed reference in the horizontal plane can all be obtained directly.

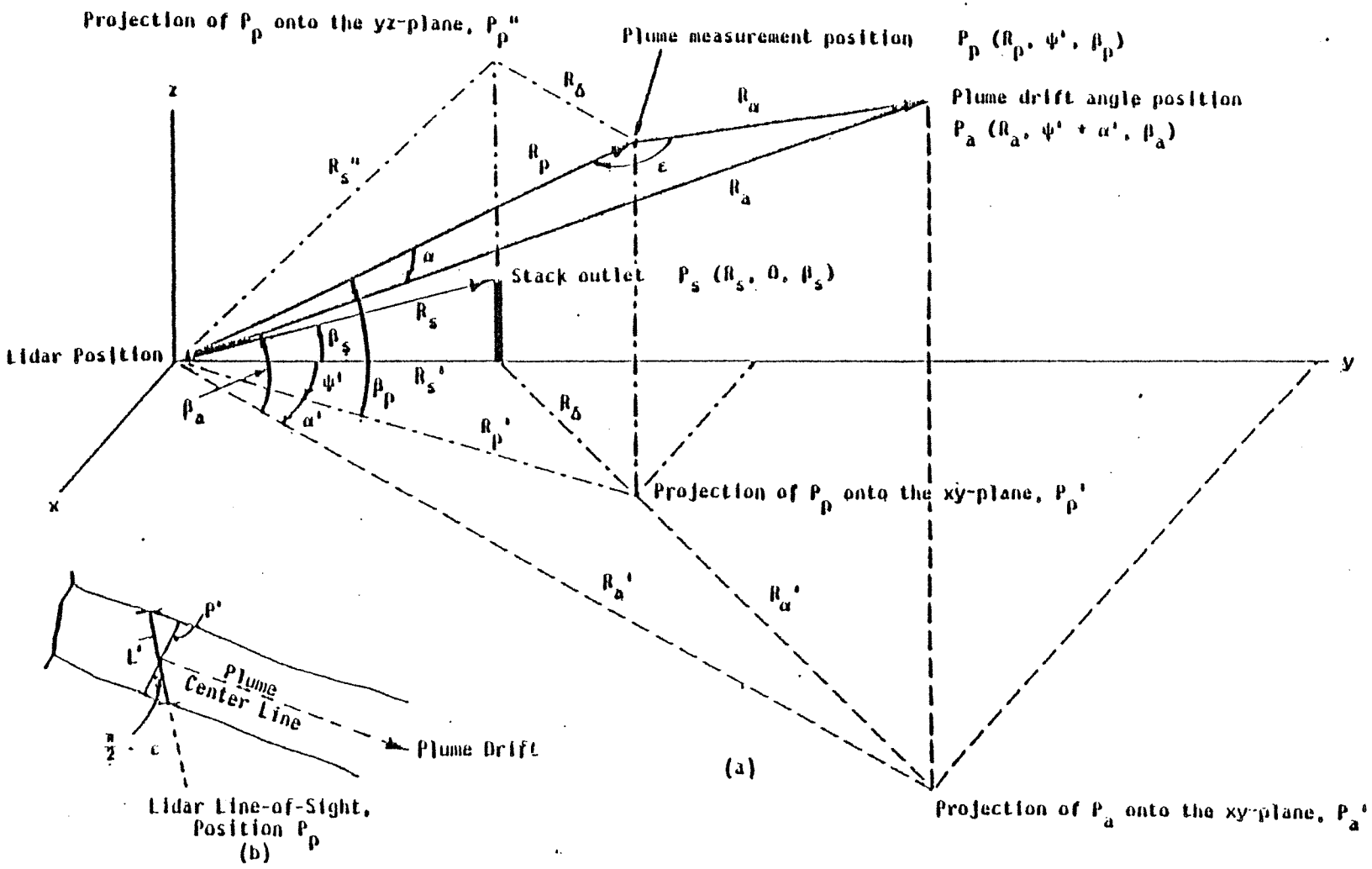


Figure AMI - IV. Correction in Opacity for Drift of the Residual Region of an Attached Steam Plume.

R_s = range from lidar to source*
β_s = elevation angle of R_s*
R_p = range from lidar to plume at the opacity measurement point*
β_p = elevation angle of R_p*
R_α = range from lidar to plume at some arbitrary point, P_α, so the drift angle of the plume can be determined*
β_α = elevation angle of R_α*
α = angle between R_p and R_α

R'_s = projection of R_s in the horizontal plane
R'_p = projection of R_p in the horizontal plane
R'_α = projection of R_α in the horizontal plane
ψ' = angle between R'_s and R'_p*
α' = angle between R'_p and R'_α*
R_δ = distance from the source to the opacity measurement point projected in the horizontal plane
R_α = distance from opacity measurement point P_p to the point in the plume P_α.

$$\varepsilon = \sin^{-1}\left[\frac{R_\alpha \sin\alpha}{R_\alpha}\right], \quad \text{(AM1-10)}$$

The correction angle ϵ shall be determined using Equation AM1-10.
where:
$\alpha = \cos^{-1}(\cos\beta_p \cos\beta_\alpha \cos\alpha' + \sin\beta_p \sin\beta_\alpha)$,
and

$R_\alpha = (R_p^2 + R_\alpha^2 - 2 R_p R_\alpha \cos\alpha)^{1/2}$

R_δ, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1-11.

$$R_\delta = (R_s'^2 + R_p'^2 - 2R'_s R'_p \cos\psi')^{1/2}, \quad \text{(AM1-11)}$$

where:
$R'_s = R_s \cos\beta_s$ and
$R'_p = R_p \cos\beta_p$

In the special case where the plume centerline at the opacity measurement point is horizontal, parallel to the ground, Equation AM1-12 may be used to determine ϵ instead of Equation AM1-10.

$$\varepsilon = \cos^{-1}\left[\frac{R_p^2 + R_\delta^2 - R_s''^2}{2 R_p R_s}\right], \quad \text{(AM1-12)}$$

where:
$R''_s = (R'^2_s + R_s^2 \sin^2\beta_s)^{1/2}$

If the angle ϵ is such that $\epsilon < 30°$ or $\epsilon > 150°$, the azimuth angle correction shall not be performed and the associated opacity value shall be discarded.

2.5.2 Elevation Angle Correction. An individual lidar-measured opacity, O_p, shall be corrected for elevation angle if the laser elevation or inclination angle, β_p (Figure AM1-V), is greater than or equal to the value calculated in Equation AM1-13.

$$\beta_p \geq \cos^{-1}\left[\frac{\ln(1.01 - O_p)}{\ln(1 - O_p)}\right] \quad \text{(AM1-13)}$$

The measured opacity, O_p, along the lidar path L_p is adjusted to obtain the corrected opacity, O_{pc}, for the actual plume (horizontal) path, P, by using Equation (AM1-14).

$$O_{pc} = 1 - (1 - O_p)^{\cos\beta_p}, \quad \text{(AM1-14)}$$

where:
β_p = lidar elevation or inclination angle,
O_p = measured opacity along path L_p and
O_{pc} = corrected opacity for the actual plume thickness P.

The values for β_p, O_p and O_{pc} should be recorded.

*Obtained directly from lidar. These values should be recorded.

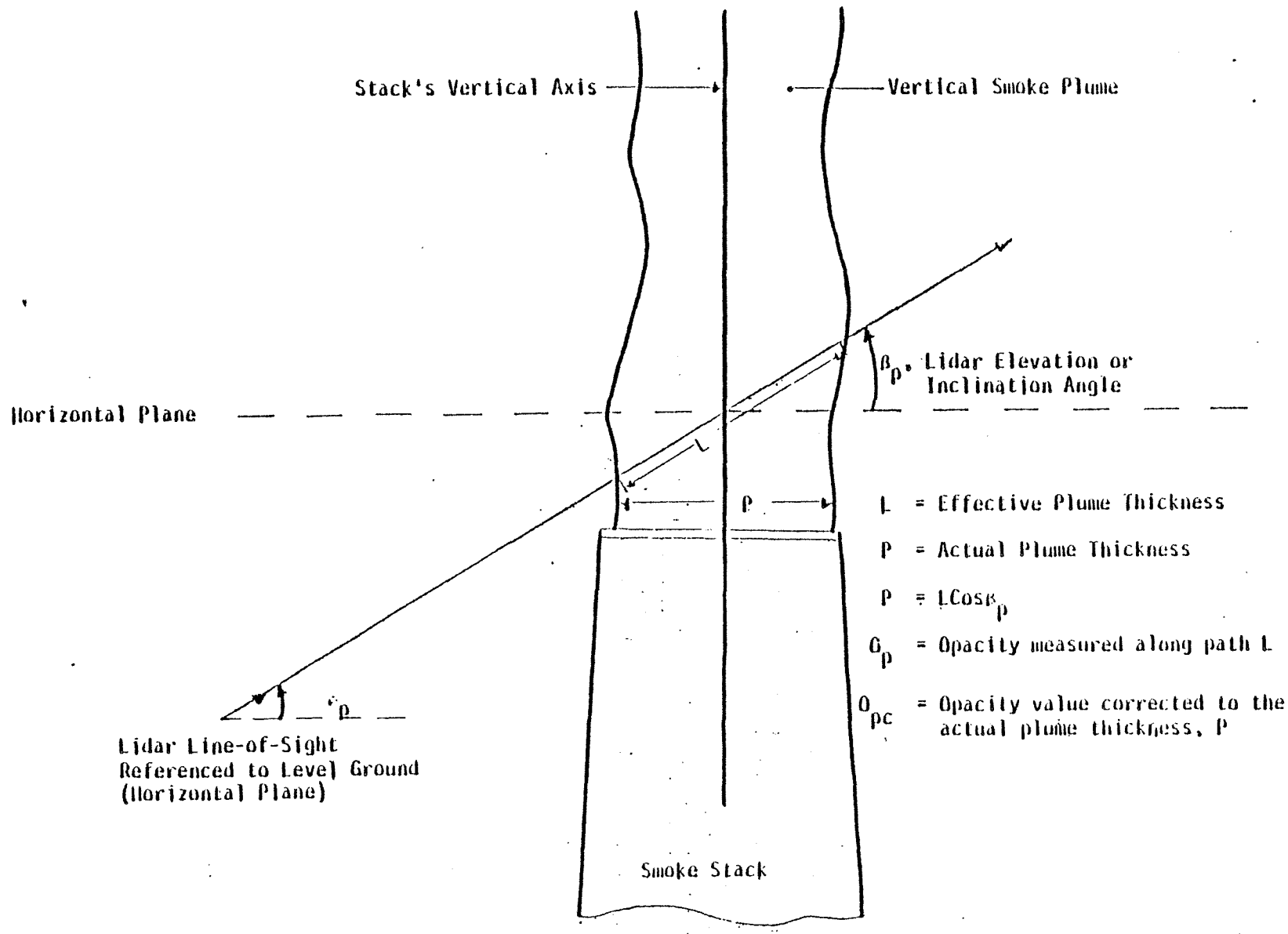


Figure AMI-V. Elevation Angle Correction for Vertical Plumes.

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1-15.

$$O_{pa} = O_{pc} - [2\ S_o + 5\%]. \qquad \text{(AM1-15)}$$

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, $\bar{O}_{pa}$, shall be calculated as the average of the consecutive individual actual opacity values, O_{pa}, by Equation AM1-16.

$$\bar{O}_{pa} = \frac{1}{n} \sum_{k=1}^{n} (O_{pa})_k \qquad \text{(AM1-16)}$$

where:

$(O_{pa})_k$ = the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

Σ = the sum of the individual actual opacity values.

n = the number of individual actual opacity values contained in the averaging interval.

$\bar{O}_{pa}$ = average actual opacity calculated over the averaging interval.

3. Lidar Performance Verification. The lidar shall be subjected to two types of performance verifications that shall be peformed in the field. The annual calibration, conducted at least once a year, shall be used to directly verify operation and performance of the entire lidar system. The routine verification, conducted for each emission source measured, shall be used to insure proper performance of the optical receiver and associated electronics.

3.1 Annual Calibration Procedures. Either a plume from a smoke generator or screen targets shall be used to conduct this calibration.

If the screen target method is selected, five screens shall be fabricated by placing an opaque mesh material over a narrow frame (wood, metal extrusion, etc.). The screen shall have a surface area of at least one square meter. The screen material should be chosen for precise optical opacities of about 10, 20, 40, 60, and 80%. Opacity of each target shall be optically determined and should be recorded. If a smoke generator plume is selected, it shall meet the requirements of Section 3.3 of Reference Method 9. This calibration shall be performed in the field during calm (as practical) atmospheric conditions. The lidar shall be positioned in accordance with Section 2.1.

The screen targets must be placed perpendicular to and coincident with the lidar line-of-sight at sufficient height above the ground (suggest about 30 ft) to avoid ground-level dust contamination. Reference signals shall be obtained just prior to conducting the calibration test.

The lidar shall be aimed through the center of the plume within 1 stack diameter of the exit, or through the geometric center of the screen target selected. The lidar shall be set in operation for a 6-minute data run at a nominal pulse rate of 1 pulse every 10 seconds. Each backscatter return signal and each respective opacity value obtained from the smoke generator transmissometer, shall be obtained in temporal coincidence. The data shall be analyzed and reduced in accordance with Section 2.6 of this method. This calibration shall be performed for 0% (clean air), and at least five other opacities (nominally 10, 20, 40, 60, and 80%).

The average of the lidar opacity values obtained during a 6-minute calibration run shall be calculated and should be recorded. Also the average of the opacity values obtained from the smoke generator transmissometer for the same 6-minute run shall be calculated and should be recorded.

Alternate calibration procedures that do not meet the above requirements but produce equivalent results may be used.

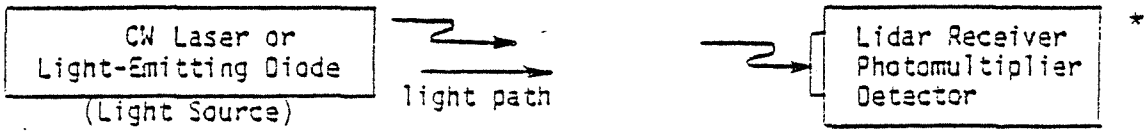
3.2 Routine Verification Procedures. Either one of two techniques shall be used to conduct this verification. It shall be performed at least once every 4 hours for each emission source measured. The following parameters shall be directly verified.

1) The opacity value of 0% plus a minimum of 3 (nominally 10, 20, 40, 60, and 80%) opacity values shall be verified through the PMT detector and data processing electronics.

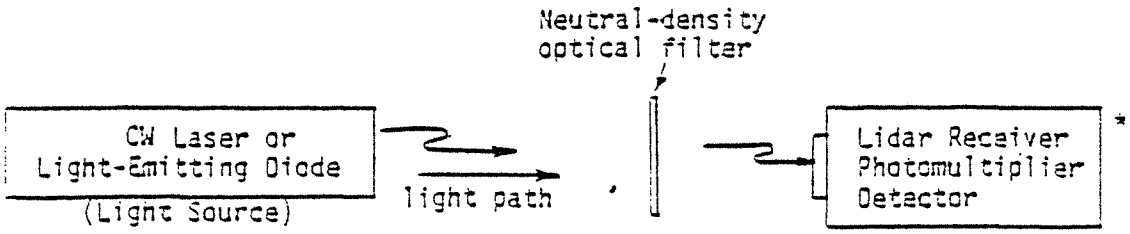
2) The zero-signal level (receiver signal with no optical signal from the source present) shall be inspected to insure that no spurious noise is present in the signal. With the entire lidar receiver and analog/digital electronics turned on and adjusted for normal operating performance, the following procedures shall be used for Techniques 1 and 2, respectively.

3.2.1 Procedure for Technique 1. This test shall be performed with no ambient or stray light reaching the PMT detector. The narrow band filter (694.3 nanometers peak) shall be removed from its position in front of the PMT detector. Neutral density filters of nominal opacities of 10, 20, 40, 60, and 80% shall be used. The recommended test configuration is depicted in Figure AM1-VI.

(a) Zero-Signal Level Test



(b) Clear-Air or 0% Opacity Test



(c) Optical Filter Test (simulated opacity values)

*Tests shall be performed with no ambient or stray light reaching the detector.

Figure AM1-VI. Test Configuration for Technique 1.

The zero-signal level shall be measured and should be recorded, as indicated in Figure AM1–VI(a). This simulated clear-air or 0% opacity value shall be tested in using the selected light source depicted in Figure AM1–VI(b).

The light source either shall be a continuous wave (CW) laser with the beam mechanically chopped or a light emitting diode controlled with a pulse generator (rectangular pulse). (A laser beam may have to be attenuated so as not to saturate the PMT detector). This signal level shall be measured and should be recorded. The opacity value is calculated by taking two pick intervals (Section 2.6) about 1 microsecond apart in time and using Equation (AM1–2) setting the ratio $R_o/R_r = 1$. This calculated value should be recorded.

The simulated clear-air signal level is also employed in the optical test using the neutral density filters. Using the test configuration in Figure AM1–VI(c), each neutral density filter shall be separately placed into the light path from the light source to the PMT detector. The signal level shall be measured and should be recorded. The opacity value for each filter is calculated by taking the signal level for that respective filter (I_f), dividing it by the 0% opacity signal level (I_o) and performing the remainder of the calculation by Equation (AM1–2) with $R_o/R_r = 1$. The calculated opacity value for each filter should be recorded.

The neutral density filters used for Technique 1 shall be calibrated for actual opacity with accuracy of ±2% or better. This calibration shall be done monthly while the filters are in use and the calibrated values should be recorded.

3.2.2 Procedure for Technique 2. An optical generator (built-in calibration mechanism) that contains a light-emitting diode (red light for a lidar containing a ruby laser) is used. By injecting an optical signal into the lidar receiver immediately ahead of the PMT detector, a backscatter signal is simulated. With the entire lidar receiver electronics turned on and adjusted for normal operating performance, the optical generator is turned on and the simulation signal (corrected for $1/R^2$) is selected with no plume spike signal and with the opacity value equal to 0%. This simulated clear-air atmospheric return signal is displayed on the system's video display. The lidar operator then makes any fine adjustments that may be necessary to maintain the system's normal operating range.

The opacity values of 0% and the other five values are selected one at a time in any order. The simulated return signal data should be recorded. The opacity value shall be calculated. This measurement/calculation shall be performed at least three times for each selected opacity value. While the order is not important, each of the opacity values from the optical generator shall be verified. The calibrated optical generator opacity value for each selection should be recorded.

The optical generator used for Technique 2 shall be calibrated for actual opacity with an accuracy of ±1% or better. This calibration shall be done monthly while the generator is in use and calibrated value should be recorded.

Alternate verification procedures that do not meet the above requirements but produce equivalent results may be used.

3.3 Deviation. The permissible error for the annual calibration and routine verification are:

3.3.1 Annual Calibration Deviation.

3.3.1.1 Smoke Generator. If the lidar-measured average opacity for each data run is not within ±5% (full scale) of the respective smoke generator's average opacity over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.1.2 Screens. If the lidar-measured average opacity for each data run is not within ±3% (full scale) of the laboratory-determined opacity for each respective simulation screen target over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.2 Routine Verification Error. If the lidar-measured average opacity for each neutral density filter (Technique 1) or optical generator selection (Technique 2) is not within ±3% (full scale) of the respective laboratory calibration value then the lidar shall be considered non-operational.

4. Performance/Design Specification for Basic Lidar System.

4.1 Lidar Design Specification. The essential components of the basic lidar system are a pulsed laser (transmitter), optical receiver, detector, signal processor, recorder, and an aiming device that is used in aiming the lidar transmitter and receiver. Figure AM1–VII shows a functional block diagram of a basic lidar system.

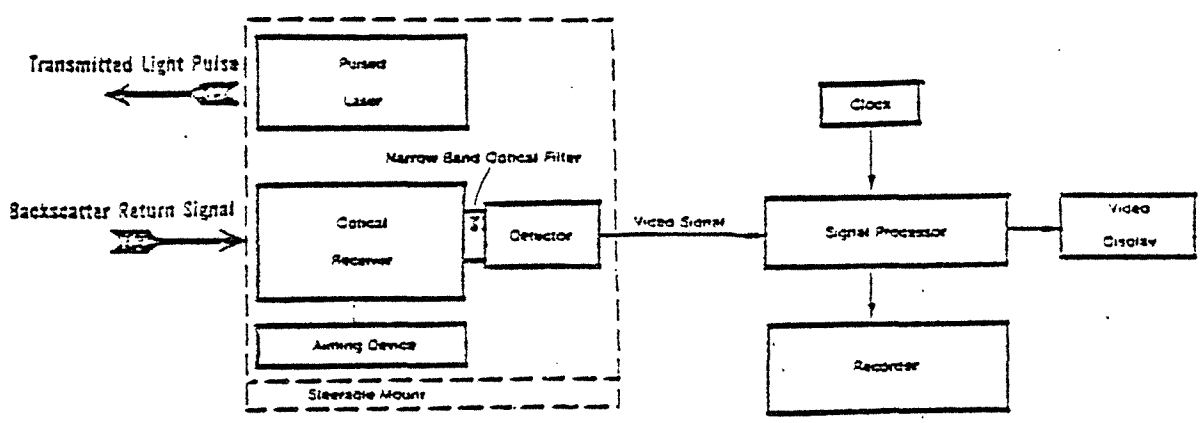


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in Section 3. The annual calibration shall be performed for three separate, complete runs and the results of each should be recorded. The requirements of Section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of Section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References.

5.1 The Use of Lidar for Emissions Source Opacity Determination. U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA-330/1-79-003-R. Arthur W. Dybdahl, current edition (NTIS No. PB81-246682).

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA/NEIC-TS-128. February 1978.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar. C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742. August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments. EPA-650/4-73-002. October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1-1976. 3 March 1976.

5.6 U.S. Army Technical Manual TB MED 279. Control of Hazards to Health from Laser Radiation. February 1969.

5.7 Laser Institute of America Laser Safety Manual. 4th Edition.

5.8 U.S. Department of Health, Education and Welfare. Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968. January 1976.

5.9 Laser Safety Handbook. Alex Mallow, Leon Chabot. Van Nostrand Reinhold Co. 1978.

Method 12. Determination of Inorganic Lead Emissions From Stationary Sources [1-5]

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the determination of inorganic lead (Pb) emissions from specified stationary sources only.

1.2 Principle. Particulate and gaseous Pb emissions are withdrawn isokinetically from the source and collected on a filter and in dilute nitric acid. The collected samples are digested in acid solution and analyzed by atomic absorption spectrometry using an air acetylene flame.

2. *Range, Sensitivity, Precision, and Interferences.*

2.1 Range. For a minimum analytical accuracy of ±10 percent, the lower limit of the range is 100 μg. The upper limit can be considerably extended by dilution.

2.2 Analytical Sensitivity. Typical sensitivities for a 1-percent change in absorption (0.0044 absorbance units) are 0.2 and 0.5 μg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

2.3 Precision. The within-laboratory precision, as measured by the coefficient of variation ranges from 0.2 to 9.5 percent relative to a run-mean concentration. These values were based on tests conducted at a gray iron foundry, a lead storage battery manufacturing plant, a secondary lead smelter, and a lead recovery furnace of an alkyl lead manufacturing plant. The concentrations encountered during these tests ranged from 0.81 to 123.3 mg Pb/m^3.

2.4 Interferences. Sample matrix effects may interfere with the analysis for Pb by flame atomic absorption. If this interference is suspected, the analyst may confirm the presence of these matrix effects and frequently eliminate the interference by using the Method of Standard Additions.

High concentrations of copper may interfere with the analysis of Pb at 217.0 nm. This interference can be avoided by analyzing the samples at 283.3 nm.

3. *Apparatus.*

3.1 Sampling Train. A schematic of the sampling train is shown in Figure 12-1; it is similar to the Method 5 train. The sampling train consists of the following components:

3.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1 to 2.1.6 and 2.1.8 to 2.1.10, respectively.

3.1.2 Impingers. Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. For the second impinger, use the Greenburg-Smith design with the standard tip. Place a thermometer, capable of measuring temperature to within 1°C (2°F) at the outlet of the fourth impinger for monitoring purposes.

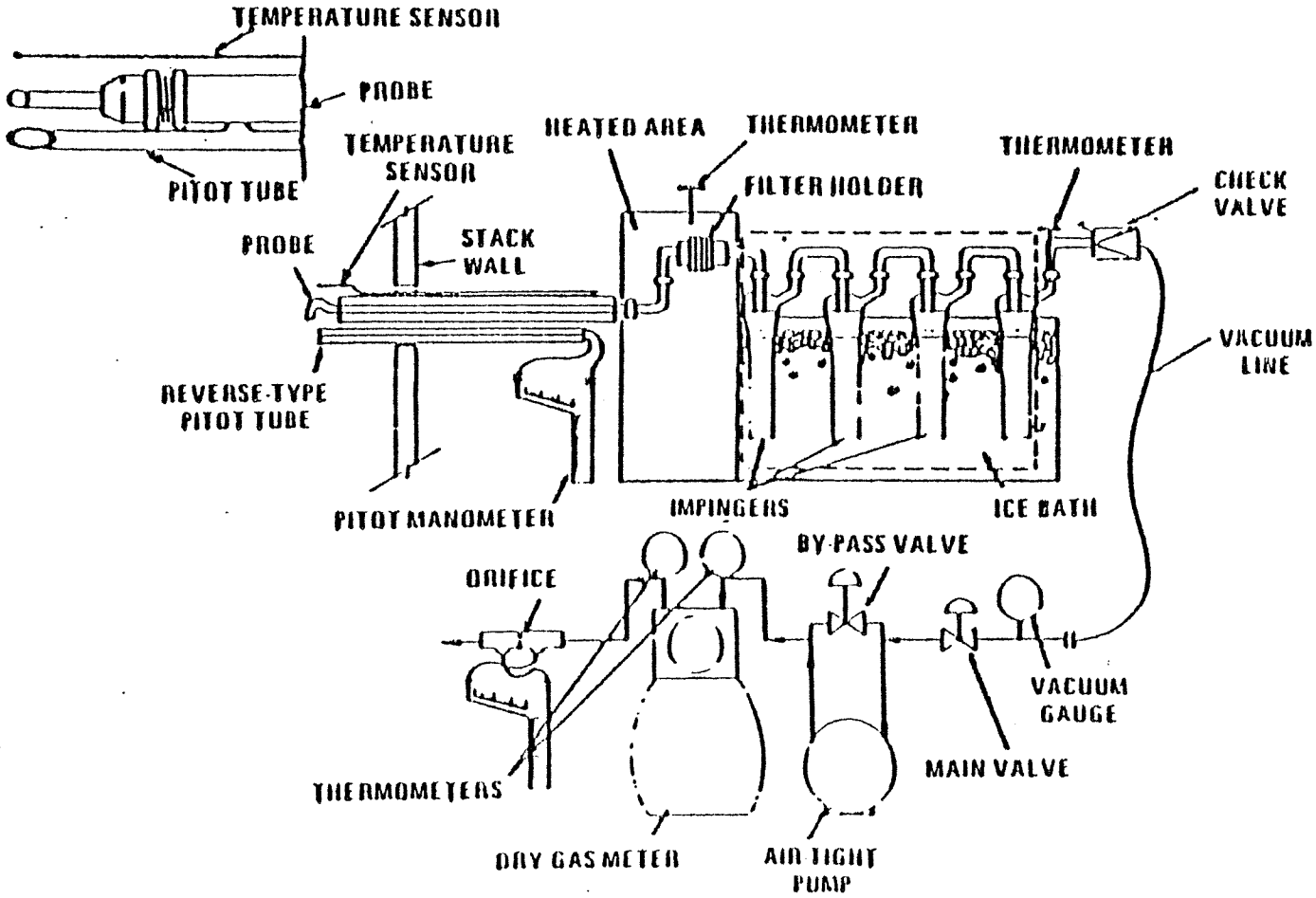


Figure 12-1. Inorganic lead sampling train.

3.2 Sample Recovery. The following items are needed:

3.2.1 Probe-Liner and Probe-Nozzle Brushes, Petri Dishes, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as Method 5, Sections 2.2.1, 2.2.4, 2.2.5, and 2.2.7, respectively.

3.2.2 Wash Bottles. Glass (2).

3.2.3 Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for 0.1 nitric acid (HNO_3) impinger and probe solutions and washes, 1000-ml. Use screw-cap liners that are either rubber-backed Teflon* or leak-free and resistant to chemical attack by 0.1 N HNO_3. (Narrow mouth glass bottles have been found to be less prone to leakage.)

3.2.4 Graduated Cylinder and/or Balance. To measure condensed water to within 2 ml or 1 g. Use a graduated cylinder that has a minimum capacity of 500 ml, and subdivisions no greater than 5 ml. (Most laboratory balances are capable of weighing to the nearest 0.5 g or less.)

3.2.5 Funnel. Glass, to aid in sample recovery.

3.3 Analysis. The following equipment is needed:

3.3.1 Atomic Absorption Spectrophotometer. With lead hollow cathode lamp and burner for air/acetylene flame.

3.3.2 Hot Plate.

3.3.3 Erlenmeyer Flasks, 125-ml, 24/40 S.

3.3.4 Membrane Filters, Millipore SCWPO 4700 or equivalent.

3.3.5 Filtration Apparatus, Millipore vacuum filtration unit, or equivalent, for use with the above membrane filter.

3.3.6 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml.

4. *Reagents.*

4.1 Sampling. The reagents used in sampling are as follows:

4.1.1 Filter. Gelman Spectro Grade, Reeve Angel 934 AH, MSA 1108 BH, all with lot assay for Pb, or other high-purity glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. Conduct the filter efficiency test using ASTM Standard Method D 2986-71 or use test data from the supplier's quality control program.

4.1.2 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Section 3.1.2, 3.1.4, and 3.1.5, respectively.

4.1.3 Water. Deionized distilled, to conform to ASTM Specification D 1193-74, Type 3. If high concentrations of organic matter are not expected to be present, the analyst may delete the potassium permanganate test for oxidizable organic matter.

4.1.4 Nitric Acid, 0.1 N. Dilute 6.3 ml of concentrated HNO_3 to 1 liter with deionized distilled water. (It may be desirable to run blanks before field use to eliminate a high blank on test samples.)

4.2 Pretest Preparation. 6 N HNO_3 is needed. Dilute 380 ml of concentrated HNO_3 to 1 liter with deionized distilled water.

*Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

4.3 Sample Recovery. 0.1 N HNO_3 (same as 4.1.4 above) is needed for sample recovery.

4.4 Analysis. The following reagents are needed for analysis (use ACS reagent grade chemicals or equivalent, unless otherwise specified):

4.4.1 Water. Same as 4.1.3 above.

4.4.2 Nitric Acid, Concentrated.

4.4.3 Nitric Acid, 20 percent (V/V). Dilute 500 ml of concentrated HNO_3 to 1 liter with deionized distilled water.

4.4.4 Stock Lead Standard Solution, 1000 µg Pb/ml. Dissolve 0.1598 g of lead nitrate ($Pb(NO_3)_2$) in about 60 ml of deionized distilled water, add 2 ml concentrated HNO_3, and dilute to 100 ml with deionized distilled water.

4.4.5 Working Lead Standards. Pipet 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the stock lead standard solution (4.4.4) into 250-ml volumetric flasks. Add 5 ml of concentrated HNO_3 to each flask and dilute to volume with deionized distilled water. These working standards contain 0.0, 4.0, 8.0, 12.0, 16.0, and 20.0 µg Pb/ml, respectively. Prepare, as needed, additional standards at other concentrations in a similar manner.

4.4.6 Air. Suitable quality for atomic absorption analysis.

4.4.7 Acetylene. Suitable quality for atomic absorption analysis.

4.4.8 Hydrogen Peroxide, 3 percent (V/V). Dilute 10 ml of 30 percent H_2O_2 to 100 ml with deionized distilled water.

5. *Procedure.*

5.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except the filter need not be weighed.

5.1.2 Preliminary Determinations. Follow the same general procedure given in Method 5, Section 4.1.2.

5.1.3 Preparation of Collection Train. Follow the same general procedure given in Method 5, Section 4.1.3, except place 100 ml of 0.1 HNO_3 in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Set up the train as shown in Figure 12-1.

5.1.4 Leak-Check Procedures. Follow the general leak-check procedures given in Method 5, Sections 4.1.4.1 (Pretest Leak-Check), 4.1.4.2 (Leak-Checks During the Sample Run), and 4.1.4.3 (Post-Test Leak-Check).

5.1.5 Sampling Train Operation. Follow the same general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in EPA Method 5, Figure 5-2.

5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

5.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the glassware inlet where the probe was fastened and cap the inlet. Remove the umbilical cord from the last impinger and cap the impinger. The tester may use ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and filter-impinger assembly to a cleanup area, which is clean and protected from the wind so that the chances of contaminating or losing the sample are minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

5.2.1 *Container No. 1* (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. If it is necessary to fold the filter, do so such that the sample-exposed side is inside the fold. Carefully transfer to the petri dish any visible sample matter and/or filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

5.2.2 *Container No. 2* (Probe). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover sample matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 0.1 N HNO_3 and placing the wash into a glass sample storage container. Measure and record (to the nearest 2-ml) the total amount of 0.1 N HNO_3 used for each rinse. Perform the 0.1 N HNO_3 rinses as follows:

Carefully remove the probe nozzle and rinse the inside surfaces with 0.1 N HNO_3 from a wash bottle while brushing with a stainless steel, Nylon-bristle brush. Brush until the 0.1 N HNO_3 rinse shows no visible particles, then make a final rinse of the inside surface.

Brush and rinse with 0.1 N HNO_3 the inside parts of the Swagelok fitting in a similar way until no visible particles remain.

Rinse the probe liner with 0.1 N HNO_3. While rotating the probe so that all inside surfaces will be rinsed with 0.1 N HNO_3, tilt the probe and squirt 0.1 N HNO_3 into its upper end. Let the 0.1 N HNO_3 drain from the lower end into the sample container. The tester may use a glass funnel to aid in transferring liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, squirt 0.1 N HNO_3 into the upper end of the probe as the probe brush is being pushed with a twisting action through the probe; hold the sample container underneath the lower end of the probe and catch any 0.1 N HNO_3 and sample matter that is brushed from the probe. Run the brush through the probe three times or more until no visible sample matter is carried out with the 0.1 N HNO_3 and none remains on the probe liner on visual inspection. With

stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which sample matter can be entrapped. Rinse the brush with 0.1 N HNO_3 and quantitatively collect these washings in the sample container. After the brushing make a final rinse of the probe as described above.

It is recommended that two people clean the probe to minimize loss of sample. Between sampling runs, keep brushes clean and protected from contamination.

After insuring that all joints are wiped clean of silicone grease, brush and rinse with 0.1 N HNO_3 the inside of the front half of the filter holder. Brush and rinse each surface three times or more, if needed, to remove visible sample matter. Make a final rinse of the brush and filter holder. After all 0.1 N HNO_3 washings and sample matter are collected in the sample container, tighten the lid on the sample container so that the fluid will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

5.2.3 *Container No. 3* (Silica Gel). Check the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to the original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow procedure for Container No. 3 under Section 5.4 (Analysis).

5.2.4 *Container No. 4* (Impingers). Due to the large quantity of liquid involved, the tester may place the impinger solutions in several containers. Clean each of the first three impingers and connecting glassware in the following manner:

1. Wipe the impinger ball joints free of silicone grease and cap the joints.

2. Rotate and agitate each impinger, so that the impinger contents might serve as a rinse solution.

3. Transfer the contents of the impingers to a 500-ml graduated cylinder. Remove the outlet ball joint cap and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within ±2 ml. Alternatively, determine the weight of the liquid to within ±0.5 g. Record in the log the volume or weight of the liquid present, along with a notation of any color or film observed in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5, Figure 5-3).

4. Transfer the contents to Container No. 4.

5. Note: In steps 5 and 8 below, measure and record the total amount of 0.1 N HNO_3 used for rinsing. Pour approximately 50 ml of 0.1 N HNO_3 into each of the first three impingers and agitate the impingers. Drain the 0.1 N HNO_3 through the outlet arm of each impinger into Container No. 4. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

6. Wipe the ball joints of the glassware connecting the impingers free of silicone grease and rinse each piece of glassware twice with 0.1 N HNO_3; transfer this rinse into Container No. 4. (*Do not rinse or brush the glass-fritted filter support.*) Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

5.2.5 Blanks. Save 200 ml of the 0.1 N HNO_3 used for sampling and cleanup as a blank. Take the solution directly from the bottle being used and place into a glass sample container labeled "0.1 N HNO_3 blank."

5.3 Sample Preparation.

5.3.1 *Container No. 1* (Filter). Cut the filter into strips and transfer the strips and all loose particulate matter into a 125-ml Erlenmeyer flask. Rinse the petri dish with 10 ml of 50 percent HNO_3 to insure a quantitative transfer and add to the flask. (Note: If the total volume required in Section 5.3.3 is expected to exceed 80 ml, use a 250-ml Erlenmeyer flask in place of the 125-ml flask.)

5.3.2 *Containers No. 2 and No. 4* (Probe and Impingers). (Check the liquid level in Containers No. 2 and/or No. 4 and confirm as to whether or not leakage occurred during transport; note observation on the analysis sheet. If a noticeable amount of leakage had occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.) Combine the contents of Containers No. 2 and No. 4 and take to dryness on a hot plate.

5.3.3 Sample Extraction for lead. Based on the approximate stack gas particulate concentration and the total volume of stack gas sampled, estimate the total weight of particulate sample collected. Then transfer the residue from Containers No. 2 and No. 4 to the 125-ml Erlenmeyer flask that contains the filter using rubber policeman and 10 ml of 50 percent HNO_3 for every 100 mg of sample collected in the train or a minimum of 30 ml of 50 percent HNO_3 whichever is larger.

Place the Erlenmeyer flask on a hot plate and heat with periodic stirring for 30 min at a temperature just below boiling. If the sample volume falls below 15 ml, add more 50 percent HNO_3. Add 10 ml of 3 percent H_2O_2 and continue heating for 10 min. Add 50 ml of hot (80°C) deionized distilled water and heat for 20 min. Remove the flask from the hot plate and allow to cool. Filter the sample through a Millipore membrane filter or equivalent and transfer the filtrate to a 250-ml volumetric flask. Dilute to volume with deionized distilled water.

5.3.4 Filter Blank. Determine a filter blank using two filters from each lot of filters used in the sampling train. Cut each filter into strips and place each filter in a separate 125-ml Erlenmeyer flask. Add 15 ml of 50 percent HNO_3 and treat as described in Section 5.3.3 using 10 ml of 3 percent H_2O_2 and 50 ml of hot, deionized distilled water. Filter and dilute to a total volume of 100 ml using deionized distilled water.

5.3.5 0.1 N HNO_3 Blank. Take the entire 200 ml of 0.1 N HNO_3 to dryness on a steam bath, add 15 ml of 50 percent HNO_3, and treat as described in Section 5.3.3 using 10 ml of 3 percent H_2O_2 and 50 ml of hot, deionized distilled water. Dilute to a total volume of 100 ml using deionized distilled water.

5.4 Analysis.

5.4.1 Lead Determination. Calibrate the spectrophotometer as described in Section 6.2 and determine the absorbance for each source sample, the filter blank, and 0.1 N HNO_3 blank. Analyze each sample three times in this manner. Make appropriate dilutions, as required, to bring all sample Pb concentrations into the linear absorbance range of the spectrophotometer.

If the Pb concentration of a sample is at the low end of the calibration curve and high accuracy is required, the sample can be taken to dryness on a hot plate and the residue dissolved in the appropriate volume of water to bring it into the optimum range of the calibration curve.

5.4.2 Mandatory Check for Matrix Effects on the Lead Results. The analysis for Pb by atomic absorption is sensitive to the chemical compositon and to the physical properties (viscosity, pH) of the sample (matrix effects). Since the Pb procedure described here will be applied to many different sources, many sample matrices will be encountered. Thus, check (mandatory) at least one sample from each source using the Method of Additions to ascertain that the chemical composition and physical properties of the sample did not cause erroneous analytical results.

Three acceptable "Method of Additions" procedures are described in the General Procedure Section of the Perkin Elmer Corporation Manual (see Citation 9.1). If the results of the Method of Additions procedure on the source sample do not agree within 5 percent of the value obtained by the conventional atomic absorption analysis, then the tester must reanalyze all samples from the source using the Method of Additions procedure.

5.4.3 *Container No. 3* (Silica Gel). The tester may conduct this step in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

6. *Calibration.*

Maintain a laboratory log of all calibrations.

6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

6.2 Spectrophotometer. Measure the absorbance of the standard solutions using the instrument settings recommended by the spectrophotometer manufacturer. Repeat until good agreement (±3 percent) is obtained between two consecutive readings. Plot the absorbance (y-axis) versus concentration in μg Pb/ml (x-axis). Draw or compute a straight line through the linear portion of the curve. Do not force the calibration curve through zero, but if the curve does not pass through the origin or at least lie closer to the origin than ±0.003

absorbance units, check for incorrectly prepared standards and for curvature in the calibration curve.

To determine stability of the calibration curve, run a blank and a standard after every five samples and recalibrate, as necessary.

7. *Calculations.*

7.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the total volume of dry gas metered corrected to standard conditions (20°C and 760 mm Hg), by using Equation 5-1 of Method 5. If necessary, adjust $V_{m(std)}$ for leakages as outlined in Section 6.3 of Method 5. See the field data sheet for the average dry gas meter temperature and average orifice pressure drop.

7.2 Volume of Water Vapor and Moisture Content. Using data obtained in this test and Equations 5-2 and 5-3 of Method 5, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas.

7.3 Total Lead in Source Sample. For each source sample correct the average absorbance for the contribution of the filter blank and the 0.1 N HNO_3 blank. Use the calibration curve and this corrected absorbance to determine the µg Pb concentration in the sample aspirated into the spectrophotometer. Calculate the total Pb content C^*_{Pb} (in µg) in the original source sample; correct for all the dilutions that were made to bring the Pb concentration of the sample into the linear range of the spectrophotometer.

7.4 Lead Concentration. Calculate the stack gas Pb concentration C_{Pb} in mg/dscm as follows:

$$C_{Pb} = K \frac{C^*_{Pb}}{V_{m(std)}}$$

Where:

$K = 0.001$ mg/µg for metric units.

$= 2.205$ lb/µg for English units.

7.5 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively. To calculate v_s, the average stack gas velocity, use Equation 2-9 of Method 2 and the data from this field test.

8. *Alternative Test Methods for Inorganic Lead.*

8.1 Simultaneous Determination of Particulate and Lead Emissions. The tester may use Method 5 to simultaneously determine Pb provided that (1) he uses acetone to remove particulate from the probe and inside of the filter holder as specified by Method 5, (2) he uses 0.1 N HNO_3 in the impingers, (3) he uses a glass fiber filter with a low Pb background, and (4) he treats and analyzes the entire train contents, including the impingers, for Pb as described in Section 5 of this method.

8.2 Filter Location. The tester may use a filter between the third and fourth impinger provided that he includes the filter in the analysis for Pb.

8.3 In-stack Filter. The tester may use an in-stack filter provided that (1) he uses a glass-lined probe and at least two impingers, each containing 100 ml of 0.1 N HNO_3, after the in-stack filter and (2) he recovers and analyzes the probe and impinger contents for Pb. Recover sample from the nozzle with acetone if a particulate analysis is to be made.

9. *Bibliography*

9.1 Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. Norwalk, Connecticut. September 1976.

9.2 American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31; Water. Atmospheric Analysis. Philadelphia, Pa. 1974. p. 40-42.

9.3 Klein, R. and C. Hach. Standard Additions—Uses and Limitations in Spectrophotometric Analysis. *Amer. Lab.* 9:21-27. 1977.

9.4 Mitchell, W.J. and M.R. Midgett. Determining Inorganic and Alkyl Lead Emissions from Stationary Sources. U.S. Environmental Protection Agency, Emission Monitoring and Support Laboratory, Research Triangle Park, N.C. (Presented at National APCA Meeting, Houston, June 25, 1978).

9.5 Same as Method 5, Citations 2 to 5 and 7 of Section 7.

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(Secs. 111, 114, and 301(a) of the Clean Air Act as amended (42 U.S.C. 7411, 7414, and 7601(a)))

[FR Doc. 82-10487 Filed 4-15-82; 8:45 am]

METHOD 13—DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES SPADNS ZIRCONIUM LAKE METHOD

[Method 13A revised by 45 FR 41852, June 20, 1980]

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of fluoride (F) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as freons.

1.2 Principle. Gaseous and particulate F are withdrawn isokinetically from the source and collected in water and on a filter. The total F is then determined by the SPADNS Zirconium Lake colorimetric method.

2. Range and Sensitivity

The range of this method is 0 to 1.4ug F/ml. Sensitivity has not been determined.

3. Interferences

Large quantities of chloride will interfere with the analysis, but this interference can be prevented by adding silver sulfate into the distillation flask (see Section 7.3.4). If chloride ion is present, it may be easier to use the Specific Ion Electrode Method (Method 13B). Grease on sample-exposed surfaces may cause low F results due to adsorption.

4. Precision, Accuracy, and Stability

4.1 Precision. The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F/m³. The within-laboratory and between-laboratory standard deviations, which include sampling and analysis errors, were 0.044 mg F/m³ with 60 degrees of freedom and 0.064 mg F/m³ with five degrees of freedom, respectively.

4.2 Accuracy. The collaborative test did not find any bias in the analytical method.

4.3 Stability. After the sample and colorimetric reagent are mixed, the color formed is stable for approximately 2 hours. A 3°C temperature difference between the sample and standard solutions produces an error of approximately 0.005 mg F/liter. To avoid this error, the absorbances of the sample and standard solutions must be measured at the same temperature.

5. Apparatus

5.1 Sampling Train. A schematic of the sampling train is shown in Figure 13A-1. It is similar to the Method 5 train except the filter position is interchangeable. The sampling train consists of the following components:

5.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1, 2.1.3, 2.1.4, 2.1.6, 2.1.8, 2.1.9, and 2.1.10. When moisture condensation is a problem, the filter heating system is used.

5.1.2 Probe Liner. Borosilicate glass or 316 stainless steel. When the filter is located immediately after the probe, the tester may use a probe heating system to prevent filter plugging resulting from moisture condensation, but the tester shall not allow the temperature in the probe to exceed 120± 14°C (248± 25°F).

5.1.3 Filter Holder. With positive seal against leakage from the outside or around the filter. If the filter is located between the probe and first impinger, use borosilicate glass or stainless steel with a 20-mesh stainless steel screen filter support and a silicone rubber gasket; do not use a glass frit or a sintered metal filter support. If the filter is located between the third and fourth impingers, the tester may use borosilicate glass with a glass frit filter support and a silicone rubber gasket. The tester may also use other materials of construction with approval from the Administrator.

5.1.4 Impingers. Four impingers connected as shown in Figure 13A-1 with ground-glass (or equivalent), vacumm-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm-inside-diameter (½ in.) glass tube extending to 1.3 cm (½ in.) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. The tester may use modifications (e.g., flexible connections between the impingers or materials other than glass), subject to the approval of the Administrator. Place a thermometer, capable of measuring temperature to within 1°C (2°F), at the outlet of the fourth impinger for monitoring purposes.

5.2 Sample Recovery. The following items are needed:

5.2.1 Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Graduated Cylinder and/or Balance, Plastic Storage Containers, Rubber Policeman, Funnel. Same as Method 5, Sections 2.2.1 to 2.2.2 and 2.2.5 to 2.2.8, respectively.

5.2.2 Sample Storage Container. Wide-mouth, high-density-polyethylene bottles for impinger water samples, 1-liter.

5.3 Analysis. The following equipment is needed:

5.3.1 Distillation Apparatus. Glass distillation apparatus assembled as shown in Figure 13A-2.

5.3.2 Bunsen Burner.

5.3.3 Electric Muffle Furnace. Capable of heating to 600°C.

5.3.4 Crucibles. Nickel, 75- to 100-ml.

5.3.5 Beakers. 500-ml and 1500-ml.

5.3.6 Volumetric Flasks. 50-ml.

5.3.7 Erlenmeyer Flasks or Plastic Bottles. 500-ml.

5.3.8 Constant Temperature Bath. Capable of maintaining a constant temperature of ±1.0°C at room temperature conditions.

5.3.9 Balance. 300-g capacity to measure to ±0.5 g.

5.3.10 Spectrophotometer. Instrument that measures absorbance at 570 nm and provides at least a 1-cm light path.

5.3.11 Spectrophotometer Cells. 1-cm pathlength.

6. *Reagents*

6.1 Sampling. Use ACS reagent-grade chemicals or equivalent, unless otherwise specified. The reagents used in sampling are as follows:

6.1.1 Filters.

6.1.1.1 If the filter is located between the third and fourth impingers, use a Whatman No. 1 filter, or equivalent, sized to fit the filter holder.

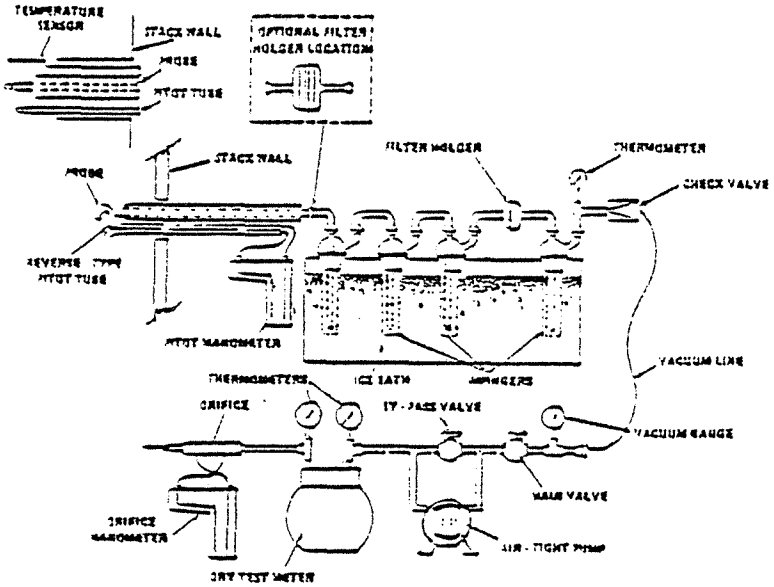


Figure 13A-1. Fluoride sampling train.

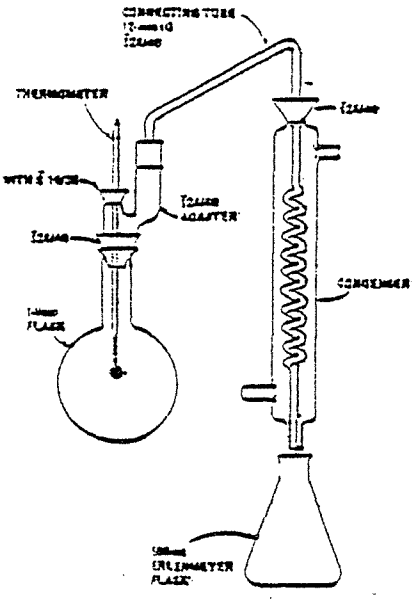


Figure 13A-2. Fluoride distillation apparatus.

8.1.1.2 If the filter is located between the probe and first impinger, use any suitable medium (e.g., paper organic membrane) that conforms to the following specifications: (1) The filter can withstand prolonged exposure to temperatures up to 135°C (275°F). (2) The filter has at least 95 percent collection efficiency (<5 percent penetration) for 0.3 μm dioctyl phthalate smoke particles. Conduct the filter efficiency test before the test series, using ASTM Standard Method D 2986-71, or use test data from the supplier's quality control program. (3) The filter has a low F blank value (<0.015 mg F/cm² of filter area). Before the test series, determine the average F blank value of at least three filters (from the lot to be used for sampling) using the applicable procedures described in Sections 7.3 and 7.4 of this method. In general, glass fiber filters have high and/or variable F blank values, and will not be acceptable for use.

8.1.2 Water. Deionized distilled, to conform to ASTM Specification D 1193-74, Type 3. If high concentrations of organic matter are not expected to be present, the analyst may delete the potassium permanganate test for oxidizable organic matter.

8.1.3 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Section 3.1.2, 3.1.4, and 3.1.5, respectively.

8.2 Sample Recovery. Water, from same container as described in Section 8.1.2, is needed for sample recovery.

8.3 Sample Preparation and Analysis. The reagents needed for sample preparation and analysis are as follows:

8.3.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F or less.

8.3.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml of deionized distilled water.

8.3.3 Silver Sulfate (Ag_2SO_4).

8.3.4 Sodium Hydroxide (NaOH). Pellets.

8.3.5 Sulfuric Acid (H_2SO_4). Concentrated.

8.3.6 Sulfuric Acid, 25 percent (V/V). Mix 1 part of concentrated H_2SO_4 with 3 parts of deionized distilled water.

8.3.7 Filters. Whatman No. 541, or equivalent.

8.3.8 Hydrochloric Acid (HCl). Concentrated.

8.3.9 Water. From same container as described in Section 8.1.2.

8.3.10 Fluoride Standard Solution, 0.01 mg F/ml. Dry in an oven at 110°C for at least 2 hours. Dissolve 0.2210 g of NaF in 1 liter of deionized distilled water. Dilute 100 ml of this solution to 1 liter with deionized distilled water.

8.3.11 SPADNS Solution (4, 5 dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene-disulfonic acid trisodium salt). Dissolve 0.960 ± 0.010 g of SPADNS reagent in 500 ml deionized distilled water. If stored in a well-sealed bottle protected from the sunlight, this solution is stable for at least 1 month.

8.3.12 Spectrophotometer Zero Reference Solution. Prepare daily. Add 10 ml of SPADNS solution (8.3.11) to 100 ml deionized distilled water, and acidify with a solution prepared by diluting 7 ml of concentrated HCl to 10 ml with deionized distilled water.

8.3.13 SPADNS Mixed Reagent. Dissolve 0.135 ± 0.005 g of zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in 25 ml of deionized distilled water. Add 350 ml of concentrated HCl, and dilute to 500 ml with deionized distilled water. Mix equal volumes of this solution and SPADNS solution to form a single reagent. This reagent is stable for at least 2 months.

7. Procedure

7.1 Sampling. Because of the complexity of this method, testers should be trained and experienced with the test procedures to assure reliable results.

7.1.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 4.1.1, except the filter need not be weighed.

7.1.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 4.1.2, except the nozzle size selected must maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

7.1.3 Preparation of Collection Train. Follow the general procedure given in Method 5, Section 4.1.3, except for the following variations:

Place 100 ml of deionized distilled water in each of the first two impingers, and leave the third impinger empty. Transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger.

Assemble the train as shown in Figure 13A-1 with the filter between the third and fourth impingers. Alternatively, if a 20-mesh stainless steel screen is used for the filter support, the tester may place the filter between the probe and first impinger. The tester may also use a filter heating system to prevent moisture condensation, but shall not allow the temperature around the filter holder to exceed 120 ± 14°C (248 ± 25°F). Record the filter location on the data sheet.

7.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Sections 4.1.4.1 (Pretest Leak-Check), 4.1.4.2 (Leak-Checks During the Sample Run), and 4.1.4.3 (Post-Test Leak-Check).

7.1.5 Fluoride Train Operation. Follow the general procedure given in Method 5, Section 4.1.5, keeping the filter and probe temperatures (if applicable) at 120 ± 14°C (248 ± 25°F) and isokinetic sampling rates below 28 liters/min (1.0 cfm). For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-2.

7.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to keep from losing part of the sample. Do not cap off the probe tip tightly while the sampling train is cooling down, because a vacuum would form in the filter holder, thus drawing impinger water backward.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate, if present. Remove the filter assembly, wipe off the silicone grease from the filter holder inlet, and cap this inlet. Remove the umbilical cord from the last impinger, and cap the impinger. After wiping off the silicone grease, cap off the filter holder outlet and any open impinger inlets and outlets. The tester may use ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and filter-impinger assembly to an area that is clean and protected from the wind so that the chances of contaminating or losing the sample is minimized.

Inspect the train before and during disassembly, and note any abnormal conditions. Treat the samples as follows:

7.2.1 *Container No. 1* (Probe, Filter, and Impinger Catches). Using a graduated cylinder, measure to the nearest ml, and record the volume of the water in the first three impingers; include any condensate in the probe in this determination. Transfer the impinger water from the graduated cylinder into this polyethylene container. Add the filter to this container. (The filter may be handled separately using procedures subject to the Administrator's approval.) Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all sample-exposed surfaces (including the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors, and filter holder) with deionized distilled water. Use less than 500 ml for the entire wash. Add the washings to the sample container. Perform the deionized distilled water rinses as follows:

Carefully remove the probe nozzle and rinse the inside surface with deionized distilled water from a wash bottle. Brush with a Nylon bristle brush, and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with deionized distilled water in a similar way.

Rinse the probe liner with deionized distilled water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, and squirt deionized distilled water into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with deionized distilled water, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Rinse the inside surface of each of the first three impingers (and connecting glassware) three separate times. Use a small portion of deionized distilled water for each rinse, and brush each sample-exposed surface with a Nylon bristle brush, to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush.

After ensuring that all joints have been wiped clean of the silicone grease, brush and rinse with deionized distilled water the inside of the filter holder (front-half only, if filter is positioned between the third and fourth impingers). Brush and rinse each surface three times or more if needed. Make a final rinse of the brush and filter holder.

After all water washings and particulate matter have been collected in the sample container, tighten the lid so that water will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container clearly to identify its contents.

7.2.2 *Container No. 2* (Sample Blank). Prepare a blank by placing an unused filter in a polyethylene container and adding a volume of water equal to the total volume in Container No. 1. Process the blank in the same manner as for Container No. 1.

7.2.3 *Container No. 3* (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow the analytical procedure for Container No. 3 in Section 7.4.2.

7.3 Sample Preparation and Distillation. (Note the liquid levels in Containers No. 1 and No. 2 and confirm on the analysis sheet whether or not leakage occurred during transport. If noticeable leakage had occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.) Treat the contents of each sample container as described below:

7.3.1 *Container No. 1* (Probe, Filter, and Impinger Catches). Filter this container's contents, including the sampling filter, through Whatman No. 541 filter paper, or equivalent, into a 1500-ml beaker.

7.3.1.1 If the filtrate volume exceeds 900 ml, make the filtrate basic (red to phenolphthalein) with NaOH, and evaporate to less than 900 ml.

7.3.1.2 Place the filtered material (including sampling filter) in a nickel crucible, add a few ml of deionized distilled water, and macerate the filters with a glass rod.

Add 100 mg CaO to the crucible, and mix the contents thoroughly to form a slurry. Add two drops of phenolphthalein indicator. Place the crucible in a hood under infrared lamps or on a hot plate at low heat. Evaporate the water completely. During the evaporation of the water, keep the slurry basic (red to phenolphthalein) to avoid loss of F. If the indicator turns colorless (acidic) during the evaporation, add CaO until the color turns red again.

After evaporation of the water, place the crucible on a hot plate under a hood and slowly increase the temperature until the Whatman No. 541 and sampling filters char. It may take several hours to completely char the filters.

Place the crucible in a cold muffle furnace. Gradually (to prevent smoking) increase the temperature to 600°C, and maintain until the contents are reduced to an ash. Remove the crucible from the furnace and allow to cool.

Add approximately 4 g of crushed NaOH to the crucible and mix. Return the crucible to the muffle furnace, and fuse the sample for 10 minutes at 500°C.

Remove the sample from the furnace, and cool to ambient temperature. Using several rinsings of warm deionized distilled water, transfer the contents of the crucible to the beaker containing the filtrate. To assure complete sample removal, rinse finally with two 20-ml portions of 25 percent H_2SO_4, and carefully add to the beaker. Mix well, and transfer to a 1-liter volumetric flask. Dilute to volume with deionized distilled water, and mix thoroughly. Allow any undissolved solids to settle.

7.3.2 *Container No. 2* (Sample Blank). Treat in the same manner as described in Section 7.3.1 above.

7.3.3 Adjustment of Acid/Water Ratio in Distillation Flask. (Use a protective shield when carrying out this procedure.) Place 400 ml of deionized distilled water in the distillation flask, and add 200 ml of concentrated H_2SO_4. (Caution: Observe standard precautions when mixing H_2SO_4 with water. Slowly add the acid to the flask with constant swirling.) Add some soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus as shown in Figure 13A-2. Heat the flask until it reaches a temperature of 175°C to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

7.3.4 Distillation. Cool the contents of the distillation flask to below 80°C. Pipet an aliquot of sample containing less than 10.0 mg F directly into the distillation flask, and add deionized distilled water to make a total volume of 220 ml added to the distillation flask. (To estimate the appropriate aliquot size, select an aliquot of the solution and treat as described in Section 7.4.1. This will be an approximation of the F content because of possible interfering ions.) Note: If the sample contains chloride, add 5 mg of Ag_2SO_4 to the flask for every mg of chloride.

Place a 250-ml volumetric flask at the condenser exit. Heat the flask as rapidly as possible with a Bunsen burner, and collect all the distillate up to 175°C. During heatup, play the burner flame up and down the side of the flask to prevent bumping. Conduct the distillation as rapidly as possible (15 minutes or less). Slow distillations have been found to produce low F recoveries. Caution: Be careful not to exceed 175°C to avoid causing H_2SO_4 to distill over.

If F distillation in the mg range is to be followed by a distillation in the fractional mg range, add 220 ml of deionized distilled water and distill it over as in the acid adjustment step to remove residual F from the distillation system.

The tester may use the acid in the distillation flask until there is carry-over of interferences or poor F recovery. Check for these every tenth distillation using a deionized distilled water blank and a standard solution. Change the acid whenever the F recovery is less than 90 percent or the blank value exceeds 0.1 µg/ml.

7.4 Analysis.

7.4.1 Containers No. 1 and No. 2. After distilling suitable aliquots from Containers No. 1 and No. 2 according to Section 7.3.4, dilute the distillate in the volumetric flasks to exactly 250 ml with deionized distilled water, and mix thoroughly. Pipet a suitable aliquot of each sample distillate (containing 10 to 40 µg F/ml) into a beaker, and dilute to 50 ml with deionized distilled water. Use the same aliquot size for the blank. Add 10 ml of SPADNS mixed reagent (8.3.13), and mix thoroughly.

After mixing, place the sample in a constant-temperature bath containing the standard solutions (see Section 8.2) for 30 minutes before reading the absorbance on the spectrophotometer.

Set the spectrophotometer to zero absorbance at 570 nm with the reference solution (8.3.12), and check the spectrophotometer calibration with the standard solution. Determine the absorbance of the samples, and determine the concentration from the calibration curve. If the concentration does not fall within the range of the calibration curve, repeat the procedure using a different size aliquot.

7.4.2 *Container No. 3* (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. The tester may conduct this step in the field.

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train. Calibrate the sampling train components according to the indicated sections in Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe heater (Section 5.4); Temperature Gauges (Section 5.5); Leak Check of Metering System (Section 5.6); and Barometer (Section 5.7).

8.2 Spectrophotometer. Prepare the blank standard by adding 10 ml of SPADNS mixed reagent to 50 ml of deionized distilled water. Accurately prepare a series of standards from the 0.01 mg F/ml standard fluoride solution (8.3.10) by diluting 0, 2, 4, 6, 8, 10, 12, and 14 ml to 100 ml with deionized distilled water. Pipet 50 ml from each solution and transfer each to a separate 100-ml beaker. Then add 10 ml of SPADNS mixed reagent to each. These standards will contain 0, 10, 20, 30, 40 50, 60, and 70 µg F (0 to 1.4 µg/ml), respectively.

After mixing, place the reference standards and reference solution in a constant temperature bath for 30 minutes before reading the absorbance with the spectrophotometer. Adjust all samples to this same temperature before analyzing.

With the spectrophotometer at 570 nm, use the reference solution (6.3.12) to set the absorbance to zero.

Determine the absorbance of the standards. Prepare a calibration curve by plotting µg F/50 ml versus absorbance on linear graph paper. Prepare the standard curve initially and thereafter whenever the SPADNS mixed reagent is newly made. Also, run a calibration standard with each set of samples and if it differs from the calibration curve by ±2 percent, prepare a new standard curve.

9. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation. Other forms of the equations may be used, provided that they yield equivalent results.

9.1 Nomenclature.

A_d = Aliquot of distillate taken for color development, ml.

A_t = Aliquot of total sample added to still, ml.

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_s = Concentration of F in stack gas, mg/m³, dry basis, corrected to standard conditions of 760 mm Hg (29.92 in. Hg) and 293°K (528°R).

F_t = Total F in sample, mg.

µg F = Concentration from the calibration curve, µg.

T_m = Absolute average dry gas meter temperature (see Figure 5-2 of Method 5), °K (°R).

T_s = Absolute average stack gas temperature (see Figure 5-2 of Method 5), °K (°R).

V_d = Volume of distillate collected, ml.

$V_{m(std)}$ = Volume of gas sample as measured by dry gas meter, corrected to standard conditions, dscm (dscf).

V_t = Total volume of F sample, after final dilution, ml.

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

9.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5-2 of Method 5).

9.3 Dry Gas Volume. Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in section 6.3 of Method 5.

9.4 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor $V_{w(std)}$ and moisture content B_{ws} from the data obtained in this method (Figure 13A-1); use Equations 5-2 and 5-3 of Method 5.

9.5 Concentration.

9.5.1 Total Fluoride in Sample. Calculate the amount of F in the sample using the following equation:

$$F_t = 10^{-3} \frac{V_t}{A_t} \frac{V_d}{A_d} (\mu g\ F) \qquad \text{Eq. 13A-1}$$

9.5.2 Fluoride Concentration in Stack Gas. Determine the F concentration in the stack gas using the following equation:

$$C_s = K \frac{F_t}{V_{m(std)}} \qquad \text{Eq. 13A-2}$$

Where:

K = 35.31 ft³/m³ if $V_{m(std)}$ is expressed in English units.

= 1.00 m³/m³ if $V_{m(std)}$ is expressed in metric units.

9.6 Isokinetic Variation and Acceptable Results. Use Method 5, Sections 6.11 and 6.12.

10. Bibliography

1. Beilack, Ervin. Simplified Fluoride Distillation Method. Journal of the American Water Works Association. *50*:5306. 1958.

2. Mitchell, W. J., J. C. Suggs, and F. J. Bergman. Collaborative Study of EPA Method 13A and Method 13B. Publication No. EPA-600/4-77-050. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1977.

3. Mitchell, W. J. and M. R. Midgett. Adequacy of Sampling Trains and Analytical Procedures Used for Fluoride. Atm. Environ. *10*:865-872. 1976.

Method 13B: Determination of Total Fluoride Emissions From Stationary Sources: Specific Ion Electrode Method

[Method 13B revised by 45 FR 41852, June 20, 1980]

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of fluoride (F) emissions from stationary sources as specified in the regulations. It does not measure fluorocarbons, such as freons.

1.2 Principle. Gaseous and particulate F are withdrawn isokinetically from the source and collected in water and on a filter. The total F is then determined by the specific ion electrode method.

2. Range and Sensitivity

The range of this method is 0.02 to 2,000 μg F/ml; however, measurements of less than 0.1 μg F/ml require extra care. Sensitivity has not been determined.

3. Interferences

Grease on sample-exposed surfaces may cause low F results because of adsorption.

4. Precision and Accuracy

4.1 Precision. The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F/m³. The within-laboratory and between-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F/m³ with 60 degrees of freedom and 0.056 mg F/m³ with five degrees of freedom, respectively.

4.2 Accuracy. The collaborative test did not find any bias in the analytical method.

5. Apparatus

5.1 Sampling Train and Sample Recovery. Same as Method 13A, Sections 5.1 and 5.2, respectively.

5.2 Analysis. The following items are needed:

5.2.1 Distillation Apparatus, Bunsen Burner, Electric Muffle Furnace, Crucibles, Beakers, Volumetric Flasks, Erlenmeyer Flasks or Plastic Bottles, Constant Temperature Bath, and Balance. Same as Method 13A, Sections 5.3.1 to 5.3.9, respectively, except include also 100-ml polyethylene beakers.

5.2.2 Fluoride Ion Activity Sensing Electrode.

5.2.3 Reference Electrode. Single junction, sleeve type.

5.2.4 Electrometer. A pH meter with millivolt-scale capable of ±0.1-mv resolution, or a specific ion meter made specifically for specific ion use.

5.2.5 Magnetic Stirrer and TFE[1] Fluorocarbon-Coated Stirring Bars.

6. Reagents

6.1 Sampling and Sample Recovery. Same as Method 13A, Sections 6.1 and 6.2, respectively.

6.2 Analysis. Use ACS reagent grade chemicals (or equivalent), unless otherwise specified. The reagents needed for analysis are as follows:

6.2.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F or less.

6.2.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml deionized distilled water.

6.2.3 Sodium Hydroxide (NaOH). Pellets.

6.2.4 Sulfuric Acid (H_2SO_4). Concentrated.

6.2.5 Filters. Whatman No. 541, or equivalent.

6.2.6 Water. From same container as 6.1.2 of Method 13A.

6.2.7 Sodium Hydroxide, 5 M. Dissolve 20 g of NaOH in 100 ml of deionized distilled water.

6.2.8 Sulfuric Acid, 25 percent (V/V). Mix 1 part of concentrated H_2SO_4 with 3 parts of deionized distilled water.

[1] Mention of any trade name or specific product does not constitute endorsement by the Environmental Protection Agency.

6.2.9 Total Ionic Strength Adjustment Buffer (TISAB). Place approximately 500 ml of deionized distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of cyclohexylene dinitrilo tetraacetic acid. Stir to dissolve. Place the beaker in a water bath to cool it. Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Cool to room temperature. Pour into a 1-liter volumetric flask, and dilute to volume with deionized distilled water. Commercially prepared TISAB may be substituted for the above.

6.2.10 Fluoride Standard Solution, 0.1 M. Oven dry some sodium fluoride (NaF) for a minimum of 2 hours at 110°C, and store in a desiccator. Then add 4.2 g of NaF to a 1-liter volumetric flask, and add enough deionized distilled water to dissolve. Dilute to volume with deionized distilled water.

7. Procedure

7.1 Sampling, Sample Recovery, and Sample Preparation and Distillation. Same as Method 13A, Sections 7.1, 7.2, and 7.3, respectively, except the notes concerning chloride and sulfate interferences are not applicable.

7.2 Analysis.

7.2.1 Containers No. 1 and No. 2. Distill suitable aliquots from Containers No. 1 and No. 2. Dilute the distillate in the volumetric flasks to exactly 250 ml with deionized distilled water and mix thoroughly. Pipet a 25-ml aliquot from each of the distillate and separate beakers. Add an equal volume of TISAB, and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than ±2°C from the temperature at which the calibration standards were measured, condition samples and standards in a constant-temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution temperature, place a piece of temperature insulating material such as cork between the stirrer and the beaker. Hold dilute samples (below 10^{-5} M fluoride ion content) in polyethylene beakers during measurement.

Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with distilled water.

7.2.2 Container No. 3 (Silica Gel). Same as Method 13A, Section 7.4.2.

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train. Same as Method 13A.

8.2 Fluoride Electrode. Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M fluoride standard solution into a 100-ml volumetric flask, and make up to the mark with deionized distilled water for a 10^{-1} M standard solution. Use 10 ml of 10^{-1} M solution to make a 10^{-2} M solution in the same manner. Repeat the dilution procedure and make 10^{-4} and 10^{-5} solutions.

Pipet 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, e.g., when 50 ml of 10^{-2} M standard is diluted with 50 ml of TISAB, the concentration is still designated "10^{-2} M."

Between measurements soak the fluoride sensing electrode in deionized distilled water for 30 seconds, and then remove and blot dry. Analyze the standards going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4} fluoride molarity on the log axis plotted versus electrode potential (in mv) on the linear scale. Some electrodes may be slightly nonlinear between 10^{-3} and 10^{-4} M. If this occurs, use additional standards between these two concentrations.

Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10^{-4} M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers. (Note: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.)

9. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

9.1 Nomenclature. Same as Method 13A, Section 9.1, in addition:

M = F concentration from calibration curve, molarity.

9.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor and Moisture Content, Fluoride Concentration in Stack Gas, and Isokinetic Variation and Acceptable Results. Same as Method 13A, Section 9.2 to 9.4, 9.5.2, and 9.6, respectively.

9.3 Fluoride in Sample. Calculate the amount of F in the sample using the following:

$$F_t = K \frac{T_t}{A_t} (V_d) (M) \qquad \text{Equation 13B-1}$$

Where:

K = 19 mg/ml.

10. References

1. Same as Method 13A, Citations 1 and 2 of Section 10.

2. MacLeod, Kathryn E. and Howard L. Crist. Comparison of the SPADNS—Zirconium Lake and Specific Ion Electrode Methods of Fluoride Determination in Stack Emission Samples. Analytical Chemistry. 45:1272–1273, 1973.

METHOD 14—DETERMINATION OF FLUORIDE EMISSIONS FROM POTROOM ROOF MONITORS FOR PRIMARY ALUMINUM PLANTS

[Method 14 revised by 45 FR 44206, June 30, 1980]

1. *Applicability and Principle.*

1.1 Applicability. This method is applicable for the determination of fluoride emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards.

1.2 Principle. Gaseous and particulate fluoride roof monitor emissions are drawn into a permanent sampling manifold through several large nozzles. The sample is transported from the sampling manifold to ground level through a duct. The gas in the duct is sampled using Method 13A or 13B—Determination of Total Fluoride Emissions from Stationary Sources. Effluent velocity and volumetric flow rate are determined with anemometers located in the roof monitor.

2. *Apparatus.*

2.1 Velocity measurement apparatus.

2.1.1 Anemometers. Propeller anemometers, or equivalent. Each anemometer shall meet the following specifications: (1) Its propeller shall be made of polystyrene, or similar material of uniform density. To insure uniformity of performance among propellers, it is desirable that all propellers be made from the same mold; (2) The propeller shall be properly balanced, to optimize performance; (3) When the anemometer is mounted horizontally, its threshold velocity shall not exceed 15 m/min (50 fpm); (4) The measurement range of the anemometer shall extend to at least 600 m/min (2,000 fpm); (5) The anemometer shall be able to withstand prolonged exposure to dusty and corrosive environments; one way of achieving this is to continuously purge the bearings of the anemometer with filtered air during operation; (6) All anemometer components shall be properly shielded or encased, such that the performance of the anemometer is uninfluenced by potroom

magnetic field effects: (7) A known relationship shall exist between the electrical output signal from the anemometer generator and the propeller shaft rpm at a minimum of three evenly spaced rpm settings between 60 and 1800 rpm: for the 3 settings, use 60±15, 900±100, and 1800±100 rpm. Anemometers having other types of output signals (e.g., optical) may be used, subject to the approval of the Administrator. If other types of anemometers are used, there must be a known relationship (as described above) between output signal and shaft rpm; also, each anemometer must be equipped with a suitable readout system (See Section 2.1.3).

2.1.2 Installation of anemometers.

2.1.2.1 If the affected facility consists of a single, isolated potroom (or potroom segment), install at least one anemometer for every 85 m of roof monitor length. If the length of the roof monitor divided by 85 m is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. For monitors that are less than 130 m in length, use at least two anemometers. Divide the monitor cross-section into as many equal areas as anemometers and locate an anemometer at the centroid of each equal area. See exception in Section 2.1.2.3.

2.1.2.2 If the affected facility consists of two or more potrooms (or potroom segments) ducted to a common control device, install anemometers in each potroom (or segment) that contains a sampling manifold. Install at least one anemometer for every 85 m of roof monitor length of the potroom (or segment). If the potroom (or segment) length divided by 85 is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. If the potroom (or segment) length is less than 130 m, use at least two anemometers. Divide the potroom (or segment) monitor cross-section into as many equal areas as anemometers and locate an anemometer at the centroid of each equal area. See exception in Section 2.1.2.3.

2.1.2.3 At least one anemometer shall be installed in the immediate vicinity (i.e., within 10 m) of the center of the manifold (See Section 2.2.1). For its placement in relation to the width of the monitor, there are two alternatives. The first is to make a velocity traverse of the width of the roof monitor where an anemometer is to be placed and install the anemometer at a point of average velocity along this traverse. The traverse may be made with any suitable low velocity measuring device, and shall be made during normal process operating conditions.

The second alternative, at the option of the tester, is to install the anemometer halfway across the width of the roof monitor. In this latter case, the velocity traverse need not be conducted.

2.1.3 Recorders. Recorders, equipped with suitable auxiliary equipment (e.g. transducers) for converting the output signal from each anemometer to a continuous recording of air flow velocity, or to an integrated measure of volumetric flowrate. A suitable recorder is one that allows the output signal from the propeller anemometer to be read to within 1 percent when the velocity is between 100 and 120 m/min (350 and 400 fpm). For the purpose of recording velocity, "continuous" shall mean one readout per 15-minute or shorter time interval. A constant amount of time shall elapse between readings. Volumetric flow rate may be determined by an electrical count of anemometer revolutions. The recorders or counters shall permit identification of the velocities or flowrate measured by each individual anemometer.

2.1.4 Pitot tube. Standard-type pitot tube, as described in Section 2.7 of Method 2, and having a coefficient of 0.99±0.01.

2.1.5 Pitot tube (optional). Isolated, Type S pitot, as described in Section 2.1 of Method 2. The pitot tube shall have a known coefficient, determined as outlined in Section 4.1 of Method 2.

2.1.6 Differential pressure gauge. Inclined manometer or equivalent, as described in Section 2.1.2 of Method 2.

2.2 Roof monitor air sampling system.

2.2.1 Sampling ductwork. A minimum of one manifold system shall be installed for each potroom group (as defined in Subpart S, Section 60.191). The manifold system and connecting duct shall be permanently installed to draw an air sample from the roof monitor to ground level. A typical installation of a duct for drawing a sample from a roof monitor to ground level is shown in Figure 14-1. A plan of a manifold system that is located in a roof monitor is shown in Figure 14.2. These drawings represent a typical installation for a generalized roof monitor. The dimensions on these figures may be altered slightly to make the manifold system fit into a particular roof monitor, but the general configuration shall be followed. There shall be eight nozzles, each having a diameter of 0.40 to 0.50 m. Unless otherwise specified by the Administrator, the length of the manifold system from the first nozzle to the eighth shall be 35 m or eight percent of the length of the potroom (or potroom segment) roof monitor, whichever is greater. The duct leading from the roof monitor manifold shall be round with a diameter of 0.30 to 0.40 m. As shown in Figure 14-2, each of the sample legs of the manifold shall have a device, such as a blast gate or valve, to enable adjustment of the flow into each sample nozzle.

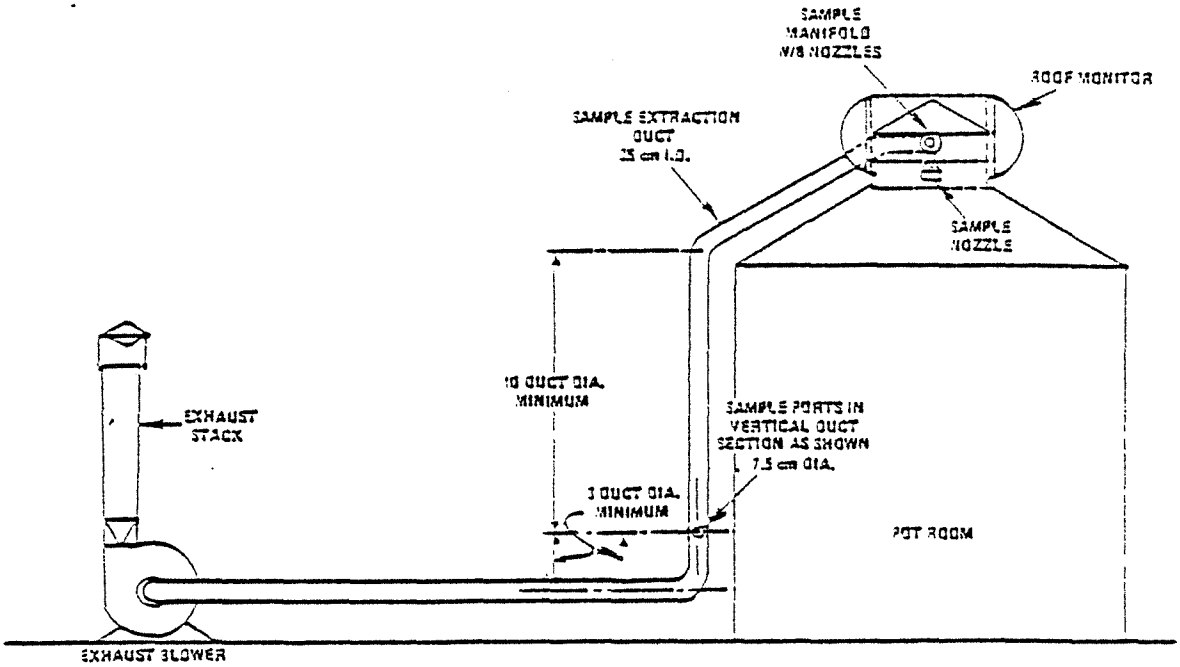


Figure 14-1. Roof monitor sampling system.

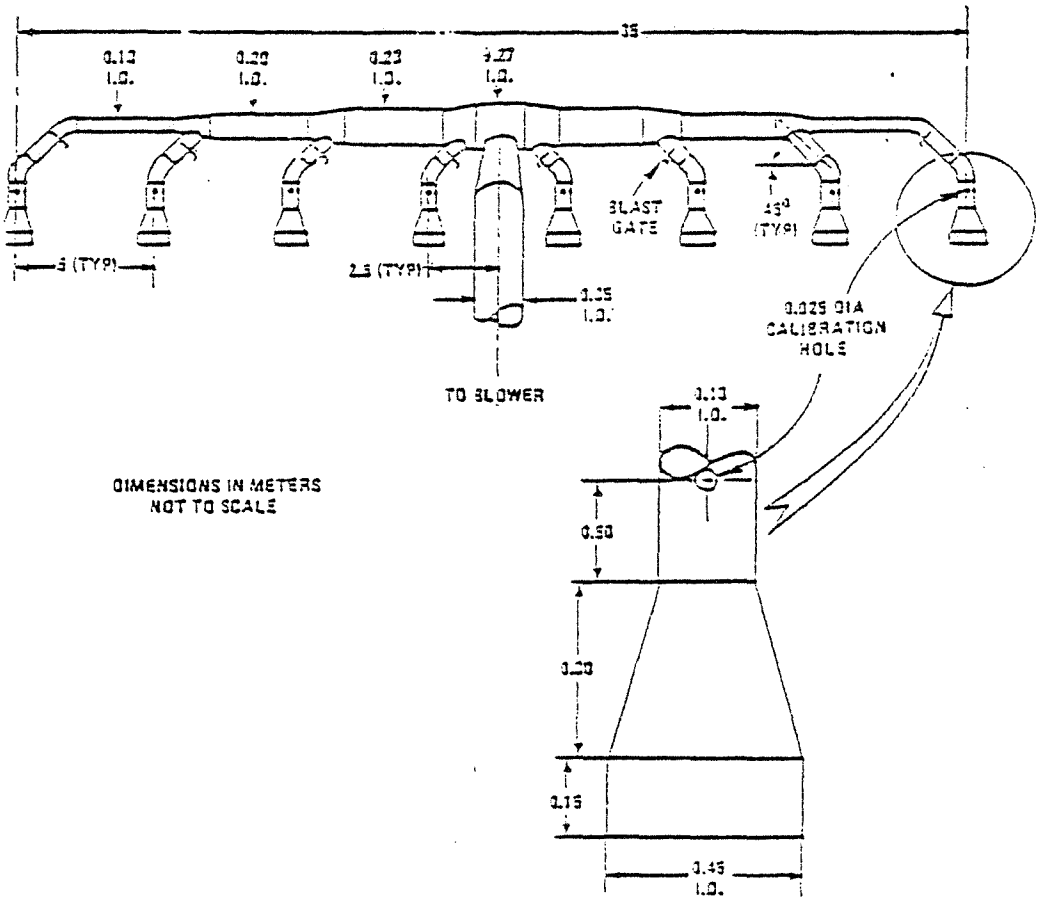


Figure 14-2. Sampling manifold and nozzles.

The manifold shall be located in the immediate vicinity of one of the propeller anemometers (see Section 2.1.2.3) and as close as possible to the midsection of the potroom (or potroom segment). Avoid locating the manifold near the end of a potroom or in a section where the aluminum reduction pot arrangement is not typical of the rest of the potroom (or potroom segment). Center the sample nozzles in the throat of the roof monitor (see Figure 14-1). Construct all sample-exposed surfaces within the nozzles, manifold and sample duct of 316 stainless steel. Aluminum may be used if a new ductwork system is conditioned with fluoride-laden roof monitor air for a period of six weeks prior to initial testing. Other materials of construction may be used if it is demonstrated through comparative testing that there is no loss of flourides in the system. All connections in the ductwork shall be leak free.

Locate two sample ports in a vertical section of the duct between the roof monitor and exhaust fan. The sample ports shall be at least 10 duct diameters downstream and three diameters upstream from any flow disturbance such as a bend or contraction. The two sample ports shall be situated 90° apart. One of the sample ports shall be situated so that the duct can be traversed in the plane of the nearest upstream duct bend.

2.2.2 Exhaust fan. An industrial fan or blower shall be attached to the sample duct at ground level (see Figure 14-1). This exhaust fan shall have a capacity such that a large enough volume of air can be pulled through the ductwork to maintain an isokinetic sampling rate in all the sample nozzles for all flow rates normally encountered in the roof monitor.

The exhaust fan volumetric flow rate shall be adjustable so that the roof monitor air can be drawn isokinetically into the sample nozzles. This control of flow may be achieved by a damper on the inlet to the exhauster or by any other workable method.

2.3 Temperature measurement apparatus.

2.3.1 Thermocouple. Install a thermocouple in the roof monitor near the sample duct. The thermocouple shall conform to the specifications outlined in Section 2.3 of Method 2.

2.3.2 Signal transducer. Transducer to change the thermocouple voltage output to a temperature readout.

2.3.3 Thermocouple wire. To reach from roof monitor to signal transducer and recorder.

2.3.4 Recorder. Suitable recorder to monitor the output from the thermocouple signal transducer.

2.4 Fluoride sampling train. Use the train described in Method 13A or 13B.

3. *Reagents.*

3.1 Sampling and analysis. Use reagents described in Method 13A or 13B.

4. *Calibration.*

4.1 Initial performance checks. Conduct these checks within 60 days prior to the first performance test.

4.1.1 Propeller anemometers. Anemometers which meet the specifications outlined in Section 2.1.1 need not be calibrated, provided that a reference performance curve relating anemometer signal output to air velocity (covering the velocity range of interest) is available from the manufacturer. For the purpose of this

method, a "reference" performance curve is defined as one that has been derived from primary standard calibration data, with the anemometer mounted vertically. "Primary standard" data are obtainable by: (1) Direct calibration of one or more of the anemometers by the National Bureau of Standards (NBS); (2) NBS-traceable calibrations; or (3) Calibration by direct measurement of fundamental parameters such as length and time (e.g., by moving the anemometers through still air at measured rates of speed, and recording the output signals). If a reference performance curve is not available from the manufacturer, such a curve shall be generated, using one of the three methods described as above. Conduct a performance-check as outlined in Section 4.1.1.1 through 4.1.1.3, below. Alternatively, the tester may use any other suitable method, subject to the approval of the Administrator, that takes into account the signal output, propeller condition and threshold velocity of the anemometer.

4.1.1.1 Check the signal output of the anemometer by using an accurate rpm generator (see Figure 14-3) or synchronous motors to spin the propeller shaft at each of the three rpm settings described in Section 2.1.1 above (specification No. 7), and measuring the output signal at each setting. If, at each setting, the output signal is within ± 5 percent of the manufacturer's value, the anemometer can be used. If the anemometer performance is unsatisfactory, the anemometer shall either be replaced or repaired.

4.1.1.2 Check the propeller condition, by visually inspecting the propeller, making note of any significant damage or warpage; damaged or deformed propellers shall be replaced.

4.1.1.3 Check the anemometer threshold velocity as follows: With the anemometer mounted as shown in Figure 14-4(A), fasten a known weight (a straight-pin will suffice) to the anemometer propeller at a fixed distance from the center of the propeller shaft. This will generate a known torque; for example, a 0.1 g weight, placed 10 cm from the center of the shaft, will generate a torque of 1.0 g-cm. If the known torque causes the propeller to rotate downward, approximately 90° (see Figure 14-4(B)), then the known torque is greater than or equal to the starting torque; if the propeller fails to rotate approximately 90°, the known torque is less than the starting torque. By trying different combinations of weight and distance, the starting torque of a particular anemometer can be satisfactorily estimated. Once an estimate of the starting torque has been obtained, the threshold velocity of the anemometer (for horizontal mounting) can be estimated from a graph such as Figure 14-5 (obtained from the manufacturer). If the horizontal threshold velocity is acceptable [<15 m/min (50 fpm), when this technique is used], the anemometer can be used. If the threshold velocity of an anemometer is found to be unacceptably high, the anemometer shall either be replaced or repaired.

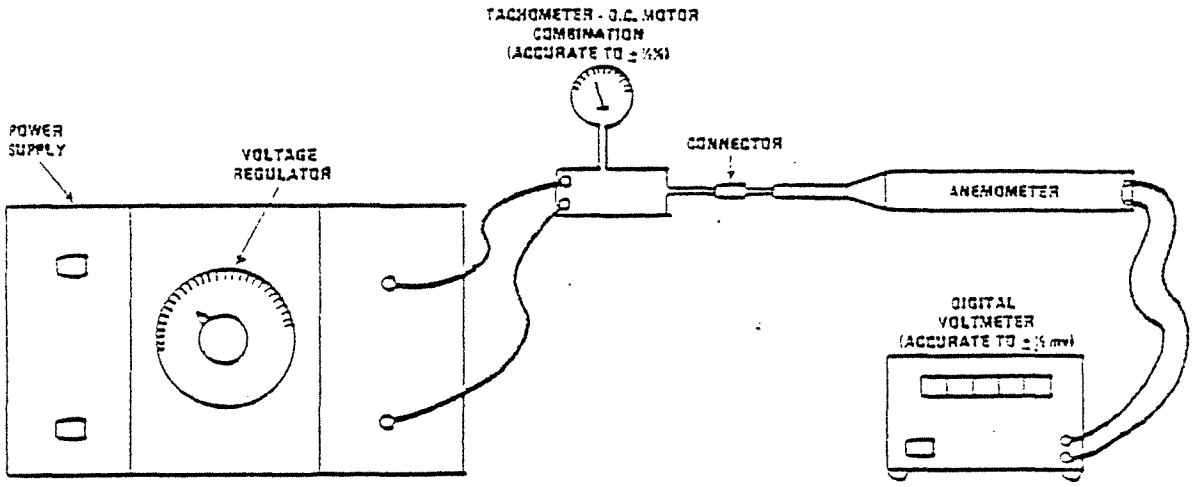


Figure 14-3. Typical RPM generator.

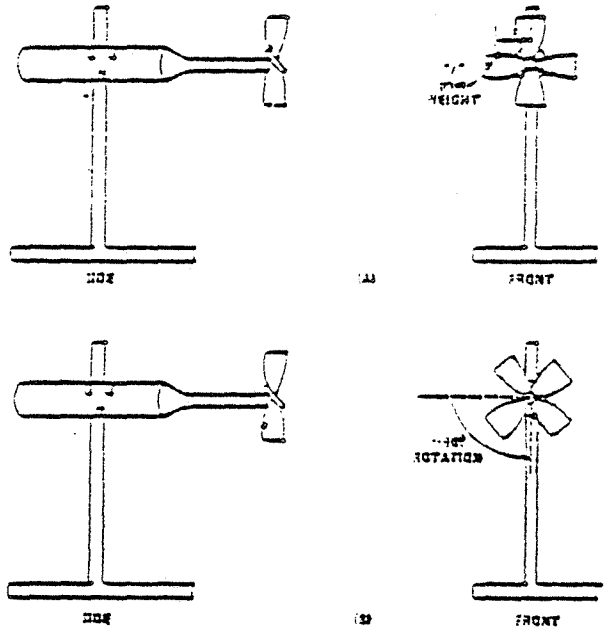


Figure 14-4. Check of anemometer starting torque. A "y" gram weight placed "x" centimeters from center of propeller shaft produces a torque of "xy" g-cm. The minimum torque which produces a 90° (approximately) rotation of the propeller is the "starting torque."

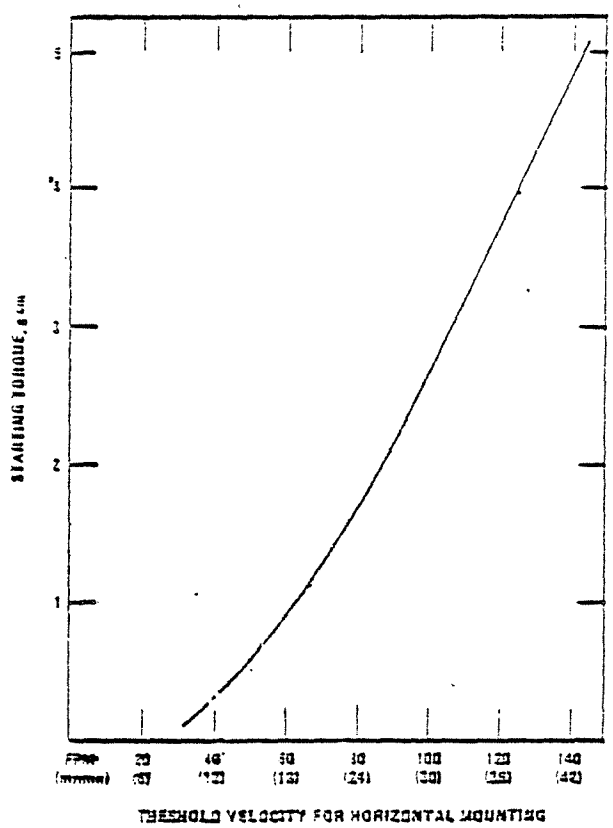


Figure 14-5: Typical curve of starting torque vs horizontal threshold velocity for propeller anemometers. Based on data obtained by R.M. Young Company, May, 1977.

4.1.2 Thermocouple. Check the calibration of the thermocouple-potentiometer system, using the procedures outlined in Section 4.3 of Method 2, at temperatures of 0, 100, and 150°C. If the calibration is off by more than 5°C at any of the temperatures, repair or replace the system; otherwise, the system can be used.

4.1.3 Recorders and/or counters. Check the calibration of each recorder and/or counter (see Section 2.1.3) at a minimum of three points, approximately spanning the expected range of velocities. Use the calibration procedures recommended by the manufacturer, or other suitable procedures (subject to the approval of the Administrator). If a recorder or counter is found to be out of calibration by an average amount greater than 5 percent for the three calibration points, replace or repair the system; otherwise, the system can be used.

4.1.4 Manifold Intake Nozzles. In order to balance the flow rates in the eight individual nozzles, proceed as follows: Adjust the exhaust fan to draw a volumetric flow rate (refer to Equation 14-1) such that the entrance velocity into each manifold nozzle approximates the average effluent velocity in the roof monitor. Measure the velocity of the air entering each nozzle by inserting a standard pitot tube into a 2.5 cm or less diameter hole (see Figure 14-2) located in the manifold between each blast gate (or valve) and nozzle. Note that a standard pitot tube is used, rather than a type S, to eliminate possible velocity measurement errors due to cross-section blockage in the small (0.13 m diameter) manifold leg ducts. The pitot tube tip shall be positioned at the center of each manifold leg duct. Take care to insure that there is no leakage around the pitot tube, which could affect the indicated velocity in the manifold leg. If the velocity of air being drawn into each nozzle is not the same, open or close each blast gate (or valve) until the velocity in each nozzle is the same. Fasten each blast gate (or valve) so that it will remain in this position and close the pitot port holes. This calibration shall be performed when the manifold system is installed. Alternatively, the manifold may be preassembled and the flow rates balanced on the ground, before being installed.

4.2 Periodical performance checks. Twelve months after their initial installation, check the calibration of the propeller anemometers, thermocouple-potentiometer system, and the recorders and/or counters as in Section 4.1. If the above systems pass the performance checks, (i.e., if no repair or replacement of any component is necessary), continue with the performance checks on a 12-month interval basis. However, if any of the above systems fail the performance checks, repair or replace the system(s) that failed and conduct the periodical performance checks on a 3-month interval basis, until sufficient information (consult with the Administrator) is obtained to establish a modified performance check schedule and calculation procedure.

Note.—If any of the above systems fail the initial performance checks, the data for the past year need not be recalculated.

5. *Procedure.*

5.1 Roof Monitor Velocity Determination.

5.1.1 Velocity estimate(s) for setting isokinetic flow. To assist in setting isokinetic flow in the manifold sample nozzles, the anticipated average velocity in the section of the roof monitor containing the sampling manifold shall be estimated prior to each test run. The tester may use any convenient means to make this estimate (e.g., the velocity indicated by the anemometer in the section of the roof monitor containing the sampling manifold may be continuously monitored during the 24-hour period prior to the test run).

If there is question as to whether a single estimate of average velocity is adequate for an entire test run (e.g., if velocities are anticipated to be significantly different during different potroom operations), the tester may opt to divide the test run into two or more "sub-runs," and to use a different estimated average velocity for each sub-run (see Section 5.3.2.2.)

5.1.2 Velocity determination during a test run. During the actual test run, record the velocity or volumetric flowrate readings of each propeller anemometer in the roof monitor. Readings shall be taken for each anemometer every 15 minutes or at shorter equal time intervals (or continuously).

5.2 Temperature recording. Record the temperature of the roof monitor every 2 hours during the test run.

5.3 Sampling.

5.3.1 Preliminary air flow in duct. During 24 hours preceding the test, turn on the exhaust fan and draw roof monitor air through the manifold duct to condition the ductwork. Adjust the fan to draw a volumetric flow through the duct such that the velocity of gas entering the manifold nozzles approximates the average velocity of the air exiting the roof monitor in the vicinity of the sampling manifold.

5.3.2 Manifold isokinetic sample rate adjustment(s).

5.3.2.1 Initial adjustment. Prior to the test run (or first sub-run, if applicable; see Section 5.1.1 and 5.3.2.2), adjust the fan to provide the necessary volumetric flowrate in the sampling duct, so that air enters the manifold sample nozzles at a velocity equal to the appropriate estimated average velocity determined under Section 5.1.1. Equation 14-1 gives the correct stream velocity needed in the duct at the sampling location, in order for sample gas to be drawn isokinetically into the manifold nozzles. Next, verify that the correct stream velocity has been achieved, by performing a pitot tube traverse of the sample duct (using either a standard or type S pitot tube); use the procedure outlined in Method 2.

$$v_s = \frac{3\,(D_n)^2}{(D_s)^2}\,(v_m)\,\frac{1\ \text{min}}{60\ \text{sec}} \qquad \text{(Equation 14-1)}$$

Where:

v_s = Desired velocity in duct at sampling location, m/sec.

D_n = Diameter of a roof monitor manifold nozzle, m.

D_s = Diameter of duct at sampling location, m.

v_m = Average velocity of the air stream in the roof monitor, m/min, as determined under Section 5.1.1.

5.3.2.2 Adjustments during run. If the test run is divided into two or more "sub-runs" (see Section 5.1.1), additional isokinetic rate adjustment(s) may become necessary during the run. Any such adjustment shall be made just before the start of a sub-run, using the procedure outlined in Section 5.3.2.1 above.

Note.—Isokinetic rate adjustments are not permissible during a sub-run.

5.3.3 Sample train operation. Sample the duct using the standard fluoride train and methods described in Methods 13A and 13B. Determine the number and location of the sampling points in accordance with Method 1. A single train shall be used for the entire sampling run. Alternatively, if two or more sub-runs are performed, a separate train may be used for each sub-run; note, however, that if this option is chosen, the area of the sampling nozzle shall be the same (± 2 percent) for each train. If the test run is divided into sub-runs, a complete traverse of the duct shall be performed during each sub-run.

5.3.4 Time per run. Each test run shall last 3 hours or more; if more than one run is to be performed, all runs shall be of approximately the same (± 10 percent) length. If question exists as to the representativeness of an 3-hour test, a longer period should be selected. Conduct each run during a period when all normal operations are performed underneath the sampling manifold. For most recently-constructed plants, 24 hours are required for all potroom operations and events to occur in the area beneath the sampling manifold. During the test period, all pots in the potroom group shall be operated such that emissions are representative of normal operating conditions in the potroom group.

5.3.5 Sample recovery. Use the sample recovery procedure described in Method 13A or 13B.

5.4 Analysis. Use the analysis procedures described in Method 13A or 13B.

6. *Calculations.*

6.1 Isokinetic sampling check.

6.1.1 Calculate the mean velocity (v_m) for the sampling run, as measured by the anemometer in the section of the roof monitor containing the sampling manifold. If two or more sub-runs have been performed, the tester may opt to calculate the mean velocity for each sub-run.

6.1.2 Using Equation 14-1, calculate the expected average velocity (v_s) in the sampling duct, corresponding to each value of v_m obtained under Section 6.1.1.

6.1.3 Calculate the actual average velocity (v_s) in the sampling duct for each run or sub-run, according to Equation 2-9 of Method 2, and using data obtained from Method 13.

6.1.4 Express each value v_s from Section 6.1.3 as a percentage of the corresponding v_s value from Section 6.1.2.

6.1.4.1 If v_s is less than or equal to 120 percent of v_a, the results are acceptable (note that in cases where the above calculations have been performed for each sub-run, the results are acceptable if the average percentage for all sub-runs is less than or equal to 120 percent).

6.1.4.2 If v_s is more than 120 percent of v_a, multiply the reported emission rate by the following factor.

$$1 + \frac{(100\ v_s/v_a) - 120}{200}$$

6.2 Average velocity of roof monitor gases. Calculate the average roof monitor velocity using all the velocity or volumetric flow readings from Section 5.1.2.

6.3 Roof monitor temperature. Calculate the mean value of the temperatures recorded in Section 5.2.

6.4 Concentration of fluorides in roof monitor air (in mg F/m³).

6.4.1 If a single sampling train was used throughout the run, calculate the average fluoride concentration for the roof monitor using Equation 13A-2 of Method 13A.

6.4.2 If two or more sampling trains were used (i.e., one per sub-run), calculate the average fluoride concentration for the run, as follows:

$$C_s = \frac{\sum_{i=1}^{n} (F_c)_i}{\sum_{i=1}^{n} (V_{m(std)})_i} \quad \text{(Equation 14-2)}$$

Where:

C_s = Average fluoride concentration in roof monitor air, mg F/dscm.

F_c = Total fluoride mass collected during a particular sub-run, mg F (from Equation 13A-1 of Method 13A or Equation 13B-1 of Method 13B).

$V_{m(std)}$ = Total volume of sample gas passing through the dry gas meter during a particular sub-run, dscm (see Equation 5-1 of Method 5).

n = Total number of sub-runs.

6.5 Average volumetric flow from the roof monitor of the potroom(s) (or potroom segment(s)) containing the anemometers is given in Equation 14-3.

$$Q_m = \frac{v_m (A)\ (M_d)\ P_m\ (293°K)}{(T_m + 273°)\ (760\ mm\ Hg)} \quad \text{(Equation 14-3)}$$

Where:

Q_m = Average volumetric flow from roof monitor at standard conditions on a dry basis, m³/min.

A = Roof monitor open area, m².

v_m = Average velocity of air in the roof monitor, m/min, from Section 6.2.

P_m = Pressure in the roof monitor equal to barometric pressure for this application, mm Hg.

T_m = Roof monitor temperature, °C, from Section 6.3.

M_d = Mole fraction of dry gas, which is given by:

$$M_d = (1 - B_{wo})$$

Note.—B_{wo} is the proportion by volume of water vapor in the gas stream, from Equation 5-3, Method 5.

7. Bibliography.

1. Shigehara, R. T. A guideline for Evaluating Compliance Test Results (Isokinetic Sampling Rate Criterion). U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, North Carolina, August 1977.

Method 22—Visual Determination of Fugitive Emissions From Material Processing Sources

[Method 22 added by 47 FR 34142, August 6, 1982]

1. *Introduction.*

This method involves the visual determination of fugitive emissions, i.e., emissions not emitted directly from a process stack or duct. Fugitive emissions include emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; and (4) are emitted directly from process equipment.

This method determines the amount of time that any visible emissions occur during the observation period, i.e., the accumulated emission time. This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether a visible emission occurs and does not require the determination of opacity levels, observer certification according to the procedures of Reference Test Method 9 are not required. However, it is necessary that the observer is educated on the general procedures for determining the presence of visible emissions. As a minimum, the observer must be trained and knowledgeable regarding the effects on the visibility of emissions caused by background contrast, ambient lighting, observer position relative to lighting, wind, and the presence of uncombined water (condensing water vapor). This training is to be obtained from written materials found in References 7.1 and 7.2 or from the lecture portion of the Method 9 certification course.

2. *Applicability and Principle.*

2.1 *Applicability.* This method applies to the determination of the frequency of fugitive emissions from stationary sources (located indoors or outdoors) when specified as the test method for determining compliance with new source performance standards.

2.2 *Principle.* Fugitive emissions produced during material processing, handling, and transfer operations are visibly determined by an observer without the aid of instruments.

3. *Definitions.*

3.1 *Emission Frequency.* Percentage of time that emissions are visible during the observation period.

3.2 *Emission Time.* Accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive Emissions.* Pollutant generated by an affected facility which is not collected by a capture system and is released to the atmosphere.

3.4 *Observation Period.* Accumulated time period during which observations are conducted, not to be less than 6 minutes.

4. *Equipment.*

4.1 *Stopwatches.* Accumulative type with unit divisions of at least 0.5 seconds; two required.

4.2 *Light Meter.* Light meter capable of measuring illuminance in the 50- to 200-lux range; required for indoor observations only.

5. *Procedure.*

5.1 *Position.* Survey the affected facility or building or structure housing the process to be observed and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (i.e., outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 15 feet, but not more than 0.25 miles, from the emission source is recommended. For outdoor locations, select a position where the sun is not directly in the observer's eyes.

5.2 *Field Records.*

5.2.1 *Outdoor Location.* Record the following information on the field data sheet (Figure 22-1): company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

5.2.2 *Indoor Location.* Record the following information on the field data sheet (Figure 22-2): company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed and note observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

5.3 *Indoor Lighting Requirements.* For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

5.4 *Observations.* Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation period; start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks, stop the stopwatch when a break begins and restart it without resetting when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of the observation period. When the observation period is completed, record the clock time.

During the observation period, continously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period, i.e., the emission time.

5.4.1 *Observation Period.* Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission regulation in the applicable subpart. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emissions are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

5.4.2 *Observer Rest Breaks.* Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

5.4.3 *Visual Interference.* Occasionally, fugitive emissions from sources other than the affected facility (e.g., road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations are terminated, and the observer clearly notes this fact on the data form.

5.5 *Recording Observations.* Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

6. *Calculations.*

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart. If the actual observation period is less than the required period and multiply this quotient by 100.

7. *References.*

7.1 Missan, Robert and Arnold Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA-340/1-75-007. April 1975.

7.2 Wohlschlegel, P. and D. E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions From Stationary Sources. EPA Publication No. EPA-650/4-74-005-i. November 1975.

Method 24—Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D 1475–60. Standard Method of Test for Density of Paint, Lacquer, and Related Products.

2.2 ASTM D 2369–81. Provisional Method of Test for Volatile Content of Paints.

2.3 ASTM D 3792–79. Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph.

2.4 ASTM Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method.

3. Procedure

3.1 Volatile Matter Content. Use the procedure in ASTM D 2369–81 to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1 = Weight of dish and sample before heating, g.

W_2 = Weight of dish and sample after heating, g.

W_3 = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-1}$$

Record the arithmetic average (W_v).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either "Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph" or "Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method." A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in section 4.3 is met. Record the arithmetic average (W_w).

3.3 Coating Density. Determine the density (D_c, kg/liter) of the surface coating using the procedure in ASTM D 1475–60.

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average (D_c).

3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W_v	1.5 pct W_v	4.7 pct W_v
Water content, W_w	2.8 pct W_w	7.5 pct W_w
Density, D_c	0.001 kg/liter	0.002 kg/liter

4.3 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD–13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate between-laboratory precision value to the measured mean value for that parameter. For W_v and D_c use the lower confidence limits, and for W_w use the upper confidence limit. Because V_s is calculated, there is no adjustment for the parameter.

5. Calculations

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-2}$$

Where:

W_o = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-3}$$

5.2 Weight fraction solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-4}$$

Where: W_s = Weight solids, g/g.

6. Bibliography

6.1 Provisional Method Test for Volatile Content of Paints. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 2369–81.

6.2 Standard Method of Test for Density of Paint, Varnish, Lacquer, and Related Products. In: 1980 Book of ASTM Standards, Part 27, Philadelphia, Pennsylvania. ASTM Designation D 1475–60, 1980.

6.3 Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 3792–79.

6.4 Provisional Method Test Water in Paint or Related Coatings by the Karl Fischer Titration Method. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon[117]

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane will, of course, also be measured. In practice, the FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and *only* the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide (CO_2) which is quantitatively collected in an evacuated vessel; then a portion of the CO_2 is reduced to methane (CH_4) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide (CO), CO_2, and CH_4; the nonmethane organics (NMO) are oxidized to CO_2, reduced to CH_4, and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

2. Apparatus

The sampling system consists of a condensate trap, flow control system, and sample tank (Figure 1). The analytical system consists of two major sub-systems: an oxidation system for the recovery and conditioning of the condensate trap contents and a NMO analyzer. The NMO analyzer is a GC with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. (Figures 2 and 3 are schematics of a typical NMO analyzer.) The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 4 is a schematic of a typical system.) TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

2.1 Sampling. The following equipment is required:

2.1.1 Probe. 12-mm OD (½-in.) stainless steel tubing.

2.1.2 Condensate Trap. Constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.1.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.1.4 Flow Control System. Any system capable of maintaining the sampling rate to within ±10 percent of the selected flow rate (50 to 100 cc/min range).

2.1.5 Vacuum Gauge. Gauge for monitoring the vacuum of the sample tank during leak checks and sampling.

2.1.6 Sample Tank. Stainless steel or aluminum tank with a volume of 4 to 6 liters, equipped with a stainless steel female quick connect for assembly to the sample train and analytical system.

2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.1.8 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2 Analysis. The following equipment is required:

2.2.1 Condensate Recovery and Conditioning Apparatus. An apparatus for recovering and catalytically oxidizing the condensate trap contents is required. Figure 4 is a schematic of such a system. The analyst must demonstrate prior to initial use that the analytical system is capable of proper oxidation and recovery, as specified in section 5.1. The condensate recovery and conditioning apparatus consists of the following major components.

2.2.1.1 Heat Source. A heat source sufficient to heat the condensate trap (including probe) to a temperature where the trap turns a "dull red" color. A system using both a propane torch and an electric muffle-type furnace is recommended.

2.2.1.2 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.1.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.1.3 Water Trap. Any leak-proof moisture trap capable of removing moisture from the gas stream.

2.2.1.4 NDIR Detector. A detector capable of indicating CO_2 concentration in the zero to 1 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.2.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the trap conditioning system at a near constant pressure.

2.2.1.6 Intermediate Collection Vessel. Stainless steel or aluminum collection vessel equipped with a female quick connect. Tanks with nominal volumes in the 1 to 4 liter range are recommended.

2.2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.2.1.8 Gas Purifiers. Gas purification systems sufficient to maintain CO_2 and organic impurities in the carrier gas and auxiliary oxygen at a level of less than 10 ppm (may not be required depending on quality of cylinder gases used).

2.2.2 NMO Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO_2, and CH_4 from nonmethane organic compounds, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the nonmethane organic compounds to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement (section 5.2). The analyzer consists of the following major components:

2.2.2.1 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.1). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.2 Reduction Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.3 Separation Column(s). Gas chromatographic column(s) capable of separating CO, CO_2, and CH_4 from NMO compounds as demonstrated according to the procedures established in this method (section 5.2.5). Addendum I of this method lists a column found to be acceptable.

2.2.2.4 Sample Injection System. A GC sample injection valve fitted with a sample

loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.2.2.5 FID. A FID meeting the following specifications is required.

2.2.2.5.1 Linearity. A linear response (± 5%) over the operating range as demonstrated by the procedures established in section 5.2.2.

2.2.2.5.2 Range. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale for a full scale range of 10 to 50000 ppm CH_4.

2.2.2.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

2.2.3 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.4 Thermometer. Capable of measuring the laboratory temperature within 1°C.

2.2.5 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2.6 Syringe (2). 10 µl and 100 µl liquid injection syringes.

2.2.7 Liquid Sample Injection Unit. 316 SS U-tube fitted with a Teflon injection septum, see Figure 6.

3. Reagents

3.1 Sampling. Crushed dry ice is required during sampling.

3.2 Analysis.

3.2.1 NMO Analyzer. The following gases are needed:

3.2.1.1 Carrier Gas. Zero grade gas containing less than 1 ppm C. Addendum I of this method lists a carrier gas found to be acceptable.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm C.

3.2.1.3 Combustion Gas. Zero grade air or oxygen as required by the detector.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent O_2 in N_2, containing less than 1 ppm C.

3.2.2.2 Auxiliary Oxygen. Zero grade oxygen containing less than 1 ppm C.

3.2.2.3 Hexane. ACS grade, for liquid injection.

3.2.2.4 Toluene. ACS grade, for liquid injection.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ± 5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required.

3.3.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

3.3.2 Flame Ionization Detector Linearity and Nonmethane Organic Calibration Gases (3). Gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.3.3 Carbon Dioxide Calibration Gases (3). Gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air. Note: total NMO less than 1 ppm required for 1 percent mixture.

3.3.4 NMO Analyzer System Check Calibration Gases (4).

3.3.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm C_3H_8, prepared in air.

3.3.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

3.3.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

3.3.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

4. Procedure

4.1 Sampling.

4.1.1 Sample Tank Evacuation and Leak Check. Either in the laboratory or in the field, evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer) then leak check the sample tank by isolating the tank from the vacuum pump and allowing the tank to sit for 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

4.1.2 Sample Train Assembly. Just prior to assembly, measure the tank vacuum using a mercury U-tube manometer. Record this vacuum (P_{ai}), the ambient temperature (T_{ai}), and the barometric pressure (P_{bi}) at this time. Assuring that the flow shut-off valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse the condensate trap body in dry ice to within 2.5 or 5 cm of the point where the inlet tube joins the trap body.

4.1.3 Pretest Leak Check. A pretest leak check is required. After the sampling train is assembled, record the tank vacuum as indicated by the vacuum gauge. Wait a minimum period of 10 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, assure that the probe tip is tightly plugged and then open the sample train flow shut-off valve. Allow the sample train to sit for a minimum period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the pretest leak rate (cm/Hg per 10 minutes). At the completion of the leak check period, close the sample flow shut-off valve.

4.1.4 Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single preselected point. If a probe extension which will not be analyzed as part of the condensate trap is being used, assure that at least a 15 cm section of the probe which will be analyzed with the trap is in the stack effluent. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open the flow shut-off valve and adjust (if applicable) the control valve of the flow control system used in the sample train maintain a constant flow rate (±10 percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter setting (if applicable) at 5-minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation and the sampling when this time period is reached or when a constant flow rate can no longer be maintained due to reduced sample tank vacuum. When the sampling is completed, close the flow shut-off valve and record the final sample time and gauge vacuum readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train) and connect another sample tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

4.1.5 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack and plug the probe tip. Open the sample train flow shut-off valve and monitor the sample tank vacuum gauge for a period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (cm Hg per 10 minutes). If the sampling train does not pass the post leak check, invalidate the run or use a procedure acceptable to the Administrator to adjust the data.

4.2 Sample Recovery. After the post test leak check is completed, disconnect the condensate trap at the flow metering system and tightly seal both ends of the condensate trap. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of connecting line to a minimum) and record the final tank vacuum (P_{af}); record the tank temperature (T_{af}) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and the sample tank(s).

4.3 Condensate Recovery and Conditioning. Prepare the condensate recovery and conditioning apparatus by setting the carrier gas flow rate and heating the catalyst to its operating temperature. Prior to initial use of the condensate recovery and conditioning apparatus, a system performance test must be conducted according to the procedures established in section 5.1 of this method. After successful completion of the initial performance test, the system is routinely used for sample conditioning according to the following procedures:

4.3.1 System Blank and Catalyst Efficiency Check. Prior to and immediately

following the conditioning of each set of sample traps, or on a daily basis (whichever occurs first) conduct the carrier gas blank test and catalyst efficiency test as specified in sections 5.1.1 and 5.1.2 of this method. Record the carrier gas initial and final blank values, B_a and B_b, respectively. If the criteria of the tests cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap Carbon Dioxide Purge and Sample Tank Pressurization. The first step in analysis is to purge the condensate trap of any CO_2 which it may contain and to simultaneously pressurize the sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry ice. Assure that the valves isolating the collection vessel connection from the atmospheric vent and the vacuum pump are closed and then attach the sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap: immediately switch the carrier flow from vent to collect. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 8. Monitor the NDIR: when CO_2 is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 300 mm Hg. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure (P_s), barometric pressure (P_{bd}), and ambient temperature (T_s). Remove the sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin. From the step just completed in section 4.3.1.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then switch the carrier so that it flows through the oxidation catalyst. Switch the carrier from vent to collect and open the valve to the collection vessel; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 9. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). Begin heating the condensate trap and probe with a propane torch. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 500°C). During the early part of the trap "burn out," adjust the carrier and auxiliary oxygen flow rates so that an excess of oxygen is being fed to the catalyst system. Gradually increase the flow of carrier gas through the trap. After the NDIR indicates that most of the organic matter has been purged, place the trap in a muffle furnace (500°C). Continue to heat the probe with a torch or some other procedure (e.g., electrical resistance heater). Continue this procedure for at least 5 minutes after the NDIR has returned to baseline. Remove the heat from the trap but continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 300 mm Hg (nominal). When the vessel is pressurized, vent the carrier, measure and record the final intermediate collection vessel pressure (P_f) as well as the barometric pressure (P_{bd}), ambient temperature (T_v), and collection vessel volume (V_v).

4.4 Analysis. Prior to putting the NMO analyzer into routine operation, an initial performance test must be conducted. Start the analyzer and perform all the necessary functions in order to put the analyzer in proper working order, then conduct the performance test according to the procedures established in section 5.2. Once the performance test has been successfully completed and the CO_2 and NMO calibration response factors determined, proceed with sample analysis as follows:

4.4.1 Daily operations and calibration checks. Prior to and immediately following the analysis of each set of samples or on a daily basis (whichever occurs first) conduct a calibration test according to the procedures established in section 5.2. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (section 5.2) before proceeding.

4.4.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values obtained for the condensable organics as CO_2 (C_{cc}).

4.4.3 Analysis of Sample Tank. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the sample tank and record the values obtained for the nonmethane organics (C_{nm}).

5. Calibration and Operational Checks

Maintain a record of performance of each item.

5.1 Initial Performance Check of Condensate Recovery and Conditioning Apparatus.

5.1.1 Carrier Gas and Auxiliary Oxygen Blank. Set equal flow rates for both the carrier gas and auxiliary oxygen. With the trap switching valves in the bypass position and the catalyst in-line, fill an evacuated intermediate collection vessel with carrier gas. Analyze the collection vessel for CO_2; the carrier blank is acceptable if the CO_2 concentration is less than 10 ppm.

5.1.2 Catalyst Efficiency Check. Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the valves isolating the collection system from the atmospheric vent and vacuum pump are closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cylinder (section 3.3.1) to the system's condensate trap connector (probe and, Figure 4). Adjust the system valving so that the standard gas cylinder acts as the carrier gas and adjust the flow rate to the rate normally used during trap sample recovery. Switch off the auxiliary oxygen flow and then switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in a normal manner until the intermediate vessel is filled to a nominal gauge pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions. Analyze the collection vessel for CO_2; the catalyst efficiency is acceptable if the CO_2 concentration is within ±5 percent of the expected value.

5.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 8. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap and set the carrier gas and auxiliary oxygen flow rates to normal operating levels. Attach an evacuated intermediate collection vessel to the system and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see 5.1.3.1 to 5.1.3.4) via the injection septum. Heat the injection unit with a torch while monitoring the oxidation reaction on the NDIR. Continue the purge until the reaction is complete. Measure the final collection vessel pressure and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery using the equation in section 6.4.

The performance test is acceptable if the average percent recovery is 100 ± 10 percent with a relative standard deviation (section 6.7) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 100 µl hexane.
5.1.3.2 10 µl hexane.
5.1.3.3 100 µl toluene.
5.1.3.4 10 µl toluene.

5.2 Initial NMO Analyzer Performance Test.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (section 3.3.1). The oxidation catalyst operation is acceptable if no FID response is noted.

5.2.2 Analyzer Linearity Check and NMO Calibration. Operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 3.3, make triplicate injections of each calibration gas and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within ± 5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate

injections is less than ± 5 percent. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{nmo}).

5.2.3 Reduction Catalyst Efficiency Check and CO_2 Calibration. An exact determination of the reduction catalyst efficiency is not required. Instead, proper catalyst operation is indirectly checked and continuously monitored by establishing a CO_2 response factor and comparing it to the NMO response factor. Operating both the oxidation and reduction catalysts make triplicate injections of each of the CO_2 calibration gases (section 3.2.3). Calculate the average response factor (area/ppm) for each calibration gas, as well as the overall mean of the response factor values. The reduction catalyst operation is acceptable if the average response factor of each calibration gas is within ± 5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ± 5 percent. Additionally, the CO_2 overall mean response factor must be within ± 10 percent of the NMO calibration response factor (RF_{nmo}) calculated in section 5.2.2. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{co_2}).

5.2.4 NMO System Blank. For the high level CO_2 calibration gas (section 3.2.3) record the NMO value measured during the CO_2 calibration conducted in section 5.2.1. This value is the NMO blank value for the analyzer (B_o) and should be less than 10 ppm.

5.2.5 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 3.2.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within ± 12 percent of the expected value.

5.3 NMO Analyzer Daily Calibration.

5.3.1 NMO Blank and CO_2. Inject triplicate samples of the high level CO_2 calibration gas (section 3.2.3) and calculate the average response factor. The system operation is adequate if the calculated response factor is within ± 10 percent of the RF_{co_2} calculated during the initial performance test (section 5.2.2). Use the daily response factor (DRF_{co_2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the collection vessel samples. In addition, record the NMO blank value (B_o); this value should be less than 10 ppm.

5.3.2 NMO Calibration. Inject triplicate samples of the mixed propane calibration cylinder (section 3.2.4.1) and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within ± 10 percent of the RF_{nmo} calculated during the initial performance test (section 5.2.1). Use the daily response factor (DRF_{nmo}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 Sample Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

5.5 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

6. Calculations

Note: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

6.1 Sample Volume. For each test run, calculate the gas volume sampled:

$$V_s = 0.386\ V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right)$$

6.2 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \left[\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right] \left[\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} - B_a \right]$$

6.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = 0.386\ \frac{V_v}{V_s} \frac{P_f}{T_f} \left[\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} - B_t \right]$$

6.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

6.5 Total Gaseous Nonmethane Organics (TGNMO) Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$M_c = 0.498\ C$$

6.6 Percent Recovery. To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system use the following equation:

$$\text{percent recovery} = 1.6\ \frac{M}{L} \frac{V_v}{\rho} \frac{P_f}{T_f} \frac{C_{cm}}{M}$$

6.7 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{X}} \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n - 1}}$$

Where:

B_a = Measured NMO blank value for NMO analyzer, ppm C.

B_b = Measured CO_2 [illegible] CO_2.

C = total gaseous nonmethane organic (TGNMO) concentration of the effluent, ppm C equivalent.

C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.

C_{ma} = Measured concentration (NMO analyzer) for the condensate trap (intermediate collection vessel), ppm CO_2

C_s = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.

C_{sa} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.

L = Volume of liquid injected, microliters.

M = Molecular weight of the liquid injected, g/g-mole.

M_c = total gaseous non-methane organic (TGNMO) mass concentration of the effluent, mg C/dscm.

N = Carbon number of the liquid compound injected ($N = 7$ for toluene, $N = 6$ for hexane).

P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.

P_o = Gas sample tank pressure prior to sampling, mm Hg absolute.

P_i = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg absolute.

P_u = Final gas sample tank pressure after pressurizing, mm Hg absolute.

T_f = Final temperature of intermediate collection vessel, °K.

T_o = Sample tank temperature prior to sampling, °K.

T_i = Sample tank temperature at completion of sampling, °K.

T_u = Sample tank temperature after pressurizing °K.

V = Sample tank volume, cm.

V_v = Intermediate collection vessel volume, cm

V_s = Gas volume sampled, dscm.

n = Number of data points.

q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 . . . q).

r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).

x_i = Individual measurements.

X = Mean value.

ρ = Density of liquid injected, g/cc.

7. Bibliography

7.1 Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75-33.2 (Presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, MA, June 15-20, 1975.) 14 p.

7.2 Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74-190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, CO, June 9-13, 1974.) 25 p.

Method 25

Addendum I. System Components

In test Method 25 several important system components are not specified; instead minimum performance specifications are provided. The method is written in this manner to permit individual preference in choosing components, as well as to encourage development and use of improved components. This addendum is added to the method in order to provide users with some specific information regarding components which have been found satisfactory for use with the method. This listing is given only for the purpose of providing information and does not constitute an endorsement of any product by the Environmental Protection Agency. This list is not meant to imply that other components not listed are not acceptable.

1. Condensate Recovery and Conditioning System Oxidation Catalyst. ⅜" OD × 14" Inconel tubing packed with 8 inches of hopcalite* oxidizing catalyst and operated at 800°C in a tube furnace. Note: At this temperature, this catalyst must be purged with carrier gas at all times to prevent catalyst damage.

2. NMO Analyzer Oxidation Catalyst. ¼" OD × 14" Inconel tubing packed with 8 inches of hopcalite oxidizing catalyst and operated at 800°C in a tube furnace. (See note above.)

3. NMO Analyzer Reduction Catalyst. Reduction Catalyst Module: Byron Instruments, Raleigh, N.C.

4. Gas Chromatographic Separation Column. ⅛ inch OD stainless steel packed with 3 feet of 10 percent methyl silicone, Sp 2100 (or equivalent) on Supelcoport (or equivalent), 80/100 mesh, followed by 1.5 feet Porapak Q (or equivalent) 60/80 mesh. The inlet side is to the silicone. Condition the column for 24 hours at 200°C with 20 cc/min N_2 purge.

During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at −78°C (dry ice bath) to elute CO and CH_4. After the CH_4 peak operate the column at 0°C to elute CO_2. When the CO_2 is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100°C in order to elute all nonmethane organics (exact timings for column operation are determined from the calibration standard).

Note.—The dry ice operating condition may be deleted if separation of CO and CH_4 is unimportant.

Note.—Ethane and ethylene may or may not be measured using this column; whether or not ethane and ethylene are quantified will depend on the CO_2 concentration in the gas sample. When high levels of CO_2 are present, ethane and ethylene will elute under the tail of the CO_2 peak.

5. Carrier Gas. Zero grade nitrogen or helium or zero air.

*MSA registered trademark.

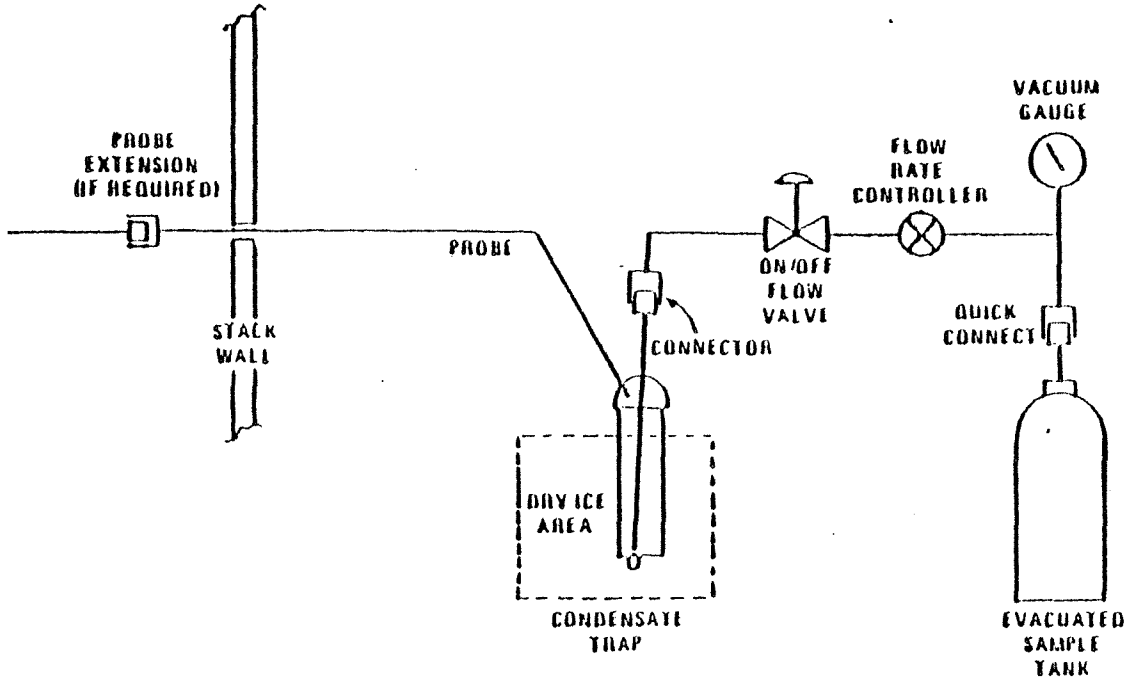


Figure 1. Sampling apparatus

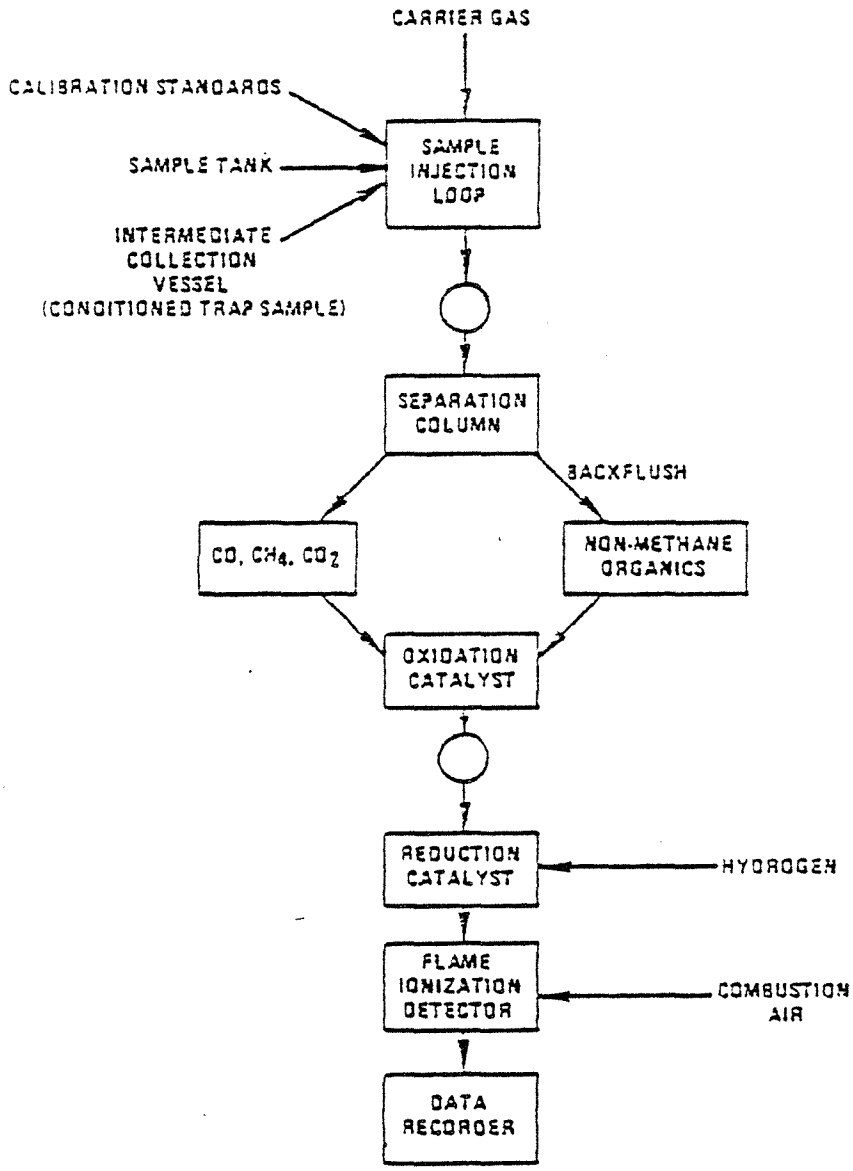


Figure 2. Simplified schematic of non-methane organic (NMO) analyzer.

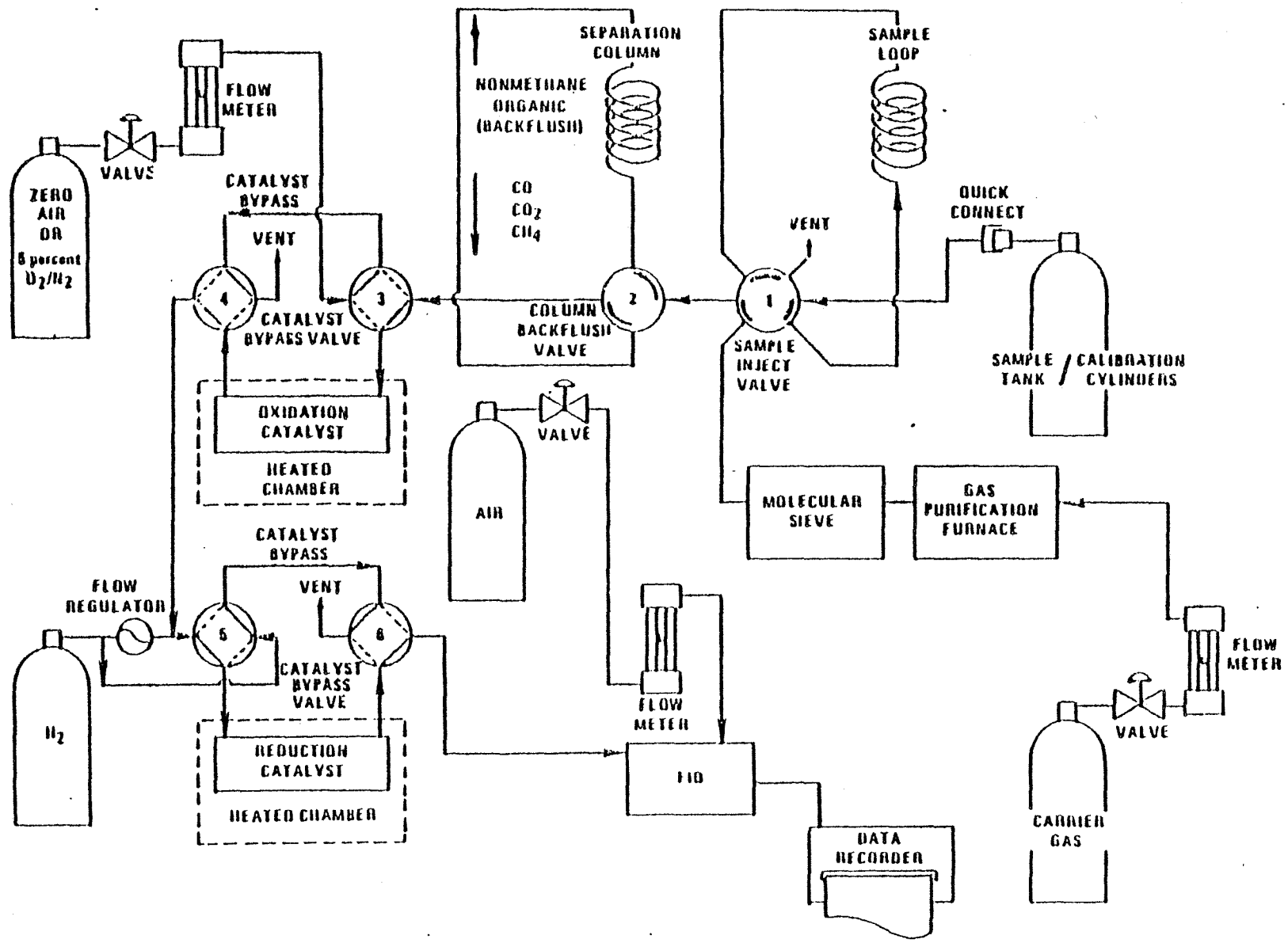


Figure 3. Nonmethane organic (NMO) analyzer.

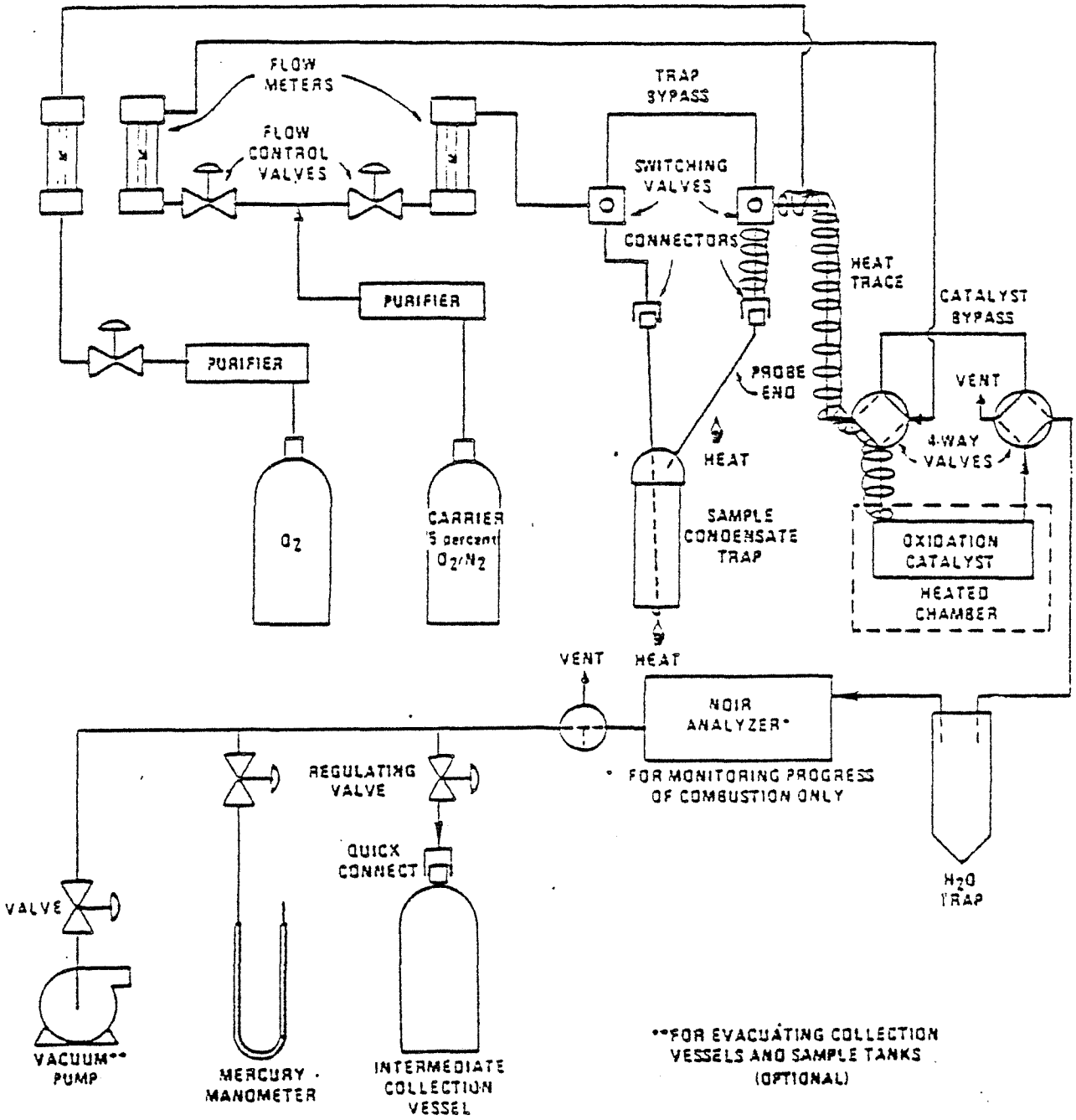


Figure 4. Condensate recovery and conditioning apparatus.

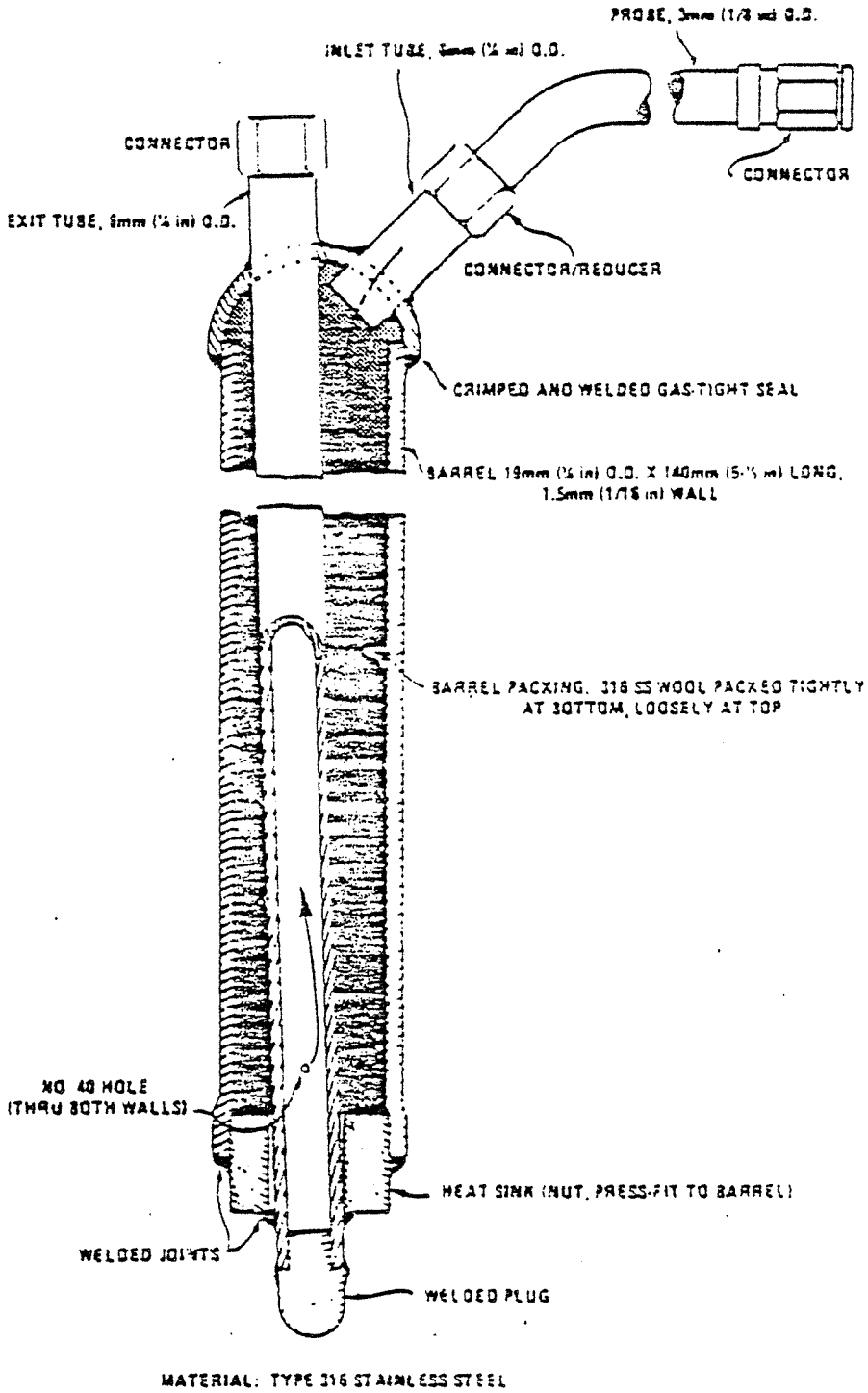


Figure 5 Condensate trap[2]

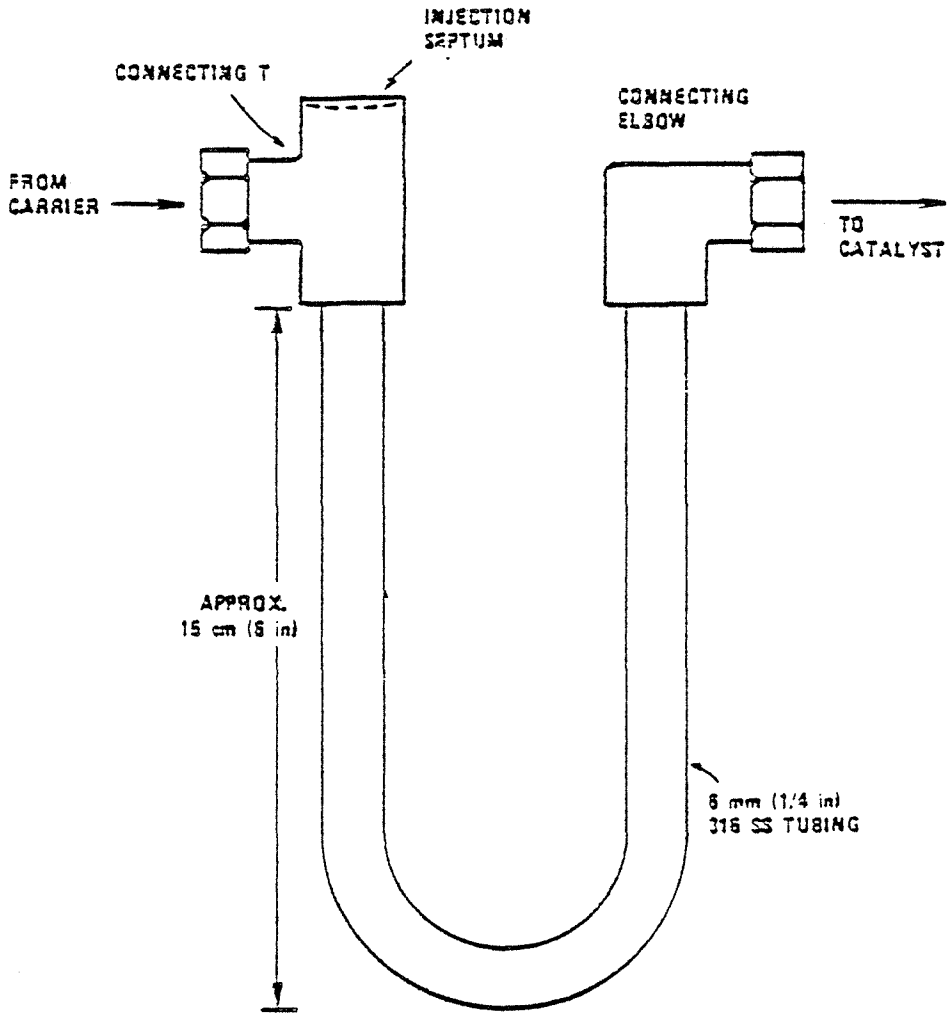


Figure 6. Liquid sample injection unit.

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

	TANK VACUUM, mm Hg	TANK VACUUM, cm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	_____	(GAUGE) _____	_____	_____
POST TEST (MANOMETER)	_____	(GAUGE) _____	_____	_____

LEAK RATE _____ cm Hg / 10 min

PRETEST _____

POST TEST _____

TIME CLOCK/SAMPLE	GAUGE VACUUM, cm Hg	FLOWMETER SETTING	COMMENTS

Figure 7. Example Field Data Form

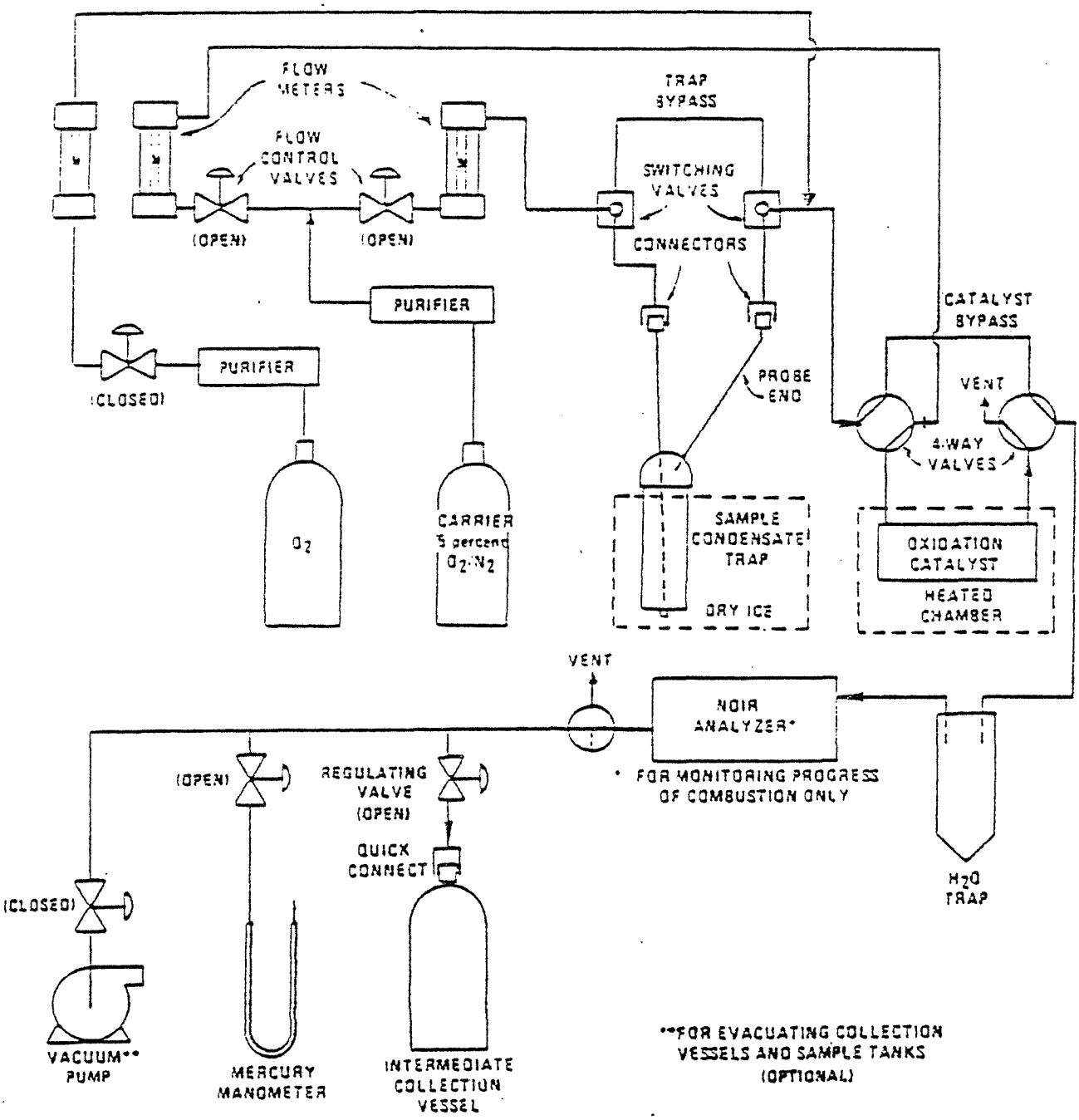


Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.

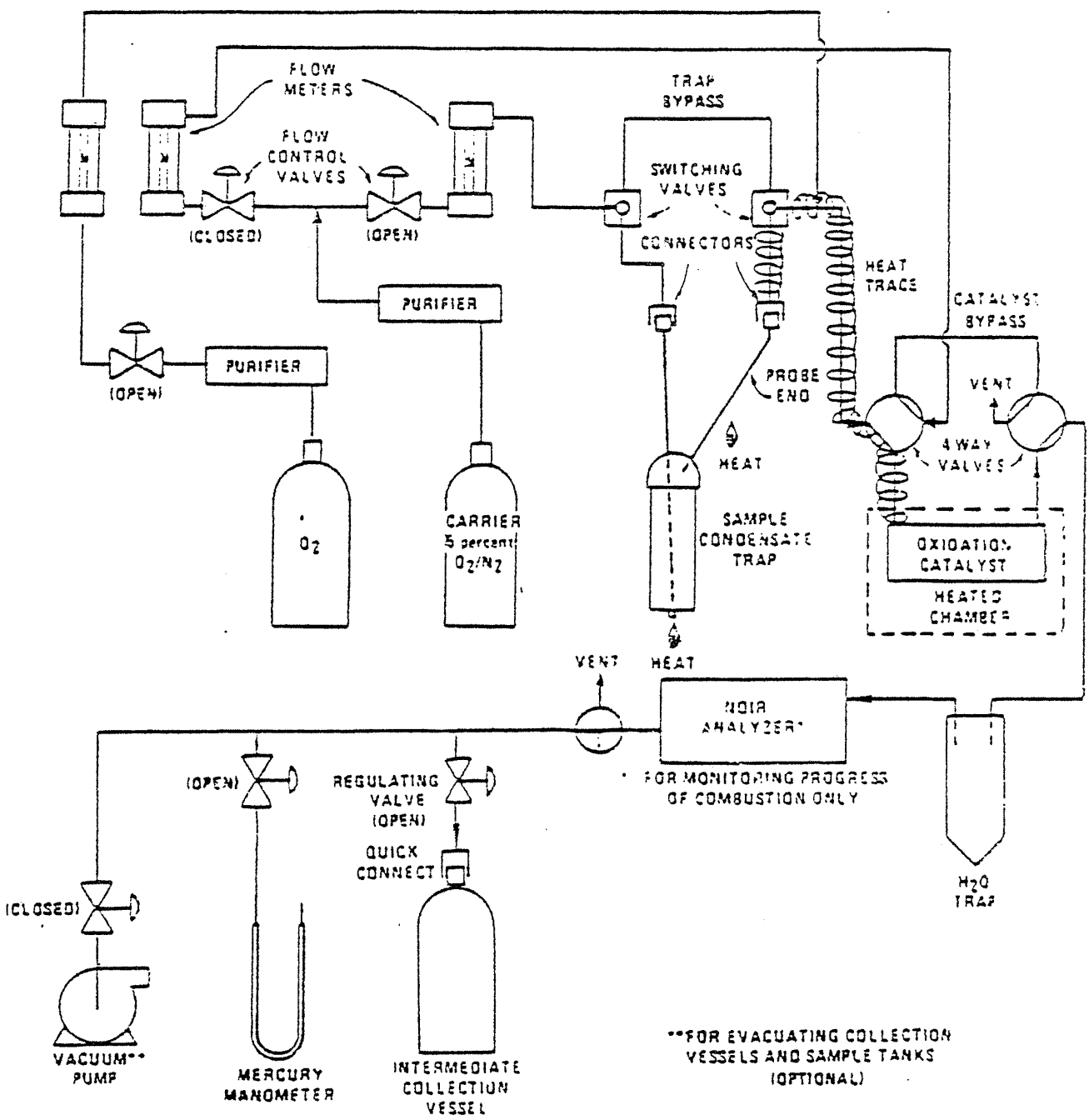


Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics

Appendix B—Test Methods

Method 101—Determination of Particulate and Gaseous Mercury Emissions From Chlor-Alkali Plants—Air Streams

[Method 101 revised by 47 FR 24704, June 8, 1982]

1. *Applicability and Principle*—1.1 *Applicability.* This method applies to the determination of particulate and gaseous mercury (Hg) emissions from chlor-alkali plants and other sources (as specified in the regulations), where the carrier-gas stream in the duct or stack is principally air.

1.2 *Principle.* Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic iodine monochloride (ICl) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

2. *Range and Sensitivity*—2.1 *Range.* After initial dilution, the range of this method is 0.5 to 120 μg Hg/ml. The upper limit can be extended by further dilution of the sample.

2.2 *Sensitivity.* The sensitivity of this method depends on the recorder/spectrophotometer combination selected.

3. *Interfering Agents*—3.1 *Sampling.* SO_2 reduces ICl and causes premature depletion of the ICl solution.

3.2 *Analysis.* ICl concentrations greater than 10^{-4} molar inhibit the reduction of the Hg (II) ion in the aeration cell. Condensation of water vapor on the optical cell windows causes a positive interference.

4. *Precision and Accuracy*—The following estimates are based on collaborative tests, wherein 13 laboratories performed duplicate analyses on two Hg-containing samples from a chlor-alkali plant and on one laboratory-prepared sample of known Hg concentration. The concentration ranged from 2 to 65 μg Hg/ml.

4.1 *Precision.* The estimated within-laboratory and between-laboratory standard deviations are 1.8 and 1.3 μg Hg/ml, respectively.

4.2 *Accuracy.* The participating laboratories that analyzed a 64.3-μg Hg/ml (in 0.1 M ICl) standard obtained a mean of 63.7 μg Hg/ml.

5. *Apparatus*—5.1 *Sampling Train.* A schematic of the sampling train is shown in Figure 101-1; it is similar to the Method 5 train (mention of Method 5 refers to Parts 60 of 40 CFR). The sampling train consists of the following components:

5.1.1 *Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment.* Same as Method 5, Sections 2.1.1, 2.1.3, 2.1.4, 2.1.5, 2.1.9, and 2.1.10, respectively.

5.1.2 *Probe Liner.* Borosilicate or quartz glass tubing. The tester may use a heating system capable of maintaining a gas temperature of 120±14° C (248±25° F) at the probe exit during sampling to prevent water condensation.

Note.—Do not use metal probe liners.

5.1.3 *Impingers.* Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, the tester may use impingers that are modified by replacing the tip with a 13-mm-ID (0.5-in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask.

5.1.4 *Acid Trap.* Mine Safety Appliances air line filter, Catalog number 31857, with acid absorbing cartridge and suitable connections, or equivalent.

5.2 *Sample Recovery.* The following items are needed:

5.2.1 *Glass Sample Bottles.* Leakless, with Teflon-lined caps, 1000- and 100-ml.

5.2.2 *Graduated Cylinder.* 250-ml.

5.2.3 *Funnel and Rubber Policeman.* To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

5.2.4 *Funnel.* Glass, to aid in sample recovery.

5.3 *Sample Preparation and Analysis.* The following equipment is needed:

5.3.1 *Atomic Absorption Spectrophotometer.* Perkin-Elmer 303, or equivalent, containing a hollow-cathode mercury lamp and the optical cell described in Section 5.3.2.

5.3.2 *Optical Cell.* Cylindrical shape with quartz end windows and having the dimensions shown in Figure 101-2. Wind the cell with approximately 2 meters of 24-gauge nichrome heating wire, and wrap with fiberglass insulation tape or equivalent; do not let the wires touch each other.

5.3.3 *Aeration Cell.* Constructed according to the specifications in Figure 101-3. Do not use a glass frit as a substitute for the blown glass bubbler tip shown in Figure 101-3.

5.3.4 *Recorder.* Matched to output of the spectrophotometer described in Section 5.3.1.

5.3.5 *Variable Transformer.* To vary the voltage on the optical cell from 0 to 40 volts.

5.3.6 *Hood.* For venting optical cell exhaust.

5.3.7 *Flowmetering Valve.*

5.3.8 *Flowmeter.* Rotameter or equivalent, capable of measuring a gas flow of 1.5 liters/min.

5.3.9 *Aeration Gas Cylinder.* Nitrogen or dry, Hg-free air, equipped with a single-stage regulator.

5.3.10 *Connecting Tubing.* Use glass tubing (ungreased ball- and socket-connections are recommended) for all tubing connections between the solution cell and the optical cell; do not use Tygon tubing, other types of flexible tubing, or metal tubing as substitutes. The tester may use Teflon, steel, or copper tubing between the nitrogen tank and flowmetering valve (5.3.7), and Tygon, gum, or rubber tubing between the flowmetering valve and the aeration cell.

5.3.11 *Flow Rate Calibration Equipment.* Bubble flowmeter or wet test meter for measuring a gas flow rate of 1.5±0.1 liters/min.

5.3.12 *Volumetric Flasks.* Class A with penny head standard taper stoppers: 100-, 250-, 500- and 1000-ml.

5.3.13 *Volumetric Pipets.* Class A: 1-, 2-, 3-, 4-, and 5-ml.

5.3.14 *Graduated Cylinder.* 50-ml.

5.3.15 *Magnetic Stirrer.* General-purpose laboratory type.

5.3.16 *Magnetic Stirring Bar.* Teflon-coated.

5.3.17 *Balance.* Capable of weighing to ±0.5 g.

5.4 *Alternative Analytical Apparatus.* Alternative systems are allowable as long as they meet the following criteria:

5.4.1 A linear calibration curve is generated and two consecutive samples of the same aliquot size and concentration agree within 3 percent of their average.

5.4.2 A minimum of 95 percent of the spike is recovered when an aliquot of a source sample is spiked with a known concentration of mercury (II) compound.

5.4.3 The reducing agent should be added after the aeration cell is closed.

5.4.4 The aeration bottle bubbler should not contain a frit.

5.4.5 Any Tygon used should be as short as possible and conditioned prior to use until blanks and standards yield linear and reproducible results.

5.4.6 If manual stirring is done before aeration, it should be done with the aeration cell closed.

5.4.7 A drying tube should not be used unless it is conditioned as the Tygon above.

6. *Reagents*—Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.

6.1 *Sampling and Recovery.* The reagents used in sampling and recovery are as follows:

6.1.1 *Water.* Deionized distilled, meeting ASTM Specifications for Type I Reagent Water—ASTM Test Method D 1193-74. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the $KMnO_4$ test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

6.1.2 *Nitric Acid (HNO_3),* 50 Percent (V/V). Mix equal volumes of concentrated HNO_3 and deionized distilled water, being careful to slowly add the acid to the water.

6.1.3 *Silica Gel.* Indicating type, 8- to 16-mesh. If previously used, dry at 175° C (350° F) for 2 hours. The tester may use new silica gel as received.

6.1.4 *Potassium Iodide (KI) Solution, 25 Percent.* Dissolve 250 g of KI in deionized distilled water and dilute to 1 liter.

6.1.5 *Iodine Monochloride (ICl) Stock Solution, 1.0 M.* To 800 ml of 25 percent KI solution, add 800 ml of concentrated hydrochloric acid (HCl). Cool to room temperature. With vigorous stirring, slowly add 135 g of potassium iodate (KIO_3) and stir until all free iodine has dissolved. A clear orange-red solution occurs when all the KIO_3 has been added. Cool to room temperature and dilute to 1800 ml with deionized distilled water. Keep the solution in amber glass bottles to prevent degradation.

6.1.6 *Absorbing Solution, 0.1 M ICl.* Dilute 100 ml of the 1.0 M ICl stock solution to 1 liter with deionized distilled water. Keep the solution in amber glass bottles and in darkness to prevent degradation. This reagent is stable for at least 2 months.

6.2 *Sample Preparation and Analysis.* The reagents needed are listed below:

6.2.1 *Tin (II) Solution.* Prepare fresh daily and keep sealed when not being used. Completely dissolve 20 g of tin (II) chloride (or 25 g of tin (II) sulfate) crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with deionized distilled water. Do not substitute HNO_3, H_2SO_4, or other strong acids for the HCl.

8.2.2 *Mercury Stock Solution, 1 mg Hg/ml.* Prepare and store all mercury standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of mercury (II) chloride in 75 ml of deionized distilled water in a 100 ml glass volumetric flask. Add 10 ml of concentrated HNO_3, and adjust the volume to exactly 100 ml with deionized distilled water. Mix thoroughly. This solution is stable for at least 1 month.

8.2.3 *Sulfuric Acid, 5 Percent (V/V).* Dilute 25 ml of concentrated H_2SO_4 to 500 ml with deionized distilled water.

8.2.4 *Intermediate Mercury Standard Solution, 10 µg Hg/ml.* Prepare fresh weekly. Pipet 5.0 ml of the mercury stock solution (8.2.2) into a 500-ml glass volumetric flask and add 20 ml of the 5 percent H_2SO_4 solution. Dilute to exactly 500 ml with deionized distilled water. Thoroughly mix the solution.

8.2.5 *Working Mercury Standard Solution, 200 ng Hg/ml.* Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Mercury Standard Solution" (8.2.4) into a 250-ml volumetric glass flask. Add 10 ml of the 5 percent H_2SO_4 and 2 ml of the 0.1 M ICl absorbing solution taken as a blank (7.2.3) and dilute to 250 ml with deionized distilled water. Mix thoroughly.

7. *Procedure*—7.1 *Sampling.* Because of the complexity of this method, testers should be trained and experienced with the test procedures to assure reliable results. Since the amount of Hg that is collected generally is small, the method must be carefully applied to prevent contamination or loss of sample.

7.1.1 *Pretest Preparation.* Follow the general procedure given in Method 5, Section 4.1.1, except omit the directions on the filter.

7.1.2 *Preliminary Determinations.* Follow the general procedure given in Method 5, Section 4.1.2, except as follows: Select a nozzle size based on the range of velocity heads to assure that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

Obtain samples over a period or periods that accurately determine the maximum emissions that occur in a 24-hour period. In the case of cyclic operations, run sufficient tests for the accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hours is recommended. In some instances, high Hg or high SO_2 concentrations make it impossible to sample for the desired minimum time. This is indicated by reddening (liberation of free iodine) in the first impinger. In these cases, the tester may divide the sample run into two or more subruns to insure that the absorbing solution is not depleted.

7.1.3 *Preparation of Sampling Train.* Clean all glassware (probe, impingers, and connectors) by rinsing with 50 percent HNO_3, tap water, 0.1 M ICl, tap water, and finally deionized distilled water. Place 100 ml of 0.1 M ICl in each of the first three impingers. Take care to prevent the absorbing solution from contacting any greased surfaces. Place approximately 200 g of preweighed silica gel in the fourth impinger. The tester may use more silica gel, but should be careful to ensure that it is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, determine and record the weight of the silica gel plus impinger to the nearest 0.5 g.

Install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260° C (500° F). Use a fiberglass string gasket if temperatures are higher. See APTD-0576 (Citation 9 in Section 10) for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as shown in Figure 101-1, using (if necessary) a very light coat of silicone grease on all ground glass joints. Grease only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease.

Note.—An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture from the sample stream.

After the sampling train has been assembled, turn on and set the probe, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

7.1.4 *Leak-Check Procedures.* Follow the leak-check procedures outlined in Method 5, Sections 4.1.4.1 (Pretest Leak Check), 4.1.4.2 (Leak Checks During Sample Run), and 4.1.4.3 (Post-Test Leak Check).

7.1.5 *Mercury Train Operation.* Follow the general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 101-4.

7.1.6 *Calculation of Percent Isokinetic.* Same as Method 5, Section 4.1.6.

7.2 *Sample Recovery.* Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling. Capping would create a vacuum and draw liquid out from the impingers.

Before moving the sampling train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and impinger assembly to a cleanup area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

Inspect the train before and during assembly, and note any abnormal conditions. Treat the sample as follows:

7.2.1 *Container No. 1* (Impinger and Probe). Using a graduated cylinder, measure the liquid in the first three impingers to within ±1 ml. Record the volume of liquid present (e.g., see Figure 5-3 of Method 5). This information is needed to calculate the moisture content of the effluent gas. (Use only glass storage bottles and graduated cylinders that have been precleaned as in Section 7.1.3.) Place the contents of the first three impingers into a 1000-ml glass sample bottle.

Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, and probe liner as follows: Rinse these components with two 50-ml portions of 0.1 M ICl. Next, rinse the probe nozzle, fitting and liner, and each piece of connecting glassware between the probe liner and the back half of the third impinger with a maximum of 400 ml of deionized distilled water. Add all washings to the 1000-ml glass sample bottle containing the liquid from the first three impingers.

After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the liquid to determine later whether leakage occurred during transport. Label the container to clearly identify its contents.

7.2.2 *Container No. 2* (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use as aids a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

7.2.3 *Container No. 3* (Absorbing Solution Blank). For a blank, place 50 ml of the 0.1 M ICl absorbing solution in a 100-ml sample bottle. Seal the container. Use this blank to prepare the working mercury standard solution (8.2.5).

7.3 *Sample Preparation.* Check the liquid level in each container to see whether liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Then follow the procedures below:

7.3.1 *Container No. 1* (Impinger and Probe). Carefully transfer the contents of Container No. 1 into a 1000-ml volumetric flask and adjust the volume to exactly 1000 ml with deionized distilled water.

7.3.2 *Dilutions.* Pipet a 2-ml aliquot from the diluted sample from 7.3.1 into a 250-ml volumetric flask. Add 10 ml of 5 percent H_2SO_4, and adjust the volume to exactly 250 ml with deionized distilled water. These solutions are stable for at least 72 hours.

Note.—The dilution factor will be 250/2 for this solution.

7.4 *Analysis.* Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in Sections 8.1 to 8.4.

7.4.1 *Mercury Samples.* Repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 5 ml) of each of the diluted samples (from

Section 7.3.2) until two consecutive peak heights agree within ±3 percent of their average value. The peak maximum of an aliquot (except the 5-ml aliquot) must be greater than 10 percent of the recorder full scale. If the peak maximum of a 1.0-ml aliquot is off scale on the recorder, further dilute the original source sample to bring the Hg concentration into the calibration range of the spectrophotometer.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the method of standard additions to confirm that matrix effects have not interfered in the analysis.

7.4.2 *Container No. 2* (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

8. *Calibration and Standards*—Before use, clean all glassware, both new and used, as follows: brush with soap and water, liberally rinse with tap water, soak for 1 hour in 50 percent HNO_3, and then rinse with deionized distilled water.

8.1 *Flow Calibration.* Assemble the aeration system as shown in Figure 101-3. Set the outlet pressure on the aeration gas cylinder regulator to a minimum pressure of 500 mm Hg (10 psi), and use the flowmetering valve and a bubble flowmeter or wet test meter to obtain a flow rate of 1.5±0.1 liters/min through the aeration cell. After the flow calibration is complete, remove the bubble flowmeter from the system.

8.2 *Optical Cell Heating System Calibration.* Using a 50-ml graduated cylinder, add 50 ml of deionized distilled water to the bottle section of the aeration cell and attach the bottle section to the bubbler section of the cell. Attach the aeration cell to the optical cell; and while aerating at 1.5 liters/min, determine the minimum variable transformer setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

8.3 *Spectrophotometer and Recorder Calibration.* The mercury response may be measured by either peak height or peak area.

Note.—The temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). Therefore, to obtain reproducible results, bring all solutions to room temperature before use.

Set the spectrophotometer wavelength at 253.7 nm, and make certain the optical cell is at the minimum temperature that will prevent water condensation. Then set the recorder scale as follows: Using a 50-ml graduated cylinder, add 50 ml of deionized distilled water to the aeration cell bottle and pipet 5.0 ml of the working mercury standard solution into the aeration cell.

Note.—Always add the Hg-containing solution to the aeration cell after the 50 ml of deionized distilled water.

Place a Teflon-coated stirring bar in the bottle. Before attaching the bottle section to the bubbler section of the aeration cell, make certain that (1) the aeration cell exit arm stopcock (Figure 101-3) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. If conditions (1) and (2) are met, attach the bottle section to the bubbler section of the aeration cell through the side arm of the cell and immediately stopper the side arm. Stir the solution for 15 sec, turn on the recorder, open the aeration cell exit arm stopcock, and then immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

8.4 *Calibration Curve.* After setting the recorder scale, repeat the procedure in Section 8.3 using 0.0-, 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquots of the working standard solution (final amount of Hg in the aeration cell is 0, 200, 400, 600, 800, and 1000 ng, respectively). Repeat this procedure on each aliquot size until two consecutive peaks agree within 3 percent of their average value. (Note: To prevent Hg carryover from one sample to another, do not close the aeration gas tank valve and do not disconnect the aeration cell from the optical cell until the recorder pen has returned to the baseline.) It should not be necessary to disconnect the aeration gas inlet line from the aeration cell when changing samples. After separating the bottle and bubbler sections of the aeration cell, place the bubbler section into a 600-ml beaker containing approximately 400 ml of deionized distilled water. Rinse the bottle section of the aeration cell with a stream of deionized distilled water to remove all traces of the tin (II) reducing agent. Also, to prevent the loss of Hg before aeration, remove all traces of the reducing agent between samples by washing with deionized distilled water. It will be necessary, however, to wash the aeration cell parts with concentrated HCl if any of the following conditions occur: (1) A white film appears on any inside surface of the aeration cell, (2) the calibration curve changes suddenly, or (3) the replicate samples do not yield reproducible results.

Subtract the average peak height (or peak area) of the blank (0.0-ml aliquot)—which should be less than 2 percent of recorder full scale—from the averaged peak heights of the 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquot standards. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Hg contamination of a reagent or carry-over of Hg from a previous sample. Plot the corrected peak height of each standard solution versus the corresponding final total Hg weight in the aeration cell (in ng) and draw the best-fit straight line. This line should either pass through the origin or pass through a point no further from the origin than ±2 percent of the recorder full scale. If the line does not pass through or very near to the origin, check for nonlinearity of the curve and for incorrectly prepared standards.

8.5 *Sampling Train Calibration.* Calibrate the sampling train components according to the procedures outlined in the following sections of Method 5: Section 5.1 (Probe-Nozzle), Section 5.2 (Pitot Tube), Section 5.3 (Metering System), Section 5.4 (Probe Heater), Section 5.5 (Temperature Gauges), Section 5.7 (Barometer). Note that the leak-check described in Section 5.8 of Method 5 applies to this method.

9. *Calculations*—9.1 *Dry Gas Volume.* Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions (corrected for leakage, if necessary) as outlined in Section 6.3 of Method 5.

9.2 *Volume of Water Vapor and Moisture Content.* Using the data obtained from this test, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

9.3 *Stack Gas Velocity.* Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity v_s.

9.4 *Total Mercury.* For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within ±3 percent of their average for the contribution of the solution blank (see Section 8.4). Use the calibration curve and these corrected averages, to determine the final total weight of mercury in nanograms in the aeration cell for each source sample. Correct for any dilutions made to bring the sample in the working range of the spectrophotometer. Then calculate the Hg in µg (m_{Hg}) in the original solution as follows:

$$m_{Hg} = \frac{C_{Hg(std)}(D.F.)\,V_t\,10^{-3}}{S} \qquad \text{Eq. 101-1}$$

Where:

$C_{Hg(std)}$ = Total nanograms of mercury in aliquot analyzed (reagent blank subtracted).

D.F. = Dilution factor for the Hg-containing solution (before adding to the aeration cell; e.g., D.F. = 250/2 if the source samples were diluted as described in Section 7.3.2.)

V_t = Solution volume of original sample, 1000 ml for samples diluted as described in Section 7.2.1.

10^{-3} = Conversion factor, µg/ng.

S = Aliquot volume added to aeration cell, ml.

9.5 *Mercury Emission Rate.* Calculate the Hg emission rate R in g/day for continuous operations using Equation 101-2. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = K\,\frac{m_{Hg}\,v_s\,A_s\,(86{,}400\times10^{-6})}{(V_{m(std)}+V_{w(std)})(T_s/P_s)} \qquad \text{Eq. 101-2}$$

Where:

A_s = Stack cross-sectional area, m^2 (ft^2).

86,400 = Conversion factor, sec/day.

10^{-6} = Conversion factor, g/µg.

T_s = Absolute average stack gas temperature, °K (°R).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

K = 0.3858 °K/mm Hg for metric units.
= 17.65 °R/in. Hg for English units.

9.6 *Isokinetic Variation and Acceptable Results.* Same as Method 5, Sections 6.11 and 6.12, respectively.

9.7 *Determination of Compliance.* Each performance test consists of three repetitions

of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all repetitions.

10. *Bibliography.* 1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS. NCAPC. December 6. 1967.

2. Determining Dust Concentration in a Gas Stream. ASME Performance Test Code No. 27. New York. NY. 1957.

3. Devorkin. Howard. et al. Air Pollution Source Testing Manual. Air Pollution Control District. Los Angeles. CA. November 1963.

4. Hatch. W.R., and W.L. Ott. Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry. Anal. Chem. *40*:2085–87. 1968.

5. Mark. L.S. Mechanical Engineers' Handbook. McGraw-Hill Book Co., Inc. New York. NY. 1951.

6. Martin. Robert M. Construction Details of Isokinetic Source Sampling Equipment. U.S. Environmental Protection Agency. Research Triangle Park. NC. Publication No. APTD–0581. April 1971.

7. Western Precipitation Division of Joy Manufacturing Co. Methods for Determination of Velocity. Volume. Dust and Mist Content of Gases. Bulletin WP–50. Los Angeles. CA. 1968.

8. Perry. J.H. Chemical Engineers' Handbook. McGraw-Hill Book Co., Inc. New York. NY. 1960.

9. Rom. Jerome J. Maintenance. Calibration. and Operation of Isokinetic Source Sampling Equipment. U.S. Environmental Protection Agency. Research Triangle Park. NC. Publication No. APTD–0576. April 1972.

10. Shigehara. R.T., W.F. Todd. and W.S. Smith. Significance of Errors in Stack Sampling Measurements. Stack Sampling News. *1*:(3):8–18. September 1973.

11. Smith. W.S., et al. Stack Gas Sampling Improved and Simplified with New Equipment. APCA Paper No. 67–119. 1967.

12. Smith. W.S., R.T. Shigehara. and W.F. Todd. A Method of Interpreting Stack Sampling Data. Stack Sampling News. *1*(2):8–17. August 1973.

13. Specifications for Incinerator Testing at Federal Facilities. PHS. NCAPA. 1967.

14. Standard Method for Sampling Stacks for Particulate Matter. In: 1971 Annual Book of ASTM Standards. Part 23. ASTM Designation D–2928–71. Philadelphia. PA. 1971.

15. Vennard. J.K. Elementary Fluid Mechanics. John Wiley and Sons. Inc. New York. 1947.

16. Mitchell. W.J., and M.R. Midgett. Improved Procedure for Determining Mercury Emissions from Mercury Cell Chlor-Alkali Plants. J. APCA. *28*: 674–677. July 1978.

17. Shigehara. R.T. Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News. *2*:4–11. October 1974.

18. Vollaro. R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency. Emission Measurement Branch. Research Triangle Park. NC. November 1978.

19. Klein. R., and C. Hach. Standard Additions: Uses and Limitation in Spectrophotometric Measurements. Amer. Lab. *9*:21. 1977.

20. Water. Atmospheric Analysis. In: Annual Book of ASTM Standards. Part 31. ASTM Designation D–1193–74. Philadelphia. PA. 1974.

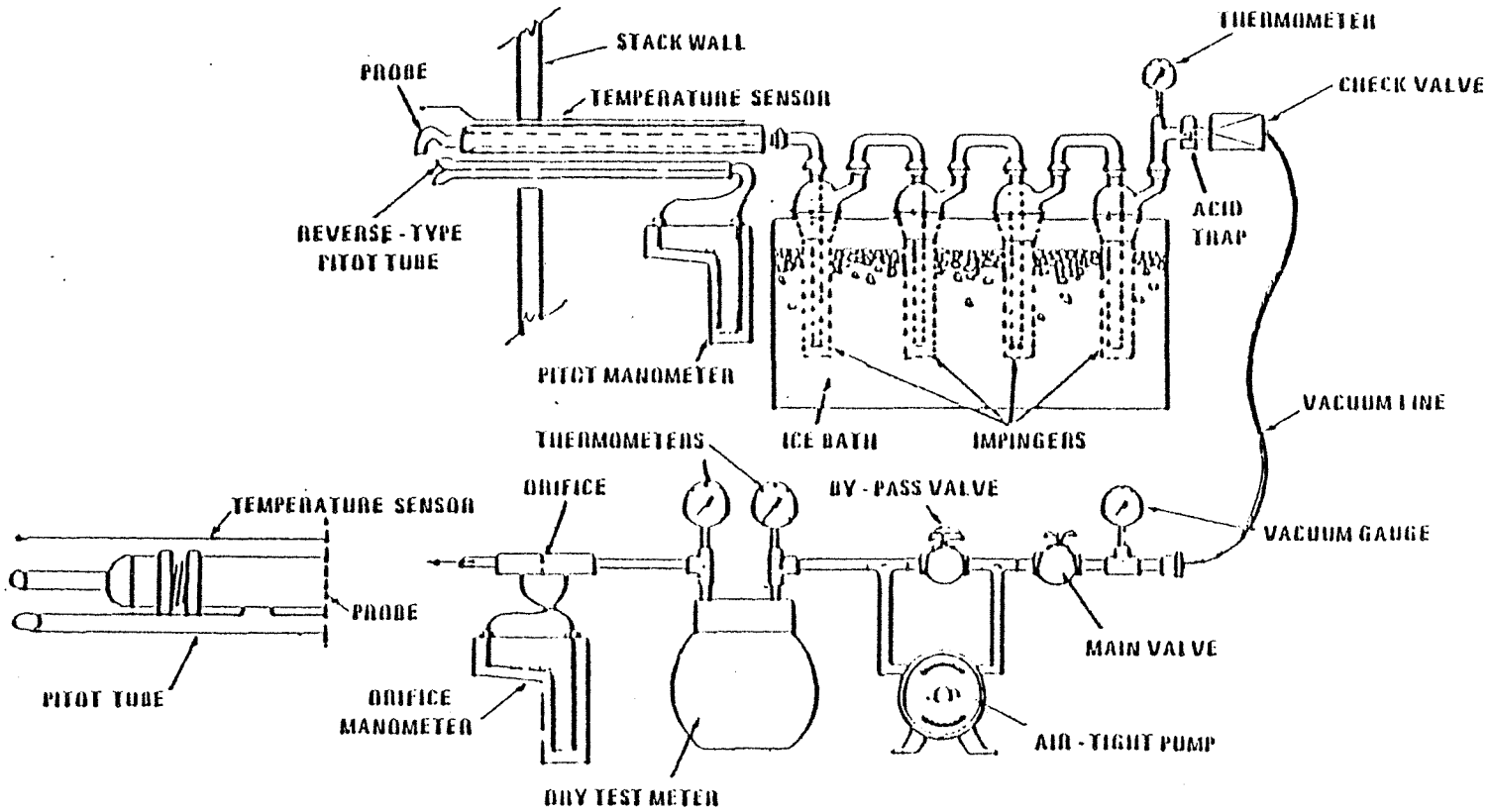
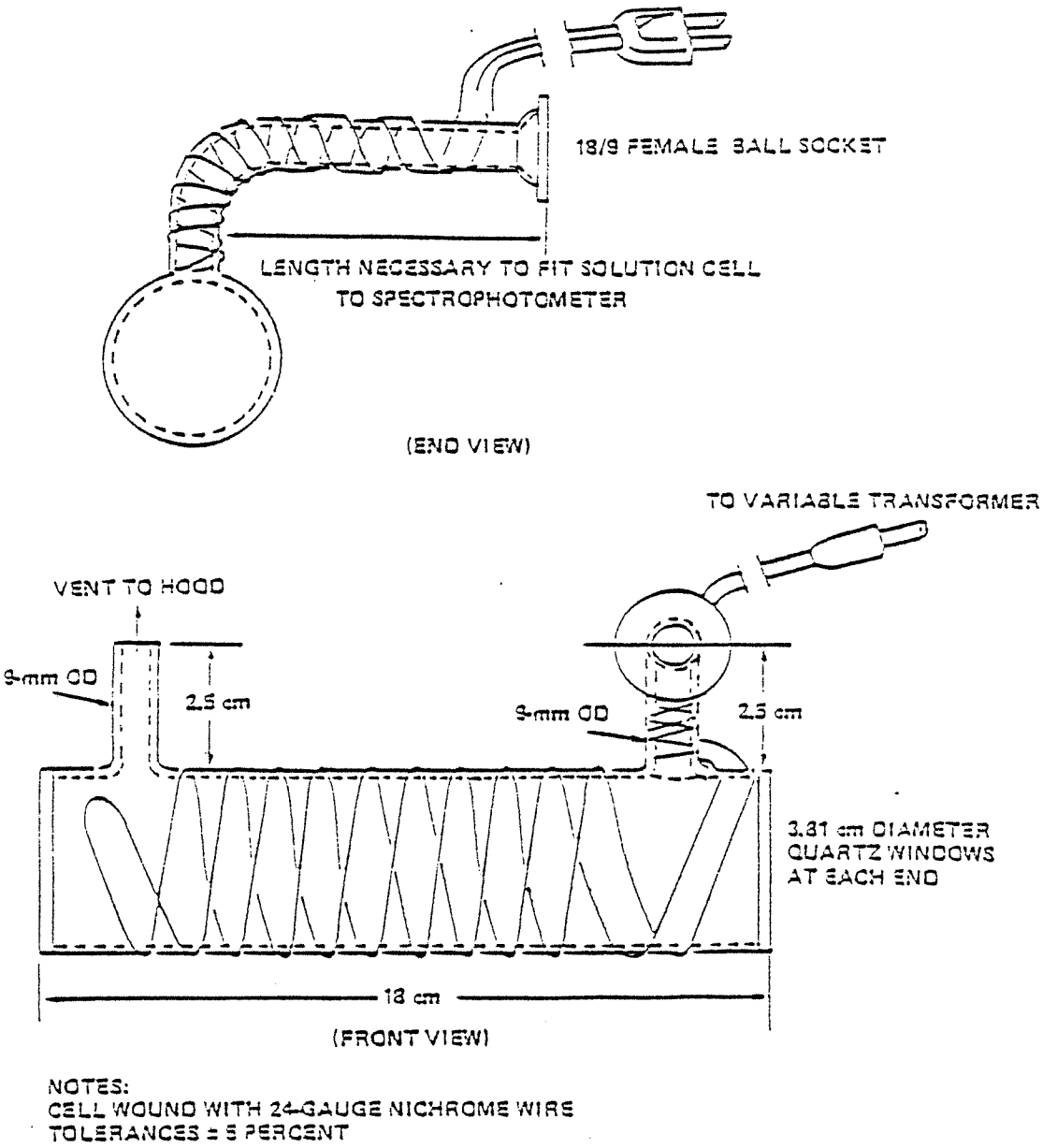


Figure 101-1 Mercury sampling train.



NOTES:
CELL WOUND WITH 24-GAUGE NICHROME WIRE
TOLERANCES ± 5 PERCENT

Figure 101-2. Optical cell.

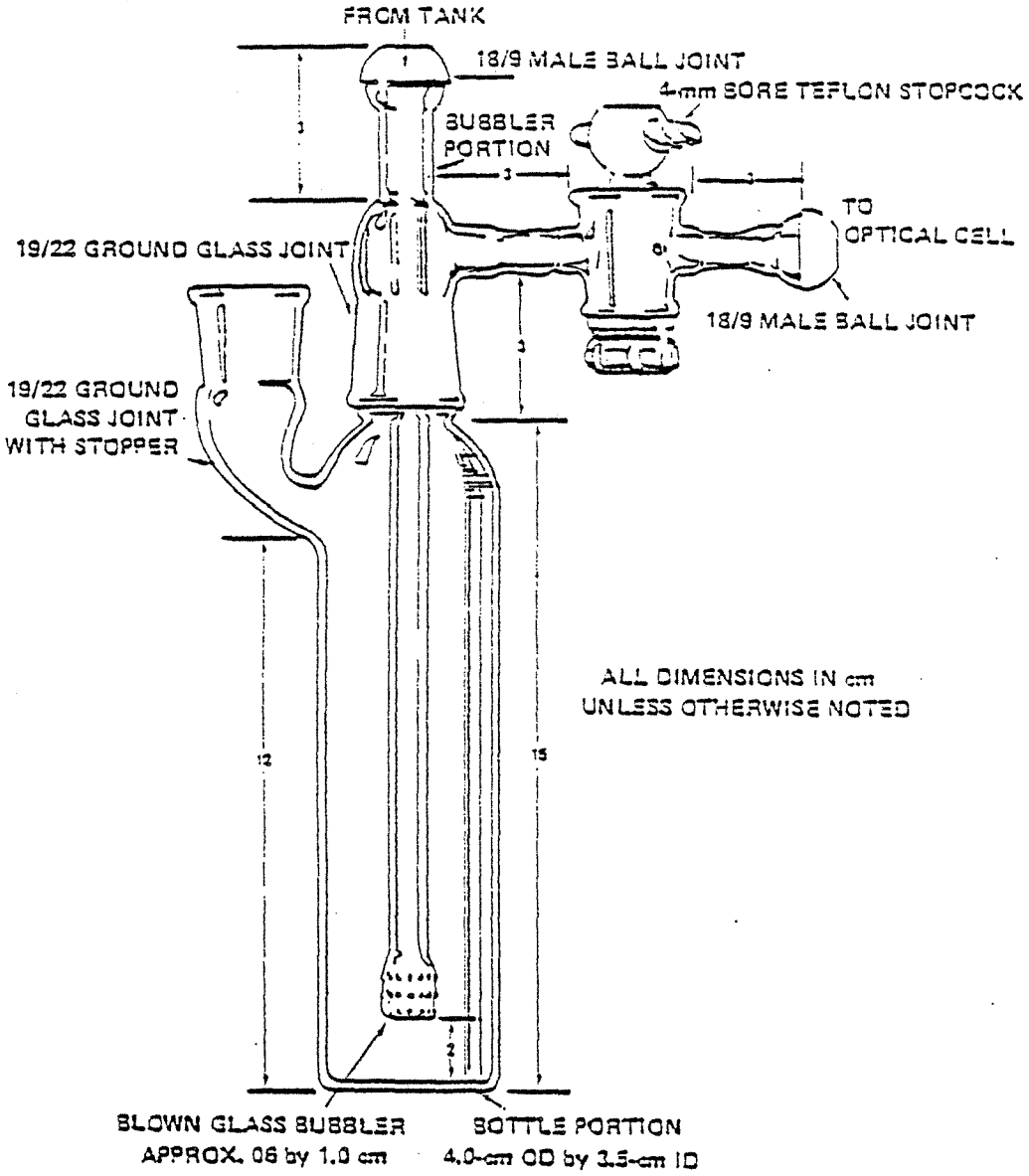


Figure 101-3. Aeration cell.

PLANT _____
LOCATION _____
OPERATOR _____
DATE _____
RUN NO. _____
SAMPLE BOX NO. _____
FILTER BOX NO. _____
METER ΔH@ _____
C FACTOR _____
PITOT TUBE COEFFICIENT, C_p _____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
ASSUMED MOISTURE, % _____
PROBE LENGTH, m (ft) _____
NOZZLE IDENTIFICATION NO. _____
AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____
PROBE HEATER SETTING* _____
LEAK RATE, m^3/min (cfm) _____
PROBE LINER MATERIAL _____
STATIC PRESSURE, mm Hg (in. Hg) _____
FILTER NO.* _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		FILTER HOLDER* TEMPERATURE °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

*IF APPLICABLE

Fig. 101-4. Mercury field data.

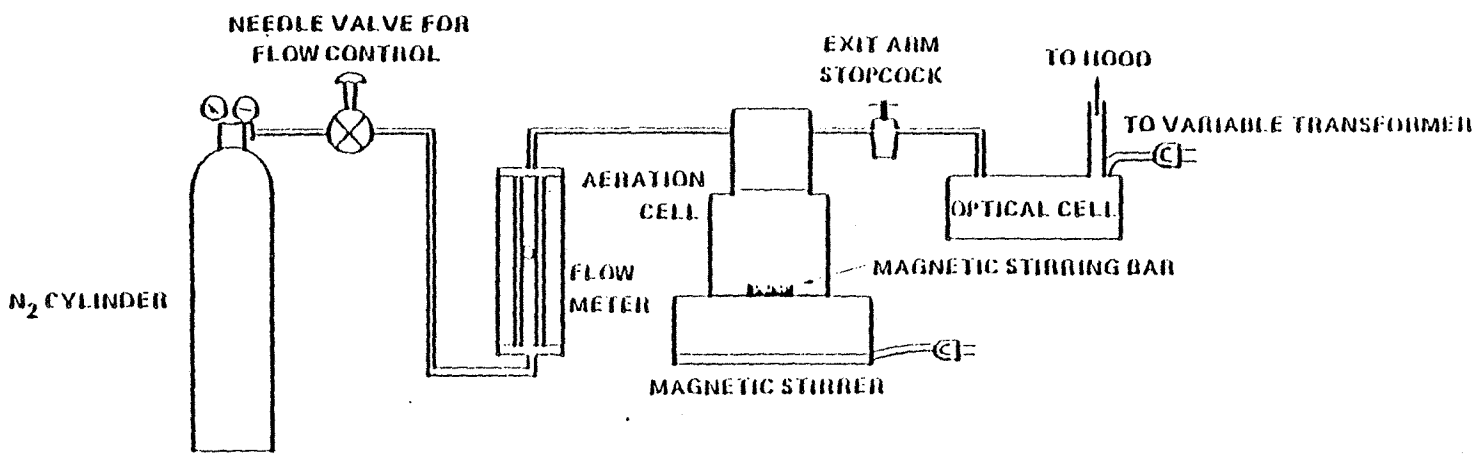


Figure 101-5. Schematic of aeration system.

Method 101A. Determination of Particulate and Gaseous Mercury Emissions From Sewage Sludge Incinerators

[Method 101A added by 47 FR 24704 June 8, 1982]

Introduction

This method is similar to Method 101, except acidic potassium permanganate solution is used instead of acidic iodine monochloride for collection.

1. *Applicability and Principle*—1.1 *Applicability.* This method applies to the determination of particulate and gaseous mercury (Hg) emissions from sewage sludge incinerators and other sources as specified in the regulations.

1.2 *Principle.* Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate ($KMnO_4$) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

2. *Range and Sensitivity*—2.1 *Range.* After initial dilution, the range of this method is 20 to 800 ng Hg/ml. The upper limit can be extended by further dilution of the sample.

2.2 *Sensitivity.* The sensitivity of the method depends on the recorder/spectrophotometer combination selected.

3. *Interfering Agents*—3.1 *Sampling.* Excessive oxidizable organic matter in the stack gas prematurely depletes the $KMnO_4$ solution and thereby prevents further collection of Hg.

3.2 *Analysis.* Condensation of water vapor on the optical cell windows causes a positive interference.

4. *Precision*—Based on eight paired-train tests, the within-laboratory standard deviation was estimated to be 4.8 µg Hg/m³ in the concentration range of 50 to 130 µg Hg/m³.

5. *Apparatus*—5.1 *Sampling Train and Sample Recovery.* Same as Method 101, Sections 5.1 and 5.2, respectively, except for the following variations:

5.1.1 *Probe Liner.* Same as Method 101, Section 5.1.2, except that if a filter is used ahead of the impingers, the tester must use the probe heating system to minimize the condensation of gaseous Hg.

5.1.2 *Filter Holder (Optional).* Borosilicate glass with a rigid stainless-steel wire-screen filter support (do not use glass frit supports) and a silicone rubber or Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter. The filter holder must be equipped with a filter heating system capable of maintaining a temperature around the filter holder of 120 ± 15° C (248 ± 25° F) during sampling to minimize both water and gaseous Hg condensation. The tester may use a filter in cases where the stream contains large quantities of particulate matter.

5.2 *Analysis.* The apparatus needed for analysis is the same as Method 101, Sections 5.3 and 5.4, except as follows:

5.2.1 *Volumetric Pipets.* Class A: 1-, 2-, 3-, 4-, 5-, 10-, and 20-ml.

5.2.2 *Graduated Cylinder.* 25-ml.

5.2.3 *Steam Bath.*

6. *Reagents*—*Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.*

6.1 *Sampling and Recovery.* The reagents used in sampling and recovery are as follows:

6.1.1 *Water.* Deionized distilled, meeting ASTM Specifications for Type I Reagent Water—ASTM Test Method D 1193-74. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the $KMnO_4$ test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

6.1.2 *Nitric Acid (HNO_3), 50 Percent (V/V).* Mix equal volumes of concentrated HNO_3 and deionized distilled water, being careful to slowly add the acid to the water.

6.1.3 *Silica Gel.* Indicating type, 6- to 16-mesh. If previously used, dry at 175° C (350° F) for 2 hr. The tester may use new silica gel as received.

6.1.4 *Filter (Optional).* Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3 µm dioctyl phthalate smoke particles. The tester may use the filter in cases where the gas stream contains large quantities of particulate matter, but he should analyze blank filters for Hg content.

6.1.5 *Sulfuric Acid (H_2SO_4), 10 Percent (V/V).* Add and mix 100 ml of concentrated H_2SO_4 with 900 ml of deionized distilled water.

6.1.6 *Absorbing Solution, 4 Percent $KMnO_4$ (W/V).* Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation.

6.2 *Analysis.* The reagents needed for analysis are listed below:

6.2.1 *Tin (II) Solution.* Prepare fresh daily and keep sealed when not being used. Completely dissolve 20 g of tin (II) chloride (or 25 g of tin (II) sulfate) crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with deionized distilled water. Do not substitute HNO_3, H_2SO_4, or other strong acids for the HCl.

6.2.2 *Sodium Chloride—Hydroxylamine Solution.* Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in deionized distilled water and dilute to 100 ml.

6.2.3 *Hydrochloric Acid (HCl), 8 N.* Dilute 67 ml of concentrated HNO_3 to 100 ml with deionized distilled water (slowly add the HCl to the water).

6.2.4 *Nitric Acid, 15 Percent (V/V).* Dilute 15 ml of concentrated HNO_3 to 100 ml with deionized distilled water.

6.2.5 *Mercury Stock Solution, 1 mg Hg/ml.* Prepare and store all mercury standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of mercury (II) chloride in 75 ml of deionized distilled water. Add 100 ml of concentrated HNO_3, and adjust the volume to exactly 100 ml with deionized distilled water. Mix thoroughly. This solution is stable for at least 1 month.

6.2.6 *Intermediate Mercury Standard Solution, 10 µg Hg/ml.* Prepare fresh weekly. Pipet 5.0 ml of the mercury stock solution (Section 6.2.5) into a 500-ml volumetric flask and add 20 ml of 15 percent HNO_3 solution. Adjust the volume to exactly 500 ml with deionized distilled water. Thoroughly mix the solution.

6.2.7 *Working Mercury Standard Solution, 200 ng Hg/ml.* Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Mercury Standard Solution" (Section 6.2.6) into a 250-ml volumetric flask. Add 5 ml of 4 percent $KMnO_4$ absorbing solution and 5 ml of 15 percent HNO_3. Adjust the volume to exactly 250 ml with deionized distilled water. Mix thoroughly.

6.2.8 *Potassium Permanganate, 5 Percent (W/V).* Dissolve 5 g of $KMnO_4$ in deionized distilled water and dilute to 100 ml.

6.2.9 *Filter.* Whatman No. 40 or equivalent.

7. *Procedure*—7.1 *Sampling.* The sampling procedure is the same as Method 101, except for changes due to the use of $KMnO_4$ instead of ICl absorbing solution and the possible use of a filter. These changes are as follows:

7.1.1 *Preliminary Determinations.* The preliminary determinations are the same as those given in Method 101, Section 7.1.2, except for the absorbing solution depletion sign. In this method, high oxidizable organic content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the $KMnO_4$ solution. In these cases, the tester may divide the sample run into two or more subruns to insure that the absorbing solution would not be depleted. In cases where an excess of water condensation is encountered, collect two runs to make one sample.

7.1.2 *Preparation of Sampling Train.* The preparation of the sampling train is the same as that given in Method 101, Section 7.1.3, except for the cleaning of the glassware (probe, filter holder (if used), impingers, and connectors) and the charging of the first three impingers. In this method, clean all the glass components by rinsing with 50 percent HNO_3, tap water, 8 N HCl, tap water, and finally deionized distilled water. Then place 50 ml of 4 percent $KMnO_4$ in the first impinger and 100 ml in each of the second and third impingers.

If a filter is used, use a pair of tweezers to place the filter in the filter holder. Be sure to center the filter and place the gasket in proper position to prevent the sample gas stream from by-passing the filter. Check the filter for tears after assembly is completed. Be sure also to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

7.1.3 *Sampling Train Operation.* In addition to the procedure given in Method 101, Section 7.1.5, maintain a temperature around the filter (if applicable) of 120° ± 14° C (248° ± 25° F).

7.2 *Sample Recovery.* Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling because the resultant vacuum would draw liquid out from the impingers.

Before moving the sample train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open

outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe, impinger assembly, and (if applicable) filter assembly to a cleanup area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

Inspect the train before and during assembly, and note any abnormal conditions. Treat the sample as follows:

7.2.1 *Container No. 1* (Impinger, Probe, and Filter Holder). Use a graduated cylinder: measure the liquid in the first three impingers to within ±1 ml. Record the volume of liquid present (e.g., see Figure 5-3 of Method 5 in Part 60 of 40 CFR). This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as in Section 7.1.2.) Place the contents of the first three impingers into a 1000-ml glass sample bottle.

(Note.—If a filter is used, remove the filter from its holder, as outlined under "Container No. 3" below.)

Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner and front half of the filter holder (if applicable) as follows: Rinse these components with a total of 250 to 400 ml of fresh 4 percent $KMnO_4$ solution: add all washings to the 1000-ml glass sample bottle: remove any residual brown deposits on the glassware using the minimum amount of 8 N HCl required: and add this HCl rinse to this sample container.

After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

7.2.2 *Container No. 2* (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use as aids a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g: record this weight.

7.2.3 *Container No. 3* (Filter). If a filter was used, carefully remove it from the filter holder, place it in a 100-ml glass sample bottle, and add 20 to 40 ml of 4 percent $KMnO_4$. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 150-ml sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Label the container to clearly identify its contents. Mark the height of the fluid level to determine whether leakage occurs during transport.

7.2.4 *Container No. 4* (Filter Blank). If a filter was used, treat an unused filter from the same filter lot used for sampling in the same manner as Container No. 3.

7.2.5 *Container No. 5* (Absorbing Solution Blank). For a blank, place 500 ml of 4 percent $KMnO_4$ absorbing solution in a 1000-ml sample bottle. Seal the container.

7.3 *Sample Preparation.* Check liquid level in each container to see if liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Then follow the procedures below.

7.3.1 *Containers No. 3 and No. 4* (Filter and Filter Blank). If a filter was used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-ml beakers and heat the beakers on a steam bath until most of the liquid has evaporated. Do not take to dryness. Add 20 ml of concentrated HNO_3 to the beakers, cover them with a glass, and heat on a hot plate at 70° C for 2 hours. Remove from the hot plate and filter the solution through Whatman No. 40 filter paper. Save the filtrate for Hg analysis. Discard the filter.

7.3.2 *Container No. 1* (Impingers, Probe, and Filter Holder). Filter the contents of Container No. 1 through Whatman 40 filter paper to remove the brown MnO_2 precipitate. Wash the filter with 50 ml of 4 percent $KMnO_4$ absorbing solution and add this wash to the filtrate. Discard the filter. Combine the filtrates from Containers No. 1 and No. 3 (if applicable), and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.3.3 *Container No. 5* (Absorbing Solution Blank). Treat this container as described in Section 7.3.2. Combine this filtrate with the filtrate with Container No. 4 and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.4 *Analysis.* Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in Sections 8.1 to 8.4. Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from Sections 7.3.2 and 7.3.3) until two consecutive peak heights agree within ±3 percent of their average value. If the 10-ml sample is below the detectable limit, use a larger aliquot (up to 20 ml), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0-ml aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration: recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the Method of Standard Additions to confirm that matrix effects have not interfered in the analysis.

8. *Calibration and Standards.*—The calibration and standards are the same as Method 101, Section 8, except for the following variations:

8.1 *Optical Cell Heating System Calibration.* Same as method 101, Section 8.2, except use a 25-ml graduated cylinder to add 25 ml of deionized distilled water to the bottle section of the aeration cell.

8.2 *Spectrophotometer and Recorder Calibration.* The mercury response may be measured by either peak height or peak area. (Note: the temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.) Set the spectrophotometer wave length at 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent water condensation.

Then set the recorder scale as follows: Using a 25-ml graduated cylinder, add 25 ml of deionized distilled water to the aeration cell bottle and pipet 5.0 ml of the working mercury standard solution into the aeration cell. (Note: Always add the Hg-containing solution to the aeration cell after the 25 ml of deionized distilled water.) Place a Teflon-coated stirring bar in the bottle. Add 5 ml of the 4 percent $KMnO_4$ absorbing solution followed by 5 ml of 15 percent HNO_3 and 5 ml of 5 percent $KMnO_4$ to the aeration bottle and mix well. Now, attach the bottle section to the bubbler section of the aeration cell and make certain that (1) the aeration cell exit arm stopcock (Figure 101-3 of Method 101) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. Add 5 ml of sodium chloride hydroxylamine in 1-ml increments until the solution is colorless. Now add 5 ml of tin (II) solution to the aeration bottle through the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

9. *Calculations.*—9.1 *Dry Gas Volume, Volume of Water Vapor and Moisture Content, Stack Gas Velocity, Isokinetic Variation and Acceptable Results, and Determination of Compliance.* Same as Method 101, Sections 9.1, 9.2, 9.3, 9.6, and 9.7, respectively, except use data obtained from this test.

9.2 *Total Mercury.* For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agreed within ±3 percent of their average for the contribution of the field blank. Then calculate the total Hg content in μg in each sample. Correct for any

dilutions made to bring the sample into the working range of the spectrophotometer.

9.3 *Mercury Emission Rate.* Calculate the Hg emission rate R in g/day for continuous operations using Equation 101A-1. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = \frac{K\, m_{Hg}\, v_s\, A_s\, (86{,}400 \times 10^{-6})}{[V_m(std) + V_{w(std)}]\,(T_s/P_s)}$$

Eq. 101A-1

Where:

m_{Hg} = Total Hg content in each sample, µg.
v_s = Average stack gas velocity, m/sec (fps).
A_s = Stack cross-sectional area, m^2 (ft^2).
86,400 = Conversion factor, sec/day.
10^{-6} = Conversion factor, g/µg.
$V_{m(std)}$ = Dry gas sample volume at standard conditions, corrected for leakage (if any), m^3 (ft^3).
$V_{w(std)}$ = Volume of water vapor at standard conditions, m^3 (ft^3).
T_s = Absolute average stack gas temperature, °K (°R).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
K = 0.3858 °K/mm Hg for metric units.
= 17.64 °R/in. Hg for English units.

10. *Bibliography.* 1. Same as Method 101, Section 10.

2. Mitchell, W. J., M. R. Midgett, J. C. Suggs, and D. Albrinck.
Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Publication No. EPA-600/4-79-058. September 1979.

Method 102. Determination of Particulate and Gaseous Mercury Emissions From Chlor-Alkali Plants—Hydrogen Streams

[Method 102 revised by 47 FR 24704, June 8, 1982]

1. *Introduction*—Although similar to Method 101, Method 102 requires changes to accommodate the sample being extracted from a hydrogen stream. Conduct the test according to Method 101, except as shown below:

2. *Mercury Train Operation*—2.1 *Probe Heating System.* Do not use, unless otherwise specified.

2.2 *Glass Fiber Filter.* Do not use, unless otherwise specified.

2.3 *Safety Procedures.* The sampler must conduct the source test under conditions of utmost safety, because hydrogen and air mixtures are explosive. Since the sampling train essentially is leakless, attention to safe operation can be concentrated at the inlet and outlet. If a leak does occur, however, remove the meter box cover to avoid a possible explosive mixture. The following specific precautions are recommended:

2.3.1 *Operate only the vacuum pump during the test.* The other electrical equipment, e.g., heaters, fans, and timers, normally are not essential to the success of a hydogen stream test.

2.3.2 *Seal the sample port to minimize leakage of hydrogen from the stack.*

2.3.3 *Vent sampled hydrogen at least 3 m (10 feet) away from the train.* This can be accomplished by attaching a 13-mm-ID (0.50-in) Tygon tube to the exhaust from the orifice meter. (Note: A smaller ID tubing may cause the orifice meter calibration to be erroneous.) Take care to ensure that the exhaust line is not bent or pinched.

2.4 *Setting of Isokinetic Rates.*

2.4.1 If a nomograph is used, take special care in the calculation of the molecular weight of the stack gas and in the setting of the nomograph to maintain isokinetic conditions during sampling (Sections 2.4.1.1 through 2.4.1.3 below).

2.4.1.1 *Calibrate the meter box orifice.* Use the techniques described in APTD—0578 (see Citation 9 in Section 10 of Method 101). Calibration of the orifice meter at flow conditions that simulate the conditions at the source is suggested. Calibration should either be done with hydrogen or with some other gas having a similar Reynolds Number so that there is similarity between the Reynolds Numbers during calibration and during sampling.

2.4.1.2 The nomograph described in APTD—0576 cannot be used to calculate the C factor because the nomograph is designed for use when the stack gas dry molecular weight is 29±4. Instead, the following calculation should be made to determine the proper C factor:

$$C = 0.00154\ \Delta H@\ C_p\ T_m (P_s / P_m) \frac{(1 - B_{ws})^2}{(1 - B_{ws}) - 18\ B_{ws} / M_s}$$

Where:

$\Delta H@$ = Meter box calibration factor obtained in Section 2.4.1.1, in. H_2O.

C_p = Pitot tube calibration coefficient, dimensionless.

T_m = Absolute temperature of gas at the orifice, °R.

P_s = Absolute pressure of stack gas, in Hg.

P_m = Absolute pressure of gas at the meter, in Hg.

B_{ws} = Fraction by volume of water vapor in the stack gas.

M_s = Dry molecular weight of stack gas, lb/lb-mole.

Note. This calculation is left in English units, and is not converted to metric units because nomographs are based on English units.

2.4.1.3 Set the calculated C factor on the operating nomograph and select the proper nozzle diameter and K factor as specified in APTD—0576. If the C factor obtained in Section 2.4.1.2 exceeds the values specified on the existing operating nomograph, expand the C scale logarithmically so that the values can be properly located.

2.4.2 If a calculator is used to set isokinetic rates, it is suggested that the isokinetic equation presented in Citation 17 in the Bibliography of Method 101 be used.

2.5 Sampling in Small (<12-in.-Diameter) Stacks. When the stack diameter (or equivalent diameter) is less than 12 inches, conventional pitot tube-probe assemblies should not be used. For sampling guidelines, see Citation 18 in the Bibliography of Method 101.

Method 106—Determination of Vinyl Chloride From Stationary Sources

[Method 106 revised by 47 FR 39170, September 7, 1982]

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Applicability and Principle

1.1 Applicability. The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. The method does not measure vinyl chloride contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to GC analysis using a flame ionization detector (FID).

2. Range and Sensitivity

This method is designed for the 0.1 to 50 ppm range. However, common GC instruments are capable of detecting 0.02 ppm vinyl chloride. With proper calibration, the upper limit may be extended as needed.

3. Interferences

The chromatographic columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic, provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

4. Apparatus

4.1 Sampling (see Figure 106-1). The sampling train consists of the following components:

4.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing (as stack temperature permits), equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Lines. Teflon, 6.4-mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon completion of the test.

4.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one pair without), located as shown in Figure 106-1.

4.1.4 Tedlar Bags. 50- to 100-liter capacity, to contain sample. Aluminized Mylar bags may be used if the samples are analyzed within 24 hours of collection.

4.1.5 Bag Containers. Rigid leak-proof containers for sample bags, with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rates.

4.1.7 Pump. Leak-free, with minimum of 2-liter/min capacity.

4.1.8 Charcoal Tube. To prevent admission of vinyl chloride and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flowmeter. For observing sampling flow rate; capable of measuring a flow range from 0.10 to 1.00 liter/min.

4.1.10 Connecting Tubing. Teflon, 6.4-mm outside diameter, to assemble sampling train (Figure 106-1).

4.1.11 Tubing Fittings and Connectors. Teflon or stainless steel, to assemble sampling train.

4.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, to connect bag to GC sample loop for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon conclusion of analysis of those bags.

4.3 Analysis. The following equipment is required:

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0- to 5.0-ml heated sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1-ppm vinyl chloride that is at least as great as the average noise level. (Response is measured from the average value of the base line to the maximum of the wave form, while standard operating conditions are in use.)

4.3.2 Chromatographic Columns. Columns as listed below. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1, "Determination of Adequate Chromatographic Peak Resolution.")

4.3.2.1 Column A. Stainless steel, 2.0 m by 3.2 mm, containing 80/100-mesh Chromasorb 102.

4.3.2.2 Column B. Stainless steel, 2.0 m by 3.2 mm, containing 20 percent GE SF-96 on 60/80-mesh Chromasorb P AW; or stainless steel, 1.0 m by 3.2 mm containing 80/100-mesh Porapak T. Column B is required as a secondary column if acetaldehyde is present. If used, column B is placed after column A. The combined columns should be operated at 120° C.

4.3.3 Flowmeters (2). Rotameter type, 100-ml/min capacity, with flow control valves.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to 1° C, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around GC during sample analysis.

4.3.7 Pump. Leak-free, with minimum of 100-ml/min capacity.

4.3.8 Recorder. Strip chart type, optionally equipped with either disc or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator on recorder, to measure chromatograph peak areas.

4.4 Calibration. Sections 4.4.2 through 4.4.4 are for the optional procedure in Section 7.1.

4.4.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar Bags. Sixteen-inch-square size, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringe. 0.5-ml and 50-ul, gas tight.

individually calibrated to dispense gaseous vinyl chloride.

4.4.4 Dry Gas Meter, with Temperature and Pressure Gauges. Singer model DTM-115 with 802 index, or equivalent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

5. Reagents

Use only reagents that are of chromatograph grade.

5.1 Analysis. The following are required for analysis.

5.1.1 Helium or Nitrogen. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen. Zero grade.

5.1.3 Oxygen or Air. Zero grade, as required by the detector.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Vinyl Chloride. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride, for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.2 Nitrogen. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (50-, 10-, and 5-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ±3 percent or better (see Section 5.2.3.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 50 and 100 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 5 and 10 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Verification of Manufacturer's Calibration Standards. Before using a standard, the manufacturer shall verify each calibration standard (a) by comparing it to gas mixtures prepared with 99 mole percent vinyl chloride in accordance with the procedure described in Section 7.1, or (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (vinyl chloride in nitrogen cylinders). The concentrations of the audit cylinder should be: one low-concentration cylinder in the range of 5 to 20 ppm vinyl chloride and one high-concentration cylinder in the range of 20 to 50 ppm. When available, the tester may obtain audit cylinders by contacting: Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711. Audit cylinders obtained from a commercial gas manufacturer may be used provided: (a) the gas manufacturer certifies the audit cylinder as described in Section 5.2.3.1, and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined here to mean analysis performed by an individual different than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within ±5 percent of the gas manufacturer's concentration.

6. Procedure

6.1 Sampling. Assemble the sample train as shown in Figure 106-1. A bag leak check should have been performed previously according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connection between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow that will fill over 50 percent of bag volume in the specific sample period. After allowing sufficient time to purge the line several times, change the vacuum line from the container to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. At all times, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample storage. Keep the sample bags out of direct sunlight. When at all possible, analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection. Aluminized Mylar bag samples must be analyzed within 24 hours.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to 100-ml/min rotameter with flow control valve followd by a charcoal tube and a 1-in. H_2O pressure gauge. The tester may maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

6.4 Analysis. Set the column temperature to 100° C and the detector temperature to 150° C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatography operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for 30 seconds at the rate of 100 ml/min, shut off flow, allow the sample loop pressure to reach atmospheric pressure as indicated by the H_2O manometer, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), sample number, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record the barometeric pressure. From the chart, note the peak having the retention time corresponding to vinyl chloride as determined in Section 7.2.1. Measure the vinyl chloride peak area, A_m, by use of a disc integrator, electronic integrator, or a planimeter. Measure and record the peak heights, H_m. Record A_m and retention time. Repeat the injection at least two times or until two consecutive values for the total area of the vinyl chloride peak do not vary more than 5 percent. Use the average value for these two total areas to compute the bag concentration.

Compare the ratio of H_m to A_m for the vinyl chloride sample with the same ratio for the standard peak that is closest in height. If these ratios differ by more than 10 percent, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2.2).

6.5 Determination of Bag Water Vapor Content. Measure the ambient temperature

and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance

7.1 Preparation of Vinyl Chloride Standard Gas Mixtures. (Optional Procedure—delete if cylinder standards are used.) Evacuate a 16-inch square Tedlar bag that has passed a leak check (described in Section 7.3.2) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5-ml syringe to inject 250 µl of 99.9+ percent vinyl chloride gas through the wall of the bag. Upon withdrawing the syringe, immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppm. In a like manner use the 50 µl syringe to prepare gas mixtures having 10- and 5-ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time new gas mixtures must be prepared. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Calibration.

7.2.1 Determination of Vinyl Chloride Retention Time. (This section can be performed simultaneously with Section 7.2.2.) Establish chromatograph conditions identical with those in Section 6.4 above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions with the equipment plumbing arranged identically to Section 6.3, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity divided by the chart speed is defined as the retention time. Since other organics may be present in the sample, positive identification of the vinyl chloride peak must be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a GC measurement of each gas mixture standard (described in Section 5.2.3 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard mixtures, and activate the sample valve. Record the concentration of vinyl chloride injected (C_c), attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the barometric pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus C_c. When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after the analysis of each emission test set of bag samples, whichever is more frequent. For each group of sample analyses, use the average of the two calibration curves which bracket that group to determine the respective sample concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by both calibration curves.

7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. Checking of bags for leaks is required after bag use and strongly recommended before bag use. After each use, connect a water manometer and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: An alternative leak check method is to pressurize the bag to 5 to 10 cm H_2O and allow it to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. *Calculations.*

8.1 Determine the sample peak area, A_c, as follows:

$$A_c = A_m A_f \qquad \text{Eq. 106-1}$$

Where:

A_m = Measured peak area.

A_f = Attenuation factor.

8.2 Vinyl Chloride Concentrations. From the calibration curves described in Section 7.2.2, determine the average concentration value of vinyl chloride, C_c, that corresponds to A_c, the sample peak area. Calculate the concentration of vinyl chloride in the bag, C_b, as follows:

$$C_b = \frac{C_c P_r T_t}{P_t T_r (1 - B_{wo})} \qquad \text{Eq. 106-2}$$

Where:

P_r = Reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_t = Sample loop temperature on the absolute scale at the time of analysis, °K.

P_t = Laboratory pressure at time of analysis, mm Hg.

T_r = Reference temperature, the sample loop temperature recorded during calibration, °K.

B_{wo} = Water vapor content of the bag sample, as analyzed.

9. *Bibliography.*

1. Brown D.W., E.W. Loy, and M.H. Stephenson. Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, KY. Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, GA. June 24, 1974.

2. G.D. Clayton and Associates. Evaluation of a Collection and Analytical Procedure for Vinyl Chloride in Air. U.S. Environmental Protection Agency, Research Triangle Park, N.C. EPA Contract No. 68-02-1408, Task Order No. 2. EPA Report No. 75-VCL-1. December 13, 1974.

3. Midwest Research Institute. Standardization of Stationary Source Emission Method for Vinyl Chloride. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/4-77-028. May 1977.

4. Scheil, G. and M.C. Sharp. Collaborative Testing of EPA Method 106 (Vinyl Chloride) that Will Provide for a Standardized Stationary Source Emission Measurement Method. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/4-78-058, October 1978.

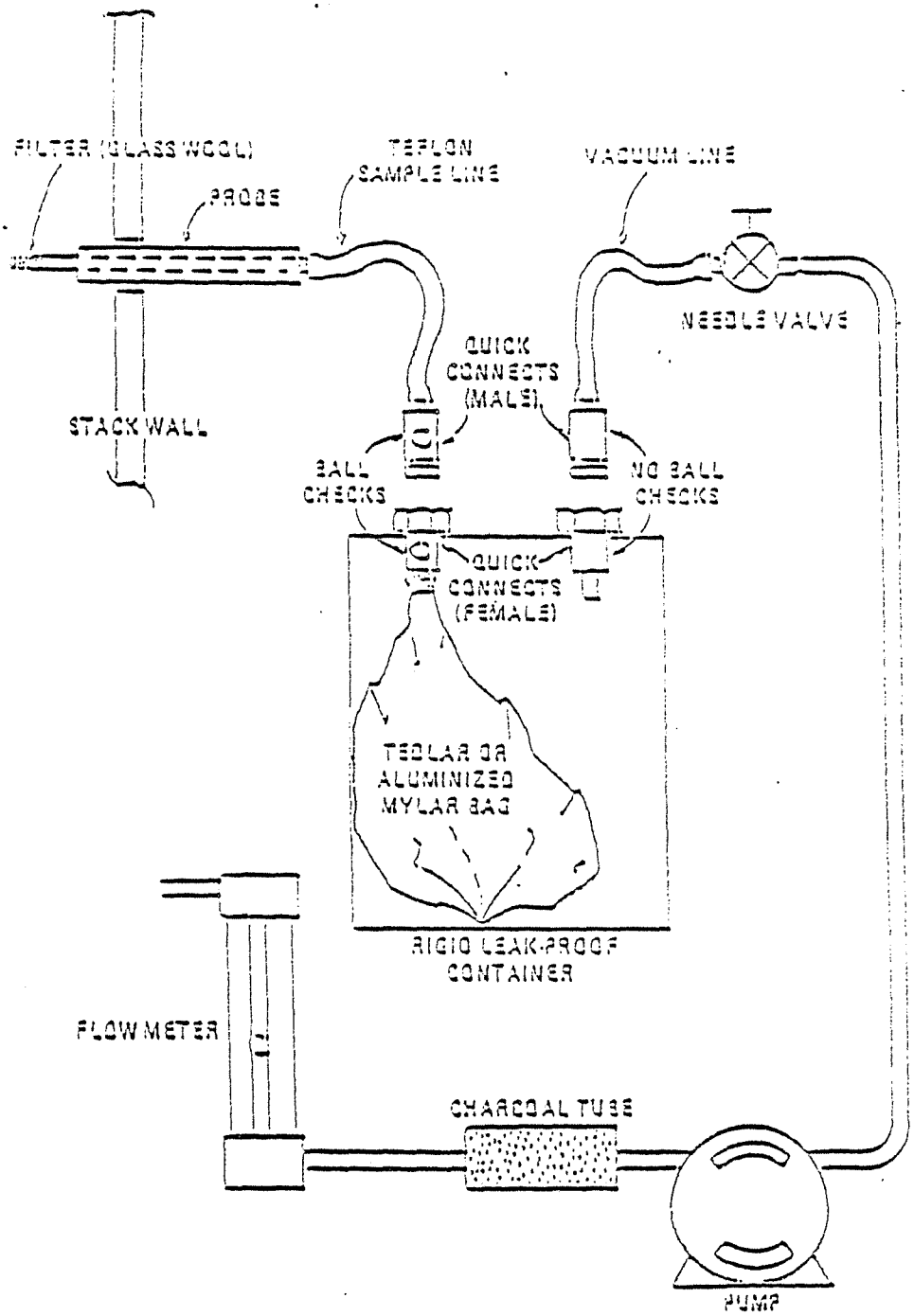


Figure 106-1. Integrated-bag sampling train. (Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

Method 107—Determination of Vinyl Chloride Content of Inprocess Wastewater Samples, and Vinyl Chloride Content of Polyvinyl Chloride Resin, Slurry, Wet Cake, and Latex Samples

[Method 107 revised by 47 FR 39170, September 7, 1982]

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC), nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the measurement of the vinyl chloride monomer (VCM) content of inprocess wastewater samples, and the residual vinyl chloride monomer (RVCM) content of polyvinyl chloride (PVC) resins, wet cake, slurry, and latex samples. It cannot be used for polymer in fused forms, such as sheet or cubes. This method is not acceptable where methods from Section 304(h) of the Clean Water Act, 33 U.S.C. 1251 et seq. (the Federal Water Pollution Control Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.2 Principle. The basis for this method relates to the vapor equilibrium that is established between RVCM, PVC resin, water, and air in a closed system. The RVCM in a PVC resin will equilibrate rapidly in a closed vessel, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

2. Range and Sensitivity. The lower limit of detection of vinyl chloride will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-7} mg. With proper calibration, the upper limit may be extended as needed.

3. *Interferences.* The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

4. *Precision and Reproducibility.* An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63 percent for a sample with a mean of 2.09 ppm, 4.16 percent for a sample with a mean of 1.66 ppm, and 5.29 percent for a sample with a mean of 32.68 ppm.

5. *Safety.* Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the gas must be vented prior to removal of the vial from the instrument turntable. Vials must be vented through a hypodermic needle connected to an activated charcoal tube to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

6. *Apparatus.*

6.1 Sampling. The following equipment is required:

6.1.1 Glass bottles, 60-ml (2-oz) capacity, with wax-lined screw-on tops, for PVC samples.

6.1.2 Glass Vials, 60-ml capacity Hypovial, sealed with Teflon faced Tuf-Bond discs, for water samples.

6.1.3 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

6.2.1 Glass Vials. With butyl rubber septa, Perkin-Elmer Corporation Nos. 0105–0129 (glass vials), 3001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalents. The seals must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.2.2 Analytical Balance. Capable of weighing to ±0.0001 gram.

6.2.3 Vial Sealer. Perkin-Elmer No. 105–0108, or equivalent.

6.2.4 Syringe. 100-µl capacity, precision series "A" No. 010025, or equivalent.

6.3 Analysis. The following equipment is required:

6.3.1 Gas Chromatograph. Perkin-Elmer Corporation Model F–40, F–42, or F–45 Head-Space Analyzer, or equivalent. Equipped with backflush accessory.

6.3.2 Chromatographic Columns. Stainless steel 1 m by 3.2 mm and 2 m by 3.2 mm, both containing 50/80-mesh Porapak Q. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.") Two 1.83 m columns, each containing 1 percent Carbowax 1500 on Carbopak B, have been suggested for samples containing acetaldehyde.

6.3.3 Thermometer. 0 to 100° C, accurate to ±0.1° C, Perkin-Elmer No. 105–0109, or equivalent.

6.3.4 Sample Tray Thermostat System. Perkin-Elmer No. 105–0103, or equivalent.

6.3.5 Septa. Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 105–1008, or equivalent.

6.3.6 Integrator-Recorder. Hewlett-Packard Model 3380A, or equivalent.

6.3.7 Filter Drier Assembly (3). Perkin-Elmer No. 2220117, or equivalent.

6.3.8 Soap Film Flowmeter. Hewlett Packard No. 0101–0113, or equivalent.

6.3.9 Regulators. For required gas cylinders.

6.3.10 Headspace Vial Pre-Pressurizer. Nitrogen pressurized hypodermic needle inside protective shield. (Blueprint available from Test Support Section, Emission Measurement Branch, Office of Air Quality Planning and Standards, Environmental Protection Agency, Mail Drop 19, Research Triangle Park, N.C. 27711.)

7. *Reagents.* Use only reagents that are of chromatographic grade.

7.1 Analysis. The following items are required for analysis:

7.1.1 Hydrogen. Zero grade.

7.1.2 Nitrogen. Zero grade.

7.1.3 Air. Zero grade.

7.2 Calibration. The following items are required for calibration:

7.2.1 Cylinder Standards (4). Gas mixture standards (50-, 500-, 2000- and 4000-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 9.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ±3 percent or better (see Section 7.2.1.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a 3-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 4000 and 3000 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 500 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the 3-point calibration.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 of Method 106 or by (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8. *Procedure.*

8.1 Sampling.

8.1.1 PVC Sampling. Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend and fill a 60-ml sample bottle under the tap, and immediately tighten a cap on the bottle. Wrap adhesive tape around the cap and bottle to prevent the cap from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

8.1.2 Water Sampling. Prior to use, the 50-ml vials (without the discs) must be capped with aluminum foil and heated in a muffle furnace at 400° C for at least 1 hour to destroy or remove any organic matter that could interfere with analysis. At the sampling location fill the vials bubble-free to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, with the Teflon side down, on the opening of the vial.

Place the aluminum seal over the disc and the neck of the vial, and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book. All samples must be kept refrigerated until analyzed.

8.2 Sample Recovery. Samples must be run within 24 hours.

8.2.1 Resin Samples. The weight of the resin used must be between 3.5 and 4.5 grams. An exact weight must be obtained (±0.0001 g) for each sample. In the case of suspension resins, a volumetric cup can be prepared for holding the required amount of sample. When the cup is used, open the sample bottle, and add the cup volume of resin to the tared sample vial (tared, including septum and aluminum cap). Obtain the exact sample weight, add 100µl or about two equal drops of distilled water, and immediately seal the vial. Report this value on the data sheet; it is required for calculation of RVCM. In the case of dispersion resins, the cup cannot be used. Weigh the sample in an aluminum dish, transfer the sample to the tared vial, and accurately weigh it in the vial. After prepressurization of the samples, condition them for a minimum of 1 hour in the 90° C bath. Do not exceed 5 hours.

Note.—Some aluminum vial caps have a center section that must be removed prior to placing into sample tray. If the cap is not removed, the injection needle will be damaged.

8.2.2 Suspension Resin Slurry and Wet Cake Samples. Decant the water from a wet cake sample, and turn the sample bottle upside down onto a paper towel. Wait for the water to drain, place approximately 0.2 to 4.0 grams of the wet cake sample in a tared vial (tared, including septum and aluminum cap) and seal immediately. Then determine the sample weight (±0.0001 g). All samples must be prepressurized and then conditioned for 1 hour at 90° C. A sample of wet cake is used to determine total solids (TS). This is required for calculating the RVCM.

8.2.3 Dispersion Resin Slurry and Geon Latex Samples. The materials should not be filtered. Sample must be thoroughly mixed. Using a tared vial (tared, including septum and aluminum cap) add approximately eight drops (0.25 to 0.35 g) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as possible. Determine sample weight (±0.0001 g). After prepressurization, condition the vial for 1 hour at 90° C in the analyzer bath. Determine the TS on the slurry sample (Section 8.3.5).

8.2.4 Inprocess Wastewater Samples. Using a tared vial (tared, including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight (±0.0001 g). Prepressurize the vial, and then condition for 1 to 2 hours as required at 90° C in the analyzer bath.

8.3 Analysis.

8.3.1 Preparation of Equipment. Install the chromatographic column and condition overnight at 180° C in the first operation. Porapak columns must be purged for 1 hour at 220° C.

Do not connect the exit end of the column to the detector while conditioning. Hydrogen and air to the detector must be turned off while the column is disconnected.

8.3.1.1 Flow Rate Adjustments. Adjust flow rates as follows:

a. Nitrogen Carrier Gas. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to produce a flow rate of 30.0 cc/min. Accurately measure the flow rate at the exit end of the column using the soap film flowmeter and a stopwatch, with the oven and column at the analysis temperature. After the instrument program advances to the "B" (backflush) mode, adjust the nitrogen pressure regulator to exactly balance the nitrogen flow rate at the detector as was obtained in the "A" mode.

b. Vial Prepressurizer Nitrogen. After the nitrogen carrier is set, solve the following equation and adjust the pressure on the vial prepressurizer accordingly.

$$p = \frac{T_1}{T_2}\left[P_1 - \frac{P_{w1} - P_{w2}}{7.50}\right] - 10 \text{ k Pa}$$

Where:

T_1 = Ambient temperature, °K.

T_2 = Conditioning bath temperature, °K.

P_1 = Gas chromatograph absolute dosing pressure (analysis mode), k Pa.

P_{w1} = Water vapor pressure @ 90° C (525.8 mm Hg).

P_{w2} = Water vapor pressure @ 22° C (19.8 mm Hg).

7.50 = mm Hg per k Pa.

10 k Pa = Factor to adjust the prepressurized pressure to slightly less than the dosing pressure.

Because of gauge errors, the apparatus may over-pressurize the vial. If the vial pressure is at or higher than the dosing pressure, an audible double injection will occur. If the vial pressure is too low, errors will occur on resin samples because of inadequate time for head-space gas equilibrium. This condition can be avoided by running several standard gas samples at various pressures around the calculated pressure, and then selecting the highest pressure that does not produce a double injection. All samples and standards must be pressurized for 60 seconds using the vial prepressurizer. The vial is then placed into the 90° C conditioning bath and tested for leakage by placing a drop of water on the septum at the needle hole. A clean, burr-free needle is mandatory.

c. Burner Air Supply. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/min. Check with bubble flowmeter.

d. Hydrogen Supply. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply approximately 35 ± 5 cc/min. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with bubble meter and record this flow.

8.3.1.2 Temperature Adjustments. Set temperatures as follows:

a. Oven (chromatograph column), 140° C.

b. Dosing Line, 150° C.

c. Injection Block, 170° C.

d. Sample Chamber, Water Temperature, 90° C ± 1.0° C.

8.3.1.3 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions.

8.3.1.4 Amplifier Balance. Balance the amplifier according to the manufacturer's instructions.

8.3.2 Programming the Chromatograph. Program the chromatograph as follows:

a. I—Dosing or Injection Time. The normal setting is 2 seconds.

b. A—"Analysis Time." The normal setting is approximately 70 percent of the VCM retention time. When this timer terminates, the programmer initiates backflushing of the first column.

c. B—Backflushing Time. The normal setting is double the "analysis time."

d. W—Stabilization Time. The normal setting is 0.5 min to 1.0 min.

e. X—Number of Analyses Per Sample. The normal setting is one.

8.3.3 Preparation of Sample Turntable. Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. All samples and standards must be pressurized for 60 seconds by using the vial prepressurizer. The numbered sample vials should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

Position 1 and 2—Old 2000-ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

Position 3—50-ppm standard, freshly prepared.

Position 4—500-ppm standard, freshly prepared.

Position 5—2000-ppm standard, freshly prepared.

Position 6—4000-ppm standard, freshly prepared.

Position 7—Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

After all samples have been positioned, insert the second set of 50-, 500-, 2000-, and 4000-ppm standards. Samples, including standards, must be conditioned in the bath of 90° C for 1 hour (not to exceed 5 hours).

8.3.4 Start Chromatograph Program. When all samples, including standards, have been conditioned at 90° C for 1 hour, start the analysis program according to the

manufacturer's instructions. These instructions must be carefully followed when starting and stopping a program to prevent damage to the dosing assembly.

3.3.5 Determination of TS. For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110° C). Samples must be dried to constant weight. After first weighing, return the pan to the oven for a short period of time, and then reweigh to verify complete dryness. The TS are then calculated as the final sample weight divided by initial sample weight.

9. *Calibration.* Calibration is to be performed each 8-hour period when the instrument is used. Each day, prior to running samples, the column should be conditioned by running two 2000-ppm standards from the previous day.

9.1 Preparation of Standards. Calibration standards are prepared as follows: Place 100ul or about two equal drops of distilled water in the sample vial, then fill the vial with the VCM/nitrogen standard, rapidly seat the septum, and seal with the aluminum cap. Use a ⅛-in. stainless steel line from the cylinder to the vial. Do not use rubber or tygon tubing. The sample line from the cylinder must be purged (into a properly vented hood) for several minutes prior to filling the vials. After purging, reduce the flow rate to 500 to 1000 cc/min. Place end of tubing into vial (near bottom). Position a septum on top of the vial, pressing it against the ⅛-in. filling tube to minimize the size of the vent opening. This is necessary to minimize mixing air with the standard in the vial. Each vial is to be purged with standard for 90 seconds, during which time the filling tube is gradually slid to the top of the vial. After the 90 seconds, the tube is removed with the septum, simultaneously sealing the vial. Practice will be necessary to develop good technique. Rubber gloves should be worn during the above operations. The sealed vial must then be pressurized for 60 seconds using the vial prepressurizer. Test the vial for leakage by placing a drop of water on the septum at the needle hole.

9.2 Preparation of Chromatograph Calibration Curve.

Prepare two 50-, 500-, 2000-, and 4000-ppm standard samples. Run the calibration samples in exactly the same manner as regular samples. Plot A_s, the integrator area counts for each standard sample, versus C_c, the concentration of vinyl chloride in each standard sample. Draw a straight line through the points derived by the least squares method.

10. *Calculations.*

10.1 Response Factor. If the calibration curve described in Section 9.2 passes through zero, a response factor, R_f, may be used to compute vinyl chloride concentrations. To compute a response factor, divide any particular A_s by the corresponding C_c.

$$R_f = \frac{A_s}{C_c} \qquad \text{Eq. 107-1}$$

Where:

A_s = Chromatograph area counts of vinyl chloride for the sample.

P_a = Ambient atmospheric pressure, mm Hg.

R_f = Response factor in area counts per ppm VCM.

T_1 = Ambient laboratory temperature, °K.

M_v = Molecular weight of VCM, 62.5 g/mole.

V_g = Volume of the vapor phase, cm^3.

R = Gas constant, (62360 cm^3) (mm Hg/mole) (°K).

m = Sample weight, g.

K_p = Henry's Law Constant for VCM in PVC @ 90° C, 6.52×10^{-4} g/g/mm Hg.

If the calibration curve does not pass through zero, the calibration curve must be employed to calculate each sample concentration unless the error introduced by using a particular R_f is known.

10.2 Residual Vinyl Chloride Monomer Concentration, (C_{rvc}) or Vinyl Chloride Monomer Concentration. Calculate C_{rvc} in ppm or mg/kg as follows:

$$C_{rvc} = \frac{A_s \; P_a}{R_f \; T_1}\left[\frac{M_v \; V_g}{R \; m} + K_p \; (TS) \; T_2 + K_w \; (1 - TS) \; T_2\right] \qquad \text{Eq. 107-2}$$

Results calculated using these equations represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

TS = Total solids expressed as a decimal fraction.

T_2 = Equilibrium temperature, °K.

K_w = Henry's Law Constant for VCM in water @ 90° C, 7×10^{-7} g/g/mm Hg.

Assuming the following conditions are met, these values can be substituted into Equation 107-2:

P_a = 750 mm Hg.

V_g = Vial volume—sample volume (Fisher vials are 22.0 cm^3 and Perkin-Elmer vials are 21.8 cm^3).

T_1 = 23° C or 296° K.

T_2 = 90° C or 363° K.

$$C_{rvc} = \frac{A_s \; 750}{R_f \; 296}\left[\frac{55.5\left(21.8 - \frac{m(TS)}{1.45} - \frac{m(1-TS)}{0.8993}\right)}{62360 \; m} + 6.25 \times 10^{-6}(TS)(363) + 7.0 \times 10^{-7}(1-TS)(363)\right]$$

11. *References.*

1. B.F. Goodrich. Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins, Latex, Wet Cake, Slurry and Water Samples. B.F. Goodrich Chemical Group Standard Test Procedure No. 1005-E. B.F. Goodrich Technical Center, Avon Lake, Ohio. October 8, 1979.

2. Berens, A.R. The Diffusion of Vinyl Chloride in Polyvinyl Chloride. ACS—Division of Polymer Chemistry, Polymer Preprints *15* (2):197, 1974.

3. Berens, A.R. The Diffusion of Vinyl Chloride in Polyvinyl Chloride. ACS—Division of Polymer Chemistry, Polymer Preprints *15* (2):203, 1974.

4. Berens, A.R., L.B. Crider, C.J. Tomanek, and J.M. Whitney. Analysis for Vinyl Chloride in PVC Powders by Head—Space Gas Chromatography. Journal of Applied Polymer Science. *19*:3169–3172, 1975.

5. Mansfield, R.A. The Evaluation of Henry's Law Constant (Kp) and Water Enhancement in the Perkin-Elmer Multifract F-40 Gas Chromatograph. B.F. Goodrich, Avon Lake, Ohio. February 10, 1978.

Method 107A—Determination of Vinyl Chloride Content of Solvents, Resin-Solvent Solution, Polyvinyl Chloride Resin, Resin Slurry, Wet Resin, and Latex Samples

[Method 107A added by 47 FR 39486, September 8, 1982]

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) or by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Applicability and Principle

1.1 Applicability. This is an alternative method and applies to the measurement of the vinyl chloride content of solvents, resin solvent solutions, polyvinyl chloride (PVC) resin, wet cake slurries, latex, and fabricated resin samples. This method is not acceptable where methods from Section 304(h) of the Clean Water Act, 33 U.S.C. 1251 et seq., (the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.2 Principle. The basis for this method lies in the direct injection of a liquid sample into a chromatograph and the subsequent evaporation of all volatile material into the carrier gas stream of the chromatograph, thus permitting analysis of all volatile material including vinyl chloride.

2. Range and Sensitivity

The lower limit of detection of vinyl chloride in dry PVC resin is 0.2 ppm. For resin solutions, latexes, and wet resin, this limit rises inversely as the nonvolatile (resin) content decreases.

With proper calibration, the upper limit may be extended as needed.

3. Interferences

The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride. In cases where resolution interferences are encountered, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis problem, subject to the approval of the Administrator. Approval

is automatic, provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

4. Precision and Reproducibility

A standard sample of latex containing 181.3 ppm vinyl chloride analyzed 10 times by the alternative method showed a standard deviation of 7.5 percent and a mean error of 0.21 percent.

A sample of vinyl chloride copolymer resin solution was analyzed 10 times by the alternative method and showed a standard deviation of 5.6 percent at a level of 35 ppm.

5. Safety

Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with vinyl chloride monomer (VCM) air mixtures must be held to minimum. When purging is required, the vapor must be routed to outside air. Vinyl chloride, even at low-ppm levels, must never be vented inside the laboratory.

6. Apparatus

6.1 Sampling. The following equipment is required:

6.1.1 Glass Bottles. 16-oz wide mouth with polyethylene-lined, screw-on tops.

6.1.2 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

6.2.1 Glass Vials. 20-ml capacity with polycone screw caps.

6.2.2 Analytical Balance. Capable of weighing to ±0.01 gram.

6.2.3 Syringe. 50-microliter size, with removable needle.

6.2.4 Fritted Glass Sparger. Fine porosity.

6.2.5 Aluminum Weighing Dishes.

6.2.6 Sample Roller or Shaker. To help dissolve sample.

6.3 Analysis. The following equipment is required:

6.3.1 Gas Chromatograph. Hewlett Packard Model 5720A or equivalent.

6.3.2 Chromatograph Column. Stainless steel, 6.1 m by 3.2 mm, packed with 20 percent Tergitol E-35 on Chromosorb W AW 60/80 mesh. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and that he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interfering peak. Calculation of area overlap is explained in Apendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.")

6.3.3 Valco Instrument Six-Port Rotary Valve. For column back flush.

6.3.4 Septa. For chromatograph injection port.

6.3.5 Injection Port Liners. For chromatograph used.

6.3.6 Regulators. For required gas cylinders.

6.3.7 Soap Film Flowmeter. Hewlett Packard No. 0101-0113 or equivalent.

6.4 Calibration. The following equipment is required:

6.4.1 Analytical Balance. Capable of weighing to ±0.0001 g.

6.4.2 Erlenmeyer Flask With Glass Stopper. 125 ml.

6.4.3 Pipets. 0.1, 0.5, 1, 5, 10, and 50 ml.

6.4.4 Volumetric Flasks. 10 and 100 ml.

7. Reagents

Use only reagents that are of chromatograph grade.

7.1 Analysis. The following items are required:

7.1.1 Hydrogen Gas. Zero grade.

7.1.2 Nitrogen Gas. Zero grade.

7.1.3 Air. Zero grade.

7.1.4 Tetrahydrofuran (THF). Reagent grade.

Analyze the THF by injecting 10 microliters into the prepared gas chromatograph. Compare the THF chromatogram with that shown in Figure 107A-1. If the chromatogram is comparable to A, the THF should be sparged with pure nitrogen for approximately 2 hours using the fritted glass sparger to attempt to remove the interfering peak. Reanalyze the sparged THF to determine whether the THF is acceptable for use. If the scan is comparable to B, the THF should be acceptable for use in the analysis.

7.1.5 N, N-Dimethylacetamide (DMAC). Spectrographic grade. For use in place of THF.

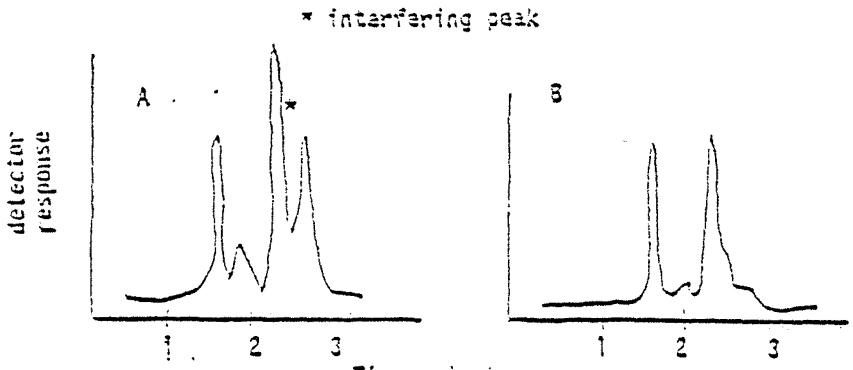


Figure 107A-1

7.2 Calibration. The following item is required:

7.2.1 Vinyl Chloride 99.9 Percent. Ideal Gas Products lecture bottle, or equivalent. For preparation of standard solutions.

8. Procedure

8.1 Sampling. Allow the liquid or dried resin to flow from a tap on the tank, silo, or pipeline until the tap has been purged. Fill a wide-mouth pint bottle, and immediately tightly cap the bottle. Place an identifying label on each bottle and record the date, time, sample location, and material.

8.2 Sample Treatment. Sample must be run within 24 hours.

8.2.1 Resin Samples. Weigh 9.00 ± 0.01 g of THF or DMAC in a tared 20-ml vial. Add 1.00 ± 0.01 g of resin to the tared vial containing the THF or DMAC. Close the vial tightly with the screw cap, and shake or otherwise agitate the vial until complete solution of the resin is obtained. Shaking may require several minutes to several hours, depending on the nature of the resin.

8.2.2 Suspension Resin Slurry and Wet Resin Sample. Slurry must be filtered using a small Buchner funnel with vacuum to yield a wet resin sample. The filtering process must be continued only as long as a steady stream of water is exiting from the funnel. Excessive filtration time could result in some loss of VCM. The wet resin sample is weighed into a tared 20-ml vial with THF or DMAC as described earlier for resin samples (8.2.1) and treated the same as the resin sample. A sample of the wet resin is used to determine total solids as required for calculating the residual VCM (Section 8.3.4).

8.2.3 Latex and Resin Solvent Solutions. Samples must be thoroughly mixed. Weigh 1.00 ± 0.01 g of the latex or resin-solvent solution into a 20-ml vial containing 9.00 ± 0.01 g of THF or DMAC as for the resin samples (8.2.1). Cap and shake until complete solution is obtained. Determine the total solids of the latex or resin solution sample (Section 8.3.4).

8.2.4 Solvents and Non-viscous Liquid Samples. No preparation of these samples is required. The neat samples are injected directly into the GC.

8.3 Analysis.

8.3.1 Preparation of GC. Install the chromatographic column, and condition overnight at 70° C. Do not connect the exit end of the column to the detector while conditioning.

8.3.1.1 Flow Rate Adjustments. Adjust the flow rate as follows:

a. Nitrogen Carrier Gas. Set regulator on cylinder to read 60 psig. Set column flow controller on the chromatograph using the soap film flowmeter to yield a flow rate of 40 cc/min.

b. Burner Air Supply. Set regulator on the cylinder at 40 psig. Set regulator on the chromatograph to supply air to the burner to yield a flow rate of 250 to 300 cc/min using the flowmeter.

c. Hydrogen. Set regulator on cylinder to read 60 psig. Set regulator on the chromatograph to supply 30 to 40 cc/min using the flowmeter. Optimize hydrogen flow

to yield the most sensitive detector response without extinguishing the flame. Check flow with flowmeter and record this flow.

d. Nitrogen Back Flush Gas. Set regulator on the chromatograph using the soap film flowmeter to yield a flow rate of 40 cc/min.

8.3.1.2 Temperature Adjustments. Set temperature as follows:

a. Oven (chromatographic column) at 70° C.

b. Injection Port at 100° C.

c. Detector at 300° C.

8.3.1.3 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions. Allow system to stabilize approximately 1 hour.

8.3.1.4 Recorder. Set pen at zero and start chart drive.

8.3.1.5 Attenuation. Set attenuation to yield desired peak height depending on sample VCM content.

8.3.2 Chromatographic Analyses.

a. Sample Injection. Remove needle from 50-microliter syringe. Open sample vial and draw 50-microliters of THF or DMAC sample recovery solution into the syringe. Recap sample vial. Attach needle to the syringe and while holding the syringe vertically (needle uppermost), eject 40 microliters into an absorbent tissue. Wipe needle with tissue. Now inject 10 microliters into chromatograph system. Repeat the injection until two consecutive values for the height of the vinyl chloride peak do not vary more than 5 percent. Use the average value for these two peak heights to compute the sample concentration.

b. Back Flush. After 4 minutes has elapsed after sample injection, actuate the back flush valve to purge the first 4 feet of the chromatographic column of solvent and other high boilers.

c. Sample Data. Record on the chromatogram strip chart the data from the sample label.

d. Elution Time. Vinyl chloride elutes at 2.8 minutes. Acetaldehyde elutes at 3.7 minutes. Analysis is considered complete when chart pen becomes stable. After 5 minutes, reset back flush valve and inject next sample.

8.3.3 Chromatograph Servicing.

a. Septum. Replace after five sample injections.

b. Sample Port Liner. Replace the sample port liner with a clean spare after five sample injections.

c. Chromatograph Shutdown. If the chromatograph has been shut down overnight, rerun one or more samples from the preceding day to test stability and precision prior to starting on the current day's work.

8.3.4 Determination of Total Solids (TS). For wet resin, resin solution, and PVC latex samples, determine the TS for each sample by accurately weighing approximately 3 to 5 grams of sample into a tared aluminum pan. The initial procedure is as follows:

a. Where water is the major volatile component: Tare the weighing dish, and add 3 to 5 grams of sample to the dish. Weigh to the nearest milligram.

b. Where volatile solvent is the major volatile component: Transfer a portion of the sample to a 20-ml screw cap vial and cap immediately. Weigh the vial to the nearest milligram. Uncap the vial and transfer a 3- to 5-gram portion of the sample to a tared aluminum weighing dish. Recap the vial and reweigh to the nearest milligram. The vial weight loss is the sample weight.

To continue, now place the weighing pan in a 130° C oven for 1 hour. Remove the dish and allow to cool to room temperature in a desiccator. Weigh the pan to the nearest 0.1 mg. Total solids is the weight of material in the aluminum pan after heating divided by the net weight of sample added to the pan originally times 100.

9. *Calibration of the Chromatograph*

9.1 Preparation of Standards. Prepare a 1 percent by weight (approximate) solution of vinyl chloride in THF or DMAC by bubbling vinyl chloride gas from a cylinder into a tared 125-ml glass-stoppered flask containing THF or DMAC. The weight of vinyl chloride to be added should be calculated prior to this operation, i.e., 1 percent of the weight of THF or DMAC contained in the tared flask. This must be carried out in a laboratory hood. Adjust the vinyl chloride flow from the cylinder so that the vinyl chloride dissolves essentially completely in the THF or DMAC and is not blown to the atmosphere. Take particular care not to volatize any of the solution. Stopper the flask and swirl the solution to effect complete mixing. Weigh the stoppered flask to nearest 0.1 mg to determine the exact amount of vinyl chloride added.

Pipet 10 ml of the approximately 1 percent solution into a 100-ml glass-stoppered volumetric flask, and add THF or DMAC to fill to the mark. Cap the flask and invert 10 to 20 times. This solution contains approximately 1,000 ppm by weight of vinyl chloride (note the exact concentration).

Pipet 50-, 10-, 5-, 1-, 0.5-, and 0.1-ml aliquots of the approximately 1,000 ppm solution into 10 ml glass stoppered volumetric flasks.

Dilute to the mark with THF or DMAC, cap the flasks and invert each 10 to 20 times. These solutions contain approximately 500, 100, 50, 10, 5, and 1 ppm vinyl chloride. Note the exact concentration of each one. These standards are to be kept under refrigeration in stoppered bottles, and must be renewed every 3 months.

9.2 Preparation of Chromatograph Calibration Curve.

Obtain the GC for each of the six final solutions prepared in Section 9.1 by using the procedure in Section 8.3.2. Prepare a chart plotting peak height obtained from the chromatogram of each solution versus the known concentration. Draw a straight line through the points derived by the least squares methods.

10. *Calculations*

10.1 Response Factor. From the calibration curve described in Section 9.2, select the value of C_{vc} that corresponds to H_s for each sample. Compute the response factor, R_s, for each sample as follows:

$$R_s = \frac{C_{vc}}{H_s} \qquad \text{Eq. 107A-1}$$

10.2 Residual vinyl chloride monomer concentration (C_{vc}) or vinyl chloride monomer concentration in resin:

$$C_{vc} = 10 H_s R_s \qquad \text{Eq. 107A-2}$$

Where:

H_s = Peak height of sample, mm.

R_s = Chromatograph response factor.

10.3 Samples containing volatile material, i.e., resin solutions, wet resin, and latexes:

$$C_{vc} = \frac{H_s R_s (1{,}000)}{TS} \qquad \text{Eq. 107A-3}$$

10.4 Samples of solvents and in process wastewater:

$$C_{vc} = \frac{H_s R_s}{0.888} \qquad \text{Eq. 107A-4}$$

Where:

0.888 = Specific gravity of THF.

11. *Bibliography*

1. Communication from R. N. Wheeler, Jr., Union Carbide Corporation. Part 61 National Emissions Standards for Hazardous Air Pollutants Appendix B. Method 107—Alternate Method. September 19, 1977.

Appendix C.—Quality Assurance Procedures

[Appendix C added by 47 FR 39170, September 7, 1982]

Procedure 1.—Determination of Adequate Chromatographic Peak Resolution

In this method of dealing with resolution, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from -2σ to -2σ. This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two peaks are separated by a known distance, b, one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compound overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over the limits $b-2\sigma_s$ to $b-2\sigma_s$, where σ_s is the standard deviation of the sample curve.

This calculation can be simplified in several ways. Overlap can be determined for curves of unit area; then actual areas can be introduced. Desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 in Texas Instruments Program Manual ST1, 1975, Texas Instruments, Inc., Dallas, Texas 75222.

In judging the suitability of alternate GC columns or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymmetric. In cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, it may be possible to define an effective width for t_s as "twice the distance from the leading edge to a perpendicular line through the maxim of the contaminant curve, measured along a perpendicular bisection of that line."

$$\frac{1}{\sqrt{2\pi}\sigma_c}\int_{b-2\sigma_s}^{b+2\sigma_s} e^{\left(\frac{-t_c^2}{2\sigma_c}\right)}dt = \frac{1}{\sqrt{2\pi}}\int_{\frac{b-2\sigma_s}{\sigma_c}}^{\infty} e^{\left(\frac{-x^2}{2}\right)}dx - \frac{1}{\sqrt{2\pi}}\int_{\frac{b+2\sigma_s}{\sigma_c}}^{\infty} e^{\left(\frac{-x^2}{2}\right)}dx$$

The following calculation steps are required:*

1. $2\sigma_s = t_s/\sqrt{2 \ln 2}$
2. $\sigma_c = t_c/2\sqrt{2 \ln 2}$
3. $x_1 = (b-2\sigma_s)/\sigma_c$
4. $x_2 = (b+2\sigma_s)/\sigma_c$
5. $Q(x_1) = \frac{1}{\sqrt{2\pi}}\int_{x_1}^{\infty} e^{\left(\frac{-x^2}{2}\right)}dx$
6. $Q(x_2) = \frac{1}{\sqrt{2\pi}}\int_{x_2}^{\infty} e^{\left(\frac{-x^2}{2}\right)}dx$
7. $I_o = Q(x_1) - Q(x_2)$
8. $A_o = I_o A_c/A_s$
9. Percentage overlap = $A_o \times 100$,

where:

A_s = Area of the sample peak of interest determined by electronic integration or by the formula $A_s = h_s t_s$.

A_c = Area of the contaminant peak, determined in the same manner as A_s.

b = Distance on the chromatographic chart that separates the maxima of the two peaks.

H_s = Peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.

t_s = Width of sample peak of interest at 1/2 peak height.

t_c = Width of the contaminant peak at 1/2 of peak height.

σ_s = Standard deviation of the sample compound of interest elution curve.

σ_c = Standard deviation of the contaminant elution curve.

$Q(x_1)$ = Integral of the normal distribution function from x_1 to infinity.

$Q(x_2)$ = Integral of the normal distribution function from x_2 to infinity.

I_o = Overlap integral.

A_o = Area overlap fraction.

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*In most instances, $Q(x_2)$ is very small and may be neglected.

Procedure 2—Procedure for Field Auditing GC Analysis

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

A. The audit supervisor verifies that audit cylinders are stored in a safe location both before and after the audit to prevent vandalism.

B. At the beginning and conclusion of the audit, the analyst records each cylinder number and pressure. An audit cylinder is never analyzed when the pressure drops below 200 psi.

C. During the audit, the analyst performs a minimum of two consecutive analyses of each audit cylinder gas. The audit must be conducted to coincide with the analysis of source test samples, normally immediately after GC calibration and prior to sample analyses.

D. At the end of audit analyses, the audit supervisor requests the calculated concentrations from the analyst and compares the results with the actual audit concentrations. If each measured concentration agrees with the respective actual concentration within ±10 percent, he directs the analyst to begin analyzing source samples. Audit supervisor judgment and/or supervisory policy determine action when agreement is not within ±10 percent. When a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analysis, with a corrective factor to be applied to the results at a later time. However, every attempt should be made to locate the cause of the discrepancy, as it may be misleading. The audit supervisor records each cylinder number, cylinder pressure (at the end of the audit), and all calculated concentrations. The individual being audited must not under any circumstance be told actual audit concentrations until calculated concentrations have been submitted to the audit supervisor.

Field Audit Report

Part A.—To be filled out by organization supplying audit cylinders.

1. Organization supplying audit sample(s) and shipping address

2. Audit supervisor, organization, and phone number

3. Shipping instructions: Name, Address, Attention

4. Guaranteed arrival date for cylinders———

5. Planned shipping date for cylinders———

6. Details on audit cylinders from last analysis

	Low conc.	High conc.
a. Date of last analysis		
b. Cylinder number		
c. Cylinder pressure, psi		
d. Audit gas(es)/balance gas		
e. Audit gas(es), ppm		
f. Cylinder construction		

Part B.—To be filled out by audit supervisor.

1. Process sampled———

2. Audit location———

3. Name of individual audit———

4. Audit date———

5. Audit results:

	Low conc. cylinder	High conc. cylinder
a. Cylinder number		
b. Cylinder pressure before audit, psi		
c. Cylinder pressure after audit, psi		
d. Measured concentration, ppm Injection #1* Injection #2* Average		
e. Actual audit concentration, ppm (Part A, 5e)		
f. Audit accuracy:[1] Low Conc. Cylinder		
High Conc. Cylinder		

$$\text{Percent accuracy} = \frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$$

g. Problems detected (if any)

[1] Results of two consecutive injections that meet the sample analysis criteria of the test method.

A.G. RULE NO: 83-111

OPEN BURNING GUIDELINES

FOR

AIR POLLUTION CONTROL

Arizona Department of Health Services

Division of Environmental Health Services

Bureau of Air Quality Control

OPEN BURNING GUIDELINES

FOR

AIR POLLUTION CONTROL

Revision Control Record

Revision	Date	Section	Description of Revision
N/C	4-27-83	All	Issued.
A	6-2-83	2.0	Revised ¶2.2 to reduce size of openings.
		3.0	Deleted reference to BWC, ADHS in ¶3.2.6.
		4.0	Added ¶4.1.3 to allow use of suitably designed smoke generator for wind drift indicators by aerial applicators.
		5.0	Added ¶5.1.1 to exclude delegation for open burning in sanitary landfills

OPEN BURNING GUIDELINES

FOR

AIR POLLUTION CONTROL

1.0 General

Open burning is prohibited in Arizona except for certain necessary or beneficial purposes defined in the law. The Director of the Department of Health Services (ADHS) or the local (air pollution) control officer must approve the manner and time of setting such fires so that adverse air quality is precluded or minimized to acceptable levels. These guidelines describe the limitations or controls imposed to assure that adverse public health and welfare effects of air pollution from open burning should not occur, and supplement the limitations on open burning by other authorities which are intended to protect the public safety.

1.1 Authority

A.R.S. § 36-789, Unlawful Open Burning: Exceptions: Violation: Classification. Defines the fires that are excepted from the prohibition against open burning and sets forth the requirement that the setting of permitted fires "be conducted in a manner and at such time as approved by the control officer or the Director of the Department of Health Services." A copy of this section of this statute is provided in Appendix A. along with a copy of the applicable regulations in Appendix B.

1.2 Applicability

These guidelines apply in the counties where the Director of ADHS has jurisdiction in matters relating to air pollution control. These are Apache, Cochise, Mohave, Navajo, Santa Cruz, and Yavapai Counties, and

will also include La Paz County on open burning matters until a local air pollution control program is implemented. The guidelines do not apply to open burning for forestry management which is controlled under another section of the regulations, or open burning by State permitted sources which is controlled by operating permit conditions when applicable.

2.0 Definitions

2.1 "Officer" or "Public Officer" is defined in Arizona Statutes, Chapter 1, Section 38-101 as "the incumbent of any office, member of any board or commission, or his deputy or assistant exercising the powers and duties of the officer, other than clerks or mere employees of the officer."

2.2 "Approved waste burner" - an incinerator constructed of fire resistant material, with a cover or screen which is closed when in use and openings in the top or sides no greater than one-half inch in diameter or heavy wire mesh spacing. A 55 gallon drum with the above modification is acceptable.

2.3 "Garbage" - discarded material resulting from the processing, storage, serving or consumption of food.

2.4 "Open burning" - the burning of any material that results in emissions directly to the atmosphere without passing through a stack, duct or chimney.

2.5 "Refuse collection service" - a public or private operation engaged in solid waste collection, transportation, and disposal in an approved sanitary landfill.

2.6 "Rubbish" - nonputrescible solid waste such as paper, cardboard, yard clippings, and other natural material not including garbage.

2.7 "Incorporated area" - a town, city or subdivision that is legally incorporated.

2.8 "Air Pollution Emergency Episodes" - Air pollution Alerts, Warnings, or Emergencies declared during adverse dispersion conditions as defined in Appendix C.

3.0 Allowable Open Burning

3.1 Burn Permit Not Required

Fires used only for cooking of food or for providing warmth for human beings or for recreational purposes or the branding of animals or the use of orchard heaters for the purpose of frost protection in farming or nursery operations do not require a Burn Permit. Such fires may be set in the manner and at the time suitable for the intended purpose, except that certain fires may be prohibited during air pollution emergency episodes.

3.2 Burn Permit Required

The following fires require a Burn Permit from the Director or the local air pollution control officer or his designee and must be conducted in the manner and at the time(s) authorized unless doing so would defeat the purpose of the fire.

3.2.1 Any fire set or permitted by any public officer in the performance of official duty, if such fire is set or permission given for the purpose of weed abatement, the prevention of a fire hazard, or instruction in the methods of fighting fires.

3.2.2 Fires set by or permitted by the State entomologist or county agricultural agents of the county for the purpose of disease and pest prevention.

3.2.3 Fires set by or permitted by the Federal Government or any of its departments, agencies or agents, the State or any of its agencies, departments or political subdivisions, for the purpose of watershed rehabilitation or control through vegetative manipulation.

3.2.4 Fires set for the disposal of dangerous materials or materials that can be defined as a hazardous waste in A.C.R.R. R9-8-1800 where there is no safe alternative method of disposal.

3.2.5 Fires for the disposal of ordinary household rubbish in an approved waste burner in non-urban areas of less than 100 well spread out dwelling units per square mile where no refuse collection and disposal service is available.

3.2.6 Segregated and controlled fires for the disposal of clean combustible materials in approved sanitary landfills.

3.2.7 Fires for the disposal of suitably prepared and combustible empty pesticide containers, also in accordance with conditions and limitations for container disposal as specified on the pesticide container label.

4.0 Limitations on Open Burning

4.1 Materials To Be Burned

4.1.1 Open burning of the following materials is forbidden: garbage resulting from the processing, storage, serving or consumption of food; asphalt shingles; tar paper; plastic and rubber products (such as tires and electrical wire insulation); landscape clippings which generate

noxious or toxic fumes as products of combustion; waste petroleum products (such as waste crankcase oil, transmission oil and oil filters); transformer oils; and, hazardous material containers including those that contained inorganic pesticides, lead, cadmium, mercury, or arsenic compounds. A partial listing of materials which can generate noxious or toxic fumes is provided in Appendix D. This list will be updated as additional information becomes available.

4.1.2 Waste petroleum oils burned for the purpose of training for fire fighting is exempted from the prohibition noted above.

4.1.3 Aerial applicators may use smoke bombs or other types of smoke generators when required to indicate wind drift provided that the smoke generator can be extinguished or will be totally consumed at or within a limited period of time after the need for wind indication is satisfied. A smudge pot using a small portion of a tire and ignitor fluid is acceptable if the above noted provision is satisfied.

4.2 Preparation for Burning

4.2.1 Material to be burned shall be readily combustible and piled, collected in a pit, or placed in an approved waste burner in such quantity that the material will be completely consumed within the permitted burn hours.

4.2.2 Piled material or material collected in a pit for burning shall be located not less than 50 feet from any structure. Material contained in an approved waste burner shall be located not less than 15 feet from any structure. A buffer zone or other adequate provisions to prevent the fire from spreading to within 50 feet of any structure shall be prepared.

4.2.3 A water hose connected to a water supply or other fire-extinguishing equipment readily available for use shall be provided.

4.2.4 Material to be burned at sanitary landfills shall be totally segregated from other refuse and collected in a pit so that the material will be consumed within the permitted burn hours. The use of equipment such as an air curtain destructor is recommended to expedite the burn and to prevent smoke and fly ash emissions associated with unaided open burning.

4.2.5 The maximum quantity of those empty pesticide containers which may be burned shall not exceed 50 pounds empty weight at any site in one day. Such burning shall not be conducted within one quarter mile upwind of any populated area.

4.3 Time for Burning

Unless doing so would defeat the purpose of the fire, all permitted open burning covered by these guidelines shall be conducted during the following time periods:

April through September	9:00 AM to 4:00 PM
October and March	9:00 AM to 3:00 PM
November through February	10:00 AM to 2:00 PM

4.4 Conditions for Burning

4.4.1 No fire shall be ignited during any air pollution emergency episode in effect in the area of the burn, or during periods when smoke can be expected to accumulate to the extent that it will significantly impair visibility. Such visibility impairment can be anticipated during periods of heavy regional haze and/or calm wind conditions.

4.4.2 The fire shall be attended at all times until it is completely extinguished.

4.4.3 Burning shall be conducted only during wind conditions which prevent dispersion of smoke into populated areas, visibility impairment on travelled roads or airports to the extent that a safety hazard results, or otherwise create a public nuisance, and do not cause uncontrollable spreading of the fire.

4.4.4 The local fire fighting agency shall be notified prior to the setting of the fire. Such agency may prohibit open burning when atmospheric conditions or local circumstances make such fires hazardous.

ARIZONA D. RTMENT OF HEALTH SERVICES
Division of Environmental Health Services
Bureau of Air Quality Control
1740 West Adams Street
Phoenix, Arizona 85007

Air Pollution
Report No. _____

Complainant _____ Phone _____

Address _____

Type: Open Burning /_/ Fugitive Dust /_/ Odors /_/ Fumes /_/

_____ Emissions /_/ Other _____ /_/

Source _____

Address _____

Description _____

Received by _____ Phone /_/ Letter /_/ Date _____ Time _____

Referred to _____ Date _____

Action by Department _____

Response Reference _____

cc: Engineering /_/ NRO /_/
Compliance /_/ SRO /_/

DHS/AQC-005 (6/77)

4.4.5 An open burning permit shall be subject to revocation if emissions from the permitted fires create excessive air pollution, a public nuisance or a safety hazard.

5.0 Delegation of Authority for Issuance of Open Burning Permits

5.1 The Director of the Department of Health Services may delegate the authority for the issuance of open burning permits to local fire fighting agencies in those areas of the state where the Director has jurisdiction in matters related to air pollution control. In applying for the delegation of such authority, the local agency must certify that it will abide by the limitations contained in these guidelines. In addition the agency shall be responsible for the enforcement of these open burning limitations in the area of its jurisdiction and shall report any violations of the air pollution regulations on open burning to the Department.

5.1.1 Authority for the issuance of permits for open burning in sanitary landfills will not be delegated. Such permits will only be issued upon the submittal of an acceptable burn plan to the Bureau of Air Quality Control, ADHS and with the concurrence of the Chief, Bureau of Waste Control, ADHS.

5.2 Permit issuing authorities shall provide the Director with a telephone number to facilitate notification by the Director that open burning shall be extinguished in the event that an air pollution problem occurs.

5.3 Records of the authorized local agency relating to open burning permits shall be subject to review by authorized representatives of the Director.

5.4 Retention of a copy of all burn permits issued in the prior two years by the agency delegated such authority by the Director is deemed to satisfy the requirement at ARS 36-789.D. that a copy of such permits be immediately submitted to the Director.

6.0 Application and Permit Requirements

Suggested formats for applications for open burning permits and an open burning permit are provided in Appendices E and F. Those entries denoted by an asterisk are required to assure conformance to air pollution control requirements.

7.0 Liability

Approval to conduct open burning does not excuse a person from the consequences, damages, or injuries which may result from said burning.

8.0 Conflicting Laws and Regulations

Nothing in these guidelines should be construed to allow open burning in those areas or under such conditions that may be prohibited by other laws, regulations or ordinances.

APPENDIX A

§ 36-789. Unlawful open burning; exceptions; violation; classification

A. Notwithstanding the provisions of any other section of this article, it is unlawful for any person to ignite, cause to be ignited, permit to be ignited, or suffer, allow, or maintain any open outdoor fire except as provided in this section.

B. "Open outdoor fire", as used in this section, means any combustion of combustible material of any type outdoors, in the open where the products of combustion are not directed through a flue. "Flue", as used in this section, means any duct or passage for air, gases or the like, such as a stack or chimney.

C. The following fires are excepted from the provisions of this section:

1. Fires used only for cooking of foods or for providing warmth for human beings or for recreational purposes or the branding of animals or the use of orchard heaters for the purpose of frost protection in farming or nursery operations.

2. Any fire set or permitted by any public officer in the performance of official duty, if such fire is set or permission given for the purpose of weed abatement, the prevention of a fire hazard, or instruction in the methods of fighting fires.

3. Fires set by or permitted by the state entomologist or county agricultural agents of the county for the purpose of disease and pest prevention.

4. Fires set by or permitted by the federal government or any of its departments, agencies or agents, the state or any of its agencies, departments or political subdivisions, for the purpose of watershed rehabilitation or control through vegetative manipulation.

5. Fires permitted by any rule or regulation issued pursuant to this article, by any conditional permit issued by a hearing board established under this article or by any rule, regulation or conditional permit issued pursuant to title 36, chapter 14, article 1[1] when the department of health services pursuant to section 36-1706 has assumed jurisdiction of the county in which the fire is located.

6. Fires set for the disposal of dangerous materials where there is no safe alternate method of disposal.

D. Permission for the setting of any fire given by a public officer in the performance of official duty under paragraph 2, 3 or 4 of subsection C shall be given in writing and a copy of such written permission shall be transmitted immediately to the director of the department of health services and the control officer of the county, district or region in which such fire is allowed. The setting of any such fire shall be conducted in a manner and at such time as approved by the control officer or the director of the department of health services, unless doing so would defeat the purpose of the exemption.

E. Nothing in this section is intended to permit any practice which is a violation of any statute, ordinance, rule or regulation.

F. A person who violates any provision of this section may be served a notice of violation and be subject to the enforcement provisions of this article to the same extent as a person violating any rule or regulation adopted pursuant to this article.

G. Any violation of this section shall be a petty offense.

Amended by Laws 1978, Ch. 201, § 620, eff. Oct. 1, 1978.

[1]Section 36-1700 et seq.

R9-3-402. Unlawful open burning

A. Notwithstanding the provisions of any other Regulation in this Chapter, it is unlawful for any person to ignite, cause to be ignited, permit to be ignited, or suffer, allow or maintain any open outdoor fire.

B. "Open outdoor fire", as used in this Regulation, means any combustion of combustible material of any type outdoors, in the open where the products of combustion are not directed through a flue. "Flue", as used in this Regulation, means any duct or passage for air, gases or the like, such as a stack or chimney.

C. The following fires are excepted from the provisions of this Regulation:

1. Fires used only for cooking of food or for providing warmth for human beings or for recreational purposes or the branding of animals or the use of orchard heaters for the purpose of frost protection in farming or nursery operations.

2. Any fire set or permitted by any public officer in the performance of official duty, if such fire is set or permission given for the purpose of weed abatement, the prevention of a fire hazard, or instruction in the methods of fighting fires.

3. Fires set by or permitted by the State entomologist or county agricultural agents of the county for the purpose of disease and pest prevention.

4. Fires set by or permitted by the Federal government or any of its departments, agencies or agents, the State or any of its agencies, departments or political subdivisions, for the purpose of watershed rehabilitation or control through vegetative manipulation.

5. Fires set for the disposal of dangerous materials where there is no safe alternative method of disposal.

D. Permission for the setting of any fire given by a public officer in the performance of official duty under Paragraphs 2., 3. or 4. of Subsection C., shall be given, in writing, and a copy of such written permission shall be transmitted immediately to the Director of the Department of Health Services and the control officer, if any, of the county, district or region in which such fire is allowed. The setting of any such fire shall be conducted in a manner and at such time as approved by the Director, unless doing so would defeat the purpose of the exemption.

E. Nothing in this Regulation is intended to permit any practice which is a violation of any statute, ordinance, Rule or Regulation.

Historical Note

Amended eff. Aug. 6, 1976 (Supp. 76-4); Former Section R9-3-402 repealed, new Section R9-3-402 adopted eff. May 14, 1979 (Supp. 79-1).

R9-3-219. Air pollution emergency episodes

A. Procedures shall be implemented by the Director in order to prevent the occurrence of ambient air pollutant concentrations which would cause significant harm to the health of persons. These concentrations are listed in the table at the end of this Section.

B. The following stages are identified by air quality criteria in order to provide for sequential emissions reductions, public notification and increased Department monitoring and forecast responsibilities. The declaration of any stage, and the area of the State affected, shall be based on air quality measurements and meteorological analysis and forecast. The procedures and actions required for each stage are described in the current edition of the Department's Manual entitled "Procedures for Prevention of Emergency Episodes".

1. STAGE I — ALERT. An air pollution alert shall be declared when any of the alert level concentrations listed in the table at the end of this Section are exceeded at any monitoring site and when meteorological conditions indicate that there will be a continuance or recurrence of alert level concentrations for the same pollutant(s) during the subsequent 24-hour period. If, 48 hours after an alert has been initially declared, air pollution concentrations and meteorological conditions do not improve, the warning stage control actions shall be implemented but no warning shall be declared, unless air quality has deteriorated to the extent described in B.2. below.

2. STAGE II — WARNING. An air pollution warning shall be declared when any of the warning level concentrations listed in the table at the end of this Section are exceeded at any monitoring site and when meteorological conditions indicate that there will be a continuance or recurrence of concentrations of the same pollutant(s) exceeding the warning level during the subsequent 24-hour period. If, 48 hours after a warning has been initially declared, air pollution concentrations and meteorological conditions do not improve, the emergency stage shall be declared and its control actions implemented.

3. STAGE III — EMERGENCY. An air pollution emergency shall be declared when any of the emergency level concentrations listed in the table at the end of this Section are exceeded at any monitoring site and when meteorological conditions indicate that there will be a continuance or recurrence of concentrations of the same pollutant(s) exceeding the emergency level during the subsequent 24-hour period.

4. Summary of emergency episode and significant harm levels

Pollutant	Averaging Time	Alert	Warning	Emergency	Significant Harm
Carbon monoxide	1-hr	—	—	—	144
	4-hr	—	—	—	86.3
	8-hr	17	34	46	57.5
Nitrogen dioxide	1-hr	1,130	2,260	3,000	3,750
	24-hr	282	565	750	938
Ozone	1-hr	.2	.4	.5	.6
Particulates	24-hr	375	625	875	1,000
Sulfur dioxide	24-hr	800	1,600	2,100	2,620
Sulfur dioxide and particules combined	24-hr	65,000	261,000	393,000	490,000

Note: Units are ug/m^3 except for carbon monoxide which has units of mg/m^3, sulfur dioxide and particulates combined which has units of $(ug/m^3)^2$, and ozone, which has units of parts per million (ppm).

Historical Note

Adopted eff. May 14, 1979 (Supp. 79-1). Editorial correction, Subsection B, Paragraph 2. (Supp. 80-1). Editorial correction, Subsection A. (Supp. 80-2). Former Section R9-3-219 repealed, new Section R9-3-219 adopted eff. May 28, 1982 (Supp. 82-3).

APPENDIX D

List of Materials Which Can Generate Noxious or Toxic Fumes or Products of Combustion

Plant materials

- Poison oak
- Poison ivy
- Poison sumac
- Oleander

Petroleum Products

- Crankcase oil
- Transmission oil or any other petroleum products
- Chlorinated hydrocarbons
- Asphalt shingles

Plastics and other synthetic materials

- Polyvinyl Chloride
- Polyester
- Polyurethane
- Polymide
- LOPAC or BAREX
- Urea Formaldehyde
- Polyethylene
- Polypropyleve
- Polystyrene

U.S. ADOT "Selected Hazardous Materials"

- Dimethyl Sulfate
- Acrolein
- Carbon Disulfide
- Ethyleneimine

Ethylene Oxide

Methyl Chloride

Vinyl Chloride

Empty Pesticide or Hazardous Material Containers that contained any of the following materials:

Inorganic Pesticides

Arsenic

Lead

Cadmium

Mercury

APPENDIX E

STATE OF ARIZONA

Open Burning Permit Application

*Burning Location - County _____

*Legal Description or Address _____

_____

_____

Material to be burned

*Type _____

_____

*Quantity of fuel _____

_____

*Anticipated duration _____

_____

*Purpose of burning _____

_____

Fire controls available _____

Nearest local fire department _____

Phone # _____

Proximity of nearby residences/businesses:

*Distance in miles or fraction of miles _____

(attach map or drawing)

*Applicant Name _____

*Address _____

*Phone # _____

_____

Signature

Additional Information

_____

_____

_____

_____

_____

APPENDIX F

STATE OF ARIZONA

Open Burning Permit

Permission to conduct open burning at the following location is granted by the Director of the Arizona Department of Health Services with the following limitations:

1. Burning of _____
(list fuels)*

_____

will take place at _____
(legal description)*

_____

between the hours of _____ for the period of
(day/time)*

_____. The responsible party,
(dates)*

_____
(name and phone #)*

will be present at all times during burning and is responsible for informing the local fire fighting agency _____
(RFD)

of all open burning activities.

*2. Burning in violation of any condition of this permit shall be punishable as a misdeameanor as provided in Arizona Revised Statutes § 36-739.01.

*3. In order to control air pollution problems as indicated by a reduction in visibility, or quality, or the registration of complaints, the Director, or his authorized representative, have the authority to order all burning to be extinguished by the Permittee.

*4. Open burning of the following materials is forbidden: garbage, asphalt shingles, tar paper, plastic and rubber products (such as tires and electrical wire insulation), waste petroleum products (such as waste crankcase oil, transmission oil & oil filters), hazardous material containers including those that contained inorganic pesticides, lead, cadmium, mercury, or arsenic compounds.

Signed _____

Agency _____

Date _____

Permit No. _____