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FINAL REVISED
SAMPLING AND ANALYSIS PLAN
DUTCH BOY SITE
CHICAGO, ILLINOIS

I.1

FINAL REVISED
SAMPLING AND ANALYSIS PLAN
DUTCH BOY SITE
CHICAGO, ILLINOIS

Prepared for
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Prepared by
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December 11, 1996

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EXECUTIVE SUMMARY

The Sampling and Analysis Plan (SAP) for the Dutch Boy site was prepared in fulfillment of the March 26, 1996 Unilateral Administrative Order issued by the U.S. EPA to NL Industries Inc. (NL). The Order requires NL to establish site security, conduct sampling, and address lead contamination at the site and in its vicinity.

The SAP outlines the sampling and analysis needed to identify the extent of soil lead contamination at and in the vicinity of this site. Quality assurance and quality control procedures to be followed for both the field and laboratory activities are also provided in the report. Data collected pursuant to the SAP will be reviewed with previously collected data from the site area to make conclusions regarding the extent of soil lead contamination.

Sampling locations and activities are discussed within the SAP. It is anticipated that over 400 environmental samples will be collected and analyzed during implementation of the program. On-site samples will be collected and analyzed for total lead. A subset of on-site soil samples will also be analyzed for volatile organic compounds and petroleum hydrocarbons (depending on the results of laboratory screening) and asbestos. Off-site sampling extends along eight radii, up to 1,600 feet away from the site. In addition, off-site sampling along the roadways (parkways) adjacent to the site is also proposed. All off-site samples will be analyzed for total lead. In order to institute the sampling program, access agreements are being obtained from property owners within the sampling area.

A second phase of sampling may be needed if the current plan does not define the extent of site-related contamination. After the sampling and analysis efforts are completed, an "Extent of Contamination" report will be submitted (planned to be sent March 1997).

I. INTRODUCTION

A. Background

On March 26, 1996, the United States Environmental Protection Agency (USEPA) issued a unilateral Administrative Order (Order) to NL Industries, Inc. (NL). The Order pertains to the property located at 12000 to 12054 South Peoria Street and 901 to 935 West 120th Street in Chicago, Illinois (the "Dutch Boy Site" or the "Site"). The Order requires NL to investigate Site related contamination and to conduct appropriate removal action activities. NL has retained ENVIRON International Corporation (ENVIRON) to implement the removal action requirements specified in the Order.

The scope of work to be performed is specified in Section V.3 of the Order. In fulfillment of Section V.3.1 and V.3.2 of the Order, ENVIRON submitted a draft Work Plan for USEPA approval for performing the removal activities set forth in the Order (the Removal Action Work Plan, "RAWP"). The draft RAWP provided a general discussion and schedule of the following major elements specified in Section V.3 of the Order:

- Site Security Plan
- Sampling and Analysis Plan
- Risk Management Plan.

In addition, requirements for Site health and safety, reporting, recordkeeping, and a preliminary project schedule were included in the RAWP. The draft RAWP was approved by USEPA on June 11, 1996.

B. Objectives and Scope

Consistent with the requirements specified in the Order, the SAP detailed herein is designed to: (1) identify the vertical and horizontal extent of on-Site soil contamination; (2) to determine the background concentrations of lead in soils in the vicinity of the Site; and (3) determine whether lead is present beyond the boundaries of the Site and the extent of such contamination. The results of the SAP will be used to establish a Site-related Extent of Contamination (EOC) survey. This information subsequently will be used in the design of an appropriate Risk Management Plan (RMP) for the Site.

C. Organization

The draft SAP is organized as follows:

- Chapter II. Site Description. This chapter includes a description of the Site's physical setting and local meteorological characteristics, describes the Site's operational history, summarizes previous investigations that have been conducted at the Site, and describes the currently known contamination present at the Site.

- Chapter III. Sampling and Analytical Work Plan. This chapter includes a discussion of the specific objectives of the sampling work plan proposed for the Site, a description of sampling locations, and a summary of sample identification, collection, and handling procedures to be employed in the field. Also included in this section is a description of the laboratory methods to be employed in the analysis of samples collected in the sampling program. Reference is also made to detailed quality assurance/quality control procedures to be employed by field personnel and the analytical laboratory to ensure that the data generated is useful to fulfill the SAP objectives. A comprehensive Quality Assurance Project Plan (QAPjP) is included herein as Appendix 1.

II. SITE DESCRIPTION

A. Site Setting

1. Physical Characteristics

The Dutch Boy Site ("the Site") is located at 12042 South Peoria Street in Chicago, Illinois (Cook County) (Figure II-1). The Site consists of a parcel of land approximately 5.2 acres in size, and is surrounded by industrial and warehouse buildings to the north and south, and vacant or abandoned lots to the east and west. The Illinois Central Gulf Railroad borders the Site to the south, and the Site is bounded on the north and east by 120th and Peoria Streets, respectively (Figure II-2). The nearest residences exist less than two blocks from the Site (approximately 600 feet to the south and 800 feet to the north). The Little Calumet River is located approximately 1.2 miles south of the Site, flows east, and eventually drains into Lake Michigan, located approximately 7.5 miles northeast of the Site. Land surface appears to slope gently to the south/southeast at the Site toward the Little Calumet.

At the present time, no buildings are present on-Site. The Mill Building, the last remaining structure, was demolished earlier this year although its basement still exists. The Site is mostly at ground surface or loading dock level. Approximately 75% of the Site is covered with concrete from former structures, and another 5% is paved with asphalt (See Figure II-2). The portion of the Site not covered with pavement or concrete consists primarily of a narrow strip containing a former railroad spur. The strip runs from north to south along the western edge of the property and diagonally across the property, extending to the southeast corner of the Site.

2. Climatic Data

The national weather station closest to the Site is located at Midway Airport, ten miles northwest of the Site. Figure II-3 is a wind rose for Midway Airport that shows the predominant wind direction is directly north, for all wind categories shown in the figure. The other primary wind vectors are in the southwest quadrant, with winds blowing to the northeast. Winds blow toward the northwest less than 5 percent of the

time, with wind speeds generally less than 15 mph. Average precipitation for the area is 38 inches per year.

B. Site Description

The Site was owned and operated from approximately 1906 to 1976 by NL Industries, Inc. (NL), and from 1976 to 1980 by the ARTRA Group, Inc., in the manufacture of lead-based paint. The Site has been inactive since that time. A series of Sanborn Maps (1939, 1950, and 1975) for the Site is included as Attachment 1 to this SAP. Site operations mainly consisted of the manufacture of white lead (i.e., lead carbonate) and lead oxide. Manufacturing operations occurred primarily in the northeast quadrant of the Site. According to Sanborn Maps and aerial photographs, building demolition on the Site occurred primarily in the early 1980s. By 1990, only the Mill Building remained at the Site. The Mill Building was demolished earlier this year.

Various industrial activities have been conducted in the immediate vicinity of the Site dating back to the early 1900s (Sanborn Maps 1911-1993). The West Pullman Car Works Co. occupied the property across S. Peoria Street to the east of the Site in 1911. By 1939, the northwest portion of this property was occupied by the Safety Vulcanizer Company, whose operations included an aluminum foundry and machine shop. These operations were no longer present in 1950. The remainder of this property was used primarily as a warehouse by Louis E. Emerman & Co., whose operations remained at the site until 1975. In 1975, the property was occupied by Caine Steel Co. By 1987, all buildings on this property had been demolished.

To the northeast of the Dutch Boy Site is a vacant lot that appears to have been used historically for storage. Presently, this property is used for vehicle and heavy equipment storage. The current occupant of the property was not identified on Sanborn Maps.

Immediately to the north, across 120th Street, is a property that by 1939 was occupied by the West Pullman Iron & Metal Company as a junkyard. This company's operations still exist at this property. The westernmost part of this property was occupied in 1939 by Neuswanger Coal Company as a coal yard. Neuswanger's operations were no longer present in 1975.

The property to the northwest has been occupied historically by the Ingersoll Steel Disc Division of Borg-Warner Corporation (Ingersoll). Ingersoll, whose historical operations included metal pressing, heat treating and finishing, electromelting, pickling, and foundry

operations, still occupies this property.

The adjacent property to the west of the Dutch Boy Site was historically occupied by International Harvester's (IH) West Pullman Works. Operations conducted by IH at this location included metal forging, heat treating, machining, and cleaning (see Sanborn Maps 1950, 1975). IH's buildings were demolished by 1987.

In 1911, the properties to the south and southeast of the Dutch Boy Site were occupied by Opaque Shade Cloth Co. & Chicago Bleachery. By 1939, these properties were occupied by Columbia Mills, Inc. for the manufacture of window shades and venetian blinds. Columbia's operations included sanding, painting, and bleaching. Between 1950 and 1987, Modern Steel Treating Co., Inc. had begun operations in the westernmost portion of this property. The historical buildings are still present on this property, many of which appear to be vacant.

In 1911, the property located to the southeast of the Dutch Boy Site housed an office and coal shed. By 1939, this property housed bulk oil storage facilities operated by The Texas Company. Between 1950 and 1975, Central States Pipe Company began warehouse operations on this property, which appear to still be present.

1. Potential On-Site Sources

Several potential sources of lead emissions existed at the Site. Specifically, manufacturing processes conducted at the Site produced airborne particulate emissions that were filtered through dust collectors (baghouses) prior to discharge to the atmosphere. Therefore, depending on the efficiency of the baghouses, some particulate emissions were likely associated with the operation of the facility. According to a report prepared by SAIC (1996), former workers at the facility indicated that the bags in the dust collectors malfunctioned (burned) at times and that other process equipment incurred spills and leaked dust at various times in the oxide plant. In addition, a potential source of airborne particulates would have been associated with building demolition activities. Building demolition activities were conducted by a previous owner (M&T) primarily in the early 1980s. One former worker described someone using an acetylene torch to cut up baghouse pipes that were encrusted with a white powder during demolition activities in 1986 (SAIC, 1996). The SAIC report noted, however, that standard (AP-42) emission factors are not applicable for the mechanical dismemberment of buildings, and that sufficient site-specific information is not

available to calculate emissions estimates from truck loading and transport activities typically associated with building demolition.

Finally, the facility had numerous storage areas and loading docks (as shown in Figure II-2), any of which could have been subject to periodic releases of lead-bearing raw materials or products to soil.

2. Potential Off-Site Sources

As described in Section II.B above, the land use surrounding the Site has been heavily industrial since the early part of this century. Moreover, the southeast Chicago area, within which the Site is located, has received considerable attention beginning in the 1980s because of the level of industrial activity in the area (USEPA, 1986). The area is one of the foremost locations for integrated steel production, chemical production of coatings and metal processing facilities. An air pollution inventory (USEPA, 1986) of a 65-kilometer square area including the Site listed about 193 facilities; 22 of which emitted 100 tons or more per year of a regulated air pollutant.

Under these circumstances, background concentrations of inorganic metals in the southeast Chicago area are expected to be elevated. Average concentrations of lead in surface soils have been summarized by USEPA (1995; Kabata-Pendias and Pendias, 1984) for different sites as follows:

- Metal processing industry; 500-6,500 mg/kg,
- Urban gardens and urban vicinity; 218-10,900 mg/kg,
- Roadside soil; 960-7,000 mg/kg.

Thus, background concentrations in this range may be expected in the area. An indication of site-specific background (i.e., natural plus non-site related anthropogenic) lead levels will be apparent from the off-site sampling program described in Section III.B.2 below.

3. Potential Sources - Conclusions

Based on the operational information discussed above, a review of historical Sanborn Maps (1911, 1939, 1950, 1975, 1987, 1990, 1993) and aerial photographs (1970, 1975, 1980, 1985, 1990, 1995), operations at the plant likely resulted in

airborne releases of lead. Furthermore, demolition activities in the 1980s would also have contributed to airborne and soil contamination of lead. Based on the prevailing wind direction and the nature and likely configuration of air emissions sources at the Site (i.e., low exit velocity, building vents on short stacks, demolition activities), the likely impact of lead emissions would be restricted to the Site, and any off-Site impact should be limited to the immediate vicinity of the Site in the northerly and possibly the northeasterly directions.

Given the historical industrial operations immediately adjacent to the Site, and the general nature of land use in the southeast Chicago area, background concentrations of lead (not Site-related) in this vicinity are expected to be elevated. The site-specific sampling to be conducted as described below will provide conclusive evidence as to whether the above preliminary observations actually apply in the vicinity of the Site.

C. Description of Site Contamination

1. Previous Site Investigations

Several investigations have been conducted at the Site beginning in 1986. The major findings of these investigations are discussed below. A summary of lead sampling data generated from these investigations is provided in Figures II-4 through II-6.

a) Envirodyne Engineers, Inc. (1986)

In 1983, wrecking and salvaging operations began at the Site by M&T Enterprises. In 1986, Envirodyne Engineers, Inc. (Envirodyne), on behalf of the IEPA, initiated an immediate removal action at the Site, which included a survey to determine the total volume of contaminated material at the Site. During the survey, an inventory of tanks, machinery, and structures remaining on the Site was completed. From the survey results, the quantity of contaminated material was estimated. The removal action included the removal of surficial solids that were either suspected or known to contain lead and/or asbestos. Envirodyne also removed the production equipment and debris associated with the manufacturing processes.

b) Toxcon Engineering Company (1987)

A field sampling program was implemented at the Site by Toxcon Engineering Company (Toxcon), on behalf of NL, in June-July 1987. Toxcon's field investigation was designed to 1) define the nature and extent of lead that may exist in native soils at the Site and adjacent properties; 2) determine if asbestos is present in the surface soils at the south end of the Site; and 3) determine the level of volatile organic compounds in the soils near the underground storage tanks on the west side of the Site.

A total of twenty on-Site native soil samples (1-17, 19 and 21), four surface soil samples adjacent to the Site (31-34), and nine surface soil samples from the parkways adjacent to the northern and eastern perimeters of the Site, were collected for lead analysis during this event (Figures II-4 and II-5). On-Site native soil samples were generally collected from the 0-1 foot depth interval beneath the base of fill material that was observed to be present under much of the Site at a depth of approximately 1.5-4 feet. Each on-Site sample was analyzed for both total and EP Toxicity lead. All parkway samples were collected from the 0-1 foot depth interval and analyzed for total lead. A subset of the parkway samples was also analyzed for EP Toxicity lead. Background samples, collected from surface soils (0-1 foot depth interval) located two blocks from the Site to the north, east, and south, were analyzed for total and EP Toxicity lead.

Background soil samples collected to the north, east, and south of the Site contained total lead concentrations of 347 mg/kg, 1,290 mg/kg, and 1,430 mg/kg, respectively. Corresponding EP Toxicity lead concentrations for these samples were all below the regulatory limit of 5 mg/L. On-Site native soil samples contained total lead to a maximum concentration of 50,000 mg/kg (sample location 12). The corresponding EP Toxicity lead concentration in this sample was 41 mg/L. Sample 12 was collected from the 0-1 foot depth interval beneath the base of an 18-inch fill layer observed to be present in the "Loading Dock Area" (see Figure II-4). Other than this area, no other on-Site samples were determined by Toxcon to have lead concentrations that were significantly elevated.

Total lead in samples from the parkways averaged 1,665 mg/kg. A

single parkway sample (33; off-Site to the northeast) contained lead at a concentration of 11,400 mg/kg which Toxcon attributed to previous demolition activities undertaken at the Site.

Based on the results of this investigation, Toxcon recommended that further investigation of the Site be conducted. Specifically, Toxcon recommended that additional samples be collected in the vicinity of sample location 12 to delineate the lead contamination found there. Additionally, Toxcon recommended resampling at location 33 and that additional sampling be conducted to delineate the observed lead contamination to the north and south.

VOCs were detected in two subsurface samples collected from a sandy stratum located at the 1-4 foot depth interval (up to 104.4 ppm) in the western part of the property during the field investigation. Based primarily on the relatively shallow depth of these samples, and the lack of evidence of any significant organic contamination in samples collected from deeper intervals, Toxcon concluded that these were the result of minor surface releases and were not attributable to any leakage from on-Site underground storage tanks. On this basis, Toxcon concluded that no further VOC sampling was required at the Site.

Asbestos sampling indicated the presence of asbestos in two of ten composite surface soil samples collected at the Site. Both samples were collected in the southern portion of the Site adjacent to the railroad spur located between the two loading docks. Toxcon therefore recommended that additional sampling be undertaken to delineate the lateral extent of soils containing asbestos.

c) Toxcon Engineering Company (1988)

Toxcon undertook a supplemental field investigation of the Site in February 1988, to better delineate the vertical and lateral extent of certain locations at the Site containing lead and asbestos.

Toxcon collected samples from two new locations (designated as samples 1214 and 1211, respectively) to delineate the lateral extent of lead contamination previously detected at sample location 12 (see Figure II-4). Samples were collected from the 0-1 and 3-4 foot depth intervals in Sample 1211, and from the 3-4 foot depth interval at Sample location 12. A sample

from the 0-1 foot interval was collected from sample location 1214[1].

Total lead concentrations of 3,390 and 6,470 mg/kg were detected from the 0-1 foot depth intervals at sample locations 1211 and 1214, respectively. EP Toxicity lead concentrations of 23.4 and 0.76 mg/L were detected in these two samples. Total lead concentrations of 26 and 3,130 mg/kg were detected from the 3-4 foot depth intervals at sample locations 12 and 1211, respectively. EP Toxicity lead concentrations in these two samples were 0.09 and 0.24 mg/L, respectively.

To obtain more information regarding lead contamination along the parkways north and east of the Site, Toxcon collected four additional samples (denoted W25P, W26P, S28P, and S29P; see Figure II-5). Toxcon also resampled at location 33 (denoted 33R) to confirm the results of the previous investigation. All sample locations included a surface sample collected from the 0-1 foot depth interval. In addition, sample location S29P included a sample collected from the 1-2 foot depth interval. All samples were analyzed for total and EP Toxicity lead. Total lead concentrations in the 0-1 foot depth interval ranged from 173 mg/kg at location W25P, to 8,120 mg/kg at location S29P. Total lead concentration in the 1-2 foot depth interval of location S29P was 20.5 mg/kg. Only one EP Toxicity sample exceeded the regulatory limit of 5 mg/L (22 mg/L at the 0-1 foot depth interval of location S29P).

At the request of IEPA, Toxcon also resampled at location number 27 to the northeast of the Site (denoted 27R) and collected samples at three additional locations in its vicinity (denoted 27SW-20, 27SE-20, 27N-20, and 27N-30; see Figure II-5). All samples appeared to be collected in soils (0-1 foot or 1-2 foot depth intervals) located above concrete. Total lead concentrations ranged from 2,570 mg/kg at sample location 27SE-20 to 12,800 mg/kg at sample location 27SW-20. EP Toxicity lead levels ranged from 0.55 mg/L at sample location 27N-30 to 9.75 mg/L at sample location 27SE-20.

Toxcon's sampling also indicated the presence of asbestos concentrations exceeding 1% in several samples collected between the two loading docks where

[1] It is not clear from the information provided in Toxcon's 1988 report, whether the on-Site sampling depths reported represent the interval beneath the fill layer.

asbestos was detected in soils during Toxcon's previous investigation.

d) Simon Hydro-Search, Inc. (1993)

In August, 1993, Simon Hydro-Search Inc. (Simon) on behalf of NL, implemented a field investigation to assess current conditions at the Site with respect to previously identified suspect contamination. Toward this end, Simon collected on-Site and off-Site soil samples for lead analysis, collected on-Site soil samples for asbestos analysis near an area of former debris that had been removed by the City of Chicago, estimated the volume and assessed the type of materials in various debris piles present on-Site, collected samples for asbestos analysis from building materials inside the Mill Building formerly existing on-Site, collected samples for analysis of VOCs, SVOCs, metals, asbestos, and cyanide from water in the basement of the Mill Building, and collected soil samples at the western end of the property along the railroad tracks for total petroleum hydrocarbon (TPH) analysis.

TPH was detected in one soil sample (sample location 12) at a concentration of 33,333 mg/kg (Figure II-4). TPH was also detected at a concentration of 1,681 mg/kg in a nearby soil sample (1211). VOCs were detected in sample location 12 at a (total) concentration of 57 mg/kg. The soil areas sampled for asbestos contained an average asbestos concentration of less than 1% and were, therefore, determined not to be of concern.

Elevated lead concentrations were detected in soil samples collected from two locations at the Site. In the vicinity of sample location 12, four soil samples from the 0-1 foot interval beneath the fill were collected. Total lead concentrations in these samples ranged from 58.7 mg/kg (12) to 26,400 mg/kg (1211). Two samples from the 1-2 foot interval beneath the fill were also collected from this area. Total lead concentrations in these samples ranged from 14,200 mg/kg (1211) to 45,700 mg/kg (12). Four of the six samples collected in the vicinity of sample location 12 had TCLP lead concentrations exceeding the regulatory limit of 5 mg/L. TCLP lead concentrations ranged up to 694 mg/L (sample location 12 at the 1-2 foot depth interval).

Elevated lead concentrations were also detected in two surface samples (33R and W26P) collected from the parkway just outside the northeast section

of the Site adjacent to Peoria Street (Figure II-5). This was an area where elevated lead concentrations had been previously detected (as described above) in surface soils. Lead concentrations in these two surface samples were 19,200 mg/kg and 1,120 mg/kg, respectively. Corresponding TCLP lead concentrations in these two samples were 98.4 mg/L and 2.53 mg/L respectively. A subsurface soil sample, collected from the 1-2 foot depth interval at sample location 33R, contained a total lead concentration of 23.1 mg/kg. TCLP lead was below the detection limit of 0.08 mg/L in this sample.

Surface and subsurface soil samples were also collected from the parkway (S29P) north of the Site adjacent to 120th Street. The surface soil sample (0-1 foot depth interval) contained lead at a concentration of 303 mg/kg. The corresponding subsurface soil sample contained lead at a concentration of 13.8 mg/kg. TCLP lead concentrations from both samples were below the detection limit of 0.08 mg/L.

e) Harza Environmental Services (1994)

Harza Environmental Services, Inc. (Harza) was retained by the City of Chicago in May 1994 to conduct a limited background review and field investigation of the Site. As part of this investigation, Harza collected scrape and wipe samples of building surfaces in the former mill building for the presence of lead. Results of this sampling event indicated the presence of lead at concentrations ranging up to 40 mg/cm^2 in the wipe samples and lead at concentrations ranging up to 25% in the scrape samples.

Harza also collected soil samples from seven discrete locations at the Site. In general, soil samples were collected from the native material at depth intervals varying between 6 and 15 feet below ground surface, just above a clay layer. One sample (B6), however, was collected from the 1-2 foot depth interval because of an elevated organic vapor monitor (OVM) reading obtained in the field. Soil samples were analyzed for selected total inorganics, TCLP lead, and Target Compound List (TCL) volatile and semi-volatile organic compounds. Lead concentrations in the native material ranged from 5.5 mg/kg to 10 mg/kg. The lead concentration in sample B6 (taken from the fill material) was 1,000 mg/kg . TCLP lead concentrations ranged from 0.041 mg/L to 0.5

concentrations.

- Surface soil samples taken from across S. Peoria Street in the empty property adjacent to the northeast corner of the Site, contained lead at concentrations up to 12,800 mg/kg. These samples were collected from soils existing above concrete that was observed below the ground surface. Previous investigations have alluded to disposal in this area under suspicious circumstances, which was confirmed based on a review of aerial photographs. The facility across from the northeast corner of the Dutch Boy Site was demolished between 1980-1985 (based on aerial photographs from 1980 and 1985), following cessation of lead operations at the Dutch Boy Site in 1980. Based on these observations, lead contaminated soil detected in this area appears to have been used as fill material, placed over the concrete and paved areas of the demolished property.

- Based on the heavy industrial activities that have occurred in this area over the last hundred years, it is expected that the surrounding vicinity may have been impacted by other metal processing facilities that have operated (or continue to operate) in this area. This inference will be substantiated by the results of the off-site sampling program described in Section III.B.2 below.

III. SAMPLING AND ANALYTICAL WORK PLAN

A. Objectives

As stated previously, the overall objective of the SAP is to delineate the horizontal and vertical extent of lead contamination in on-Site and off-Site soils, and to determine the background concentrations of lead in soils in the vicinity of the Site. The results of the SAP will be used to establish a Site-related Extent of Contamination (EOC) survey. This information subsequently will be used in the design of an appropriate Risk Management Plan (RMP) for the Site.

This section of the SAP describes the methodologies, locations, sample identification, collection, and handling procedures, and analytical test methods that will be used to fulfill the above objectives and to ensure that sampling and analysis tasks are performed in a manner that will provide reliable data. This assessment is generally consistent with standard procedures for the collection and analysis of soil samples (USEPA 1992; USEPA 1995). In particular, the five steps that have been applied in this assessment include:

Step 1 - Evaluation of Land Use History and Existing Data;
Step 2 - Establishment of Data Quality Objectives
Step 3 - Determination of Sample Locations and Numbers
Step 4 - Sample Collection, Preservation, Handling, Analysis, and Data Reporting
Step 5 - Statistical Analysis of Data

B. Sampling Locations

To fulfill the objectives stated in Section I-B, ENVIRON has proposed a sampling program consisting of on-Site sampling of surface and subsurface soils, off-Site sampling of surface soils from the parkways in the vicinity of the Site, and off-Site sampling of surface soils on adjacent properties extending to approximately 1,600 feet from the Site. A summary of the sampling program is provided in Table III-1 below.

TABLE III-1 SUMMARY OF SAMPLING PROGRAM DUTCH BOY SITE CHICAGO, ILLINOIS		
Sampling Location	**Number of Samples**	**Comments**
Off-Site; Adjacent Properties	80 (Includes samples to be sieved)	Samples will be collected on 100-foot radii extending out from the Site in each of eight transects. Additional samples will be collected on 400-foot radii in each of four transects. Samples will be collected from the 0-2 inch interval and analyzed for total lead. An additional four samples will be collected at two locations where the soil boring will be extended to the base of the fill material. Ten samples, selected at random, will be sieved and the fine and total fractions analyzed for total lead.
Note: All sample numbers are approximate.		

I. On-Site

The SAP has been designed to investigate various areas of the site depending on their respective physical condition (e.g., presence or absence of pavement) and operating history. Specifically, the Site has been divided into two zones. Zone 1 represents that area of the Site that is presently not under pavement. Zone 2 represents those areas of the site that are presently under some type of paved surface (e.g., concrete pavement, loading docks, etc.).

Sample locations for each of the zones were developed by overlaying sampling grids and then selecting sampling locations within the specified zone that fall at the nodes of the grid. For Zone 1, a grid with sampling nodes on 40-foot centers was chosen as being sufficiently representative for the purposes of this SAP. Because the remaining areas of the Site comprising Zone 2 have been under pavement or concrete for much of the Site's operating life, a grid with nodes on 100-foot centers was chosen for these areas. Use of these sampling grids results in approximately 32 and 22 sample locations designated for Zones 1 and 2, respectively. Proposed sampling locations for each of the zones are shown in Figure III-1.

For all on-site soil sampling locations, ENVIRON proposes to install soil borings via a standard coring device to the base of the fill material overlying the native soils of the

Site. Soil cores will be collected from one-foot vertical intervals until the base of the fill material is encountered. A one-foot depth sampling increment was selected based on USEPA (1995) recommendations for silty/sandy soils (silts and loams, 1.0-2.5-foot intervals; sands, 1.0-5-foot intervals). Each core will be collected in an acetate liner, sealed in the field, and sent to the laboratory for potential analysis. Initially, a portion of each soil boring, representing the upper two-inch vertical interval below ground surface, will be homogenized in the laboratory and analyzed for total lead. The remaining portion of the soil core (representing the 2-12 inch depth interval below ground surface) will be preserved for potential future analysis. In cases where the 0-2 inch homogenized sample exceeds 1,400 ppm total lead, a homogenized sample from the underlying interval (i.e., 2-12 inches) will be analyzed. If the 2-12 inch interval is also above 1,400 ppm total lead, a homogenized sample of the underlying one foot vertical interval will then be analyzed. This procedure will be repeated until a vertical interval containing lead at less than the 1,400 ppm cleanup level is encountered at each boring location. As required by USEPA, ten on-site soil samples, selected at random, will be sieved (250 um) and both the fine and total fractions analyzed for total lead.

To investigate the native material underlying the fill, soil borings will be extended to a depth of five feet below the fill base at nineteen locations (eighteen borings along and near the loading dock area between the debris pile and 120th Street, and one boring underneath the concrete paving nearest the loading dock; see Figure III-1). These locations were chosen based on previous sampling results that showed lead contamination at depth in certain areas near the loading dock. Soil samples at each of the nineteen locations will be collected from each one foot vertical interval, beginning at the one foot below surface depth, and extending into the native material to the total depth of the boring. The base of the fill is at a depth of 2-4 feet at most locations. Each soil sample will be analyzed for total lead.

Based on previous sampling that has been conducted at the Site, the presence of significant concentrations of organic compounds appears to be limited only to certain areas within Zone 1. Therefore, all Zone 1 soil cores will be screened in the laboratory using a head space solid phase microextraction (SPME) technique. A detailed description of the SPME screening procedure is provided in Section III.D.2 below. A grab sample will be collected from the one-foot vertical interval of each boring location that exhibits the highest SPME reading and analyzed for VOCs and Petroleum Hydrocarbons as specified in Section III.E. In addition, all soil cores (Zone 1 and Zone 2) will be inspected

by the laboratory for any (visual or olfactory) evidence of contamination. A grab sample will be collected from any core interval exhibiting such evidence of contamination and will be analyzed for VOCs and Petroleum Hydrocarbons as specified in Section III.E.

To confirm (and update) the results obtained previously by Toxcon, ENVIRON proposes to conduct asbestos analyses on ten Zone 1 samples collected from the 0-1 foot depth interval, between the loading docks (where asbestos was previously detected). In addition, a small area within the loading dock in the southwest corner of the Site (Figure III-1) contains construction debris from the demolition of the Mill Building earlier this year. To characterize the nature of this material, four representative samples of this material will be collected and analyzed for TCLP lead and asbestos. TCLP lead and asbestos analyses will be conducted according to the procedure described in Section III.D.2 below.

One sediment sample will be collected from the southeast corner of the sub-basement of the former mill building, where accumulated sediment has been reported during previous site visits. In addition, one soil core will be collected from beneath the sub-basement of the former mill building and analyzed for lead.

Assuming an average of three samples per boring location where the boring is extended to the base of the fill material, and nine samples where the boring is extended to five feet below the base of the fill material, a total of approximately 288 samples will be analyzed in this sampling component. The actual number of samples to be analyzed will be determined according to the protocol outlined above. In addition, anticipated sampling locations may change if significant physical impediments (e.g., underground utilities or tanks, obstructions to the drill rig, etc.) are observed during the implementation of the sampling program.

2. Off-Site

a) Adjacent Properties

To characterize off-Site soil quality on properties adjacent to the Site, ENVIRON proposes to establish a stratified radial sampling scheme as shown in Figure III-2. Adjacent properties will be targeted for sampling by extending radii, at 100-foot intervals from the Site within a 45 degree angle in each of eight compass directions. A single soil sample will be collected, where feasible, within each area defined by the 45 degree angle and the 100-foot radii interval. In addition, a total of eight soil samples will be collected from two outer rings spaced

dd = Depth Interval:

01 = 0-1 foot depth interval

12 = 1-2 foot depth interval

SS = Site:

DB = Dutch Boy Site

OA = Off-Site; adjacent property

OP = Off-Site; parkways

BG = Background

MMDDYY = Date:

Month, day, and year in number format (e.g., 062196 = June 21, 1996).

AAAA = Location:

QA/QC samples (i.e., duplicate samples, field equipment rinsate blanks, and trip blanks) will be assigned fictitious numbers starting with 99 (e.g., 9901, 9902, etc.).

2. Sample Labels

The sample labels will be placed on the sample containers so as not to obscure any data on the containers. Sample information will be printed on the labels in a legible manner using waterproof ink. The label will contain sufficient information so the sample can be identified on the sampling information form or sample collection log. Sample labels will contain the following information:

- The project name and number (i.e., Dutch Boy Site, 01-4598A).
- A unique sample identification (see Section IV.A.1.).
- The date and time.
- Designation of the sample as a composite, if appropriate.
- Identification of preservatives used, if any.
- A list of analytical tests to be performed on the sample.
- Other necessary remarks.
- Name of the sampler.

D. Sample Collection and Handling

This section describes the equipment and procedures to be used during the field portions of the investigation.

1. Sample Collection

All samples will be collected using a standard coring device. For those soil borings installed to depths below the 0-1 foot interval below ground surface (all on-site locations and a portion of the off-site locations), a direct-push method (e.g., Geoprobe) will be used for installation of the borehole and sample collection. For those soil borings to be installed to the 0-1 foot depth interval (off-site locations only), a stainless-steel hand-auger will be used for installation of the borehole and sample collection where feasible. For Zone 2 on-site sample locations, a power concrete coring device will be used to install a borehole through the concrete/pavement, through which the coring device can be inserted for soil sample collection.

For soil cores collected via the direct push method, each one-foot core will be collected in an acetate liner, sealed in the field, and sent to the laboratory for analysis (or retention for potential future analysis). For soil cores collected via hand-auger (0-1 foot depth interval only), the top 0-2 inch interval will be placed into a glass vial, sealed in the field, and sent to the laboratory for analysis. The sample will then be homogenized in the laboratory and analyzed for total lead.

Samples will be delivered to a certified laboratory within 48 hours of collection. Detailed chain-of-custody and other quality assurance procedures, as specified in the Quality Assurance Project Plan (QAPjP; Appendix 1) will be followed at all times during sample collection. Analyses will then be conducted as described in Section III.E.

Depending on the results of the total metals analyses generated in this investigation, a subset of these samples will be selected for TCLP lead analysis in order to determine whether soils at the Site exhibit hazardous waste characteristics. Specifically, samples containing different levels of lead will be submitted for TCLP analysis in order to establish a relationship between TCLP level and soil lead concentrations.

Analyses for VOCs and Petroleum Hydrocarbons will be specified for the vertical interval of each boring location exhibiting the highest SPME reading (see Section D.2 below) or for any interval exhibiting any visual or olfactory evidence of contamination.

Debris samples will be collected by identifying various debris types (e.g., concrete, transite pipe, wallboard, etc.) and taking a representative sample. The laboratory will be responsible for all sample preparation that may be required to conduct the appropriate

analyses.

2. Organic Constituent Screening Procedure

All Zone 1 soil cores collected from beneath the 0-1 foot depth interval will be screened for organic constituents in the laboratory using headspace solid phase microextraction and gas chromatography with flame ionization detection. The screening analysis will be performed by slitting each (one-foot) soil core down the middle. One half of the core (referred to as the "retained sample") will be retained by the laboratory for potential further analyses. The remaining half of the core (referred to as the "original sample") will be examined for any visual or olfactory evidence of contamination. A grab sample will be collected from any interval exhibiting such evidence and will be analyzed for VOCs and Petroleum Hydrocarbons as specified in Section III.E below. For those intervals not exhibiting visual or olfactory evidence of contamination, a representative grab sample from the interior portion of the original sample (i.e., approximately six-inches from either end) will be collected and analyzed using the SPME screening procedure. A standard operating procedure for this screening technique is provided in the QAPjP (Appendix 1). A grab sample from the one-foot vertical interval from each boring location that exhibits the highest SPME reading will be collected and analyzed for VOCs and Petroleum Hydrocarbons.

3. Decontamination Procedure

Prior to and between sample collection, all sampling equipment (e.g., coring devices) will be thoroughly cleaned using a high pressure steam cleaner and/or rinsed with tap water, rinsed with non-phosphate detergent solution, rinsed with tap water to remove detergent, rinsed with distilled/deionized water, and air dried.

4. Waste Management

All water used during decontamination will be stored in drums and labeled appropriately. The drums will be placed in an on-site waste storage area pending analytical test results. Similarly, all waste soils generated during the sampling program will be drummed and stored on-Site pending analytical results. The decontamination water and waste soils will then be disposed of appropriately.

E. Laboratory Test Methods

Chemical analyses will be performed by a qualified laboratory for the analytes specified

below. Total lead analyses will be performed by the Atomic Absorption, Furnace technique (SW-846, 3050/7421). Volatile organic compound analysis will be performed by the Gas Chromatography/Mass Spectrometry technique (SW-846, 8260). Petroleum Hydrocarbons will be analyzed (diesel and gasoline ranges) by the Gas Chromatography/Flame Ionization Detection Technique (SW-846, 8015). Asbestos sampling will be conducted by Polarized Light Microscopy (USEPA Method 600/M4-E2-020). TCLP lead analysis will be conducted in accordance with the procedure specified in SW-846, 1311. A detailed discussion of quality assurance/quality control procedures to be followed by field and laboratory personnel is provided in the QAPjP (Appendix 1).

F. Data Reporting and Statistical Evaluation

Data generated during the site investigation will be appropriately identified, validated and summarized in the final report. ENVIRON has developed a data storage and information system to facilitate data for tracking and data calculations, and for the transfer of data to various forms and reports. Quality control procedures have been designed to eliminate errors during these steps.

Appropriate documents will be prepared and distributed to summarize the field activities performed and the results of all data collected during the site investigation. These reports, to the extent possible, will include:

- Presentation of results;
- Summaries of field data from field measurements such as water levels and soil moisture and water-quality parameters; and
- Field location of sampling points.

In addition, USEPA will be provided with copies of the following documents for each sampling event:

- All field measurements, data logbooks, and notebooks;
- Laboratory reports; and
- Data validation reports summarizing the validation process used and specific comments pertaining to a sample or group of samples.

An inventory of all documents contained in the project file will be developed. This document inventory shall contain the following information:

- Document date;
- Author(s), including title and affiliation;
- Recipient(s), including title and affiliation;
- Title of document;
- Summary of content; and
- Number of pages.

All documents supplied to USEPA shall include a cover sheet containing the following information:

- Site name (Dutch Boy Superfund Site);
- Date; and
- Authors.

Upon completion of the data validation and assessment of the data with respect to precision, accuracy, and completeness, ENVIRON will develop QA/QC reports for each analytical data package. This report, along with a field activities documentation report, will be prepared to summarize the results obtained for all samples collected during the investigation.

Statistical analysis that may be conducted on-Site and off-Site data will depend on the results and the proposed use of the data. Appropriate statistical analyses will be employed to evaluate spatial trends.

It should be recognized that further sampling may be required depending on the results of this sampling event to fulfill the objectives of the program.

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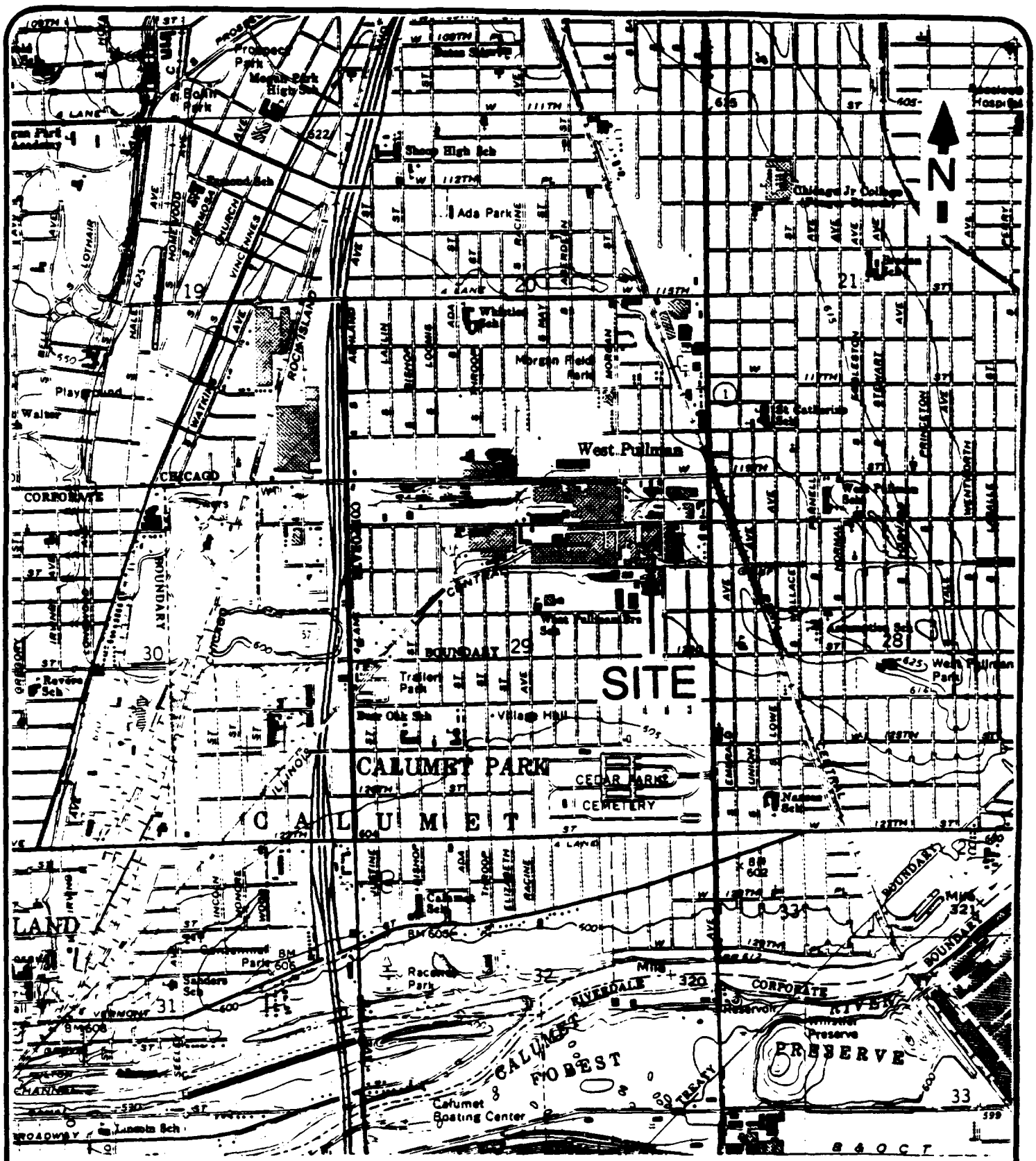
FIGURES



SOURCE: USGS 7.5 MINUTE (TOPOGRAPHIC) SERIES; BLUE ISLAND, ILLINOIS QUADRANGLE

c:\acad\FILE_SPECIFICATION

ENVIRON

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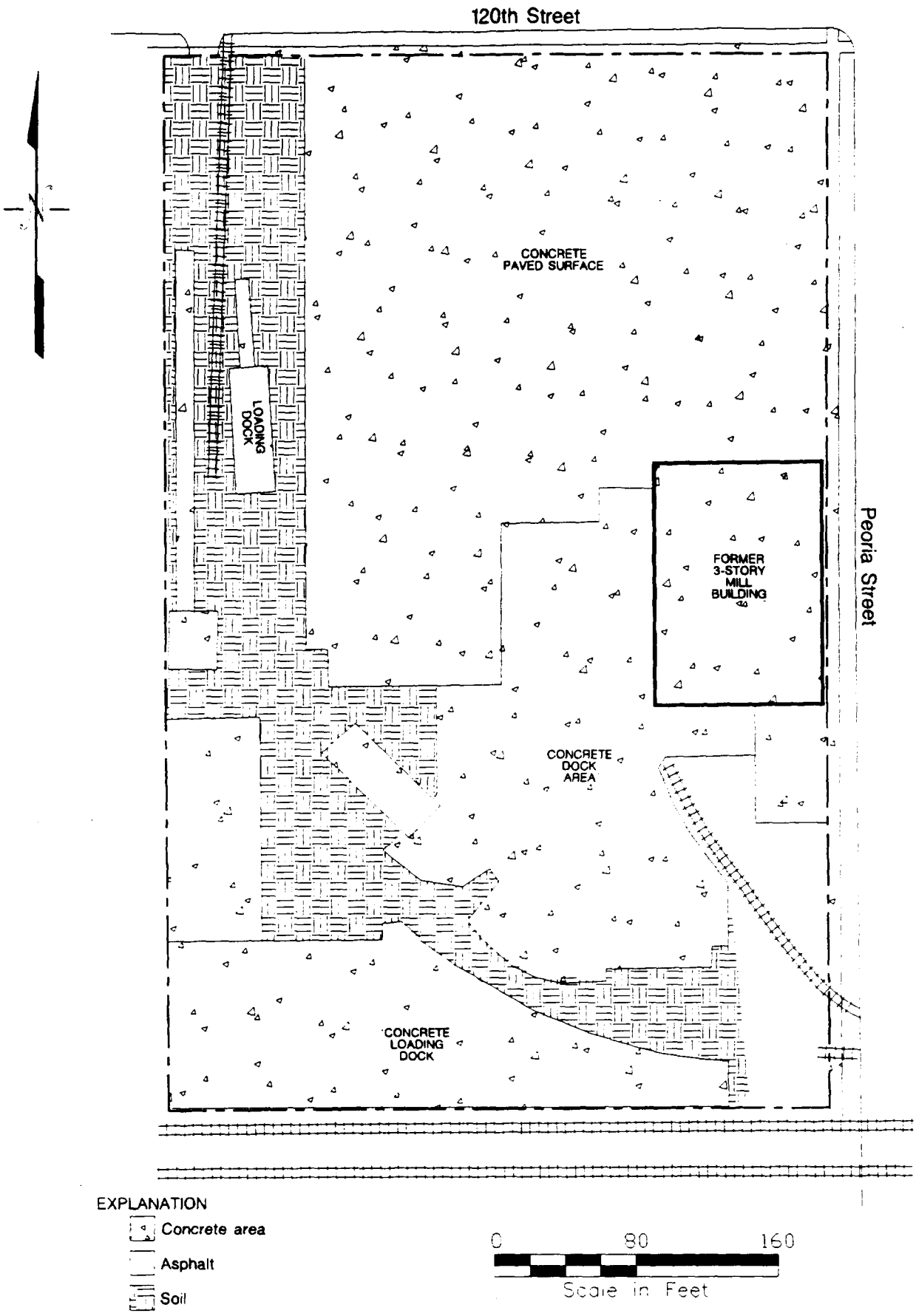
SITE LOCATION MAP
DUTCH BOY SITE
CHICAGO, ILLINOIS

Figure
II-1



ENVIRON

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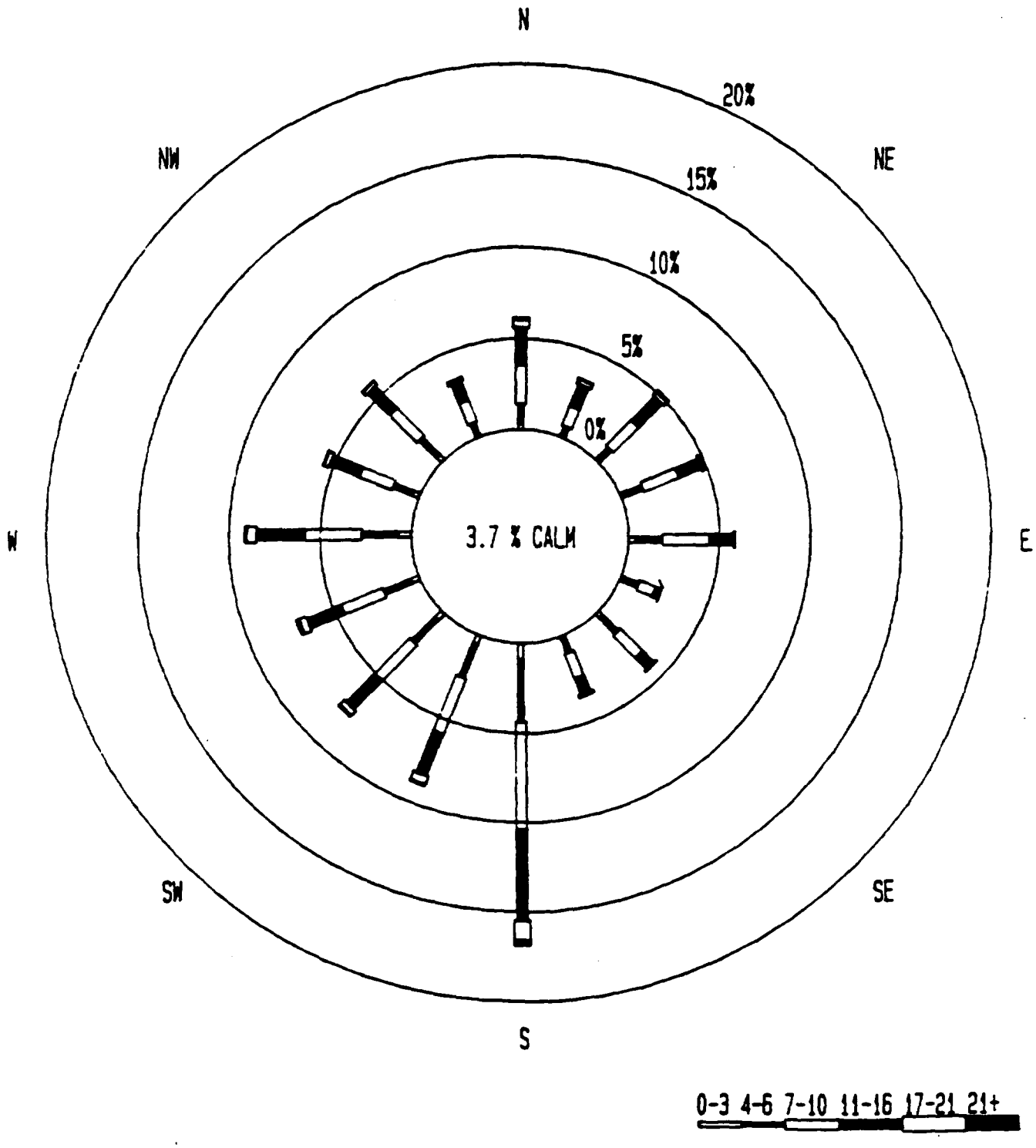
SITE LAYOUT
DUTCH BOY SITE
CHICAGO, ILLINOIS

Figure II-2



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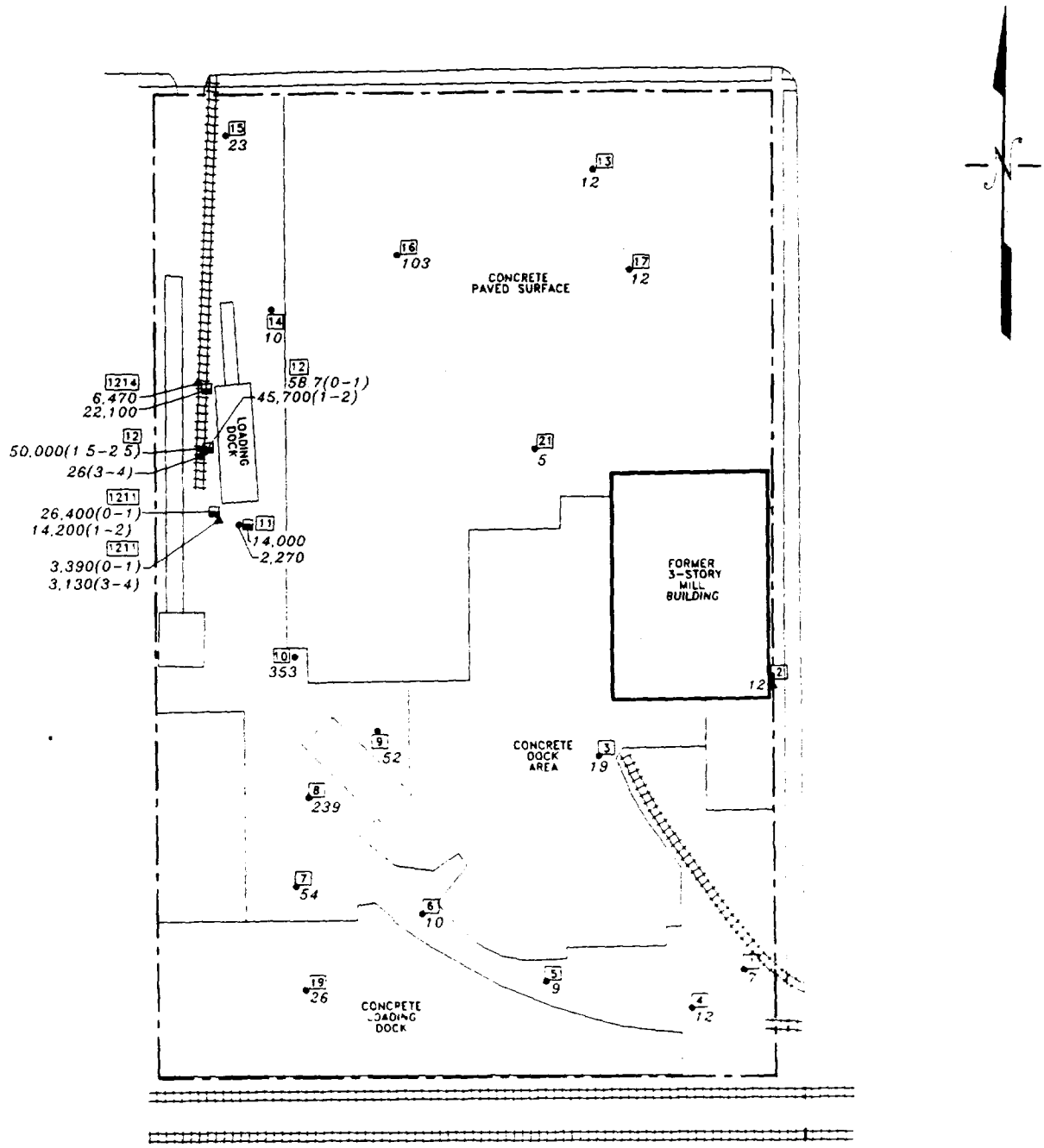
WIND ROSE
MIDWAY AIRPORT
JANUARY 1965-DECEMBER 1974

Figure
II-3



0 100 200
Scale in Feet

EXPLANATION

1211 Sample number

26(0-1) Total lead, mg/kg (ppm) and sample interval in feet

LEGEND FOR SAMPLING RESULTS

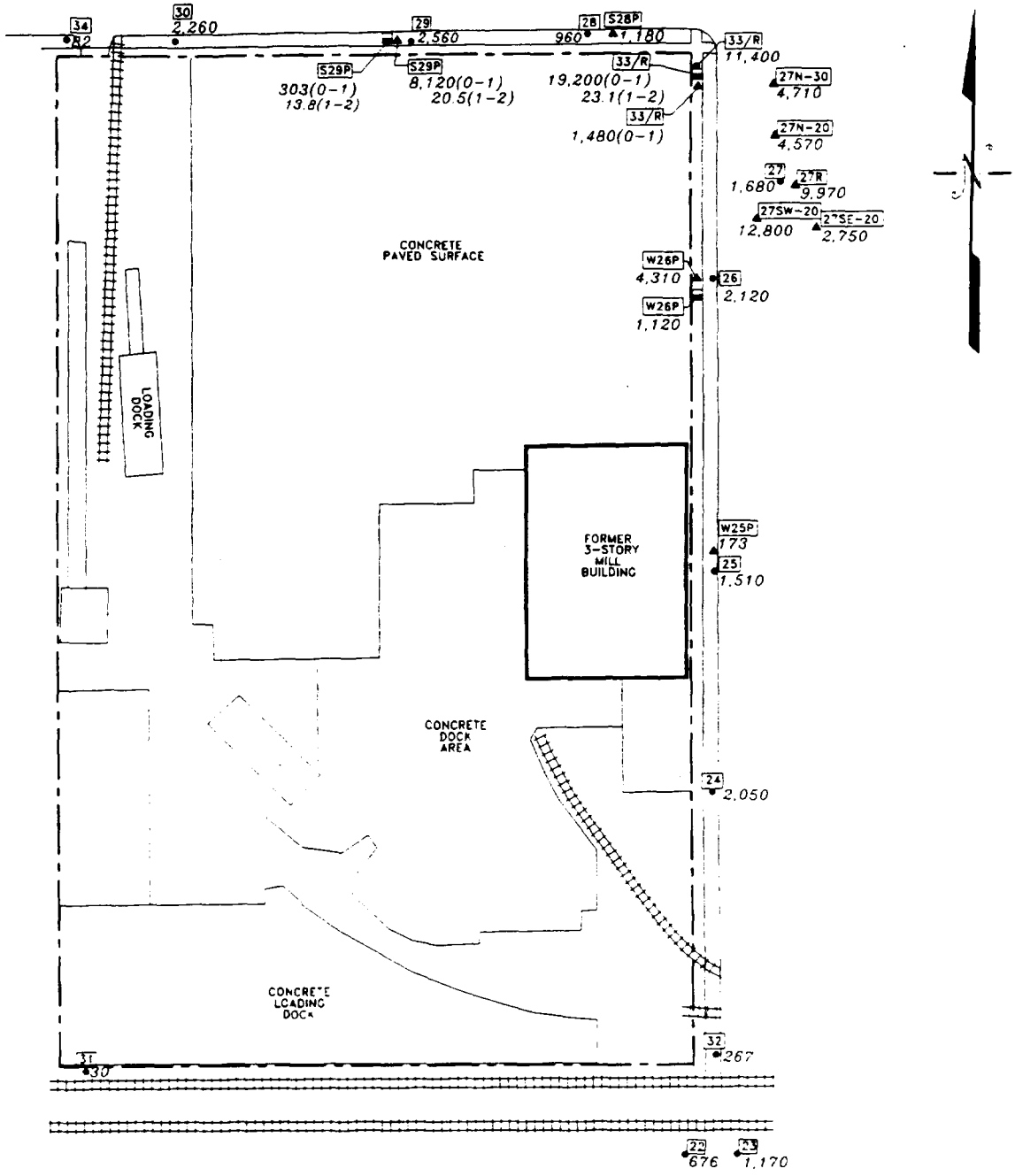
- Simon Hydro-Search, 1993
- ▲ Toxcon Engineering Company, 1989
- ● Toxcon Engineering Company, 1987.

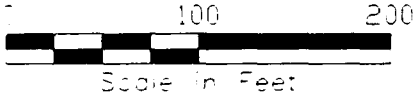
NOTE: All sample locations are approximate.
Samples collected from beneath base of fill material (0-1 feet except where noted).

ENVIRON

NATIVE MATERIAL
ON-SITE SAMPLING RESULTS

Figure
II-4





EXPLANATION

[1211] Sample number

26(0-1) Total lead, mg/kg (ppm) and sample interval in feet

LEGEND FOR SAMPLING RESULTS

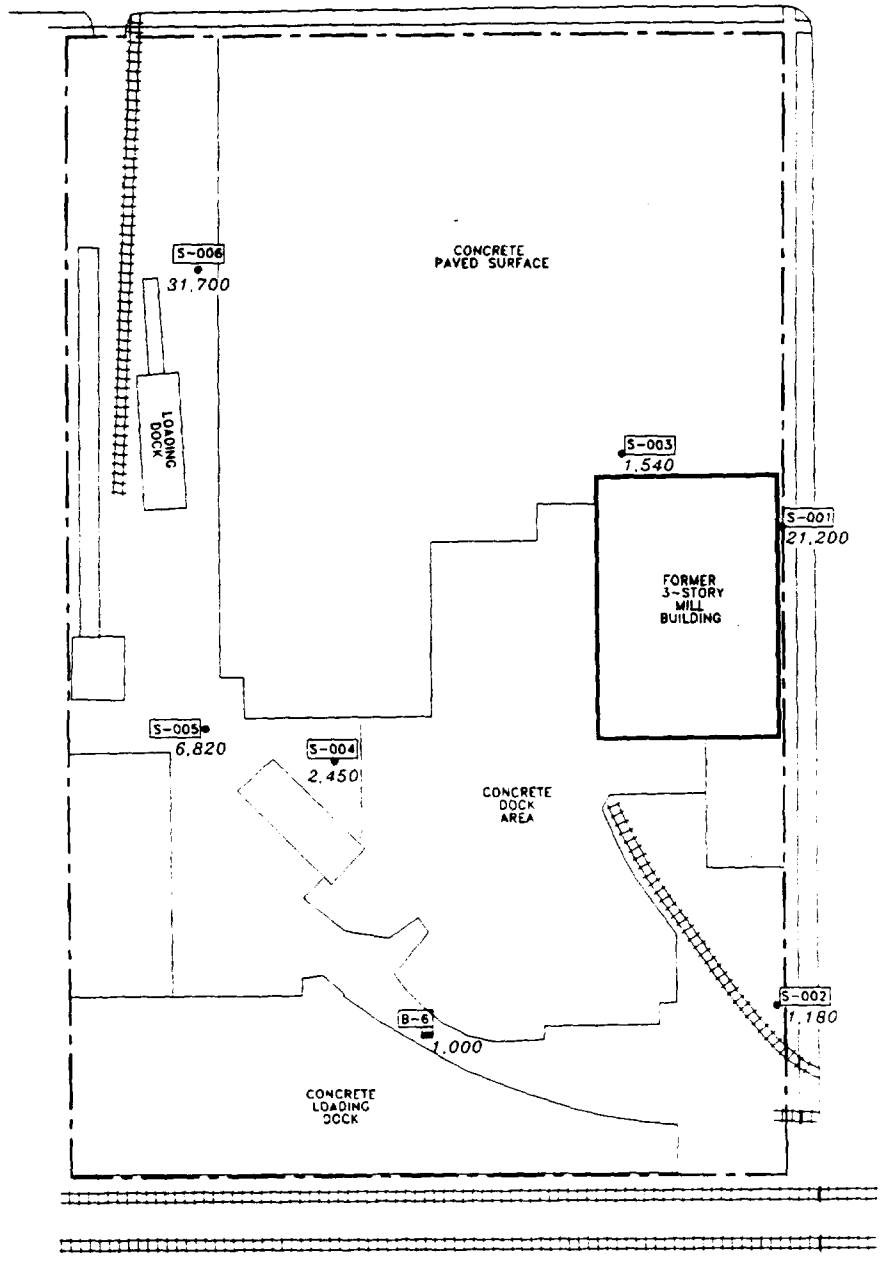
- Simon Hydro-Search, 1993
- ▲ Toxcon Engineering Company, 1989
- ● Toxcon Engineering Company, 1987

NOTE: All sample locations are approximate.
Samples collected from 0-1 feet below ground surface except where noted.

ENVIRON

FILL MATERIAL
OFF-SITE SAMPLING RESULTS

Figure
II-5



0 100 200
Scale in Feet

EXPLANATION

1211 Sample number
26 Total lead, mg/kg (ppm)

LEGEND FOR SAMPLING RESULTS

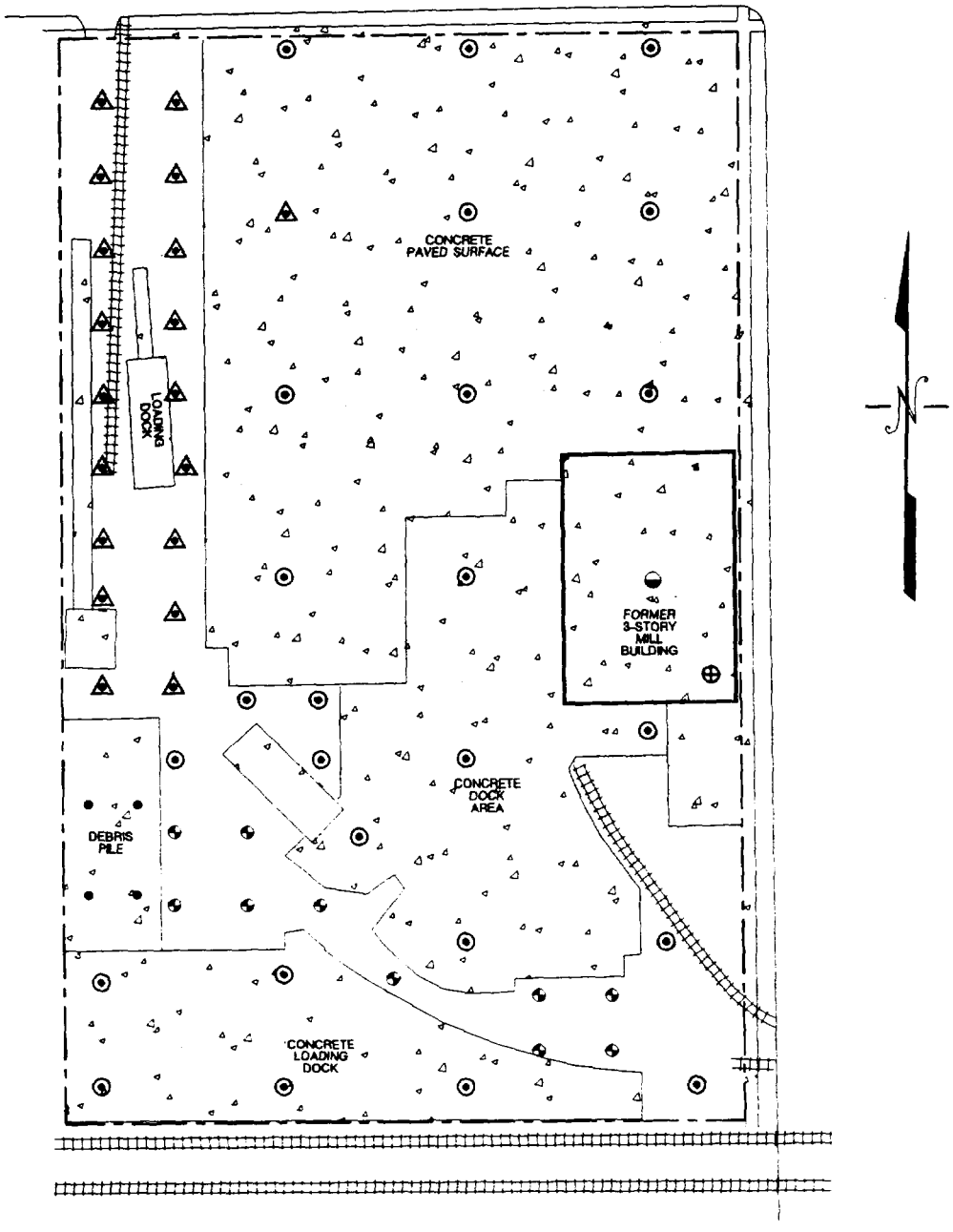
- Ecology and Environment Inc., 1995; Grab samples collected from 0–1 feet below gound surface
- Harza Environmental Services, 1994; Sample collected at depth of 1–2.5 feet below ground surface.

NOTE: All sample locations are approximate

ENVIRON

FILL MATERIAL
ON-SITE SAMPLING RESULTS

Figure
II–6



EXPLANATION

- Soil core to 5 feet below base of fill
- Soil core to base of fill
- Soil core to base of fill; includes asbestos analysis
- Debris sample
- Sediment sample
- Soil sample from below sub-basement

0 100 200
Scale in Feet

NOTE: Sampling intervals at each core location are detailed in report.
10 samples will be selected at random, sieved (250 um), and the fine and total fractions analyzed for total lead.

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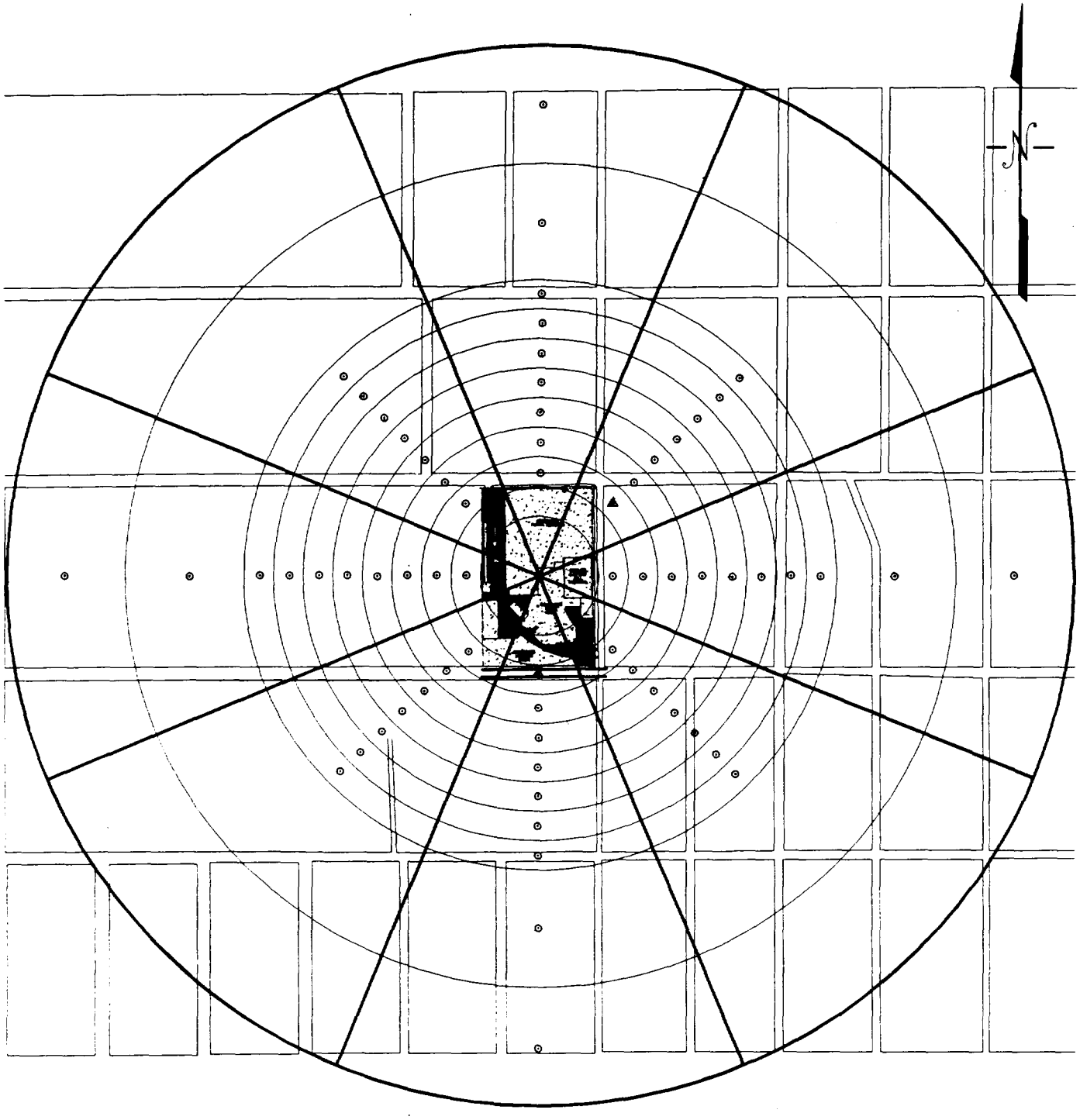
ON-SITE SAMPLING LOCATIONS
DUTCH BOY SITE
CHICAGO, ILLINOIS

Figure
III-1



EXPLANATION

⊙ Soil sample 0-2 inch depth interval location to be determined in field

▲ Soil boring to be installed to base of fill

0 500 1,000

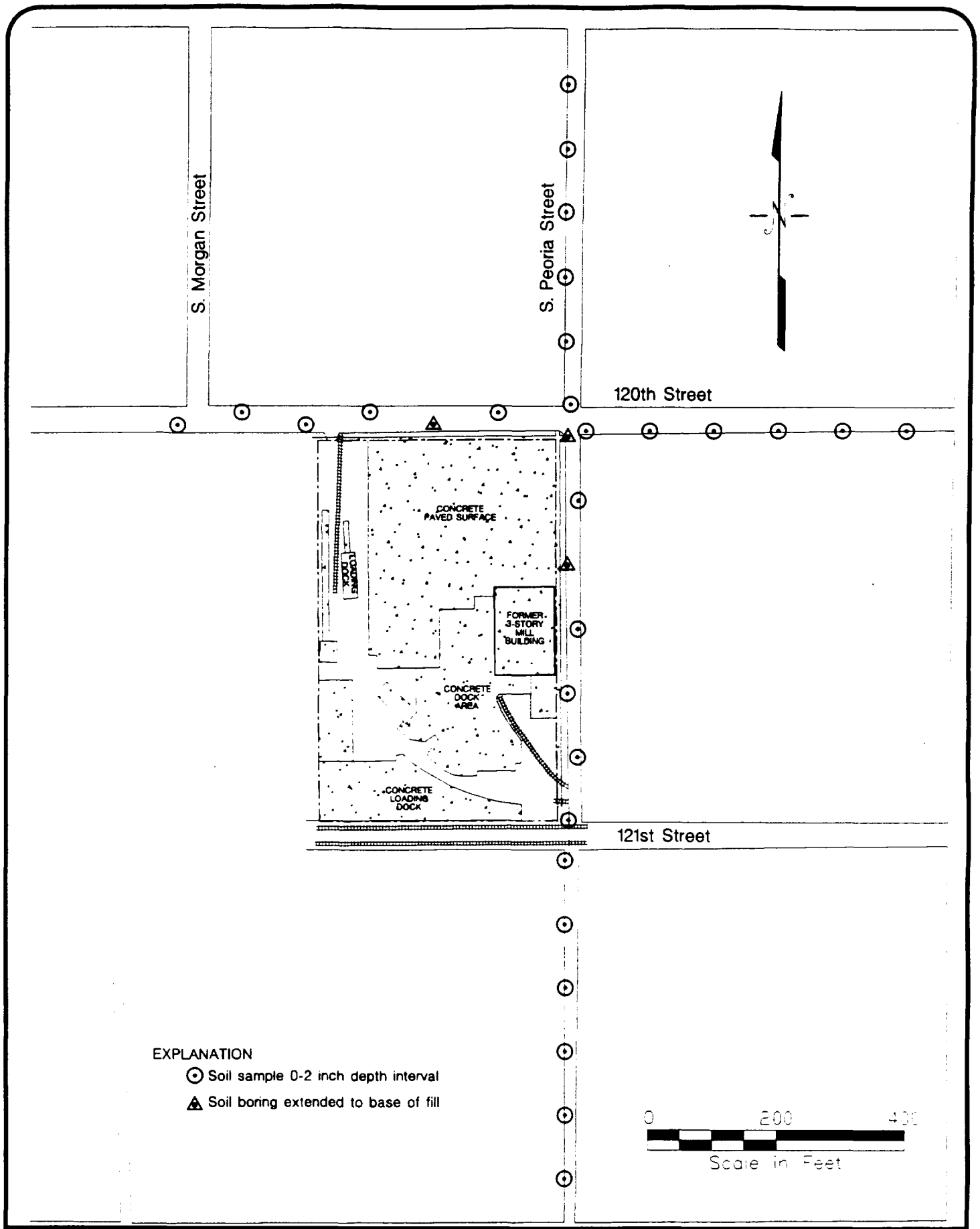
Scale in Feet

NOTE: 10 samples will be selected at random, sieved (250 um), and the fine and total fractions analyzed for lead.

ENVIRON

OFF-SITE ADJACENT PROPERTY
SAMPLING LOCATIONS
DUTCH BOY SITE
CHICAGO, ILLINOIS

Figure
III-2



ENVIRON

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OFF-SITE PARKWAY SAMPLING LOCATIONS
DUTCH BOY SITE
CHICAGO, ILLINOIS

Figure
III-3

APPENDIX 1
QUALITY ASSURANCE PROJECT PLAN

QUALITY ASSURANCE PROJECT PLAN
DUTCH BOY SITE
CHICAGO, ILLINOIS

Prepared for
NL Industries, Inc.

Prepared by
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FIGURES

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ATTACHMENT C Lancaster Laboratories Standard Operating Procedures

I. BACKGROUND

This Quality Assurance project Plan (QAPjP) has been developed for the Dutch Boy Site in Chicago, Illinois (the "Site"). Consistent with the requirements of a unilateral Administrative Order, issued by USEPA to NL Industries, Inc. (NL), NL retained ENVIRON International Corporation (ENVIRON) to design and implement a Sampling and Analysis Plan (SAP) at the Site. The SAP calls for the collection of approximately 405 soil and debris samples. All soil samples will be analyzed for total lead. In addition, certain soil samples will be analyzed for total petroleum hydrocarbons (TPH), volatile organic compounds (VOCs), TCLP lead, and asbestos. Debris samples will be analyzed for TCLP lead and asbestos. This Quality Assurance Project Plan (QAPjP) was prepared in accordance with the EPA guidance document *Quality Assurance/Quality Control Guidance for Removal Activities; Sampling QA/QC Plan and Data Validation Procedures* (USEPA 1990). Detailed information regarding the site setting, site description, and description of site contamination are provided in Chapter II.A., II.B., and II.C., of the SAP, respectively.

II. DATA USE OBJECTIVES

The data will be used to: (1) identify the vertical and horizontal extent of on-Site soil contamination; (2) determine the background concentrations of lead in soils in the vicinity of the Site; and (3) determine whether lead is present beyond the boundaries of the Site and the extent of such contamination. To fully characterize the Site, certain samples will also be analyzed for total petroleum hydrocarbons (TPH), volatile organic compounds (VOCs), TCLP lead, and asbestos. The results of the SAP will be used to establish a Site-related Extent of Contamination (EOC) survey. This information subsequently will be used in the design of an appropriate Risk Management Plan (RMP) for the Site.

III. QUALITY ASSURANCE OBJECTIVES

The overall quality assurance (QA) objective is to collect data that are of known and usable quality. This objective will be achieved and documented using the procedures and criteria set forth in this QAPjP. For each measurement used to obtain quantitative data, a set of quality objectives is used to aid in collecting usable data. Typically, quality objectives are categorized under precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters. Definitions of each parameter are provided below. PARCC parameters can be applied to both field measurements and laboratory analytical measurements. Measured media can include soil, water, air, or other media.

Outlined below are the PARCC parameters that will be addressed during the Sampling and Analysis Plan. Reporting and validation requirements are addressed in Chapters VIII and IX, respectively. Quality assurance reporting requirements are presented in Chapter VI.

A. Precision

Precision is the degree of agreement between replicate measurements of the same source or sample. Precision is expressed by relative percent differences (RPD) between replicate measurements. Replicate measurements can be made on the same sample or on two samples from the same source. Precision is generally assessed using a subset of the measurements made.

Field precision is assessed through the collection and measurement of field duplicates at the rate of one duplicate per every 10 analytical samples (i.e., 10% of primary samples collected). For original and duplicate sample values greater than five times the contract required detection limit (CRDL), the limits for precision for field duplicates will be ±20 and ±35 RPD for water and soil, respectively. If either the sample or duplicate value is less than five times the CRDL, a control limit of ± the CRDL and ± 2x the CRDL will be used for water and soil, respectively. In the case where only one result is greater than five times the CRDL and the other is less than five times the CRDL, the ± the CRDL criteria applies.

The laboratory limits for precision, as measured by the RPD between laboratory Duplicate Control Sample (DCS) analyses, will be the laboratory control limits based on historic data calculated as specified in the analytical methods. If these limits are not met, the laboratory will follow the actions specified in the analytical method and the laboratory's SOPs.

Precision of a set of analyses will also be evaluated by determining the RPDs for matrix spike and matrix spike duplicate (MS/MSD) samples for organics and duplicate samples for

inorganics. Specific quality control (QC) criteria for precision of MS/MSD analyses and duplicate sample analyses are presented in Table III-1. The formula for calculating precision is presented in Chapter VII.

B. Accuracy

Accuracy measures the level of bias that an analytical method or measurement exhibits. To measure accuracy, a standard or reference material containing a known concentration is analyzed or measured and the result is compared to the known value. Several QC parameters are used to evaluate the accuracy of reported analytical results:

- Holding times;
- Laboratory control sample (LCS) percent recovery;
- MS/MSD percent recovery (organics);
- Spike sample recovery (inorganics)
- Surrogate spike recovery; and
- Blank sample results.

The accuracy of analytical results may depend upon analysis within specified holding times. In general, a longer holding time is assumed to result in a less accurate measurement due to the potential for loss or degradation of the analyte over time. The acceptance limits for holding times are presented in Table III-2.

The laboratory limits for accuracy, as measured by the percent recoveries for LCSs, the Single Control Samples (SCS) and DCS analyses, will be the laboratory control limits based on historic data calculated as specified in the analytical methods. If these limits are not met, the laboratory will follow the actions specified in the analytical method and the laboratory's SOPs.

Accuracy is also measured by the percent recoveries for MS/ MSD analyses for organics and spike sample recoveries for inorganics. Specific QC criteria for accuracy are presented in Table III-1. The formula for calculating accuracy is presented in Chapter VII.

Surrogate spike recovery will also be used to evaluate the accuracy of reported measurements. A surrogate standard is a distinct chemical that behaves similarly to the target chemical and is purposely added to the sample prior to cleanup and extraction. The surrogate spike recovery is used to assess recovery of the target chemical from the sample matrix. A known amount of a surrogate standard is added to the sample prior to cleanup. The amount of the

TABLE III-1
Dutchboy Site
Project Required Detection Limits

Analyte	Method	Detection Limits[1] (ppm)		Accuracy [2] (%)	Precision [3] (RPD)
		Solids[4]	Aqueous[5]	Solids[4] and Aqueous[5]	
Volatile Organic Compounds					
Acetone	SW-846, 8260A	0.005	0.005	60 - 132	30
Benzene	SW-846, 8260A	0.005	0.005	42 - 150	30
Bromobenzene	SW-846, 8260A	0.005	0.005	41 - 155	30
Bromochloromethane	SW-846, 8260A	0.005	0.005	35 - 155	30
Bromodichloromethane	SW-846, 8260A	0.005	0.005	48 - 150	30
Bromoform	SW-846, 8260A	0.005	0.005	41 - 143	30
Bromomethane	SW-846, 8260A	0.005	0.005	29 - 155	30
2-Butanone	SW-846, 8260A	0.005	0.005	66 - 126	30
n-Butylbenzene	SW-846, 8260A	0.005	0.005	33 -177	30
sec-Butylbenzene	SW-846, 8260A	0.005	0.005	39 -171	30
tert-Butylbenzene	SW-846, 8260A	0.005	0.005	41 -167	30
Carbon Disulfide	SW-846, 8260A	0.005	0.005	12 - 174	30
Carbon tetrachloride	SW-846, 8260A	0.005	0.005	49 - 163	30
Chlorobenzene	SW-846, 8260A	0.005	0.005	49 -145	30
Chlorodibromomethane	SW-846, 8260A	0.005	0.005	48 - 144	30
Chloroethane	SW-846, 8260A	0.005	0.005	21 - 171	30
Chloroform	SW-846, 8260A	0.005	0.005	44 - 152	30
Chloromethane	SW-846, 8260A	0.005	0.005	22 - 172	30
2-Chlorotoluene	SW-846, 8260A	0.005	0.005	42 - 162	30
4-Chlorotoluene	SW-846, 8260A	0.005	0.005	40 - 160	30
1,2-Dibromo-3-chloropropane	SW-846, 8260A	0.005	0.005	23 -143	30
1,2-Dibromoethane	SW-846, 8260A	0.005	0.005	37 - 151	30
Dibromomethane	SW-846, 8260A	0.005	0.005	38 - 164	30

TABLE III-1
Dutchboy Site
Project Required Detection Limits

Analyte		Method	Detection Limits[1] (ppm)		Accuracy [2] (%)	Precision [3] (RPD)
			Solids[4]	Aqueous[5]	Solids[4] and Aqueous[5]	
Styrene		SW-846, 8260A	0.005	0.005	50 -140	30
1,1,1,2-Tetrachloroethane		SW-846, 8260A	0.005	0.005	39 -159	30
1,1,2,2-Tetrachloroethane		SW-846, 8260A	0.005	0.005	44 - 140	30
Tetrachloroethene		SW-846, 8260A	0.005	0.005	45 - 171	30
Toluene		SW-846, 8260A	0.005	0.005	49 - 151	30
1,2,3-Trichlorobenzene		SW-846, 8260A	0.005	0.005	1 - 162	30
1,2,4-Trichlorobenzene		SW-846, 8260A	0.005	0.005	16 -154	30
1,1,1-Trichloroethane		SW-846, 8260A	0.005	0.005	49 - 163	30
1,1,2-Trichloroethane		SW-846, 8260A	0.005	0.005	46 - 142	30
Trichloroethene		SW-846, 8260A	0.005	0.005	43 - 163	30
Trichlorofluoromethane		SW-846, 8260A	0.005	0.005	3 - 201	30
1,2,3-Trichloropropane		SW-846, 8260A	0.005	0.005	37 -157	30
1,2,4-Trimethylbenzene		SW-846, 8260A	0.005	0.005	43 - 163	30
1,3,5-Trimethylbenzene		SW-846, 8260A	0.005	0.005	38 - 170	30
Vinyl chloride		SW-846, 8260A	0.005	0.005	28 - 172	30
o-Xylene		SW-846, 8260A	0.005	0.005	41 - 161	30
m+*p*-Xylene		SW-846, 8260A	0.005	0.005	78 - 138	30
Other Analyses						
Total Lead		SW-846, 3050/7421	1	0.003	75 - 125[6]	20[7]
TCLP Lead		SW-846, 1311	1	0.003	75 - 125[6]	20[7]
TPH	Gasoline Only	SW-846, 8015	1	0.05	75 - 125[8]	20
	Diesel		7	1	61.75 - 128.25[9]	20
Asbestos		EPA 600/M4-E2-020	1%	NA	See Table 2-1 of EPA method.	

surrogate detected in the analysis is compared to the amount added and the percent recovery is determined. Quality control limits for surrogate recovery are presented in Table III-3.

In addition, accuracy will be evaluated by comparing results for the analysis of field, trip, and method blank samples to results for investigative samples. Blanks are artificial samples designed to evaluate the nature and extent of contamination of environmental samples that may be introduced by field or laboratory procedures. Contaminant concentrations in blanks should be less than detection or reporting limits.

C. Representativeness

Representativeness is the degree to which data accurately and precisely represent a characteristic of the population, natural variation at a sampling point, and/or an environmental condition. There is no standard method or formula for evaluating representativeness. The SAP has been developed to allow collection of samples that are representative of the media at the Site through selection of sampling locations that are appropriate relative to the objective of the specific sampling task, and by collection of an adequate number of samples from all locations both on and off-Site.

D. Completeness

Completeness is commonly expressed as a percentage of measurements that are valid and usable relative to the total number of measurements made. Analytical completeness is a measure of the number of overall accepted analytical results, including estimated values, compared to the total number of analytical results requested on samples submitted for analysis after review of the analytical data. The overall analytical completeness goal for laboratory data is 90 percent. If the analytical completeness goal is not met, the ENVIRON Program Manager and other senior project personnel will decide if the missing data are critical, i.e., necessary to meet the project objectives. If it is decided that the data are insufficient, additional field samples may be collected and analyzed. The formula for calculating completeness is presented in Chapter VII.

E. Comparability

Comparability is a qualitative characteristic expressing the confidence with which one data set can be compared with another. The desire for comparability is the basis for specifying the analytical methods chosen. The comparability goal is achieved through using standard techniques

to collect and analyze representative samples and reporting analytical results in appropriate units. Only when precision and accuracy are known can data sets be compared with confidence.

TABLE III-3
Dutch Boy site
Analytical Quality Control Objectives for Surrogate Recoveries

Surrogate Compound		Method	Percent Recovery	
			Solids[1]	Aqueous[2]
Volatile Organic Compounds				
4-Bromofluorobenzene		SW-846, 8260A	74 - 121	86 - 115
Dibromofluoromethane			80 - 120	NA
1,2-Dichloroethane-d4			NA	76 - 114
1,4-Dichloroethane-d4			80 - 120	NA
Toluene-d8			81 - 117	88 - 110
Total Petroleum Hydrocarbons				
Gasoline (only)	1-Chloro-3-fluorobenzene (FID)	SW-846, 8015	75 - 125	75 - 125
	Trifluorotoluene (PID)		75 - 125	75 - 125
Diesel	Chlorobenzene		50 - 135	50 - 135
	o-Terphenyl		75 - 135	75 - 135
Other Analyses				
Total Lead		SW-846, 3050/7421	NA	NA
TCLP Lead		SW-846, 1311	NA	NA
Asbestos		EPA 600/M4-E2-020	NA	NA

NOTES:

NA: Not applicable.

[1]Solid samples include soils and debris.

[2]Aqueous samples include water blanks.

IV. APPROACH AND SAMPLING METHODOLOGIES

Chapter III of the SAP describes the methodologies, locations, sample identification, collection, handling procedures, and analytical test methods that will be used in the sampling phase of the Removal Action. The SAP and QAPjP are generally consistent with standard procedures for the collection and analysis of soil samples (USEPA 1992; USEPA 1995). Several sections of the SAP relating to sampling approach and methodology are reiterated or summarized in this chapter of the QAPjP.

A. Sample Matrices

With the exception of equipment (rinsate) and trip blanks, all samples collected will be soil and debris samples only.

B. Sampling Design

A total of approximately 405 soil and debris samples will be collected on-Site and off-Site. The Site has been divided into two zones. Zone 1 represents that area of the Site that is presently not under pavement. Zone 2 represents those areas of the Site that are presently under some type of paved surface (e.g., concrete pavement, loading docks, etc.). All on-Site samples will be collected using a standard coring device. For Zone 2 sample locations, a power concrete coring device will be used to install a borehole through the concrete/pavement, through which the coring device can be inserted for soil sample collection. Most of the on-Site samples will be collected in one foot vertical intervals to the base of the fill material. At nineteen on-Site locations, soil borings will be extended to a depth of five feet below the fill base. Approximately 286 soil samples will be collected on-Site. In addition, approximately four samples will be collected from debris piles on the former loading dock in the southwestern portion of the Site.

For all off-Site sampling locations, ENVIRON proposes to install soil borings to the 0-1 foot depth interval via a stainless-steel hand auger. At one off-Site sample location (see Chapter III.B.2. of the SAP), the soil boring will be extended to a depth of five feet below the base of the fill material. Approximately 37 and 78 soil samples will be collected from two areas located off-Site: parkways in the vicinity of the Site and adjacent properties, respectively. Selected on-Site and off-Site soil samples (as described in Chapter III of the SAP) will be sieved (250 μm) and both the fine and total fractions analyzed for total lead. The frequency of QA samples (duplicates and blanks) is shown in Table IV-1.

Table IV-1 Dutch Boy Site Field Quality Control Samples[1]	
Sample Type	Frequency
Duplicates	At least 10% of primary samples collected for each matrix. (i.e., approximately 1 duplicate every 10 samples for a total of approximately 30 duplicate samples)
Equipment (Rinsate) Blanks	At least 10% of primary samples collected (i.e., approximately 1 rinsate blank every 10 samples for a total of approximately 30 rinsate blanks)
Trip Blanks	One per day that samples are shipped to analytical laboratory
[1]Each quality control sample is to be analyzed for the same constituents as those in the primary samples.	

TABLE IV-2
Dutchboy Site
Project Required Retention Times and Quantitation Ions
(Method SW-846, 8260A)

Analyte	Retention Times*	Quantitation Ions
Acetone	5.45	43
Benzene	9.94	78
Bromobenzene	16.72	156
Bromochloromethane	8.94	128
Bromodichloromethane	11.67	83
Bromoform	16.03	173
Bromomethane	3.67	94
2-Butanone	8.63	72
n-Butylbenzene	18.75	91
sec-Butylbenzene	17.93	105
tert-Butylbenzene	17.60	134
Carbon Disulfide	5.82	76
Carbon tetrachloride	9.64	117
Chlorobenzene	14.84	112
Chlorodibromomethane	13.97	129
Chloroethane	3.85	64
Chloroform	9.12	83
Chloromethane	2.90	50
2-Chlorotoluene	17.00	91
4-Chlorotoluene	17.16	91
1,2-Dibromo-3-chloropropane	19.96	75
1,2-Dibromoethane	14.14	107
Dibromomethane	11.44	93
1,2-Dichlorobenzene	18.80	146
1,3-Dichlorobenzene	18.10	146

TABLE IV-2
Dutchboy Site
Project Required Retention Times and Quantitation Ions
(Method SW-846, 8260A)

Analyte	Retention Times*	Quantitation Ions
1,4-Dichlorobenzene	18.25	146
Dichlorofluoromethane	2.72	85
1,1-Dichloroethane	7.58	63
1,2-Dichloroethane	9.98	62
1,1-Dichloroethene	5.34	96
cis-1,2-Dichloroethene	8.58	96
trans-1,2-Dichloroethene	6.82	96
1,2-Dichloropropane	11.25	63
1,3-Dichloropropane	13.64	76
2,2-Dichloropropane	8.56	77
1,1-Dichloropropene	9.63	75
cis-1,3-Dichloropropene	12.31	75
trans-1,3-Dichloropropene	13.12	75
Ethylbenzene	14.97	91
Hexachlorobutadiene	21.74	225
2-Hexanone	13.73	43
Isopropylbenzene	16.26	105
p-Isopropyltoluene	18.15	119
Methylene chloride	6.28	84
4-Methyl-2-pentanone	12.53	43
Naphthalene	21.88	128
n-Propylbenzene	16.87	91
Styrene	15.74	104
1,1,1,2-Tetrachloroethane	14.94	131
1,1,2,2-Tetrachloroethane	16.70	83

TABLE IV-2
Dutchboy Site
Project Required Retention Times and Quantitation Ions
(Method SW-846, 8260A)

Analyte	Retention Times*	Quantitation Ions
Tetrachloroethene	13.60	166
Toluene	12.80	92
1,2,3-Trichlorobenzene	22.39	180
1,2,4-Trichlorobenzene	21.40	180
1,1,1-Trichloroethane	9.37	97
1,1,2-Trichloroethane	13.39	83
Trichloroethene	10.94	95
Trichlorofluoromethane	4.30	101
1,2,3-Trichloropropane	16.75	110
1,2,4-Trimethylbenzene	17.67	105
1,3,5-Trimethylbenzene	17.11	105
Vinyl chloride	3.12	62
o-Xylene	15.73	106
m+*p*-Xylene	15.16	106

*Retention times may vary per instrument. The retention times provided are approximate.

- VOC analysis will be performed by the Gas Chromatography/Mass Spectrometry technique (GC/MS; SW-846, 8260A) (USEPA 1986)[4].

- TPH will be analyzed (diesel and gasoline ranges) by the Gas Chromatography/Flame Ionization Detection Technique (SW-846, 8015) (USEPA 1986)[5].

- Asbestos sampling will be conducted by Polarized Light Microscopy (USEPA Method 600/M4-E2-020).

D. Schedule of Work

Implementation of the field and analytical activities specified in the SAP will be completed within eight weeks of USEPA approval of the SAP.

E. Sample Handling, Preservatives, Containers, and Holding Times

Field sampling personnel are responsible for the proper description, documentation, labeling, packaging, storage, handling, and shipping of samples obtained in the field. Proper practices are necessary in the field and laboratory[6] to ensure the integrity of the sample from collection to reporting.

All samples will be collected using a standard coring device. For those soil borings installed to depths below the 0-1 foot interval below ground surface (all on-Site locations and a portion of the off-Site locations), a direct-push method (e.g., Geoprobe) will be used for installation of the borehole and sample collection. For those soil borings to be installed to the 0-1 foot depth interval (off-Site locations only), a stainless-steel hand-auger will be used for installation of the borehole and sample collection where feasible. For Zone 2 on-Site sample

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[4]See Attachment C - Laboratory Standard Operating Procedures: Lancaster SOP 0374, 1508, 1265, 1266, 1358, 1384, 1131, 3981, 4592, 5121, 5122, 5222, 5243, 5244, 5441, 5442, and 6292.

[5]See Attachment C - Laboratory Standard Operating Procedures: Lancaster SOP 2213, 2540, 6868, 6869, 6976, 1837, 2379, 5899, 4833, 2376, 5321, 5322, 5323, 5325, 6175, 7003, and 7004.

[6]See Attachment C - Laboratory Standard Operating Procedures: Lancaster SOP QA-102, QA-103, QA-104, and QA-109.

locations, a power concrete coring device will be used to install a borehole through the concrete/pavement, through which the coring device can be inserted for soil sample collection.

For soil cores collected via the direct push method, each one-foot core will be collected in an acetate liner, sealed in the field, and sent to the laboratory for analysis (or retention for potential future analysis). For soil cores collected via hand-auger (0-1 foot depth interval only), the one foot core will be separated into two components: the top 0-2 inch interval, and the lower 2-12 inch interval. Each component will be placed into a glass vial, sealed in the field, and sent to the laboratory for analysis. The upper two-inch vertical interval from each soil core will be homogenized in the laboratory and analyzed for total lead. The remaining portion of the soil core will be preserved for potential future analysis. Sample collection is described in detail in Chapter III of the SAP.

Field personnel will package, label, and place samples in coolers with blue ice (or equivalent) as indicated below. At the end of each sampling day, all samples will be shipped via overnight carrier or by courier to reduce processing time, unless otherwise determined. Samples will be delivered to a certified laboratory within 48 hours of collection. Sample holding times are stated in Table III-2[7].

F. Sample Packaging and Shipping

The following procedures will be followed for packing samples for shipment to the laboratory:

- Make sure all sample containers are tightly sealed.
- Place the sample containers in the cooler, allowing sufficient space for the addition of packing material between the containers.
- Place blue ice packs (or equivalent) on top of and between the samples.
- Place a copy of the Chain-of-Custody form in a sealed clear plastic envelope and place in the cooler.
- Place custody seals on outside of each cooler.
- Tape the shipping coolers shut if being transported by air courier.

[7]See Attachment C - Laboratory Standard Operating Procedures: Lancaster SOP IO-001.

Samples will be shipped every one or two days to the laboratory via overnight courier. Immediately upon arrival at the contract laboratory, the laboratory will record the condition of the shipping container and sample containers. The original Chain-of-Custody form will be returned from the laboratory as part of the final analytical report to the Program Manager. This record will be used to document sample custody transfers from the sampler to the laboratory and will become a permanent part of the project file.

G. Documentation

1. Photographic Documentation

Color photographs may be taken of representative sampling locations and the surrounding site to show the area, sampling equipment, and related Site activities. A camera that automatically places the date and time of each photograph on the image will be used, and frame and roll numbers will also be logged on a Photograph Log form to identify photographs with the correct sampling location.

2. Field Activity Daily Log

A field activity daily log will be used as a record of daily field activities showing the sequence of events. At a minimum, the log will include the following information:

- Project name and number;
- Date;
- Starting/ending time and nature of each major field activity;
- Names of all personnel on the site (including visitors), and a description of their involvement with the tasks being conducted;
- Weather conditions;
- References to appropriate field logs for details of each activity performed (e.g., reference sample collection logs for details of all samples collected that day);
- Identification of any photographs taken; and
- Signature of Task Leader or other reviewer.

The Field Activities Manager is responsible for ensuring that all activities are documented in the field activity daily log and that the details of each activity are recorded on the appropriate field documentation form. Contractor daily documents will be submitted to the ENVIRON Field Activities Manager no later than the start of business on the following day.

3. Variances

Significant variances from the field procedures specified in the SAP, QAPjP, and the Health and Safety Plan (HASP) will be approved by a representative of USEPA and documented on a Sample Alteration Form (Attachment A). If problems with the specified field procedures are encountered, corrective actions will be documented with a Corrective Action Report (Attachment B). Variances affecting project scope and/or schedule must be approved by the Project Manager. Any variance from the HASP must be signed off by the Site Health and Safety Officer prior to task implementation. Copies of the completed Sample Alteration Forms and Corrective Action Reports will be retained permanently in the project file.

4. Document Maintenance

Field personnel are responsible for recording field activities on the appropriate field documentation form in sufficient detail to allow the event to be reconstructed without relying on memory. It is the responsibility of the Field Activities Manager to ensure that all documents are complete and legible. At the end of each day, all documents completed that day will be reviewed by the Field Activities Manager for accuracy, completeness, and legibility.

The following field documentation forms or records will be used during the field activities, at a minimum:

- Sample Chain-of-Custody record (described below);
- Soil Sampling Log;
- Equipment Calibration Log;
- Photograph Log;

- Field Activity Daily Log;
- Sample Alteration Form; and
- Corrective Action Report.

Each completed form (a copy or original depending on the type of form) will be maintained on the Site in chronological order with other completed forms of the same type until the completion of the field activity. Copies of specific forms will be sent to the project office on a weekly basis for filing unless waived by the Program Manager.

5. Chain-of-Custody Record

a. Sampling Custody Procedures

The chain-of-custody record for each sample will originate at the Site, where samples will be prepared for shipment to the laboratory. ENVIRON will be responsible for completion of the chain-of-custody record throughout the sampling program until the samples have been delivered to the laboratory. The chain-of-custody record will be continued through sample collection, shipment, and analysis by the laboratory. This record will be completed in order to establish the documentation necessary to trace sample possession from sample collection through sample analysis. The sampling portion of the chain-of-custody record will contain:

- List of sampling team members;
- Sample number;
- Signature of sampler or bottle preparer;
- Date and time of sample collection;
- Sample depth;
- Medium type;
- Signatures of persons involved in the chain of possession;
- Inclusive dates of possession; and
- Preservation.

b. Laboratory Custody Procedures

A member of the Sample Administration Group will receive shipment of the samples from the field, sign the chain-of-custody, and create an internal laboratory chain of custody. The Sample Administrative Group will track the custody of the samples from the time they are received until the time the samples are entered into the Sample Management System. The appropriate data from the chain-of-custody record will be entered into the laboratory sample tracking system (both a written file and an electronic database) using the sample number from the sample label or assigning a unique laboratory number to each sample. The samples will then be transferred to a sample custodian who will store the samples in an assigned secure location. The internal COC will accompany the samples from the storage to the laboratory for analysis and during any other transfers. After analysis, the samples will be returned to the Sample Support Group, which will ensure that the COCs are complete. This laboratory record will serve as the documentation for all evidentiary considerations.

The a member of the Sample Administration Group will notify ENVIRON's QA Manager or Field Activities Manager of any discrepancies noted on the chain-of-custody or sample labels. Samples will not be analyzed until the discrepancy is resolved. Any changes made will be documented by the laboratory and ENVIRON's QA Manager.

Any unused portions of samples remaining after completion of analysis by the laboratory will be disposed of in accordance with procedures developed by the laboratory and consistent with applicable laws and regulations governing sample disposal.

The Sample Administration Receipt Documentation Log should be completed by a member of the Sample Administration Group upon receipt of the sample and will contain:

- Name of person receiving the samples;
- Date and time of sample receipt by the laboratory;
- Sample condition and temperature; and
- Any paperwork discrepancies or unpacking problems.

The laboratory portion of the chain-of-custody form will be completed each time the sample is transferred and will contain:

- Name of person receiving the samples;
- Laboratory sample number;
- Date and time of transfer; and
- Reason for change of custody.

Lancaster's SOPs for sample receiving, log in, storage, and tracking during sample preparation and analysis are provided as Attachment C.

H. Sample Identification and Labeling Procedures

Each sample collected for testing will be assigned a unique sample identification (ID) code. The sample ID will facilitate data management by referencing the analytical laboratory, depth interval, site, date, and location. All samples will be labeled with the sample ID code and other field information.

1. Sample Identification

To ensure correct identification of all samples collected, a unique alphanumeric code will be assigned to each sample.

The 15-character sample ID scheme to be used is summarized below. The hyphens included in this sample ID are provided for clarity and will be eliminated for database management.

Sample ID: ndd-SS-MMDDYY-AAAA
Where:

n = Laboratory designator
L = Lancaster

dd = Depth Interval:
01 = 0-1 foot depth interval
12 = 1-2 foot depth interval

SS = Site:

DB = Dutch Boy Site

OA = Off-Site; adjacent property

OP = Off-Site; parkways

BG = Background

MMDDYY = Date:

Month, day, and year in number format (e.g., 062196 = June 21, 1996).

AAAA = Location:

QA/QC samples (i.e., duplicate samples, field equipment (rinsate) blanks, and trip blanks) will be assigned fictitious numbers starting with 97, 98, and 99, respectively (e.g., 9701, 9702, etc.).

2. Sample Labels

The sample labels will be placed on the sample containers so as not to obscure any data on the containers. Sample information will be printed on the labels in a legible manner using waterproof ink. The label will contain sufficient information so the sample can be identified on the sampling information form or sample collection log. Sample labels will contain the following information:

- The project name and number (i.e., Dutch Boy Site, 01-4598A).
- A unique sample identification (see above).
- The date and time.
- Designation of the sample as a composite, if appropriate.
- Identification of preservatives used, if any.
- A list of analytical tests to be performed on the sample.
- Other necessary remarks.
- Name of the sampler.

I. Sampling Equipment and Procedures

This section describes the procedures to be used during the field portions of the investigation.

1. Decontamination Procedure

Prior to and between sample collection, all sampling equipment (e.g., stainless steel shovels and trowels) will be thoroughly cleaned using a high pressure steam cleaner and/or rinsed with tap water, rinsed with non-phosphate detergent solution, rinsed with tap water to remove detergent, rinsed with distilled/deionized water, and air dried.

2. Waste Management

All water used during decontamination will be stored in drums and labeled appropriately. The drums will be placed in an on-site waste storage area pending analytical test results. Similarly all waste soils generated during the sampling program will be drummed and stored on-Site pending analytical results. The decontamination water and waste soils will then be disposed of appropriately.

J. Corrective Action

This section describes the field and laboratory corrective action program developed for the site investigation. The criteria for data acceptability are established elsewhere in this QAPjP and include data precision, accuracy, representativeness, comparability, and completeness. These PARCC criteria shall serve as the predetermined limits for data acceptability beyond which corrective action is required. If the ENVIRON Program Manager or QA Manager determines that data do not meet these criteria or procedures are not implemented as described herein, then corrective action is required. All proposed corrective actions shall be approved by the Principal-in-Charge. The Program Manager or QA Manager shall initiate the corrective action by notifying the project team members in a written corrective action memorandum detailing the corrective action to be implemented.

1. Field Situations

If problems originating in the field are identified, immediate corrective action will take place. If such action does not resolve the problem, appropriate personnel will be assigned to investigate and evaluate the cause of the problem. Once a corrective action is implemented, the Field Activities Manager will verify that the problem has been eliminated.

2. Laboratory Situations

Corrective action, if necessary, will be initiated by the Laboratory QA Manager in consultation with ENVIRON's QA Manager. Corrective action may include, but is not limited to:

- Reanalyzing the samples, if holding-time criteria permit;
- Evaluating and amending sampling and analytical procedures;
- Accepting data with an acknowledged level of uncertainty; and
- Resampling and analyzing only if ENVIRON determines that the data are critical to an effective characterization of the site.

In the event that the above corrective actions are deemed unacceptable, an alternate laboratory will be selected to perform necessary or appropriate verification analyses.

3. Immediate Corrective Action

Any equipment and instrument malfunctions will require immediate corrective actions. The laboratory QC charts are working tools that identify appropriate immediate corrective actions to be taken when a control limit has been exceeded. They provide the framework for uniform actions as part of normal operating procedures. The actions taken should be noted in field or laboratory logbooks, but no other formal documentation is required unless further corrective action is necessary. These on-the-spot corrective actions will be applied daily as necessary.

4. Long-term Corrective Action

The need for long-term corrective action may be identified by standard QC procedures, control charts, and/or performance or system audits. Any procedural or data quality problem that cannot be solved by immediate corrective action falls into the long-term category. The essential steps in a corrective action system are:

- Identification and definition of the problem;
- Investigation and determination of the cause of the problem;

- Determination and implementation of a corrective action to eliminate the problem; and
- Verification that the corrective action has eliminated the problem.

Documentation of the problem is important in corrective action. The responsible person may be an analyst, the Field Activities Manager, the laboratory QA Manager, the sampler, ENVIRON's QA Manager, or the Program Manager. In general, the respective QA Manager will investigate the situation and determine who will be responsible for implementing the corrective action. ENVIRON's QA Manager will verify that the corrective action has been taken, and appears effective, and that the problem has been resolved.

The required corrective action will be documented by ENVIRON's QA Manager and the Field Activities Manager for site activities. The corrective action will be discussed with the Program Manager and the USEPA Remedial Project Manager (RPM) prior to implementation if the severity of the problem warrants such discussion.

Any changes proposed for amending sampling and analytical procedures will be documented in addenda to the SAP or QAPjP and/or with an appropriate Corrective Action Report or Sample Alteration Form.

5. Corrections to Documentation

Original data recorded in field logbook, chain-of-custody records, and other forms may be written in ink. None of these documents will be altered, destroyed, or discarded even if they are illegible or contain inaccuracies that require a replacement document.

If an error is made on a document assigned to one individual, that individual will make the correction by drawing a line through the error, entering the correct information, and initialing and dating the change. The erroneous information will not be obliterated. Any additional error(s) discovered on a document will be corrected by the person who made the entry. All corrections will be initialed and dated by the author. In addition, the author will complete a Sample Alteration Form or Corrective Action Report, as appropriate (see Attachment A and B, respectively, for copies of these forms).

V. PROJECT ORGANIZATION AND RESPONSIBILITIES

A. Project Staffing

Joyce Schlesinger, Managing Principal of ENVIRON's Arlington, Virginia office will serves as Principal-in-Charge for the project. Ranjit Machado of ENVIRON, the designated Project Coordinator, will manage and coordinate all aspects of the project in conjunction with Ed Hanlon, USEPA's On-Scene Coordinator. Gavin P. Thompson, Ph.D., will be the QA Manager. Steve Dielman will be the Health and Safety Coordinator and the Field Activities Manager. The primary project responsibilities for the key personnel at ENVIRON and the contract laboratory are identified below. The project management structure is represented in Figure V-1.

JOYCE SCHLESINGER, P.E.: Ms. Schlesinger is a Managing Principal at ENVIRON. Her project responsibilities will include supervision of all ENVIRON staff and their efforts, and overall project QA/QC. Her address is ENVIRON Corporation, 4350 N. Fairfax Dr., Arlington, VA 22203. Her phone number is (703) 516-2340.

RANJIT MACHADO, P.E.: Mr. Machado is a manager at ENVIRON. He will serve as the ENVIRON Program Manager and will oversee project activities. Mr. Machado is responsible for monitoring the work effort, schedule, costs, and communication. The Program Manager will provide the focal point for communications between NL, the USEPA, and the project staff. This liaison activity will provide clear lines of communication among all parties to minimize the chance for misconceptions concerning any aspect of the project. Mr. Machado will ensure that the activities of all Site personnel comply with the approved work plans and will recommend or provide disciplinary action, as appropriate, if noncompliance occurs. Mr. Machado's address is ENVIRON Corporation, 4350 N. Fairfax Dr., Arlington, VA 22203. His phone number is (703) 516-2358.

GAVIN P. THOMPSON, Ph.D.: Dr. Thompson is a Senior Science Advisor with ENVIRON. He will serve as ENVIRON's QA Manager. His project responsibilities include overall QA/QC for the analytical data generated by the sampling and analysis activities, supervision and maintenance of data processing and data processing QC, performance of data review, and conducting laboratory performance and system audits. His address is ENVIRON Corporation, 4350 N. Fairfax Drive, Arlington, VA 22203. His phone number is (703) 516-2364.

STEVE A. DIELMAN: Mr. Dielman is a manager with ENVIRON. He will serve as the Field Activities Manager for this project. His project responsibilities include supervision of the sampling operations and the sampling QC; supervising and reporting on field performance; and performance of system audits related to field activities. His address is ENVIRON Corporation, 4350 N. Fairfax Drive, Arlington, VA 22203. His phone number is (703) 516-2363.

DOUGLAS H. ERRETT: Mr. Errett is an Associate with ENVIRON. He will serve as the Health and Safety Coordinator for the project. His responsibilities include development and review of safety protocols and procedures necessary to field operations, and investigation of all site-related injuries. His address is ENVIRON Corporation, 4350 N. Fairfax Drive, Arlington, VA 22203. His phone number is (703) 516-2384.

LEE-ANN TRACY: Ms. Tracy is an Associate with ENVIRON. She is the Data Validation Specialist for the project. Her project responsibilities include performing the validation of field and analytical data. Her address is ENVIRON Corporation, 4350 N. Fairfax Dr., Arlington, VA 22203. Her phone number is (703) 516-2382.

B. Laboratory Responsibilities

Lancaster Laboratories (Lancaster) of Lancaster, Pennsylvania will provide services for analyses of samples collected during the site investigation. All organic and inorganic analyses will be performed under the conditions of relevant USEPA methods.

TIMOTHY OOSTDYK, Ph.D.: is the Project Manager/Chemist for Lancaster. He is responsible for all operations including technical and client services. His address is Lancaster Laboratories, 2425 New Holland Pike, P.O. Box 12425, Lancaster, PA 17605-2425. His phone number is (717) 656-2681.

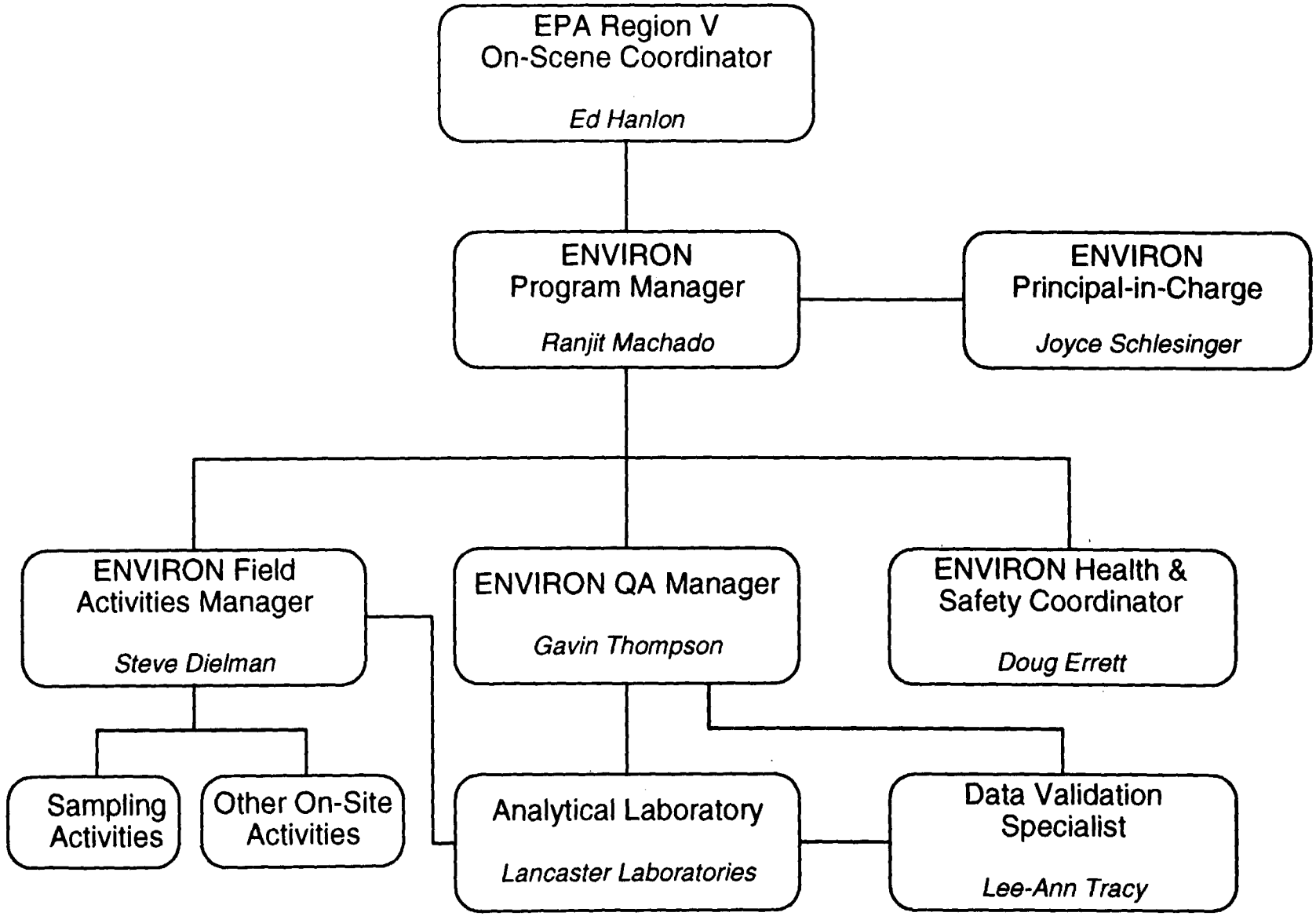
M. LOUISE HESS, B.S.: is QA Manager for Lancaster. Her responsibilities include supervision and review of the laboratory analyses and the laboratory QC effort, the data processing and data processing QC. Her address is Lancaster Laboratories, 2425 New Holland Pike, P.O. Box 12425, Lancaster, PA 17605-2425. Her phone number is (717) 656-2681.

ANNELIESE HUTCHISON, B.S., M.B.A.: is the Sample Receipt/Sample Entry Group Leader for Lancaster. Her project responsibilities will include the supervision of the sample receipt, unpacking, and entry of information into the laboratory information management system. Her address is Lancaster Laboratories, 2425 New Holland Pike, P.O. Box 12425, Lancaster, PA 17605-2425. His phone number is (717) 656-2681.

CYNTHIA AYARS, B.S., M.B.A.: is the Sample Support Group Leader at Lancaster. Her responsibilities include the supervision of storage and retrieval of samples. Her address is Lancaster Laboratories, 2425 New Holland Pike, P.O. Box 12425, Lancaster, PA 17605-2425. His phone number is (717) 656-2681.

C. USEPA Responsibilities

ED HANLON: is the EPA project manager and on-scene coordinator and will oversee project activities. He is responsible for monitoring the work effort and communication, and serves as a focal point for communications between NL, USEPA, and the public. This liaison activity includes coordinating reviews of the QAPjP with EPA's QAPjP staff. Mr. Hanlon's address is USEPA, 77 West Jackson, Mailcode SR-6J, Chicago, IL 60604. His phone number is (312) 886-4071.



ENVIRON

PROJECT MANAGEMENT STRUCTURE: DUTCH BOY SITE

Figure
V-1

VI. QUALITY ASSURANCE REQUIREMENTS

A. Sample Documentation and Handling

To assure the integrity of the samples collected prior to analyses, the sample handling, documentation, custody, packaging, shipping, identification, and labeling procedures are outlined in Chapter IV.

B. Initial and Continuing Instrument Calibration

Instrument calibration consists of the establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristics of known standards. The calibration standards must be prepared using the same type of acid or concentration of acids as used in the sample preparation. Initial instrument calibration should consist of analysis of analytical standards for a series of different specified concentrations, used to define the quantitative response, linearity, and dynamic range of the instrument to target compounds. Continuing calibration should consist of an analytical standard run every ten analytical samples or every twelve hours, whichever is more frequent, to verify the calibration of the analytical system.

C. Blanks

1. Calibration Blank

A calibration blank is prepared by the laboratory using acidified distilled/deionized water to ensure that contamination is not present in the preparation water or in the analytical instrument due to carry over from other samples or standards. The initial calibration blank (ICB) is analyzed after the analytical standards, but not before analysis of the initial calibration verification (ICV) solution(s), during the initial calibration of the instrument.

A continuing calibration blank (CCB) is analyzed after every initial and continuing calibration verification. The CCB shall be analyzed at a frequency of 10% or every twelve hours during the run, whichever is more frequent. The CCB result (absolute value) must not exceed the CRDL.

2. Method (or Preparation) Blank

The method blank is used to detect any contamination introduced by the laboratory. A method blank is a quality control sample prepared by the laboratory that contains distilled/deionized water and the same reagents used with the field samples and carried through the entire analytical procedures (digested and analyzed). An aqueous method blank is treated with the same reagents as a sample with a water matrix; a solid method blank is treated with the same reagents as a soil sample. Method blanks shall be generated and analyzed at a frequency of at least one per ten samples of a given matrix (e.g., soil or water).

3. Equipment Rinsate Blanks

One equipment rinsate blank is required per parameter per ten samples (i.e., 10% of the primary samples), and at least two equipment rinsate blanks will be collected in the field. These samples are used to test for residual contamination of the sampling equipment. The equipment rinsate blanks will be collected by pouring laboratory-supplied analyte-free water over decontaminated sampling equipment into labeled sample bottles. Pre-cleaned sample bottles with appropriate preservatives will be supplied by the analytical laboratory. Decontamination procedures are described in Chapter IV. Immediately after filling, the sample bottles will be securely closed, placed in a cooler, and kept chilled with blue ice (or equivalent) until delivery to the analytical laboratory. Equipment rinsate blanks will be considered associated with all samples collected since the last equipment rinsate blank was collected.

4. Trip Blanks

One trip blank is required per cooler used to ship samples. Trip blanks will be shipped by the analytical laboratory with the sample containers. These samples are used to identify contamination introduced in the field or by the laboratory. Trip blanks will be labeled in the field at a specific sample location, and shipped to the analytical laboratory with the associated samples. At least one trip blank sample will be included in each shipment to the analytical laboratory. Trip blanks will be considered to be associated with all samples in the same shipment to the laboratory.

D. Performance Evaluation Samples

Project QA/QC checks will be employed to evaluate the analytical performance of the laboratory. Each item of equipment used in laboratory analyses will be calibrated at a frequency specified by the appropriate USEPA method. Calibration data will be recorded and reported along with other QC parameters.

Analytical QA/QC for laboratory testing will be based on: (1) method requirements as stated in the current USEPA procedure; (2) the laboratory Standard Operating Procedures (SOPs) developed for target analytes quantified by the methods requested; and (3) the laboratory's specified QA/QC procedures. Laboratory precision and accuracy will be evaluated based on USEPA method-required system checks and results of required laboratory QA/QC samples introduced into the sample analysis stream. The types and frequency of required system checks and laboratory QA/QC samples are provided in the specific USEPA methods. Should problems be encountered, the laboratory will undertake corrective action procedures as described in Chapter IV. At a minimum, the following laboratory QA/QC checks will be performed.

- Calibration Check Compounds (CCCs): Target compounds used to evaluate the calibration stability of the instrument. Maximum percent deviations of the CCCs are defined in the protocol.

- System Performance Check Compounds (SPCCs): Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factor criteria for the SPCCs are defined in the protocol.

- Internal Standards: Compounds added to every standard, blank, matrix spike, matrix spike duplicate, sample (for VOCs), and sample extract at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

In addition to the laboratory QA/QC described above, project QA/QC checks will be employed to evaluate the analytical performance of the laboratory. Project QA/QC checks will consist of submitting controlled samples that are introduced to the laboratory from the field. Project QC samples will consist of field (equipment rinsate) blanks, trip blanks, and duplicate

samples. Duplicate samples will be collected for each matrix (soil and debris) at a rate of at least 10% of the primary samples (see Table IV-1). Spiked samples will also be part of the QA/QC program.

E. Detection Limit

Detection limits for each analyte are presented in Table III-1.

VII. ERROR DETERMINATION

A. Calculation of Precision

The procedure for assessing precision based on duplicate samples will be as follows:

Tabulate duplicate data and calculate the relative percent difference (RPD) as shown below for each duplicate pair:

$$RPD(\%) = (X_1 - X_2)/X_{avg} \times 100\%$$

where:

X_1 = concentration for sample 1 of duplicate or replicate

X_2 = concentration for sample 2 of duplicate or replicate

X_{avg} = average of concentrations in samples 1 and 2 or replicates 1 and 2

B. Calculation of Accuracy

The procedure for assessing accuracy based on spike sample results will be as follows:

Tabulate sample data and calculate the recovery (R) percentage as shown below for each sample:

$$R\% = (SSR - SR)/SA \times 100\%$$

where:

SSR = spike sample result

SR = sample result

SA = spike added

C. Calculation of Completeness

Overall completeness for the sample data collected will be calculated according to the following equation:

$$C(\%) = V/T \times 100\%$$

where:

C	= completeness of analytical effort in percent
V	= amount of valid data obtained
T	= amount of valid data expected under normal conditions

The data collected will be validated using the procedures described in Chapter IX. Completeness of the data will be calculated on this basis.

VIII. DELIVERABLES

A. Laboratory Deliverables

After the Laboratory QC Manager has qualified the analytical results and the Laboratory Project Manager has approved the report, the laboratory will provide ENVIRON with a report in the following scheme:

Sample Analytical Results: General Reporting Requirements

The following information will be provided with each sample delivery group or laboratory report:

- A transmittal letter, signed by the Laboratory Project Manager and QC Manager, identifying the laboratory report number and issuance date;
- A master list of laboratory tracking identification numbers correlated with field sample identification numbers and sample analysis batch identification to correlate QC samples to sample analysis batch;
- Chain-of-Custody forms signed by the Laboratory Sample Control Area Leader; and
- A narrative summary identifying any QA or sample problems encountered and the corrective action taken.

The following information will be contained on the sample analytical results summary forms:

- The results of sample analysis;
- The analytes of interest;
- The method of analysis;
- The method detection limit for each analyte;
- Sample collection date;
- Sample receipt date;
- Sample preparation (e.g., extraction) date; and
- Sample analysis date.

The following QA data for inorganics analyses will be provided where applicable:

- Results of method and field blank analyses;
- Results of LCS and control limits;
- Results of laboratory duplicate analyses;
- Results of pre-digestion sample spike analysis; and
- Results of post-digestion sample spike analysis.

The following QA data for organics analyses will be provided where applicable:

- Results of method, trip, and field blank analyses;
- Results of LCS analyses and control limits;
- Results of matrix spikes and calculated percent recovery, control limit, and source. Matrix spikes must be sample-specific for submitted sample batches;
- Results of matrix spike duplicates, calculated percent recoveries for matrix spike duplicate, RPD between matrix spike and matrix spike duplicate, control limits, and source. Matrix spike duplicates must be sample-specific for submitted sample batches; and
- Results of surrogate spikes, percent recoveries, control limits, and source.

B. Data Reporting

Data generated during the site investigation will be appropriately identified, validated and summarized in the final report. ENVIRON has developed a data storage and information system to facilitate data for tracking and data calculations, and for the transfer of data to various forms and reports. Quality control procedures have been designed to eliminate errors during these steps.

Appropriate documents will be prepared and distributed to summarize the field activities performed and the results of all data collected during the site investigation. These reports, to the extent possible, will include:

- Presentation of results;
- Summaries of field data from field measurements such as water levels and soil moisture and water-quality parameters; and
- Field location of sampling points.

In addition, USEPA will be provided with copies of the following documents for each sampling event:

- All field measurements, data logbooks, and notebooks;
- Laboratory reports; and
- Data validation reports summarizing the validation process used and specific comments pertaining to a sample or group of samples.

An inventory of all documents contained in the project file will be developed. This document inventory shall contain the following information:

- Document date;
- Author(s), including title and affiliation;
- Recipient(s), including title and affiliation;
- Title of document;
- Summary of content; and
- Number of pages.

All documents supplied to USEPA shall include a cover sheet containing the following information:

- Site name (Dutch Boy Site);
- Date; and
- Authors.

Upon completion of the data validation and assessment of the data with respect to precision, accuracy, and completeness, ENVIRON will develop QA/QC reports for each analytical data

package. This report, along with a field activities documentation report, will be prepared to summarize the results obtained for all samples collected during the investigation.

IX. DATA VALIDATION

Validation for analytical results generated by methods will be performed in accordance with and *EPA CLP Functional Guidelines for Organic Data Review* (USEPA 1994a) and *EPA CLP Functional Guidelines for Inorganic Data Review* (USEPA 1994b). These guidelines are collectively referred to herein as the "Functional Guidelines." For analytes for which the functional guidelines are not applicable, specific QA/QC requirements and actions are presented herein.

The following is a description of the validation steps that will be used by ENVIRON's Data Validation Team to validate the laboratory data. All sample data within each case will be checked, and the results will be summarized in the final report. The validation steps are as follows:

- Compile a list of all investigative samples;

- Compile a list of all QC samples, including:
  - Field blanks;
  - Trip blanks;
  - Blind duplicate samples (replicated or co-located samples), if applicable;
  - Split samples taken by other parties, if applicable;
  - Laboratory replicates;
  - QC performance samples;
  - Bottle blanks;
  - Matrix spikes; and
  - Matrix spike duplicates.

- Review laboratory analytical procedures and instrument performance criteria as outlined below.

  <u>Organic Analysis</u>
  - Sample holding time;
  - Blanks;
  - LCS recovery;

- Surrogate recovery;
- Matrix spike/matrix spike duplicate; and
- Method detection limits.

Inorganic Analysis

- Sample holding time;
- Blanks;
- LCS recovery;
- Duplicate sample analysis;
- Spike sample analysis; and
- Method detection limits.

- Summarize data, including the following elements:
  - Results;
  - Sample media identification;
  - Sample location and descriptions;
  - Appropriate concentration units;
  - Appropriate significant figures;
  - Data qualifiers; and
  - Definitions.

- Review data summary for potential data quality problems, including:
  - Unexpected results;
  - Common laboratory contaminants;
  - Unusual spatial concentration/identification relationships;
  - Unexpected compound or parameter relationships;
  - Samples in which dilution was necessary;
  - Samples that may have exhibited carry-over; and
  - Time and date of sample collection.

The performance criteria for organics analyses will be evaluated as follows. These criteria are derived from the USEPA National Functional Guidelines (EPA 1994a, 1994b) where applicable.

flag associated analytical results as estimated quantities (validation flag "J") or as unusable (validation flag "R"), depending upon the determination of the severity of the impact on the quality of the results.

- Matrix spike recovery: Accuracy is measured by the percent recoveries for MS/MSD analyses. The Data Validation Specialist will determine if deviations outside the QC limits for percent recovery impact on the quality of the associated sample results. If so, the Data Validation Specialist will flag associated analytical results as estimated quantities (validation flag "J") or as unusable (validation flag "R"), depending upon the determination of the severity of the impact on the quality of the results.

- Matrix spike duplicate: Precision of a set of analyses will be evaluated by determining the RPDs for MS/MSD samples. The Data Validation Specialist will determine if deviations outside the QC limits for RPDs affect the quality of the associated sample results. If so, the Data Validation Specialist will flag associated analytical results as estimated quantities (validation flag "J") or as unusable (validation flag "R"), depending upon the severity of the QC problem.

- Surrogate spike recovery: Surrogate spike recovery will also be used to evaluate the accuracy of reported measurements. A surrogate standard is a distinct chemical that behaves similarly to the target chemical and is purposely added to the sample prior to cleanup and extraction. The surrogate spike recovery is used to assess recovery of the target chemical from the sample matrix. A known amount of a surrogate standard is added to the sample prior to cleanup. The amount of the surrogate detected in the analysis is compared to the amount added and the percent recovery is determined. If surrogate recoveries do not meet QC criteria, sample data are considered estimated quantities (data qualification flag "J") or unusable (data qualification flag "R"), depending upon the severity of the excursion beyond QC limits.

- Method detection limits: Reported method detection limits will be compared against those specified in this SAP. The Data Validation Specialist will determine the cause

of any elevated detection limits and the impact on the data usability. The laboratory will be contacted if a significant number of samples have elevated detection limits.

The performance criteria for lead analyses will be evaluated as follows. These criteria are derived from the USEPA Functional Guidelines where applicable.

- Holding times: The accuracy of analytical results may depend upon analysis within specified holding times. In general, a longer holding time is assumed to result in a less accurate measurement due to the potential for loss or degradation of the analyte over time. The data reviewer will qualify results for samples analyzed outside holding times based upon professional judgment. In general, data will be qualified as estimated quantities (qualification flag "J") or unusable (qualification flag "R"), depending upon the determination of the severity of the impact on the quality of the results.

- Blanks: Accuracy will be evaluated by comparing results for the analysis of field and method blank samples to results for investigative samples. Contaminant concentrations in blanks should be less than detection or reporting limits. If a contaminant is found in a blank and the concentration of the same analyte in an associated sample is less than five times that detected in the blank, then the data reviewer will qualify associated result as non-detect (data qualification flag "U") (USEPA 1994a). If the result is greater than five times the concentration in the blank, no data qualification is required.

- Laboratory control sample: The laboratory limits for precision, as measured by the RPD between laboratory DCS analyses, will be the laboratory control limits based on historic data calculated as specified in the analytical methods. If these limits are not met, the Data Validation Specialist will flag associated analytical results as estimated quantities (validation flag "J") or as unusable (validation flag "R"), depending upon the determination of the severity of the impact on the quality of the results. The laboratory limits for accuracy, as measured by the percent recoveries for LCSs, the Single Control Samples (SCS) and DCS analyses, will be the laboratory control limits based on historic data calculated as specified in the

analytical methods. If these limits are not met, the Data Validation Specialist will flag associated analytical results as estimated quantities (validation flag "J") or as unusable (validation flag "R"), depending upon the determination of the severity of the impact on the quality of the results.

- Duplicate sample analysis: Duplicate samples are field samples that are split into two aliquots. Each aliquot is then prepared and analyzed separately. The RPD between the duplicate measurements is a measure of the precision of the analysis. If the duplicate sample RPD is outside of QC limits, the associated sample results are considered estimated quantities (data qualification flag "J").

- Spike sample analysis: For spike sample analysis, a standard metal is spiked into an investigative sample either prior to or after sample digestion. The percent recovery of the standard is then determined in order to evaluate the accuracy of analytical results. If the spike recoveries are outside of QC limits, the associated sample results are considered estimated quantities (data qualification flag "J"). Post-digestion spikes are not required if the pre-digestion spike results are within QC limits.

A sample summary will be prepared to address precision, accuracy, and completeness of the analytical data. Laboratory records and data package requirements will be checked to assess completeness of the data package. The validation effort will be performed by personnel qualified and experienced in the field of laboratory data validation.

Despite all efforts to achieve the objectives of the project, the potential for error exists in laboratory chemical analyses and in the data reporting process. Every reasonable effort will be made to compare and double-check data reported from the laboratory.

X. REFERENCES

USEPA. 1986. (1992 Revision). *Test Methods for Evaluating Solid Waste*. Office of Solid Waste and Emergency Response, Washington, D.C., November, (July 1992 Revisions).

USEPA. 1990. *Quality Assurance/Quality Control Guidance for Removal Activities; Sampling QA/QC Plan and Data Validation Procedures*. Interim Final, Office of Emergency and Remedial Response, Washington, D.C., April. EPA/540/G-90/004.

USEPA. 1992. *Options for Addressing High Background Levels of Hazardous Substances at CERCLA Sites*, Draft Issue Paper, Office of Emergency and Remedial Response, Washington, D.C., June.

USEPA. 1994a. *EPA CLP Functional Guidelines for Organic Data Review*. EPA540/R-94/012, Office of Emergency and Remedial Response, Washington, D.C., February.

USEPA 1994b. *EPA CLP Functional Guidelines for Inorganic Data Review*. EPA540/R-94/013, Office of Emergency and Remedial Response, Washington, D.C., February.

USEPA. 1995. *Determination of Background Concentrations of Inorganics in Soils and Sediments at Hazardous Waste Sites*. EPA/540/5-96/500, Office of Solid Waste and Emergency Response, December.

ATTACHMENT A

Sample Alteration Form

Sample Alteration Form

Project Name	
Project Number	

Material to be Sampled
Measurement Parameter
Standard Procedures for Field Collection and Laboratory Analysis (cite reference)
Reasons for Change in Field Procedures or Analysis Variation
Variation from Field of Analytical Procedure
Special Equipment, Materials, or Personnel Required

Initiators Name		Date	
Project Officer		Date	
QA Officer		Date	

ATTACHMENT B

Corrective Action Report

Corrective Action Report

Project Name			
Project Number			
Sample Dates Involved			
Measurement Parameter			
Acceptable Data Range			
Problem Areas Requiring Corrective Action			
Measures Required to Correct Problem			
Means of Detecting Problems and Verifying Correction			
Initiators Name		Date	
Project Officer		Date	
QA Officer		Date	

ATTACHMENT C

Laboratory Standard Operating Procedures:
Lancaster Laboratories

Attachment C Lancaster Laboratories Standard Operating Procedures (SOPs)		
SOP ID	Title	Pages
General Procedures		
QA-102	QAOM - Sample Login	3
QA-103	QAOM - Sample Storage and Disposal	5 + 1
QA-104	QAOM - Internal Chain-of-Custody Documentation	17
QA-109	QAOM - Laboratory Notebooks and Documentation	4 + 1
IO-001	Preservation Conditions, and Holding Times for Inorganic Samples	3
IO-004	QA for Graphite Furnace	10
IO-005	Department 23 Quality Control Procedures	12
IO-007	Preparation of Standards and Solutions Purpose and Contents A. Reagents B. Atomic Absorption Solutions F. Graphite Furnace Solutions G. Prep Room Solutions (waters) H. Prep Room Solutions (solids)	 11 + 1 2 16 8 11 14
IO-011	Inorganic Analysis Safety Procedures	6
Volatile Organic Compounds		
Draft SPME	Prescreening of Water and Soil Samples for Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) and Volatile Organic Content (VOC) Using Headspace Solid Phase Microextraction (SPME) and Gas-Chromatography with Flame Ionization Detection (GC/FID)	9
0374	Solid Matrix Sample Preparation	9
1508, 1265, 1266, 1358, 1384, 1131, 3981, 4592, 5121, 5122, 5222, 5243, 5244	Waters and Wastewaters for Priority Pollutant Volatile Target Compounds	37
5441, 5442, 6292	Soils and Solids for Volatile Target Compounds by Gas Chromatograph/Mass Spectrometry (GC/MS): Capillary Column Technique	27
Lead		
0947, 1339	Toxicity Characteristic Leaching Procedure TCLP Nonvolatile Leachates	15
1055-200.9	Lead in Drinking Water and Wastewater by Graphite Furnace	9
1055, 1155	Lead by Graphite Furnace	6
1056	Sample Preparation of Wastewater for Graphite Furnace Analysis of Metals	3

Attachment C Lancaster Laboratories Standard Operating Procedures (SOPs)		
SOP ID	Title	Pages
1156	Sample Preparation of Soil/Sediment for Graphite Furnace Analysis of Metals	4
5704	Sample Preparation of Extracts and Other Wastewater for Graphite Furnace Analysis of Total Metals	4
5710	Sample Preparation of Soil, Sediment, and Sludges for Graphite Furnace Analysis of Metals	4
5715	Sample Preparation of Potable Water and NPDES Wastewater for Graphite Furnace Analysis of Metals	4
Total Petroleum Hydrocarbons		
2213, 2540, 6868, 6869, 6976, 1837	Purgeable Aromatics in Soil Samples	16
2379, 5899	Preparation and Extraction of Soil and Solid Samples for the Determination of Purgeable Aromatics, Purgeable Halocarbons, and Gasoline Range Organics	3
4833	Extraction Procedure for the Determination of GC Fingerprint on Petroleum Products in Soil or Solid Waste Matrices	7 + 1
2376	Extraction Procedure for the Determination of GC Fingerprint on Petroleum Products in Water and Wastewater	7 + 1
5321, 5322	TPH-DRO API (Diesel Range Organics)	13 + 3
5323, 5325, 6175	BTEX/Gasoline Range Organics (GRO) - API	23 + 4
7003	Extraction Procedure for the Determination of Diesel Range Organics in Water and Wastewater	7 + 1
7004	Extraction Procedure for the Determination of Diesel Range Organics in Soil or Solid Waste Matrices	7
QAOM - Quality Assurance Operations Manual		

Initiated Date: 03/87
Effective Date: FEB 15 1996

CONFIDENTIAL

QUALITY ASSURANCE OPERATIONS MANUAL
SOP-QA-102

Title: Sample Log-in

Purpose:

In order to provide accountability of our results and to prevent sample loss or mix-up, a unique identification number is assigned to each sample.

Scope:

This SOP will cover the procedure used to log samples into the computerized sample management system (SMS) which are received for analysis.

Procedures:

1. All samples received by laboratory personnel shall be delivered to the Sample Administration Group immediately upon arrival at the laboratory. The only exception to this requirement will be samples which are not tracked using the SMS. There are only a few cases where samples will be not be tracked using the SMS. These include samples which will be stored for a long period of time prior to analysis, (e.g., stability storage) and samples for special projects that will be reported in a narrative R&D report instead of on the usual computerized analytical reports.

   The procedures for sample log-in described in this SOP apply only to samples which are logged into the SMS. However, a written procedure for tracking any samples not entered into the SMS must be developed by the technical department responsible for the project or analysis of those samples.

2. All client correspondence relating to samples shall also be transferred to the Sample Administration Group. This includes purchase orders, quotes, letters, and analysis request forms.

3. Personnel of the Sample Administration Group shall log the samples into the computer as soon as practical after receipt. The computer will assign a unique identification number to each sample. Samples shall be logged in on the same day they are received with the following exceptions:

   a. Samples received on a holiday will not be logged-in until the next normal work day. Samples received from 6 p.m. on Saturday through 11 p.m. on Sunday will be logged-in Sunday evenings by third shift Sample Administration.

   b. Samples submitted by clients without any indication of the tests to be performed or with unclear or incomplete information. Every effort shall be made to contact the client on the same day as sample receipt. These samples will be tracked in a Q&A hold database. This database is maintained by the Sample Administration Group.

   If same day entry is not possible, any special storage requirements (e.g., refrigeration) will be observed.

4. Upon assignment of a sample number, the computer will generate a label which shall be attached to the sample container. Every effort will be made as to not obscure the client label. The information on the label will include the Lancaster Laboratories' sample number, the client name, the storage location, a list of analyses requested (by analytical method number), a bottle code indicating container and preservative type, a unique bar code, and any notes to laboratory personnel.

5. Adjustment of sample pH, if necessary, will be the responsibility of the Sample Support Group. Preservation should be performed immediately after log-in. A list of preservatives required for routine analyses may be

UNCONTROLLED

6. All entries in preservation notebooks and on client paperwork shall be made in ink. The error correction procedure given in SOP-QA-109, "Laboratory Notebooks and Documentation," shall be followed for any changes made to this documentation.

7. After samples are logged-in (or preserved, homogenized, subsampled, if required) they shall be stored in the computer-assigned location. If the computer-assigned location is inappropriate for the samples, the location code may be changed by manually overriding the computer.

8. The Lancaster Laboratories' sample number assigned to each sample shall be used to identify the sample in all records, including laboratory notebooks, instrument printouts, and laboratory reports. The sample number will also be used to identify all additional containers of the sample which may be created during the sample preparation and analysis. This includes subsamples, extracts, and digestates.

SOPQA102.W60
012496

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Prepared by: Kathy L. DiMunzio Date: 1/25/96

Approved by: [illegible] Date: 1/26/96

Approved by: [illegible] Date: 2/2/96

Lancaster Laboratories
Where quality is a science.

Initiated Date: 03/87
Effective Date: JUL 30 1993

QUALITY ASSURANCE OPERATIONS MANUAL

SOP-QA-103

Title: Sample Storage and Disposal

Purpose:

Sample integrity can be compromised by improper storage conditions. The objective of these procedures is to prevent samples from deteriorating prior to analysis. The computerized sample management system (CSMS) is used to assign storage locations and to monitor the orderly storage of samples in locations from which they are easily retrieved for analysis or discard at the appropriate date.

Scope:

This SOP will outline procedures used in storing samples, retrieving and returning samples for analysis, and discarding samples when their holding time expires.

Procedures:

1. Personnel of the Sample Administration Group will designate the approximate size and type (e.g., refrigerator, freezer or room temperature) of sample storage required for each group of samples as they are logged onto the CSMS. The computer will assign the storage location and record the length of time the sample must be retained after the analysis report has been issued. Samples will be stored in the assigned

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location. If the location is not suitable (e.g., insufficient space), the storage location may be changed using the manual override on the computer. If refrigerated space has been requested and all the computerized refrigerator locations are occupied, samples will be assigned locations in overflow refrigerators and will be tracked using a manual system until computerized locations are available.

2. Analysts requiring the use of a sample may determine its location by referring to the daily sample status sheet. There are varying degrees of security on sample storage locations. The procedures for removal of samples from these locations are as follows:

   a. Free access locations are those which are neither locked nor attended by a sample custodian. These areas are usually located within an individual group's laboratory and samples may be removed from and returned to these locations without documentation. However, if the sample must be taken out of the laboratory, documentation may be requested. Care shall be exercised in returning the sample to its appropriate location.

   b. Controlled access areas are attended by a sample custodian and are usually large areas used by more than one group. Samples stored in controlled access areas can be removed only after requisitioning the sample via the CSMS. The sample custodian will retrieve the requisitioned samples from the storage locations and scan the bar code label. This process

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documents the sample transfer from the sample custodian to laboratory personnel. After use, the samples are returned to the sample storage center, scanned by the sample custodian and returned to the designated storage location. Only Sample Administration personnel shall be admitted to controlled access areas. The only exception to this rule will be during weekend hours when no sample custodians are on duty. During these hours, samples must be requisitioned as above, but analysts must retrieve the samples themselves, by obtaining a key to the controlled access area from the security desk. Samples must be scanned out as above. After use, samples must be scanned in and placed on the return cart inside WK. Sample custodians will return these samples to their location when they come on duty.

c. Locked storage areas are available in several individual lab areas. Access to these storage areas is limited to analysts who are responsible for the analysis of the samples stored there. These areas are locked when the laboratories are unattended and keys are available from members of the department where they are located. Samples are removed and returned as needed by analysts.

d. Forensic storage areas are locked and admission to these areas is only permitted to sample custodians. Most of the samples stored in these areas require strict chain-of-custody documentation as outlined in SOP QA-104, and should be requisitioned as described

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in (b) above. Samples may not be removed or returned to these areas without signing chain-of-custody forms.

3. To prevent unnecessary deterioration of the samples, the aliquots needed for analysis shall be removed and the sample returned to storage with a minimum of delay.

4. The Sample Administration Group will generate a discard list of samples with retention dates that have expired. The retention dates are based upon client requirements or defaulted to a given number of days past the date when the report is generated, if no client requirements were given. These samples will be removed from storage by a member of the Sample Support Group or a member of the department responsible for the given storage location. Hazardous samples shall either be returned to clients, decontaminated or disposed of at the direction of supervisory personnel. Other samples will be discarded or returned to the client, if requested. Prior to discarding each sample, the bar code will be scanned to prevent discard of the wrong sample.

5. The temperature of each refrigerator or freezer used for storing samples or reagents requiring temperature control should be checked during each normal working day by an assigned member of the group responsible for the samples stored within and recorded on a log posted on the outside of the unit. Units containing samples requiring more complete documentation of storage conditions are monitored by use of a computerized recording device or a temperature wheel. Refrigerator

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temperatures should be maintained at 4° ± 2°C and freezer temperatures should be maintained at -15° ± 5°C. If the temperature recorded does not fall within these ranges, the Maintenance Department should be contacted. Any repairs should be recorded and filed with the temperature log. All documentation of temperature checks and maintenance shall be kept in ink and any changes made shall follow the error correction procedure given in SOP-QA-109.

SOPQA103.W51
QA SOPs #1
071493

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Prepared by: M Louise Vess Date: 7/23/93

Approved by: J. William Hershey Date: 7/23/93

Read and understood by: _____ Date: _____

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Procedural Amendment #1

Number: SOP-QA-103

Title: Sample Storage and Disposal

Effective Date (listed on procedure): 07/30/93

Section(s) affected by change: Procedures

Reason for addition(s) or change(s): To allow flexibility for client-specified methods or protocols refrigeration requirements

Change will be effective from (date): 12/20/93

Samples or project affected: Project/samples with sample/standard storage temperature ranges other than those specified in this SOP.

List change(s) or addition(s) (specify which section):

Procedures:

Change third sentence in #5 to read as follows:

5. Refrigerator temperatures should be maintained at 4° ± 2°C and freezer temperatures should be maintained at -15° ± 5°C, unless otherwise specified in a client-supplied method or protocol.

SOPQA103.W60
QA SOP #1
122093

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Prepared by: _____ Date: 12-20-93

Approved by: _____ Date: 12/20/93

Approved by: _____ Date: 12/21/93

Lancaster Laboratories
A Thermo Analytical Laboratory
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Initiated Date: 03/87
Effective Date: DEC 0 1 1995

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QUALITY ASSURANCE OPERATIONS MANUAL

SOP-QA-104

Title: Internal Chain-of-Custody Documentation

Purpose:

In order to demonstrate reliability of data which may be used as evidence in a legal case or required by a regulatory agency or client, an accurate written record tracing the possession of samples must be maintained from the time they are received at the laboratory until the last requested analysis is verified. The chain of custody is to ensure traceability of samples while they are in the possession of the laboratory.

Scope:

Procedures for initiating and maintaining chain-of-custody (COC) documentation are described in this procedure.

Definition:

A sample is in custody if it is in any one of the following states:

1. In actual physical possession.

2. In view after being in physical possession.

3. Locked up so no one can tamper with it.

4. In a secured area, restricted to authorized personnel (e.g., in the ASRS system).

A. Procedure

1. Chain-of-custody documentation shall be kept upon the request of the client or for any samples which are known to be involved in a legal dispute. As with all analytical data, it is extremely important that this documentation is filled out completely and accurately with every sample transfer. **Everyone who handles the COC has the responsibility to check for documentation compliance to the point of their acquisition.** If changes need to be made to the form, they shall be made in accordance to the error correction procedure addressed in SOP-QA-109, "Laboratory Notebooks and Documentation." It will be the responsibility of the person who made an error in documentation to correct the error.

2. If requested by the client, the COC documentation will begin with the preparation of sampling containers. A form (Figure 1, attached) will be initiated by the person packing the bottle order for shipment to the client. If the delivery of containers is via Lancaster Laboratories Transportation Department, the driver shall sign the form when they relinquish the bottles to the client. Drivers must also sign COC forms when they pick up samples for analysis.

3. When samples arrive at the laboratory for analysis, a member of the Sample Administration Group will receive them and sign the external COC form that accompanies the samples, if provided. If the samples were picked up by our Transportation Department, the driver must sign the COC to relinquish the samples to sample administration.

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4. The Sample Administration Group will track the custody of samples between receipt and entry into the Sample Management System on the SA Receipt Documentation Log (Figure 2, attached). The client's sample designation will be used for identification purposes until a unique Lancaster Laboratories' number is assigned.

5. Samples will be entered into the Sample Management System as described in SOP-QA-102, "Sample Log-in." Sample Administration will enter an analysis number for "Laboratory Chain of Custody" if requested. A lab note will print to inform analysts of the need for COC documentation. This note will also be automatically added to the sample labels.

B. Creating the Internal Chain of Custody

1. Sample Administration personnel shall initiate an internal Laboratory Chain of Custody form at the time of sample entry (Figure 3, attached) for each type of container in the sample group. A master list of all chains created will also be initiated for each sample group at the time of entry (Figure 4, attached). The samples will then be relinquished to a sample custodian who will store the samples in an assigned secure location. This change of custody from sample entry to storage shall be documented on the chain, as well as any interim exchanges for rush analysis, preservation, homogenization, or temporary storage in the SA HOLD. The internal COC forms will then accompany the samples from storage to the laboratory for analysis.

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2. If samples need to be checked out from the Sample Administration Group before Lancaster Laboratories' numbers have been assigned to them, SA will be responsible for starting a COC form. They will note the available header information, the samples being relinquished (documented by the client sample designation), and the reason for transfer.

3. After sample entry, the original copy of the external client COC/analysis request form will be filed with Accounts Receivable, to be returned to the client with their invoice. Other copies of the external form will stay within SA to be filed within the client's paperwork file.

C. Documentation of Custody Changes

1. An example of how to document changes in sample custody is shown in Figures 3 and 5. Each change of sample custody must be accurately documented in a consistent format. All signatures documenting changes of custody will use the following format:

Signatures: first initial, full last name, employee number
Date: Month/day/year
Time: Documented as military time
Ink: Black ink is preferred, red ink and pencil are not acceptable

a. When sample support releases samples to an analyst they must:

Note the sample number(s) released, and sign the released by column of the chain.

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b. When an analyst receives samples from sample support they must:

Sign the received by column, note the date and time samples are received and note the reason why they are taking the samples (reason for change of custody).

c. When an analyst returns samples to sample support they must:

Note all sample numbers being returned, sign the released by column, and note time and date of return.

d. When sample support receives samples from an analyst they must:

Sign the received by column and note the reason for sample transfer.

2. Sample handling should be kept to a minimum. Analysts requiring use of a sample will requisition it through the computer requisition program. During the hours when sample support is manned by sample custodians, a custodian will receive the computerized requisition and remove the sample from storage. The custodian will ensure that the bottle type listed on the COC form matches the bottle type being distributed. **It will be the shared responsibility of the analyst and sample custodian to insure that forms are signed, dated, and reason for sample transfer are recorded with each change of custody, as directed by Item C1 above.**

3. Each specific test that an analyst performed in conjunction with the associated sample number(s) must be accurately documented by the analyst before the samples are returned to a sample custodian in the sample storage area.

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4. When an analyst requires the use of samples when a sample custodian will not be on duty, they must requisition samples earlier in the day or on the previous day. These samples and associated COCs will be pulled by a sample custodian and placed in the locked SA HOLD storage area. The sample custodian will note on the COC the change in transfer to the SA HOLD in addition to the time, date, and the sample numbers. The analyst picking up the samples will document the specific samples being checked out, record SA HOLD in the "Released by" column, sign the Received by column, note the time, date and reason for transfer. When the analyst returns the samples to the SA HOLD, they must sign the samples back into the SA HOLD.

5. The following changes of custody will be handled in the following manner:

   a. Documentation is required for all shift changes. Signatures involving transfers from one shift to another shall be the responsibility of the analyst who originally acquired the samples from sample support.

   b. Occasionally a sample container will be needed for analysis by an analyst in a department while it is in the custody of an analyst in another department. It will be the responsibility of the first person who received the sample to note on the COC the specific sample numbers requested by the second person, and to sign the released by column. The second person will sign the received by column and note the time, date, and reason for sample transfer. After the second person is finished with the sample, the sample will be returned back to the first person or to the sample storage area.

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c. In situations where a sample group must be split between departments working on different analyses, a supplemental COC must be initiated by the Sample Support Group. The supplemental chain will be used to accompany that portion of the sample group which is needed by a second department, when another department has part of the sample group and the COC for the entire group. This supplemental COC will be created only when absolutely necessary to minimize paperwork and confusion. This chain must also be documented on the master list of chains initiated for the sample group.

d. Some original samples are released by Sample Support or Sample Administration to be stored in other areas of the laboratory (e.g. GC/MS Volatiles, Foods, Pharmaceuticals). During this time they may be accessed by several people in that area. Each of these people must note the specific sample numbers in their custody in addition to date, time, and reason for removal from storage. An example of a COC is attached as Figure 6.

It will be the responsibility of the department who held the samples to assure that all necessary, signatures, dates, times, and reasons for sample custody are noted on the COC forms. It is also very important to return all samples and COCs to storage as soon as possible after data verification, because the chains may be required for a client data packages.

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e. If COC samples are stored in other areas of the laboratory or in a specific department, they must be stored in a locked area. When samples are taken from a departmental storage area, the released by column of the COC is documented as "department XX storage." If samples are returned to this area when complete the received by column will be noted as department XX storage.

D. Additional Chain-of-Custody Issues

1. Analysts in possession of samples shall remove the aliquot required for their analysis and return the samples to the Sample Support Group with a minimum of delay. During this time of possession, samples must fall under the definition of sample custody.

2. If additional containers of the sample are created (e.g. subsamples, extracts, distillates, leachates, digests, etc.), an additional COC form must be created by the department if they do not document this information on the original COC form (Figure 5, attached). This form will be marked with the container type and will be initiated to accompany the new sample container. Each department in the lab has specifically designed COC forms which will be used if new containers are created. All changes of custody involving handling of new containers in the department (e.g. analysis, storage, vials on instruments, etc.) will be documented on the departmental specific COC form or on the original COC form. Any specific handling or documentation requirements for departmental chains can be described in a departmental SOP.

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E. When Sample Analysis is Complete

1. After sample analysis, samples shall be returned to the Sample Support Group as soon as possible. Original COC forms shall also be returned with the samples and this change of custody noted. At this time it will be the responsibility of the Sample Support Group to review the COC forms to ensure that all documentation on the forms is complete before they file the forms in their area. Sample custodians will not return a sample to its assigned storage location without signing the accompanying chain and performing this completeness check. All chains should either end with a note of "Discard" or "Storage" for the final reason of transfer.

2. All completed COC forms for the original sample containers will be retained in files within Sample Support. The Data Package Group will retrieve these forms so a copy can be included in the data package. All departmental created COC forms will be collected by the department's data package group so a copy can be included in the data package. These forms will not be returned to the Sample Support Group since these sample containers will not be returned to the Sample Support Group. The original copy of all COC forms will be retained on file by the laboratory.

3. All personnel who handle sample containers shall make every attempt to ensure that all changes of custody are accurately and completely documented. **Disciplinary action may be taken for employees who fail to comply with these important requirements.**

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4. In the event that a signature or other information is inadvertently not recorded on a COC form, the Sample Support and Data Package Groups in conjunction with the technical centers shall determine what information is missing by checking computer requisition records, raw data, or the sample support work schedule. The responsible party shall add the missing information or make the necessary correction at the bottom of the COC form, in addition to noting the situation that caused the error in documentation. The person making this note needs to sign and date the information using the current date. Any errors in COC documentation that cause noncompliances must be noted in the case narrative of the sample data package. Examples of specific cases are on file in the data package department.

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SOPQA104.W60
112895

Prepared by: Kathy L. DeNunzio Date: 11/28/95

Approved by: M Louise Hess Date: 11/29/95

Figure 1

Analysis Request/ Environmental Services Chain of Custody

Lancaster Laboratories
A Thermo Analytical Laboratory

For LLI use only
Acct. # _____ Sample # _____

Please print. Instructions on reverse side correspond with circled numbers.

(1)
Client: _____ Acct. #: _____
Project Name/#: _____ PWSID #: _____
Project Manager: _____ P.O.# _____
Sampler: _____ Quote #: _____
Name of state where samples were collected: _____

(2) (4) (5) (6)

Sample Identification	Date Collected	Time Collected	Grab	Composite	Matrix: Soil	Matrix: Water (☐ Potable ☐ Non-Potable ☐ NPDES)	Matrix: Other	Total # of Containers	Analyses Requested								Remarks	Temperature of samples upon receipt (if requested)

For LLI use only
FSC: _____
SCR #: _____

(7)
Turnaround Time Requested (TAT) (please circle): Normal Rush
(Rush TAT is subject to LLI approval and surchage.)
Date results are needed: _____
Rush results requested by (please circle): Phone Fax
Phone #: _____ Fax #: _____

(8)
Data Package Options (please circle if requested)
QC Summary — Type VI
Type I (Tier I) — GLP
Type II (Tier II) — Other
Type III (NJ Red. Del.)
Type IV (CLP)

SDG Complete? Yes No

Site-specific QC required? Yes No
(If yes, indicate QC sample and submit triplicate volume.)

Internal Chain of Custody required? Yes No

(9)

Relinquished by:	Date	Time	Received by:	Date	Time
Relinquished by:	Date	Time	Received by:	Date	Time
Relinquished by:	Date	Time	Received by:	Date	Time
Relinquished by:	Date	Time	Received by:	Date	Time
Relinquished by:	Date	Time	Received by:	Date	Time

Figure 1 - (Continued)

DIRECTIONS FOR COMPLETING THIS FORM

Client: Your company's name

Acct. #: Your account number with Lancaster Laboratories

Project Name/#: The way your company refers to the work involved with these samples. You may want to include project location as part of the description.

PWSID: Potable Water Source ID#

Project Manager: The person at your company responsible for overseeing the project

P.O. #: Your company's purchase order number

Sampler: The name of the person who collected the samples

Quote #: The reference number that appears on your quote (if Lancaster Laboratories gave you a number)

State where sample was collected: Please indicate where the sample was taken, e.g., Pa., N.J., etc.

Sample Identification: The unique sample description you want to appear on the analytical report

Date Collected/Time Collected: When the sample was collected

Grab: Check here if sample was taken at one time from a single spot.

Composite: Check here if samples were taken from more than one spot, or periodically, and combined to make one sample.

Matrix: Check the type of sample you are submitting. If it is a water sample, please indicate if it is a potable water or if it is an NPDES sample.

Number of Containers: Indicate the total number of containers for each sampling point.

(5) **Analyses Requested:** Write the name of each analysis (or an abbreviation of it) here, and use the **catalog number** that appears at the beginning of each line in the *Schedule of Services*. Be sure to indicate which analyses are to be performed on which samples

(6) **Remarks:** List special instructions about the sample here (e.g., hazardous elements, high levels of analyte, etc.). The space can also be used (if needed) for listing additional analyses.

(7) **Turnaround time Requested:** Circle **Normal** if you want routine TAT, which is usually within 10-15 days. If you need your results faster, call ahead to schedule **Rush** work.

Rush Results Requested by: Circle **Fax** or **Phone** and include the number.

(8) **Data Package Options:** Call our Client Services Group (717-656-2301) if you have questions about these choices.

SDG Complete? Indicate **Yes** if this is a complete sample delivery group or **No** if you will be submitting additional samples to be included in the same data package.

Note: We need to have one quality control (QC) sample for every 20 samples you send, if you are requesting site-specific QC. Please give us this sample in triplicate volume and identify it by writing "QC" in the **Remarks** column.

The internal chain of custody is a hand-to-hand documentation recording a sample's movement throughout the company. We routinely start a chain of custody for data-package samples unless we are told otherwise. There is a $25 **per sample** charge for the chain-of-custody documentation.

(9) **Relinquished by/Received by:** The form must be signed each time the sample changes hands. We can supply chain-of-custody seals for the outside of your packages if you require them.

Thank you for using Lancaster Laboratories.

Please call our Client Services Group (717-656-2301) if you have any questions about completing this form.

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Figure 2

Lancaster Laboratories
2425 New Holland Pike • Lancaster, PA 17601-5994

Sample Administration Receipt Documentation Log

Client/Project: XYZ Associates / Well Monitoring Project
COC Seal: (Present) / Not Present on cooler
Date of Receipt: 11/27/95
Broken / (Intact)
Time of Receipt: 1350
Package: (Chilled) / Not Chilled
Source Code: 60
Unpacker Emp. No.: 210

Temperature of Samples		
#1	**#2**	**#3**
Thermometer ID: 123	Thermometer ID:	Thermometer ID:
Corrected Temp.: N/A	Corrected Temp.:	Corrected Temp.:
(Bottle) / Air	Bottle / Air	Bottle / Air
(Wet Ice) / Ice Packs	Wet Ice / Ice Packs	Wet Ice / Ice Packs
Ice Present? (Yes) No	Ice Present? Yes No	Ice Present? Yes No
#4	**#5**	**#6**
Thermometer ID:	Thermometer ID:	Thermometer ID:
Corrected Temp.:	Corrected Temp.:	Corrected Temp.:
Bottle / Air	Bottle / Air	Bottle / Air
Wet Ice / Ice Packs	Wet Ice / Ice Packs	Wet Ice / Ice Packs
Ice Present? Yes No	Ice Present? Yes No	Ice Present? Yes No

Paperwork Discrepancy/Unpacking Problems: 40 ml vial broken upon Receipt
Client ID# ABC-1. Client Called 11/27/95

Sample Administration Chain of Custody				
Released by	**Received by**	**Date**	**Time**	**Reason for Transfer**
A. Hutchison 210	SA Hold	11/27/95	1400	Storage
SA Hold	D. Neslund 208	11/27/95	1600	Entry

ORIGINAL

Figure 3

Lancaster Laboratories
2425 New Holland Pike • Lancaster, PA 17601-5994

Locked Storage Chain of Custody
Original Sample

Client/Project: XYZ Associates

Preservative: HCl Matrix: Water SDG: XYZ01

Sample # Range of Entry Group: 2420638-39 Bottle Type: #38 40 ml vial

Sample Number(s) in Custody	Released By	Received By	Date of Transfer	Time of Transfer	Reason for Change of Custody	Dist., Extr., or Digest Chain Created (X)
2420638-39	D. 208 Peslund	SS Storage	11/27/95	1600	Entry & Storage	
2420638-39	SS Storage	B. 705 Weaver	11/28/95	700	Remove from SS Storage	
2420638-39	B. 705 Weaver	dept 21 Storage	11/28/95	715	VOA Storage	
2420638-39	dept 21 Storage	K. 396 Wittman	11/29/95	1315	VOA Analysis	X
2420638-39	K. Wittman 396	L. 513 Taylor	11/29/95	1700	VOA Analyst Shift Change	
2420638-39	L. 513 Taylor	dept 21 Storage	11/29/95	2100	VOA Storage	
2420638-39	dept 21 Storage	C. 206 Dupro	12/3/95	800	Transfer to SS Storage	
2420638-39	C. Dupro 206	L. 630 Reesler	12/3/95	815	Storage	

SAMPLE MATERIAL

Figure 4

Lancaster Laboratories
2425 New Holland Pike • Lancaster, PA 17601-5994

Master List of Chain of Custodies

Client/Project: XYZ associates

Sample # Range of Entry Group: 2420632-39

SDG: XYZ01 Matrix: (Liquid) Solid Mixed Other

Original Sample Chains		
Bottle Type	**Started By**	**Date Started**
40 ml Glass Vial (#38)	D. Neeland 208	11/27/95
1000 ml Amber Glass (#45)		
1000 ml Plastic (#09)		
1000 ml Amber Glass (#29)		

Supplemental Chains		
Bottle Type	**Started By**	**Date Started**
77	C. Ayala 266	11/27/95
21	C. Ayala 266	11/27/95

Extraction, Digestion, Distillates, Etc.		
Bottle Type	**Started By**	**Date Started**

Figure 5

Lancaster Laboratories
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Locked Storage Chain of Custody
Metals

Client/Project: XYZ Associates

Sample #: 2420632-39 SDG: XYZ01

Digest Type (circle one): Hg (Metals) GF Hydrides Trial No: 2 (If not 1, fill in)

Batch No: 95305 1849 004

Sample Number(s) in Custody	Released By	Received By	Date of Transfer	Time of Transfer	Reason for Change of Custody	Dist., Extr., or Digest Chain Created (X)
2420632, 34, 36	S. 523 Correa	J. 428 Garrett	12/1/95	1631	Metals Prep Shift Change	
2420632, 34, 36	J. 428 Garrett	B. 811 Stocko	12/1/95	1920	ICP Storage	
2420632, 34, 36	ICP Storage	DR 142 Sackett	12/1/95	2115	ICP Analysis	
2420632, 34, 36	DR 142 Sackett	ICP Storage	12/1/95	2135	ICP Storage	

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Figure 6

Lancaster Laboratories
2425 New Holland Pike • Lancaster, PA 17601-5994

Pharmaceutical
Locked Storage Chain of Custody
Original Sample

Client/Project: Smith Pharmaceutical

Preservative: N/A Matrix: Tablets

Sample # Range of Entry Group: 2420320-30

Bottle Type: 40ml Vial

Sample Number(s) in Custody	Released By	Received By	Date of Transfer	Time of Transfer	Reason for Change of Custody
2420320-30	S. 074 Carruthers	M. 589 Coho	12/1/95	1300	Entry / Transfer to Pharm. Storage
2420320-30	M. 589 Coho	Pharm. Storage	12/1/95	1315	Storage
2420320-30	Pharm. Storage	E. 572 Ortiz	12/3/95	800	pH Analysis
2420320-30	E. Ortiz 572	Pharm. Storage	12/3/95	1000	Storage
2420320-30	Pharm Storage	D. 330 Wright	12/5/95	930	GC Assay Analysis
2420320-30	D. Wright 330	Pharm Storage	12/5/95	1400	Storage

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Lancaster Laboratories
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Initiated Date: 3/87
Effective Date: DEC 9 1991

QUALITY ASSURANCE OPERATIONS MANUAL
STANDARD OPERATING PROCEDURE
QA-109

Title: Laboratory Notebooks and Documentation

Purpose:

The objective of these procedures is to ensure traceability of the raw data used to derive analytical reports, and to establish a system to protect analysts against any suggestion of tampering with raw data.

Scope:

This SOP will cover the processes of obtaining laboratory notebooks, controlling distribution of laboratory notebooks, and use of laboratory notebooks.

Raw data is defined as any laboratory notebooks, worksheets, instrument printouts, or other records that are the result of original observations made in the laboratory and are necessary for the reconstruction and evaluation of the results reported. Some computerized devices, such as integrators, provide tentative data which is further manipulated by the computer prior to determination of final results. In this case, the final data is considered raw data and the intermediate data will not be subject to the requirements set forth for raw data. For example, a chromatographic run may generate several hundred thousand data points which are then reduced to peak areas and fit to a calibration curve to determine concentration. The intermediate data points and the electronic media on which they are stored are not part of the raw data, but peak areas and final fit, which are recorded on instrument printouts or manually in notebooks, are considered raw data. This definition will be used unless regulations for a specific program require retention of all data; in which case the more stringent definition will apply.

Procedures:

1. Analysts shall record data, observations and other information relevant to technical operations in a laboratory notebook. Laboratory notebooks must be bound and have sequentially numbered pages. Notebooks may consist of blank sheets or pre-printed data

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sheets. No data used in the production of analytical results may be recorded on loose sheets of paper. The only exception to this rule is in the case of printouts or charts from data systems or instruments. These shall be labeled with sample and analyst identification. Analysts may use an electronic notebook system instead of a paper notebook if the system conforms to our internal standards of development, validation, implementation and maintenance outlined in SOP-QA-121.

2. Upon request by an analyst, notebooks will be issued by one of the Archivists. The Archivists will maintain a master index used to assign sequential numbers to notebooks as they are issued. The number will be marked on the front cover of the notebook. The name of the person to whom the notebook was issued, the date of issue, the date of return, the number of pages filled when returned and, the place of storage of the notebook will be recorded in the master index.

3. The following rules apply to the use of notebooks:

   a. All entries shall be in ink.

   b. No erasures or "whiting-out" will be permitted. Erroneous entries shall be corrected by drawing a line through the error and then entering the correct information. The original entry shall not be obliterated or rendered unreadable. Any change must also be dated, initialed, and explained.

      The following error code numbers may be used to explain changes in the data:

      1 - Misspelled
      2 - Mathematical error
      3 - Wrong entry (date, word, sample #, etc.)
      4 - Transcription or transposition error
      5 - Procedural error
      6 - Illegible entry
      7 - Unnecessary entry
      8 - Footnoted explanation

   c. Blank pages or substantial portions of pages which are blank shall be crossed out to eliminate the possibility of entry of data at a later time.

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d. Each entry shall be dated and signed by the individual making the entry. Initials may be used if used in conjunction with the employee number or if an initial key is available. An initial key must list the full names of each individual making entries in the notebooks, along with initials as they will be used in the raw data. Initial keys shall be placed in the front of each notebook. As an alternative, a master initial key for an entire department may be kept in a separate file, provided all employees are listed and care is taken to prevent loss.

e. At periodic intervals (e.g., every 25th page, the end of a project, etc.), the supervisor or his designate shall check the notebook for completeness, legibility, and conformance to this SOP. This check should be documented with the statement:

"Read and understood by _____ _____"
Signature Date

If notebooks are checked at the time of computer verification, documentation of this step will suffice as a notebook review.

4. Completed notebooks shall be returned to the Archivist who will complete the entry on the master index sheet and store the notebook in the archives. Incomplete notebooks should be returned to the Archivist when an employee leaves the company or transfers to another department, or if the project for which it was used is complete. The last page used in any incomplete notebook should be marked "LAST PAGE USED FOR ENTRY", along with an explanation of reason for the blank pages. Completed notebooks shall be returned to the Archivist within three months of the last entry.

5. Because of differences in programs, and our ability to alter them, it is not possible to provide specific procedures for computer generation of data. The following guidelines apply to computer generated raw data.

a. Identity of the samples(s), date, instrument identifiction, and person operating the instrument must be made either on the printouts or on a cover sheet attached to the printouts.

b. Any manual notations or interpretations made on printouts shall be initialed and shall not obliterate the original entry.

c. Documentation of parameters or calculations used to manipulate data must be maintained. See SOP-QA-121 for further information.

QA109
SOP QA #1
112091

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Prepared by: M. Louise Hess Date: 11/26/91

Approved by: Julian Hershey Date: 12/6/91

Read and understood by: _____ Date: _____

Lancaster Laboratories
Where quality is a science.

Procedural Amendment #1

Number: SOP-QA-109

Title: Laboratory Notebooks and Documentation

Effective Date (listed on procedure): 12/09/91

Section(s) affected by change: Procedures

Reason for addition(s) or change(s): To allow temperature records for laboratory equipment to be kept on logs posted on refrigerators

Change will be effective from (date): 12/27/94

Samples or project affected: All

List change(s) or addition(s) (specify which section):

Procedures: - *Add the following paragraph to Item #1*

An additional exception to the requirement for recording data in bound notebooks applies to temperature records for various pieces of equipment such as incubators, refrigerators, and freezers. Temperature logs for equipment used to store samples or reagents may be maintained on individual sheets of paper posted on or near the unit to facilitate documentation of temperature checks. Laboratories that use this option must develop a system for ensuring that all temperature records are accounted for after completion (e.g., transfer to a file or notebook).

QA109.W51
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Prepared by: [signature] Date: 12/27/94

Approved by: [signature] Date: 12/28/94

Read and understood by: _____ Date: _____

SOP-IO-001
Initiated Date: 04/29/88
Effective Date: DEC 1 1 1995

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Preservation, Storage Conditions, and Holding Times for Inorganic Samples

Purpose:

The purpose of this standard operating procedure is to document the procedures used for preserving and storing samples for metals determinations and to outline the various holding times related to metals determinations.

Background Information:

The procedures and requirements described in this protocol are adopted from the following references:

1. USEPA CLP SOW No. ILM04.0, Exhibit D, Section II.

2. Chapter 3, Test Methods for Evaluating Solid Waste, USEPA SW-846, Revision 2, September 1994.

3. "Metals" Chapter, Methods for Chemical Analysis of Water and Wastes, USEPA 600/4-79-020, Revised March 1983.

Scope:

This protocol is applicable to the preservation, storage, and holding times of solid (soils and sludges) and water samples (waste, potable, and drinking waters) for metals determinations.

Procedure:

A. Sample preservation

Samples for metals determinations should be submitted in plastic or glass containers.

Upon receipt at the laboratory, Sample Administration personnel check the pH of water samples. If the pH is greater than two, the pH of the sample is adjusted to a pH less than two following the protocol outlined in SOP-SS-002, "Liquid Sample Preservation."

Samples requiring dissolved (soluble) metal determinations are submitted to the laboratory unpreserved. Preservation of these samples does not occur until after the sample has been filtered through a 0.45-μm filter membrane.

Solid samples require no chemical preservation.

B. Storage conditions

Both solid and water samples are stored at 4° ± 2°C. This is a requirement for soils and sludges. Water samples may be stored at room temperature after preservation with the exception of samples to be analyzed for mercury; storage at 4° ± 2°C is required until the mercury analysis is complete.

Digestions of samples are stored at room temperature in either plastic bottles or glass volumetric flasks.

C. Holding times

With the exception of mercury, the holding time for samples requiring metals determinations is 6 months (180 days). The following holding times apply to mercury:

1. SW-846 solids and waters - 28 days

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2. EPA 600 waters - 28 days

3. CLP solids and waters - 26 days

Both solid and water digestions have a 6-month holding time with the exception of mercury digestions. Mercury digestions are discarded immediately after analysis.

The general practice in the metals group is to discard the digestions after all the required metals from a batch of samples have been analyzed and verified in the computer. Digestions of samples requiring data packages are held until the package has been sent to the client. Digestions of air filter are held for about 2 weeks after the results have been reported.

SOPIO001.W60
120495

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Prepared by: Betsy S. Menefee Date: 12/8/95

Approved by: Ramona Nayman Date: 12/8/95

Approved by: [illegible] Date: 12/11/95

SOP-IO-004
Initiated Date: 09/87
Effective Date: MAR 1 2 1996

QA for Graphite Furnace

Scope:

All QC requirements listed are necessary for graphite furnace data. This supplements the standard QC protocol specified in SOP-IO-005, "Department 23 Quality Control Procedures."

Procedure:

A. CLP protocol

1. All furnace analyses, except during full method of standard addition (MSA), require duplicate injections for which the average absorbance or concentration will be reported. All analyses must be in the calibration range. For concentrations greater than the limit of quantitation, the relative percent difference (RPD) of the duplicate injections must be <20.0%. If the RPD is >20.0%, rerun the sample one more time.

2. Analysis of each sample requires at least one post digest (analytical) spike run immediately after the sample to determine if MSA is required for the analysis method. This requirement includes the LCS and the digest blank. MSA is not be to be performed on the LCS or digest blank, which must be quantitated from the calibration curve. For CLP analyses, if the analytical spike of the digest blank is out of control (<85.0% or >115.0%), the analysis must be repeated and verified by respiking and reanalyzing once with all associated samples. If the recovery is still out of the control limits, correct the problem, and redigest/analyze all samples associated with that digest blank. A post digest spike (PDS) is not required on the digest spike sample. The concentration of spike added for arsenic, selenium, and thallium must be 2 × the contract required detection limit. The concentration of spike added for lead determinations is 20 ppb. The percent recovery will determine how the sample will be quantitated using the following protocol:

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a. If the recovery is less than 40.0%, the sample must be diluted 5 to 10× and rerun once with another spike. If, after the dilution, the spike recovery is still <40.0%, raise the limit of quantitation by the factor of the dilution and report the data with Comment #180 to indicate interference problems, "The quantitation limit(s) for ********** was/were increased due to the nature of the sample matrix."

b. If the spike recovery is greater than 40.0% and the sample concentration is <50.0% of the spike concentration, report the results to the reporting limit.

c. If the sample absorbance is >50.0% of the spike and the recovery is between 85.0% and 115.0%, the results may be quantitated directly from the calibration curve.

d. If the sample absorbance is >50.0% of the spike and recovery is <85.0% or >115.0%, the sample must be run by three-point MSA.

Please refer to the furnace atomic absorption analysis scheme (Figure 1) for analytical protocol for CLP.

3. The following protocol must be incorporated into three-point MSA analyses.

   a. For samples requiring dilutions, obtain approximately a midpoint reading within the MSA spiking range. Spikes must be approximately 50%, 100%, and 150% of sample absorbance. All data must be within the linear range of the analysis.

   b. The sample and three spikes must be run consecutively. Only single injections are required for MSA quantitation.

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c. MSA can be used for the QC duplicate during a run of MSA analyses.

d. If the correlation coefficient of the MSA is less than 0.9000, dilute the sample 5 to 10x to achieve a correlation coefficient of greater than 0.9000. A correlation coefficient of greater than 0.9000 but less than 0.9950 must be repeated once. If the correlation coefficient is still less than 0.9950, report the data from the trial with the better of the two coefficients and enter Comment #1010, "The Method of Standard Additions was required for the ********** analysis due to matrix interference. Correlation coefficients of ***** and ***** were observed. The result was taken from the better of the two trials." as an analysis comment.

B. SW-846 protocol requirements

1. All furnace analyses require duplicate injections for which the average absorbance or concentration will be reported. All analyses must be in the calibration range. For concentrations greater than the limit of quantitation, the RPD of the duplicate injections must be <20.0%. If the RPD is >20.0%, rerun the sample one more time.

2. If the digest blank or LCS is out of control, the whole batch must be rerun. If the digest blank or LCS is still out of control, the batch must be redigested and reanalyzed.

3. For SW-846 protocol, all analyses data for each digest batch will require one post digest (analytical) spike and a serial dilution. The post digest spike (UP) and serial dilution (UL) should be performed on the background sample (U). If the post digest spike for the background is out of control (<85.0% or >115.0%), the whole batch requires one-point MSA (excluding the UP, UL, digest blank, and LCS). Report the corrected value.

4. If the recovery of the one-point MSA is <40.0% or >150.0%, the sample must be diluted 5 to 10× and rerun with another analytical spike. Repeat this step until the percent recovery is >40.0% and <150.0%. Report the data from this trial, raising the limit of quantitation by the factor of the dilution and enter Comment #180 indicating interference problems, "The quantitation limit(s) for ********** was/were increased due to the nature of the sample matrix. Report the corrected value." as an analysis comment.

Please refer to the furnace atomic absorption analysis scheme (Figure 2) for analytical protocol for SW-846.

C. EPA600 protocol requirements

1. All furnace analyses, except during full method of standard additions (three-point MSA), require duplicate injections for which the average absorbance or concentration will be reported. For concentrations greater than the limit of quantitation, the RPD of the duplicate injections must be <20.0%. If the RPD is >20.0%, rerun the sample one more time.

2. If the digest blank or LCS is out of control, the whole batch must be rerun. If the digest blank or LCS is still out of control, the whole batch must be redigested and reanalyzed.

3. For EPA600, the matrix spike must be within specifications (80.0% to 120.0%). If the matrix spike is out of control, all samples in the batch must be analyzed with a PDS, excluding the digest blank and LCS.

   a. If the PDS recovery is out of control (<85.0% or >115.0%) a three-point MSA is required for that sample.

   b. If the PDS recovery is <40.0%, the sample should be diluted 5 to 10× prior to spiking with the MSA spikes.

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4. The following protocol must be incorporated into MSA analyses.

   a. For samples requiring dilutions, obtain approximately a midpoint reading within the MSA spiking range. Spike must be approximately 50%, 100%, and 150% of the sample absorbance. All data must be within the linear range of the analysis.

   b. The sample and three spikes must be run consecutively. Only single injections are required for MSA quantitation.

   c. MSA can be used for the QC duplicate during a run of MSA analyses.

   d. If the correlation coefficient of the MSA is less than 0.9000, dilute the sample 5 to 10× to achieve a correlation coefficient greater than 0.9000. A correlation coefficient of greater than 0.9000 but less than 0.9950 must be repeated once. If the correlation coefficient is still less than 0.9950, report the data from the trail with the better of the two coefficients and enter Comment #1010, "The Method of Standard Additions was required for the ******* analysis due to matrix interference. Correlation coefficients of ***** and *****were observed. The result was taken from the better of the two trials." as an analysis comment.

Please refer to the furnace atomic absorption analysis scheme (Figure 3) for analytical protocol for EPA600.

NOTE: Change in protocols may be necessary due to client specific requirements.

Calculations:

Spike added

$$S = G \times \frac{e}{d}$$

Percent recovery (for matrix spike or PDS)

$$\%R = \frac{H - I}{S} \times 100\%$$

Corrected result (SW-846 one-point MSA)

$$Z = \frac{a}{\%R}$$

$$X = a \times \frac{b}{c} \times \frac{d}{e}$$

Where:

S = spike added

G = concentration of spike

%R = percent recovery

H = AA reading for spiked sample

I = AA reading for the unspiked sample

Z = corrected result for one-point MSA (SW-846)

X = result in µg/L or µg/kg

a = AA reading

b = dilution volume

c = dilution aliquot

d = final sample volume

e = initial sample volume/weight

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Method of standard addition calculations are performed in the metals departments' PC network system.

NOTE: Autosampler vials must be kept soaking in approximately 10.% HNO_3 prior to analysis (minimum 4 hours) and rinsed four times with deionized water before use.

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Prepared by: [signature] 159 Date: 3/7/96

Approved by: [signature] 383 Date: 3-7-96

Approved by: [signature] 972 Date: 3/8/96

Figure 1

Furnace Atomic Absorption Analysis Scheme

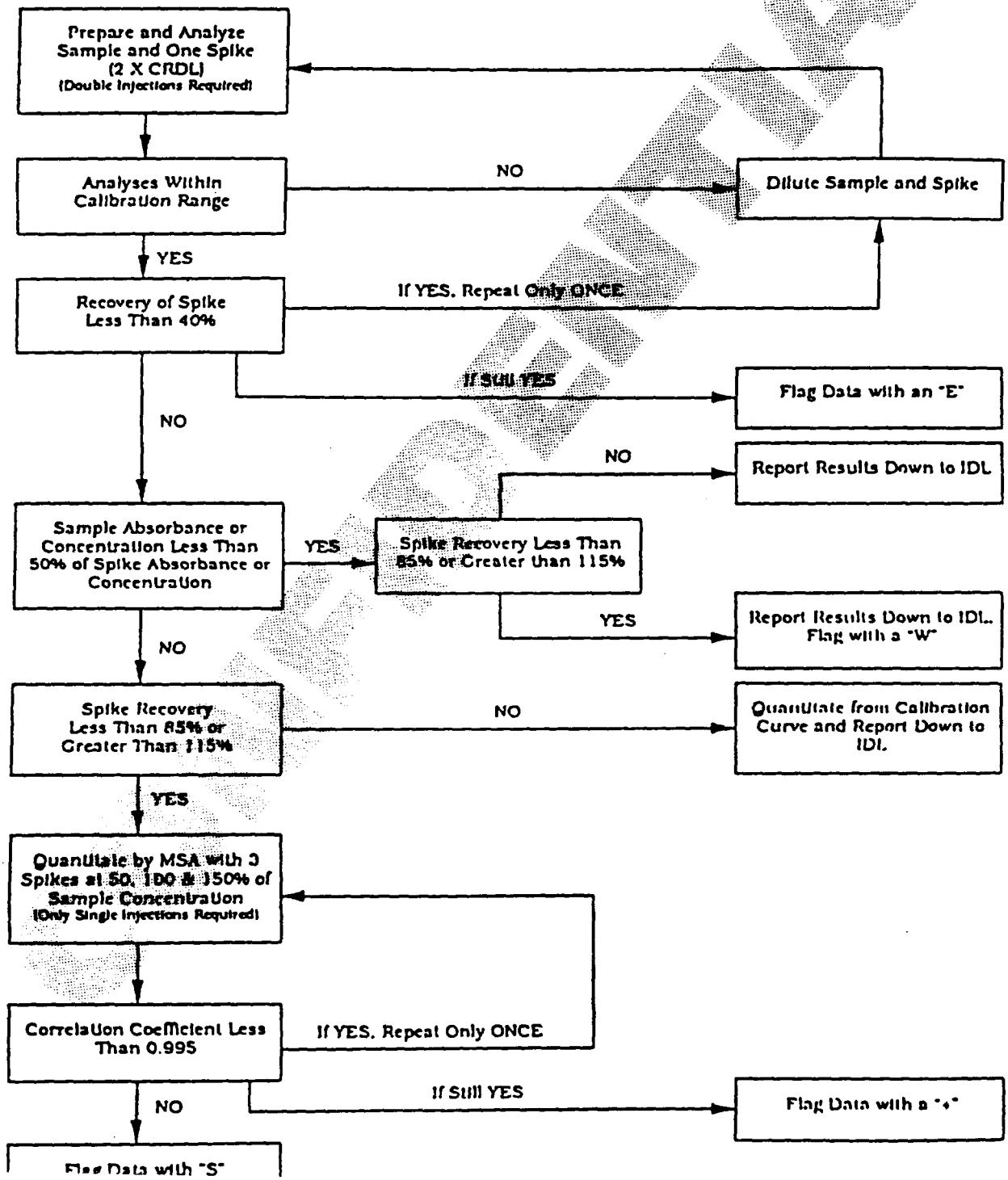

Figure 2

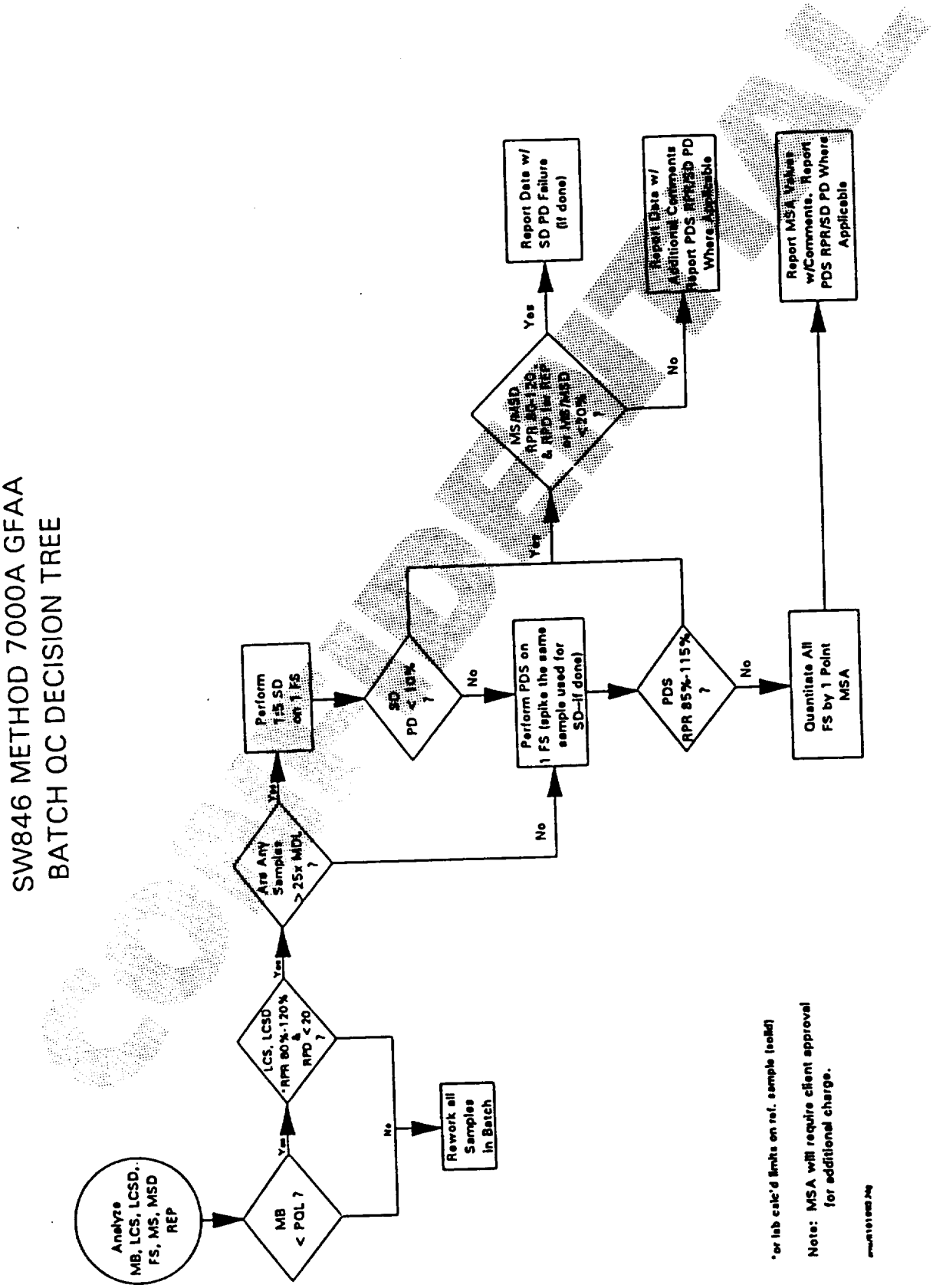

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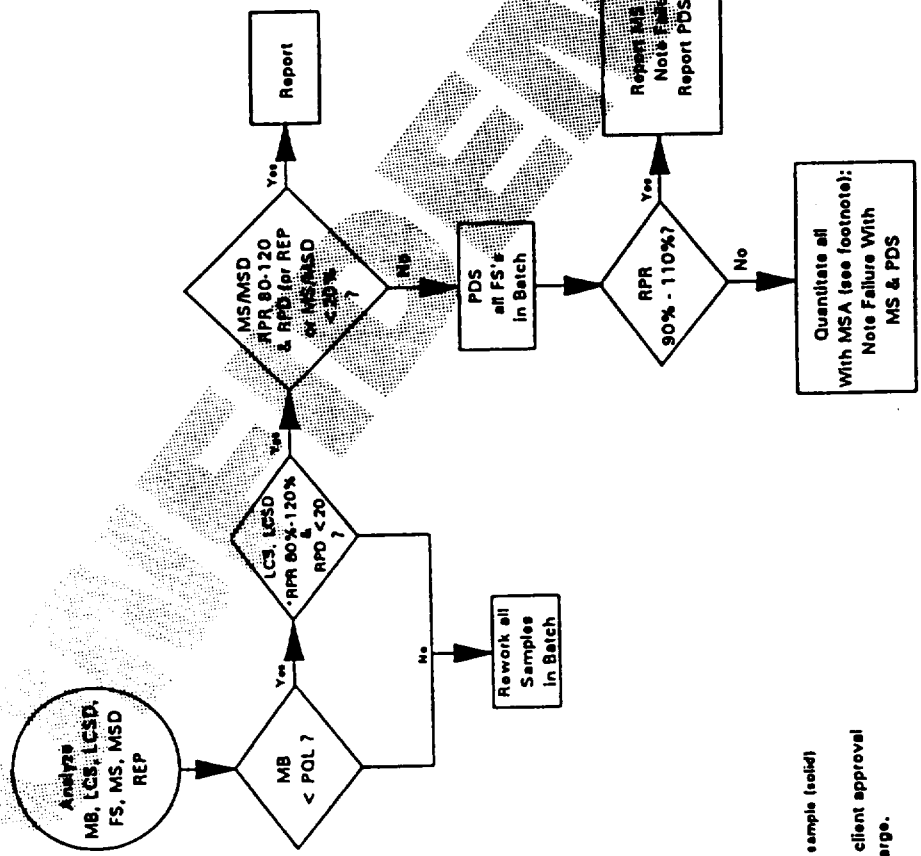
Figure 3

EPA 2XX.X METHODS GFAA
BATCH QC DECISION TREE



*or lab calc'd limits on ref. sample (solid)

Note: MSA will require client approval for additional charge.

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SOP-IO-005
Initiated Date: 06/05/89
Effective Date: SEP 19 1996

Department 23 Quality Control Procedures

Purpose:

The purpose of these quality control activities is to provide the means of assuring and maintaining the quality of results generated by Department 23 of Lancaster Laboratories. In addition, the quality control activities are designed to meet the quality control requirements that are established by various regulatory agencies.

Scope:

This SOP describes the routine quality control activities performed by Department 23, Inorganics by AA.

Definitions:

Analytical batch - A group of field samples which are digested and analyzed together. A batch consists of no more than 10 samples for EPA 600 methods and for hydride generation or no more than 20 samples for other methods.

Reagent blank or preparation blank - A deionized water sample that is carried through the digestion and analytical processes with the field samples. The reagent blank is prepared and analyzed in a manner identical to that of the accompanying samples. Reagent blanks are performed as a means of identification of any contamination that may occur during the preparation, storage, or measurement process of the analyses.

Duplicate - The preparation and measurement of two separate aliquots of the same sample. Duplicates determine the precision of an analysis.

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Matrix spike - A field sample to which the analyte(s) of interest is(are) intentionally introduced (spiked) at a known concentration. The unspiked sample and the spiked sample are then carried through the preparation and analysis process with the other samples in the batch. The matrix spike is used to document the appropriateness of the method for the matrix by calculating the recovery of the added analyte(s).

Matrix spike duplicates - Two aliquots of a sample spiked with known quantities of the analyte(s) of interest and subjected to the entire digestion and analytical procedure. They are used to document both the bias and the precision of a method.

Laboratory control sample (LCS) - A sample of known value which is prepared with and analyzed in the same manner as samples submitted by clients. LCS samples are performed as a means of assessing the accuracy of an analytical method. Duplicate LCSs may be used for samples in the environmental lead program when samples are too small to homogenize and split for QC.

For water samples, the LCS consists of a spiked aliquot of deionized water.

For solid samples, using CLP and SW-846 methods, a purchased certified solid control standard is used. Special exceptions to this are boron, lithium, and tin, for which a spiked aliquot of deionized water is used, and lead in paint, for which a standard reference material is utilized.

For the proper LCS for an oil sample, see Analysis #1015, "Sample Preparation of Oils for Graphite Furnace Analysis of Metals."

Reference material - A sample having well established properties which is analyzed to assess the accuracy of an analytical method.

Analytical spikes - Postdigestion spikes (PDS) that are prepared prior to analysis by adding a known quantity of an analyte to an aliquot of digested sample. Analytical spikes are used to assist in the identification of matrix interferences.

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Initial calibration verification (ICV) - An independent standard (i.e., a standard which is diluted from a source other than the source used for the calibration standards) within the calibration range that is used to determine the accuracy of the calibration.

Continuing calibration check (CCV) - A laboratory prepared standard solution that is intermittently analyzed during the run to ensure calibration accuracy throughout the run. It is analyzed at a midpoint in the calibration range and at a level different from that of the ICV.

Calibration blank (ICB/CCB) - A deionized water blank that is acidified at the same concentration as the calibration standards. Calibration blanks are performed as a means of identifying instrumental baseline instability and/or analyte carryover from previous samples.

Contract required detection limit (CRA) - A standard analyzed at the Contract Laboratory Program (CLP) required detection limit. This standard must be at the beginning of each sample analysis run, but not before the ICV/ICB. This sample verifies linearity near the limit of quantitation.

Serial dilution - The dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

Instrument detection limit (IDL) -

CLP Analyses - A value determined from analyzing seven standard solutions (undigested) at a concentration 3x to 5x the anticipated IDL on three nonconsecutive days. The standard deviation obtained for these multiplied by three is the IDL. These must be performed quarterly on each instrument used for an analyte.

Non-CLP Analyses - A value determined for the purpose of evaluating the ICB/CCBs for data package samples. It is determined by analyzing seven standard solutions at a concentration 3x to 5x the anticipated IDL. This value is obtained annually for each element analyzed on an instrument.

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Method detection limit (MDL) - The minimum concentration of a substance that can be reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven digested standards at an estimated concentration 2.5× to 5× the signal/noise ratio. MDLs are performed on all instruments used to determine each analyte.

Limits of quantitation - The level above which quantitative results may be obtained with a specified degree of confidence. It is based on a value 3× to 5× the MDL. CLP samples are reported on the IDL and CRDL; the statement of work for the program specifies required limits.

Procedure:

A. Each analytical batch consists of no greater than 20 field samples with the exception of EPA 600 methods and hydrides; these require no more than 10 samples per batch. Whenever possible, batches should be composed of samples of similar type, similar matrix, or common reporting group.

In addition to the field samples, each batch will contain a reagent blank (B), laboratory control sample (Q), sample duplicate (D), sample matrix spike (R), and matrix spike duplicate (M) for hydrides and SW-846 methods. All related batch QC data is entered into the computerized laboratory QC system.

1. The reagent or preparation blank is prepared and analyzed in a manner identical to that of the accompanying field samples. In order to be within quality control specifications, the analyte concentration observed in the blank must be below the established analyte limit of quantitation (LOQ) for SW-846 or EPA 600, or CRDL for CLP. For blank values greater than the LOQ or CRDL, the following criteria must be met. The lowest concentration of that analyte in the associated samples must be 20× the concentration observed in the blank for SW-846, and 10× the concentration observed in the blank for CLP and EPA 600. Following SW-846, if these parameters are not met, all associated samples with the observed concentrations above the LOQ, but less than 20× greater than the blank must be redigested and reanalyzed. If

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with the observed concentrations above the CRDL (CLP) or LOQ (EPA 600), but less than 10× greater than the blank, must be redigested and reanalyzed.

2. Recovery for the aqueous laboratory control sample must be within ±20% of the true value. Recovery for the solid laboratory control sample must be within the certified limits. For analytes falling outside the recovery criteria, all associated samples must be redigested.

   The percent recovery is calculated in the following manner:

$$\%R = \frac{\textit{Observed result}}{\textit{True value}} \times 100$$

3. Sample duplicates are prepared by taking two separate aliquots of a sample, then preparing and analyzing the aliquots as separate samples within the batch. The two samples are arbitrarily designated as background and duplicate. The acceptance criteria for duplicates is a 20% relative percent deviation (RPD). The following formula is used to calculate the relative percent difference:

$$R = \frac{X_1 - X_2}{X_1 + \frac{X_2}{2}} \times 100$$

   Where:

   X_1 = Background result

   X_2 = Duplicate result

   R = Relative percent difference

   The above acceptance criteria is only applicable for samples with concentrations greater than 5× the LOQ of the particular analyte. For

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samples with concentrations below this 5× limit, the duplicate results must be within ± the LOQ of one another to be considered within specification.

No redigestion or reanalysis is required for out-of-specification duplicates if the blank and LCS are within specifications.

The RPD is ±25% for duplicate samples (5× greater than the LOQ) in the environmental lead program.

4. Matrix spikes are samples to which the analyte(s) of interest is (are) purposely introduced to a duplicate aliquot of a background sample. The acceptance range for matrix spikes is 80% to 120%, except CLP and environmental lead samples for which the range is 75% to 125%.

$$R = \frac{\textit{Result of spike} - \textit{Result of background}}{\textit{Concentration of spike added}} \times 100$$

To calculate the amount of spike added:

$$\textit{Spike added} = \frac{C \times V_s}{V_s + V}$$

Where:

C = Concentration of spike solution

V_s = Volume of spike solution added

V = Volume or weight of sample

The above acceptance criteria is valid for samples with analyte concentrations no greater than 4× the concentration of spike added to the sample. For samples with analyte concentrations greater than 4× the amount of spike added, the spike is considered to be insignificant.

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Analytical spikes (PDS) are to be performed on the background sample for those matrix spikes where the recovery falls outside the acceptance limits or where the spike is considered to be insignificant. The performance of the analytical spike allows the analyst to determine whether the out-of-specification recovery is analytical method related or sample matrix related.

No redigestion or reanalysis is required for out-of-specification matrix spikes, if the blank and LCS are within specifications.

5. Matrix spike duplicates are prepared the same way as duplicates except that the analyte(s) of interest is(are) added to each of the two samples at identical known concentrations. One sample is arbitrarily designated as the matrix spike (R) and the other as the matrix spike duplicate (M). The calculation formula for the relative percent difference (RPD) is the same as the one used for the duplicates (see above). The acceptance criteria is ±20%. No redigestion or reanalysis is required if the RPD is out of specification when the blank and LCS are within range.

6. Toxic characteristic leachate procedure (TCLP) matrix spikes (QA spikes) are spikes added by the leachate department at the time of filtration. This QA spike is a separate sample and accompanies the unspiked sample. The recovery is calculated in the same manner as the PDS for the EP toxicity leachate. For TCLP samples (toxic leachates), an MSA (method of standard additions) is required if the sample concentration falls between 80% to 100% of the regulatory limit established in the March 29, 1990, Federal Register.

$$\textit{Corrected value} = \frac{100\ (\textit{measured value of the unspiked sample})}{\%R}$$

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B. Each analytical run must contain one initial calibration verification (ICV) standard and an appropriate number of continuing calibration verification (CCV) standards per instrument calibration. The ICV must be prepared from a standard independent from that of the calibration standards. It is analyzed immediately following calibration. The associated analytes must be within ten percent (±10%) of their true values. The exception is CLP mercury, which must be within ±20%. Should an analyte be outside these parameters, the analytical run should be stopped, the problem corrected, and the instrument recalibrated.

CCV samples are performed at a frequency of 10% or once in every ten analytical samples. For graphite furnace with analytical spikes, this would be every five samples (see SOP-IO-004, "QA for Graphite Furnace"). ICVs, initial calibration blanks (ICBs), CCVs, and continuing curve blanks (CCBs) are not considered analytical samples and, therefore, are not counted when determining the 10% frequency interval. In addition, a CCV and CCB are performed following the last analytical sample of a run.

For EPA 600, NIOSH, and CLP methodology, CCV standards must read within **10%** of their true value. The exception to this rule is mercury (Hg) by CLP protocol for which the CCVs must read within 20% of their true value. For SW-846 procedures, the CCVs must read within **20%** of their true value. In those instances where the CCV exceeds its established parameters, the run must be stopped, the problem corrected, and the instrument recalibrated. All samples following the previous in range CCV must be reanalyzed. Reslope of an instrument is acceptable if it is performed after the initial calibration verification and before the CCV (or CCB) has failed. The reslope must be bracketed by valid CCVs and CCBs.

The CRA must be analyzed after the ICV and ICB and must be immediately followed by a CCV and CCB. There is no criteria set for an allowable range.

Environmental lead samples analyzed by flame AA require the CCV to read within 10% of true value even when digested by SW-846 procedures.

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C. Each analytical run must contain one ICB and an appropriate number of CCBs. The calibration blanks are performed in conjunction with the calibration verification standards. All calibration verification standards are immediately followed by calibration blanks.

To be considered within specification, the analyte concentration observed in the blank must be less than the absolute value of the LOQ for that analyte. If this requirement is not met, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze all analytical samples analyzed since the last in-specification calibration blank (CCB).

D. Instrument and method detection limits are performed on each analytical instrument on a yearly basis. In addition, instruments used for the Contract Laboratory Program samples must have instrument detection limits on a quarterly basis for those required elements. These detection limit checks assist in the identification of potential instrument problems and assure that the reported quantitation limits are obtainable

E. Contamination controls for lead shall be performed quarterly on counters and in hoods used for environmental lead preparation. This is performed by moistening 9.0 cm circles of #41 Whatman filter paper, wiping the surface, and digesting by SW-846 3050A. The results are documented in a bound notebook in the prep room labeled for this purpose. The limit for lead permitted is 10 $\mu g/ft^2$. If this level is exceeded, all preparations in that area must be discontinued until the area is thoroughly cleaned and tested again. Once the area tested is determined to be "clean," digestions in that area may be resumed.

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QC Summary:

QC Type	Parameters	Corrective Actions
Preparation Blank SW-846	≤analyte LOQ	None required
	>analyte LOQ - related sample concentrations >20x the observed blank concentration	None required
	>analyte LOQ - related sample concentrations <20x the observed blank concentration	Redigest and reanalyze all related samples in batch.
EPA 600	≤analyte LOQ	None required
	>analyte LOQ - related sample concentrations >10x the observed blank concentration	None required
	>analyte LOQ - related sample concentrations <10x the observed blank concentration	Redigest and reanalyze all related samples in batch.
CLP	≤analyte CRDL	None required
	>analyte CRDL - related sample concentrations >10x the observed blank concentration	None required
	>analyte CRDL - related sample concentrations <10x the observed blank concentration	Redigest and reanalyze all related samples in batch.
Laboratory Control Sample (All protocols)		
LCS - aqueous	80% to 120% recovery	None required
	<80% or >120% recovery	Redigest and reanalyze all related samples in batch.
LCS - solid	Within certified limits	None required
	Outside certified limits	Redigest and reanalyze all related samples in batch
Sample Duplicates (All protocols)	±20% RPD	None required
	>20% RPD	None required Flagged in data packages.
HUD Pb	±25% RPD	None required
	>25% RPD	None required

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QC Type	Parameters	Corrective Actions
SW-846, EPA 600	<80% or >120% spike recovery	Perform analytical spike on background sample. (Spike and background must be analyzed at same dilution level.) Flagged in data packages.
CLP	±25% spike recovery	None required
	<75% or >125% spike recovery	Perform analytical spike on background sample. (Spike and background must be analyzed at same dilution level.) Flagged in data packages.
HUD Pb	±25% recovery	None required
	<75% or >125%	Perform analytical spike on background sample. Flag if data package.
Matrix Spike Duplicates (SW-846)	±20% RPD	None required
	>20% RPD	Flagged in data packages.
	±20% spike recovery	None required
	<80% or >120% recovery	None required
HUD Pb	±25% RPD	None required
	<75% or >125%	None required
Initial Calibration Blank/ Continuing Calibration Blank	≤analyte LOQ	None required
	>analyte LOQ	Identify and correct problem. Reanalyze sample.
Initial Calibration Verification (ICV)	±10% of true value (all methods except ±20% for CLP mercury)	None required
	<90% or >110% of true value	Identify and correct problem. Recalibrate instrument.
Continuing Calibration Verification (CCV)	±10% of true value (EPA 600, NIOSH, and CLP, except ±20% for CLP mercury)	None required
	±20% of true value (EPA SW-846)	None required

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<90% or >110% of true value (EPA 600, NIOSH, and CLP, except <80% or >120% for CLP for mercury)	Identify and correct problem. Reanalyze samples.
<80% or >120% of true value (EPA SW-846)	Identify and correct problem. Reanalyze samples.

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Prepared by: 383 Date: 9/13/96

Approved by: Ramona Nayman Date: 9/17/96

Approved by: 972 Date: 9/17/96

SOP-IO-007
Initiated Date: 06/15/89
Effective Date: OCT 16 1995

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Preparation of Standards and Solutions

Purpose:

The following procedures should be used to prepare standards and solutions to be used in AAS analysis for various metals. Unless otherwise stated:

Intermediate standard solutions have a 6-month holding time.
Calibration standards have a 1-month holding time.
Reference to acid is concentrated acid.
Reference to water is deionized water.
Storage containers are polyethylene bottles.
General solutions have a 6-month holding time.

All standards and reagents must be labeled with the solution name, concentration, date prepared, the expiration date, the initials of the person preparing the solution, and the storage conditions.

If larger or smaller volumes are needed, adjust all additions according to final solution volume.

After diluting to volume, all solutions are thoroughly mixed.

Contents:

A. Reagents

B. Atomic absorption solutions

C. ICP solutions

D. Hydride solutions

E. Mercury solutions

F. Graphite furnace solutions

G. Prep room solutions (waters)

H. Prep room solutions (solids)

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A. Reagents

B. Atomic absorption solutions

B.1 Calibration standards

B.1.1 Al, Ba, Cr
B.1.2 Ag
B.1.3 Cd, Co, Cu, Pb, Ni, Zn
B.1.4 Ca, Mg
B.1.5 Na, K
B.1.6 Li
B.1.7 Fe, Mn
B.1.8 Be
B.1.9 Sb
B.1.10 Mo, V
B.1.11 Tl
B.1.12 Si (Bomb)
B.1.13 Pt
B.1.14 Ag (Buffer)

B.2 Control (ICV) intermediate solutions

B.2.1 Soln 1 - Al, Sb, Co, Cu, Mo, Ni, Tl, Sr, V, Zn, Ba, Be, Cd, Ca, Li, Mg, K, Na, Cr, Pb, Sn, Si, Fe, Mn
B.2.2 Soln 2 - Ag

B.3 Control (ICV) solutions

B.3.1 Soln 1 - Al, Sb, Co, Cu, Fe, Mn, Mo, Ni, Tl, Sr, V, Zn, Ba, Be, Cd, Cr, Pb, Sn, Si, Ag
B.3.2 Soln 2 - Ca, Mg
B.3.3 Soln 3 - Na, K, Li

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B.4 Low-level (CRA) intermediate solutions

B.4.1 Soln 1 - Al, Sb, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, K, Si, Na, Tl, V, Zn, Mo, Sr, Sn
B.4.2 Soln 2 - Ag

B.5 Low-level (CRA) solutions

B.5.1 a. Soln 1a - Al, Sb, Ba, Tl, Be, Cd, Fe, V, Cr, Co, Sr, Cu, Mn, Zn, Ni, Mo, Sn, Ag
b. Soln 1b - Pb
B.5.2 Soln 2 - Ca, Mg
B.5.3 Soln 3 - Na, K, Li

B.6 IDL composite solutions

B.6.1 Soln 1 - Ca, Mg, Na, K, Li
B.6.2 Soln 2 - Al, Tl, Ba, Mo, V, Sb, Fe, Pb
B.6.3 Soln 3 - Cd, Cr, Mn, Ni, Sr, Zn, Be, Co, Cu
B.6.4 Ag

B.7 MDL composite solution

B.8 General solutions

B.8.1 Lanthanum matrix modifier
B.8.2 Cesium matrix modifier
B.8.3 Potassium matrix modifier
B.8.4 Aluminum nitrate matrix modifier
B.8.5 Acid cocktail
B.8.6 Bomb matrix
B.8.7 Sodium thiosulfate (2M)
B.8.8 Sodium hydroxide (2M)
B.8.9 Silver buffer

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C. ICP solutions

C.1 ICP rinse solutions

C.1.1 ICP rinse solution for dilutions
C.1.2 ICP rinse solutions for instrument

C.2 ICP blank solution

C.3 ICP standard 1

C.4 ICP standard 2

C.5 ICP standard 3

C.6 ICP standard 4

C.7 Initial and continuing calibration verification (ICV/CCV)

C.8 ICP initial and continuing calibration blank (ICB/CCB)

C.9 ICP CRI solution

C.9.1 CRDL intermediate-A
C.9.2 CRDL intermediate-B
C.9.3 CRI working solution

C.10 ICP ICSA solution

C.11 ICP (old) ICSAB solution

C.11.1 ICP (new) ICSAB solution

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C.12 ICP 61E trace standard 1

C.13 ICAP 61E trace standard 2

C.14 ICAP 61E trace standard 3

C.15 ICAP 61E trace ICV/CCV

C.16 ICP multipoint blank solution (ICAP 61 and 1100)

C.17 ICP multipoint standard 1 (ICAP 61 and 1100)

C.18 ICP multipoint standard 2 (ICAP 61 and 1100)

C.19 ICP multipoint standard 3 (ICAP 61 and 1100)

C.20 ICP multipoint standard 4 (ICAP 61 and 1100)

C.21 ICP multipoint standard 5 (ICAP 61 and 1100)

C.22 ICP multipoint standard 6 (ICAP 61 and 1100)

C.23 ICP multipoint standard 7 (ICAP 61 and 1100)

C.24 ICP IDL solution

C.25 ICP MDL solution

D. Hydride solutions

D.1 Calibration standards

D.1.1 Intermediate (10 mg/L)

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D.2 Control (ICV) intermediate (2.5 mg/L)

D.3 Control (ICV) (0.025 mg/L)

D.4 Low-level (CRA) (0.001 mg/L)

D.5 General solutions

D.5.1 Hydride acid cocktail 1
D.5.2 Sodium borohydride
D.5.3 Potassium iodide (40%)
D.5.4 Urea (40%)

E. Mercury solutions

E.1 Intermediate calibration standards

E.1.1 Intermediate (10 mg/L)
E.1.2 Intermediate (1.0 mg/L)
E.1.3 Intermediate (0.1 mg/L)

E.2 Manual digestion standards

E.2.1 Calibration standards
E.2.2 Control (ICV) (0.0020 mg/L)
E.2.3 Low level (CRA) (0.0002 mg/L)

E.3 Leeman Labs AP200 digestion standards

E.3.1 1% nitric acid soln.
E.3.2 Calibration standards
E.3.3 Control (ICV) (0.0020 mg/L)
E.3.4 Control (CCV/LCS) (0.0010 mg/L)
E.3.5 Low level (CRA) (0.0002 mg/L)

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E.4 General solutions

E.4.1 Potassium permanganate (5%)
E.4.2 Potassium persulfate (5%)
E.4.3 Sodium chloride/hydroxylamine hydrochloride
E.4.4 Stannous chloride varian (25%)
E.4.5 Stannous chloride Leeman Labs (10%)
E.4.6 1% solution nitric acid

F. Graphite furnace solutions

F.1 Calibration standards

F.1.1 Calibration blank
F.1.2 Stock solutions
F.1.3 Beryllium and cadmium intermediate
F.1.4 Calibration stock
F.1.5 Calibration standard
F.1.6 Lead intermediate
F.1.7 Lead calibration stock
F.1.8 Lead calibration standard
F.1.9 Silver calibration stock
F.1.10 Silver calibration standard
F.1.11 Thallium potable water calibration standard

F.2 Control solutions

F.2.1 Initial calibration verification stock (ICV)
F.2.2 Initial calibration verification standard (ICV)
F.2.3 Thallium potable waters initial calibration verification standard (ICV)
F.2.4 Arsenic, antimony, thallium intermediate (CCV)
F.2.5 Beryllium and cadmium intermediate (CCV)

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F.2.6 Continuing calibration verification stock (CCV)
F.2.7 Continuing calibration verification standard (CCV)
F.2.8 Silver calibration verification stock
F.2.9 Silver calibration verification standard (CCV)
F.2.10 Thallium potable waters continuing calibration verification standard (CCV)
F.2.11 Contract required detection limit check (CRA)
F.2.12 Lead contract required detection limit check (CRA)
F.2.13 Silver contract required detection limit check (CRA)
F.2.14 Thallium potable waters contract required detection limit check

F.3 Modifiers

F.3.1 Ammonium phosphate - magnesium nitrate
F.3.2 Ammonium phosphate - magnesium nitrate - ascorbic acid
F.3.3 Palladium nitrate

F.4 Silver spike

G. Prep room solutions (waters)

G.1 CLP spike solutions

G.1.1 Soln 1 - Ca, Mg, K, Na, Li
G.1.2 Soln 2 - Ag, Be, Cd
G.1.3 Soln 3 - Cr, Cu, Fe, Mn, Ni, Tl, Zn
G.1.4 Soln 4 - Al, Ba, Pb, Mo, Sn, V, B
G.1.5 Soln 5 - Si, Sr, Ti, Co, Sb, As, Se
G.1.6 Soln 6 - Hg
G.1.7 Soln 7 - As, Se
G.1.8 Soln 8 - GF - As, Cd, Pb, Se, Tl, Sb, Cu, Ni, Cr, Be
G.1.9 Soln 10 - Tl, Cu, Pb for nondigested drinking water
G.1.10 Soln 11 - Cr, Cu, Fe, Mn, Ni, Tl, Zn, Pb, As, Se
G.1.11 Soln 12 - Al, Ba, Mo, Sn, V, B
G.1.12 Soln 13 - Si, Sr, Ti, Co, Sb

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G.2 CLP spike solution addition/theoretical recovery for spiked samples

G.3 Graphite furnace silver spike (also used for solids)

G.4 General solutions

G.4.1 Methyl orange
G.4.2 Sodium hydroxide solution (8 g/L)
G.4.3 Potassium permanganate (5%)
G.4.4 Calcium chloride (15 g/L)
G.4.5 Nitric acid (1:1)
G.4.6 Hydrochloric acid (1:1)
G.4.7 100 mg/L Cr spike soln.

H. Prep room solutions (solids)

H.1 CLP spike solutions

H.1.1 Soln 1 - Ca, Mg, K, Na, Li
H.1.2 Soln 2 - Ag, Ba, Cd
H.1.3 Soln 3 - Cr, Cu, Fe, Mn, Ni, Tl, Zn
H.1.4 Soln 4 - Al, Ba, Pb, Mo, Sn, V, B
H.1.5 Soln 5 - Sr, Ti, Co, Sb, As, Se, Si
H.1.6 Soln 6 - Hg
H.1.7 Soln 7 - As, Se
H.1.8 Soln 8 - GF - As, Cd, Pb, Se, Tl, Sb, Cu, Ni, Cr, Be
H.1.9 Soln 11 - Cr, Cu, Fe, Mn, Ni, Tl, Zn, Pb, As, Se
H.1.10 Soln 12 - Al, Ba, Mo, Sn, V, B
H.1.11 Soln 13 - Si, Sr, Ti, Co, Sb

H.2 CLP spike solutions addition/theoretical recovery for spiked samples

H.3 Graphite furnace silver spike

H.4 General solutions

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H.4.1 Acetic acid (4%)
H.4.2 Nitric acid, bottle rinse (2N)
H.4.3 Nitric acid (1:1)
H.4.4 Hydrochloric acid (0.07N)
H.4.5 Hydrochloric acid (2N)
H.4.6 Glassware cleaning soln
H.4.7 Aqua regia
H.4.8 Air filter acid cocktail
H.4.9 Hydride acid cocktail
H.4.10 100 mg/L Cr spike soln.

H.5 Mercury solutions

H.5.1 Potassium permanganate (5%)
H.5.2 Potassium persulfate (5%)
H.5.3 Sodium chloride/hydroxylamine hydrochloride
H.5.4 Stannous chloride (25%) varian
H.5.5 Stannous chloride (10%) Leeman Labs PS200
H.5.6 Mercury intermediate (10 mg/L)
H.5.7 Mercury intermediate (1.0 mg/L)
H.5.8 Mercury intermediate (0.1 mg/L)
H.5.9 Mercury calibration standards
H.5.10 Mercury control (ICV) (0.0020 mg/L)
H.5.11 Mercury low-level (CRA) (0.0002 mg/L)

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Prepared by: 383 Date: 10/6/95

Approved by: Ramona Vayman Date: 10/10/95

Approved by: 972 Date: 10/10/95

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Where quality is a science.

Procedural Amendment #1

Number: SOP-IO-007

Title: Preparation of Standards and Solutions

Effective Date (listed on procedure): 10/16/95

Section(s) affected by change: Purpose

Reason for addition(s) or change(s): Qualify use of variable stock solution concentrations

Change will be effective from (date): 02/29/96

Samples or project affected: All

List change(s) or addition(s) (specify which section):

Purpose: *(Add)*

If solutions of higher or lower concentrations are used for stock or intermediate standard preparation, adjust all additions according to final solution concentration.

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Prepared by: 383 Date: 3/7/96

Approved by: Pamona Hayman Date: 3/7/96

Approved by: 972 Date: 3/7/96

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A subsidiary of Thermo Process Systems Inc., a Thermo Electron company

SOP-IO-007 A
Initiated Date: 06/15/89
Effective Date: JUL 11 1995

A. Reagents*

Acetic acid, glacial ($HC_2H_3O_2$) 99.7%, Fisher, Reagent A.C.S

Aluminum nitrate ($Al[NO_3]_3 \bullet 9H_2O$) Fisher, Certified A.C.S.

Ammonium phosphate, monobasic crystal ($[NH_4]H_2PO_4$) Baker Analyzed Reagent

Boric acid (H_3BO_3) Baker Analyzed, A.C.S.

Calcium chloride, dihydrate ($CaCl_2 \bullet 2H_2O$) Fisher, Certified A.C.S.

Cesium chloride (CsCl) Mallinckrodt, GenAR

Hydrochloric acid (HCl) 36.5% to 38%, Baker Instra-Analyzed Reagent, 1.194 g/mL

Hydrofluoric acid (HF) 48.0% to 51.0%, Baker Analyzed Reagent

Hydrogen peroxide, 30% (H_2O_2) Fisher, Certified A.C.S.

Hydroxylamine hydrochloride ($NH_2OH \bullet HCl$) Fisher, Certified A.C.S.

L-(+)-Ascorbic acid, powder ($C_6H_8O_6$) Baker Analyzed Reagent

Lanthanum oxide (La_2O_3) 99.9+%, Aldrich, AAS Grade

Magnesium nitrate, 6 hydrate, crystal ($Mg[NO_3]_2$) Baker Analyzed Reagent

Methyl orange indicator, Fisher

Nitric acid (HNO_3) 70.0% to 71.0%, Baker Instra-Analyzed Reagent, 1.428 g/mL

Palladium nitrate (1% $Pd[NO_3]_2$) Perkin Elmer

Perchloric acid, 60% ($HClO_4$) Fisher, Reagent A.C.S.

Potassium chloride (KCl) Baker Analyzed Reagent, A.C.S.

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Potassium dichromate ($K_2Cr_2O_7$) Mallinckrodt, primary standard

Potassium iodide (KI) Fisher, Certified A.C.S.

Potassium permanganate ($KMnO_4$) Baker Analyzed Reagent, A.C.S.

Potassium persulfate ($K_2S_2O_8$) Baker Instra-Analyzed Reagent, A.C.S.

Sodium borohydride ($NaBH_4$) 98%, Aldrich

Sodium chloride (NaCl) Fisher, Certified A.C.S.

Sodium hydroxide (NaOH) beads, Fisher

Sodium thiosulfate, anhydrous ($Na_2S_2O_3$) Baker Analyzed

Stannous chloride ($SnCl_2 \bullet 2H_2O$) Mallinckrodt, AR

Sulfuric acid, 95.0% to 98.0% (H_2SO_4) 36 N, Fisher, Reagent A.C.S., 1.84 g/mL

Urea ($[NH_2]_2CO$) Mallinckrodt, A.C.S.

*Use these or equivalent reagents.

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Prepared by: _____ Date: 7/10/95

Approved by: Ramona Layman Date: 7/10/95

Approved by: _____ Date: 7/11/95

B. Atomic absorption solutions

B.1 Calibration standards

B.1.1 Aluminum, barium and chromium composite calibration standards

Calibration Standard Concentration (mg/l) Al Ba/Cr	Volume of Intermediate Standard Added (ml) Al Ba/Cr	*Concentration of Stock/Intermediate Standard (mg/l) Al Ba/Cr	**Final Volume (ml)
Blank	0.0/ 0.0	----	500
1.0/0.10	0.5/ 1.0	1000/50	500
2.5/0.25	1.25/ 2.5	1000/50	500
5.0/0.50	2.5/ 5.0	1000/50	500
10.0/1.0	5.0/ 10.0	1000/50	500
20.0/5.0	10.0/ 50.0	1000/50	500

*Cr intermediate standard (50 mg/l) - Pipette 25.0 ml of Cr 1000 mg/l standard into a 500-ml volumetric flask, add 25 ml HNO_3, and dilute to volume with water.

**After pipetting the intermediate standard into the 500-ml volumetric flasks, add 5 ml HCl, 5 ml HNO_3, and 5 ml of potassium matrix modifier solution to each flask. Dilute to volume with water. Store in polyethylene containers.

B.1.2 Silver calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
0.01	1.0	* 1.0	100
0.05	5.0	* 1.0	100
0.10	10.0	* 1.0	100
0.50	0.50	100	100
1.00	1.0	100	100

Ag intermediate standard (100 mg/l) - Pipette 1.0 ml of 1000 mg/l Ag standard into a 10-ml volumetric flask, add 0.5 ml HNO_3, and dilute to volume with water. Prepare 0.50 and 1.00 mg/l standards using this solution.

*Prepare 0.01, 0.05, and 0.10 mg/l standards from the 1.00 mg/l solution.

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**After pipetting the intermediate standards into the 100-ml volumetric flasks, add 4 ml HNO_3 to each flask and dilute to volume with water. Store in a dark place. Prepare weekly.

B.1.3 Cadmium, cobalt, copper, lead, nickel, and zinc composite calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
0.05	1.0	50	1000
0.10	2.0	50	1000
0.25	5.0	50	1000
0.50	10.0	50	1000
1.00	20.0	50	1000
2.50	50.0	50	1000
5.00	100.0	50	1000

*Cd, Co, Cu, Pb, Ni, and Zn composite intermediate standard (50 mg/l) - Pipette 50 ml of 1000 mg/l standard of each of the above elements into a 1000-ml volumetric flask. Add 50 ml HNO_3 and dilute to volume with water.

**After pipetting the intermediate standard into the 1000-ml volumetric flasks, add 10 ml HNO_3 to each flask and dilute to volume with water. Store in polyethylene containers.

B.1.4 Calcium and magnesium composite calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
Blank	---	---	500
0.05	0.25	100	500
0.20	1.0	100	500
0.50	2.5	100	500
1.00	5.0	100	500
2.00	10.0	100	500

*Ca, Mg composite intermediate standard (100 mg/l) - Pipette 20 ml each of Ca and Mg 1000 mg/l standards into a 200-ml volumetric flask and dilute to volume with water.

**After pipetting the intermediate standard into the 500-ml volumetric flasks, add 25 ml of lanthanum matrix modifier solution to each flask and dilute to volume with water. Store in polyethylene containers.

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B.1.5 Sodium and potassium composite calibration standards

NOTE: Rinse all glassware and containers with water prior to using for Na and K.

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
Blank	---	---	500
0.10	0.5	100	500
0.30	1.5	100	500
0.50	2.5	100	500
1.00	5.0	100	500
1.50	7.5	100	500

*Na and K Composite Intermediate Standard (100 mg/l) - Pipette 20 ml each of Na and K 1000 mg/l standards into a 200-ml volumetric flask and dilute to volume with water.

**After pipetting the intermediate standard into the 500-ml volumetric flasks, add 5 ml of cesium matrix modifier solution to each flask and dilute to volume with water. Store in polyethylene containers.

B.1.6 Lithium calibration standard

NOTE: Rinse all glassware and containers with water prior to using for Li.

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
Blank	---	---	500
0.10	0.5	100	500
0.30	1.5	100	500
0.50	2.5	100	500
1.00	5.0	100	500
1.50	7.5	100	500

*Li Intermediate Standard (100 mg/l) - Pipette 20 ml of Li 1000 mg/l standard into a 200-ml volumetric flask and dilute to volume with water.

**After pipetting the intermediate standard into the 500-ml volumetric flask, add 5 ml of cesium matrix modifier solution and dilute to volume with water. Store in polyethylene container.

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B.1.7 Iron and manganese composite calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
Blank	---	---	1000
0.10	1.0	50	500
0.25	2.5	50	500
0.50	10.0	50	1000
1.00	10.0	50	500
2.50	25.0	50	500
5.00	50.0	50	500

*Fe, Mn Composite Intermediate Standard (50 mg/l) - Pipette 10 ml each of Fe and Mn 1000 mg/l standards into a 200-ml volumetric flask and dilute to volume with water.

**After pipetting the intermediate standard into the 500-ml volumetric flasks, add 5 ml HNO_3 and 25 ml HCl to each 500-ml flask. Add 10 ml HNO_3 and 50 ml HCl to each 1000-ml flask. Dilute to volume with water.

B.1.8 Beryllium calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
.025	0.25	10	100
.050	0.50	10	100
.100	1.0	10	100
.200	2.0	10	100

*Be Intermediate Standard (10 mg/l) - Pipette 1.0 ml of 1000 mg/l Be standard into a 100-ml volumetric flask and dilute to volume with acid cocktail.

**After pipetting the intermediate standard into the 100-ml volumetric flasks, add 3 ml HNO_3 and 2 ml HCl to each flask. Dilute to volume with water.

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B.1.9 Antimony calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
Blank	---	---	100
0.50	0.5	100	100
1.00	1.0	100	100
2.50	0.25	1000	100
5.00	0.50	1000	100
10.00	1.0	1000	100

*Sb Intermediate Standard (100 mg/l) - Pipette 1.0 ml of 1000 mg/l Sb standard into a 10-ml volumetric flask. Add 1 ml HNO_3, 0.25 ml HCl, and dilute to volume with water.

**After pipetting the intermediate standard into the 100-ml volumetric flasks, add 10 ml HNO_3 and 2.5 ml HCl to each flask. Dilute to volume with water.

B.1.10 Molybdenum and vanadium composite calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
Blank	---	---	100
0.50	0.50	100	100
1.00	1.0	100	100
2.50	0.25	1000	100
5.00	0.50	1000	100
10.00	1.0	1000	100

*Mo, V composite intermediate standard (100 mg/l) - Pipette 1.0 ml each of Mo and V 1000 mg/l standards into a 10-ml volumetric flask, add 1 ml HCl, 0.25 ml HNO_3, and dilute to volume with water.

**After pipetting the intermediate standards into the 100-ml volumetric flasks, add 10 ml HCl, 2 ml HNO_3, and 2 ml of aluminum matrix modifier solution to each flask. Dilute to volume with water.

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B.1.11 Thallium calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
0.10	0.10	100	100
0.25	0.25	100	100
0.50	0.50	100	100
1.00	1.0	100	100
5.00	5.0	100	100

*Tl intermediate standard (100 mg/l) - Pipette 1.0 ml of 1000 mg/l Tl standard into a 10-ml volumetric flask, add 0.5 ml HNO_3, and dilute to volume with water.

**After pipetting the intermediate standard into the 100-ml volumetric flasks, add 4 ml HNO_3 to each flask and dilute to volume with water.

B.1.12 Silicon (Bomb Matrix) calibration standards

NOTE: Use polyethylene volumetric flasks.

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	Concentration of Intermediate Standard (mg/l)	* Final Volume (ml)
Blank	---	---	100
2.5	0.25	1000	100
5.0	0.50	1000	100
10.0	1.0	1000	100
20.0	2.0	1000	100
30.0	3.0	1000	100
50.0	5.0	1000	100

*After pipetting the intermediate standard into the 100-ml volumetric flasks, dilute each to volume with bomb matrix solution. Store in polyethylene containers.

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B.1.13 Platinum calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	Concentration of Intermediate Standard (mg/l)	* Final Volume (ml)
Blank	---	---	100
0.50	0.5	100	100
2.00	2.0	100	100
5.00	0.5	1000	100
10.00	1.0	1000	100
15.00	1.5	1000	100

*Pt intermediate standard (100 mg/l) - Pipette 1.0 ml of 1000 mg/l Pt standard into a 10-ml volumetric flask and dilute to volume with deionized water.

**After pipetting the appropriate standard into the 100-ml volumetric flasks, add 10 ml of lanthanum matrix modifier solution to each flask and dilute to volume with deionized water.

B.1.14 Silver (Buffer Solution) calibration standards

Calibration Standard Concentration (mg/l)	Volume of Intermediate Standard Added (ml)	*Concentration of Intermediate Standard (mg/l)	**Final Volume (ml)
Blank	---	---	25
0.10	0.05	50	25
0.20	0.10	50	25
0.50	0.25	50	25
1.00	0.5	50	25
2.00	1.0	50	25

*Ag intermediate standard (50 mg/l) - Pipette 5 ml of 1000 mg/l Ag standard into a 100-ml volumetric flask and dilute to volume with water.

**After pipetting the intermediate standard into the 25-ml volumetric flasks, add 20 ml of silver buffer solution to each flask and dilute to volume with water.

NOTE: Prepare samples using 20 ml of silver buffer solution in a 25-ml volumetric flask.

B.2 Control (ICV) intermediate solutions

B.2.1 Solution 1 - High Purity Standards Custom Multi-Element Solution Standard Lancaster Laboratories ICV-AA or equivalent:

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200 ppm each of Al, Sb, Co, Cu, Fe, Mn, Mo, Ni, Tl, Sr, V, and Zn
500 ppm Ba
10 ppm each of Be and Cd
100 ppm each of Ca, Li, Mg, K, and Na
50 ppm each of Cr and Pb
2000 ppm each of Sn and Si
in 5% HNO_3/Tr. HF

B.2.2 Solution 2 - (50 mg/l Ag): Transfer 20 ml of water and 4 ml HNO_3 to a 100-ml volumetric flask. Pipette 5 ml of SPEX Industries, Inc. 1000 mg/l Ag standard solution or equivalent into the flask. Dilute to volume with water. Store in a dark bottle. Prepare monthly.

B.3 Control (ICV) solutions

B.3.1 Control solution 1 - Pipette 0.25 ml of control intermediate solution 1 and 2 into a 25-ml volumetric flask. Add 0.25 ml of 10% KCl per 25 ml of solution. Dilute to volume with acid cocktail. Prepare daily. The concentrations in this solution are:

Element	Concentration mg/l
Al	2.0
Sb	2.0
Ba	5.0
Be	0.1
Cd	0.1
Cr	0.5
Co	2.0
Cu	2.0
Fe	2.0
Pb	0.5
Mn	2.0
Mo	2.0
Ni	2.0
Sr	2.0
Sn	20.0
V	2.0
Zn	2.0
Tl	2.0
Si	20.0
Ag	0.5

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B.3.2 Control solution 2 - Rinse a 25-ml volumetric flask and stopper with water. Pipette 0.25 ml of control intermediate Solution 1 into the flask. Add 1.25 ml of 10% La_2O_3 per 25 ml final volume. Dilute to volume with water. Prepare daily as needed for analysis. The concentrations in this solution are:

Element	Concentration (mg/l)
Ca	1.0
Mg	1.0

B.3.3 Control Solution 3 - Rinse a 25-ml volumetric flask and stopper with water prior to making solution. Pipette 0.25 ml of Control Intermediate Solution 1 into the flask. Add 0.25 ml of 10% CsCl per 25 ml of solution. Dilute to volume with water. Prepare daily as needed. The concentrations in this solution are:

Element	Concentration (mg/l)
Na	1.0
K	1.0
Li	1.0

B.4 Low-level (CRA) intermediate solutions

B.4.1 Solution 1 - High purity standards custom multi-element solution standard Lancaster Laboratories CRA-AA or equivalent:

20 ppm each of Al, Sb, Ba, Tl, and V
5 ppm each of Ca, Fe, Pb, Li, Mg, K, and Na
1 ppm of Cr, Be, and Cd
10 ppm each of Co and Sr
2 ppm each of Cu, Mn, and Zn
4 ppm of Ni
50 ppm of Mo
100 ppm of Sn
in 2% HNO_3

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B.4.2 Solution 2 - Silver solution (1.0 mg/l Ag): Transfer 50 ml of water, 5 ml HCl, 7.5 ml HNO_3 to a 250-ml volumetric flask. Pipette 0.25 ml of SPEX Industries, Inc. 1000 mg/l Ag standard solution or equivalent into the flask. Dilute to volume with water. Store in a dark bottle. Prepare weekly.

B.5 Low-level (CRA) solutions

B.5.1.a. Solution 1a - Pipette 0.25 ml each of low-level (CRA) Intermediate Solution 1 and 2 into a 25-ml volumetric flask. Add 0.25 ml of 10% KCl per 25 ml final volume. Dilute to volume with acid cocktail. Prepare daily as needed. The concentrations of this solution are:

Element	Concentration (mg/l)
Al	0.20
Sb	0.20
Ba	0.20
Be	0.01
Cd	0.01
Cr	0.01
Co	0.10
Cu	0.02
Fe	0.05
Mn	0.02
Ni	0.04
Ag	0.01
Tl	0.20
V	0.05
Zn	0.02
Mo	0.50
Sr	0.10
Sn	1.0
Ag	0.01

B.5.1.b. Solution 1b - Pipette 0.50 ml of low-level (CRA) intermediate Solution 1 into a 25-ml volumetric flask. Dilute to volume with acid cocktail. Prepare daily as needed. The concentration of this solution is as follows:

Concentration
(mg/l)

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B.5.2 Solution 2 - Rinse a 25-ml volumetric flask and stopper with water. Pipette 0.25 ml of low-level (CRA) intermediate Solution 1 into the flask. Add 1.25 ml of 10% La_2O_3 per 25 ml final volume. Dilute to volume with water. Prepare daily as needed for analysis. The concentrations in the solution are:

Element	Concentration (mg/l)
Ca	0.05
Mg	0.05

B.5.3 Solution 3 - Rinse a 25-ml volumetric flask and stopper with water prior to making solution. Pipette 0.25 ml of low-level (CRA) intermediate Solution 1 into the flask. Add 0.25 ml of 10% CsCl per 25 ml of solution. Dilute to volume with water. Prepare daily as needed for analysis. The concentrations in this solution are:

Element	Concentration (mg/l)
Na	0.05
K	0.05
Li	0.05

B.6 IDL composite solutions

Prepare IDL composite Solutions 1, 2, and 3 from 1000 mg/l standard solutions as shown in the following tables. Dilute these solutions daily as needed for IDL determination.

B.6.1 IDL composite Solution 1

Element	**Final Concentration (mg/l)	Volume of 1000 mg/l Standard (ml)	Composite Concentration (mg/l)	*Final Volume of Composite (ml)
Ca	0.10	1.0	10	100
Mg	0.10	1.0	10	
Na	0.50	5.0	50	
K	0.50	5.0	50	
Li	0.50	5.0	50	

*Add 1 ml HNO_3 and dilute to volume with water.

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**For IDL determination, pipette 0.5 ml of composite solution into a 50-ml volumetric flask, add matrix modifier as required, and dilute to volume with water.

B.6.2 IDL composite Solution 2

Element	** Final Concentration (mg/l)	Volume of 1000 mg/l Standard (ml)	Composite Concentration (mg/l)	*Final Volume of Composite (ml)
Al	0.25	2.5	25	100
Tl	0.50	5.0	50	
Ba	0.25	2.5	25	
Mo	0.25	2.5	25	
V	0.20	2.0	20	
Sb	1.00	10.0	100	
Fe	0.20	2.0	20	
Pb	0.20	2.0	20	

*Add 5 ml HNO_3, 3 ml HCl, and dilute to volume with water.

**For IDL determination, pipette 0.5 ml of composite solution into a 50-ml volumetric flask, add matrix modifier as required, and dilute to volume with acid cocktail.

B.6.3 IDL composite Solution 3

Element	**Final Concentration (mg/l)	Volume of 1000 mg/l Standard (ml)	Composite Concentration (mg/l)	*Final Volume of Composite (ml)
Cd	0.025	0.5	5	100
Cr	0.05	1.0	10	
Mn	0.025	0.5	5	
Ni	0.10	2.0	20	
Sr	0.01	0.2	2	
Zn	0.025	0.5	5	
Be	0.025	0.5	5	
Co	0.10	2.0	20	
Cu	0.05	1.0	10	

*Add 5 ml HNO_3, 3 ml HCl, and dilute to volume with water.

**For IDL determination, pipette 0.5 ml of composite solution into a 100-ml volumetric flask, add matrix modifier as required, and dilute to volume with acid cocktail.

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B.6.4 Silver IDL solution

Silver intermediate solution (10 mg/l) - Into a 100-ml volumetric flask, place about 20 ml water and add 4 ml HNO_3. Pipette 1.0 ml of 1000 mg/l Ag standard into the flask and dilute to volume with water. Store in a dark bottle. For IDL determination, dilute daily.

Final Concentration (mg/l)	Intermediate Concentration (mg/l)	Volume HNO_3 (ml)	Volume Intermediate (ml)	Final Volume (ml)
0.05	10	4	0.5	100

B.7 MDL composite solution

Prepare MDL composite solution from 1000 mg/l standard solutions as shown in the following table:

Element	Volume of 1000 mg/l Standard (ml)	Final Volume of Composite (ml)
Ag	1	1000
Al	10	
Ba	10	
Be	0.5	
Ca	10	
Cd	0.5	
Co	3	
Cr	3	
Cu	0.5	
Fe	5	
K	40	
Mg	10	
Mn	1	
Mo	5	
Na	50	
Ni	5	
Pb	7	
Sb	25	
Tl	25	
V	25	
Zn	4	

Add 50 ml HNO_3 to approximately 500 ml deionized water. Dilute to volume with deionized water and mix well.

Final concentrations in the solution are the same as the volume pipetted. The holding time for this solution is one month.

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Water MDL Solution:

Pipette 10 ml of the AA MDL composite solution to two 1000-ml volumetric flasks. Dilute to volume with deionized water.

Using the water MDL solution prepared above, digest seven 100-ml aliquots and one deionized water blank by the 0820 and 5706 digests.

Solid MDL Solution:

Pipette 10 ml of the AA MDL Composite Solution to two 1000-ml volumetric flasks. Dilute to volume with deionized water.

Using the solid MDL solution prepared above, digest seven 100-ml aliquots and one deionized water blank by the 5709 digest.

Once digested, the MDLs should be read on each instrument used for the analysis of the elements. Each digest's MDLs should be analyzed in succession and readings should be bracketed by valid CCV and CCBs with as many decimal places as possible on the instrument.

B.8 General solutions

B.8.1 Lanthanum matrix modifier solution (10%) - Weigh approximately 117.32 g lanthanum oxide (La_2O_3) into a 1000-ml volumetric flask. Add approximately 200 ml of water. Add 250 ml HCl, with swirling. Cool. Dilute to volume with water. The holding time for this solution is 6 months. **NOTE:** Each new batch of La_2O_3 should be checked for Ca and Mg content before using.

B.8.2 Cesium matrix modifier solution (10%) - Weigh approximately 63.34 g of cesium chloride (CsCl) into a 500-ml volumetric flask. Dilute to volume and shake until dissolved. Store in a polyethylene container. The holding time for this solution is 6 months. **NOTE:** Each new batch of CsCl solution should be checked for Na and K content before using.

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B.8.3 Potassium matrix modifier solution (10%) - Weigh approximately 95.35 g of potassium chloride (KCl) into a 200-ml beaker. Add approximately 150 ml water and heat gently until dissolved. Transfer to a 500-ml volumetric flask and dilute to volume with water. Store in a polyethylene container. The holding time for this solution is 6 months.

B.8.4 Aluminum nitrate matrix modifier solution (40%) - Weigh approximately 139.0 g of aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] into a 200-ml volumetric flask, dilute to volume with water, and mix. The holding time for this solution is 6 months.

B.8.5 Acid cocktail (3% HNO_3/2% HCl) - Mix 60 ml HNO_3 and 40 ml HCl with 1900 ml of water.

B.8.6 Bomb matrix solution - Weigh approximately 28.20 g of boric acid (H_3BO_3) into a 1000-ml Nalgene bottle. Add 2 ml HNO_3, 5 ml HCl, and 30 ml of HF **(Caution: Wear rubber gloves and pour under hood).** Fill the bottle with water to the 1000 ml line, cap and mix. The holding time for this solution is 6 months.

B.8.7 Sodium thiosulfate (2M) - Weigh approximately 316 g of sodium thiosulfate, anhydrous, ($Na_2S_2O_3$) into a 1000-ml volumetric flask, dilute to volume with water, and mix dissolve. The holding time for this solution is 6 months.

B.8.8 Sodium hydroxide (2M) - Weigh approximately 80 g of sodium hydroxide beads (NaOH) into a 600-ml beaker. Add about 300 ml water and stir to dissolve. Cool. Transfer to a 1000-ml volumetric flask and dilute to volume with water. The holding time for this solution is 6 months.

B.8.9 Silver buffer solution - Mix 10 ml of 2M $Na_2S_2O_3$ with 10 ml of 2M NaOH prior to using.

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Approved by: Carol R. Johnson Date: 5/23/95

Approved by: [illegible] Date: 5/25/95

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F. Graphite furnace solutions

F.1 Calibration standards

F.1.1 Calibration blank - Dilute 10 mL of concentrated HNO_3 and 20 mL of 30% H_2O_2 to 1000 mL with deionized water. This solution should be made daily. Store at room temperature.

F.1.2 Stock solutions - Use 1000 mg/L Baker instra-analyzed atomic spectral standard or other commercially prepared standard of equal quality. This standard is good for 1 year unless otherwise specified by the manufacturer. Store at room temperature.

F.1.3 Beryllium and cadmium intermediate stock solution - Dilute 1 mL of both the Be and Cd 1000 mg/L standard to 10 mL with deionized water. The final concentration of this intermediate solution is 100 mg/L Be and Cd. This solution is good for 1 month. Store at room temperature.

F.1.4 Calibration stock solution - Pipet the following volumes (in mL) of 1000-mg/L stock solutions (except the Be/Cd solution into a 100-mL volumetric flask containing approximately 10 mL of deionized water):

Analyte	Volume of Stock Soln. (mL)	Concentration of Standard (mg/L)	Final Volume (mL)	**Final Concentration (mg/L)
As	1.00	1000	100	10.0
Sb	1.00	1000	100	10.0
Tl	1.00	1000	100	10.0
Cu	0.50	1000	100	5.0
Pb	0.50	1000	100	5.0
Ni	0.50	1000	100	5.0
Se	0.50	1000	100	5.0
Cr	0.25	1000	100	2.5
Be/Cd*	0.50	100	100	0.5

*Use the beryllium and cadmium intermediate stock solution.

** After pipetting all of the standards into the 100-mL volumetric flask, add 5.0 mL of concentrated HNO_3 and bring to volume with deionized water. This standard is good for 1 month. Store at room temperature.

F.1.5 Calibration standard - Dilute 1.0 mL of the calibration stock solution to 100 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentrations are:

As/Tl/Sb	100 µg/L
Pb*/Ni/Cu/Se	50 µg/L
Cr	25 µg/L
Be/Cd	5 µg/L

This standard should be made daily. Store at room temperature.

*This solution is not used in calibrating for the lead analysis. It is used only as a spike. See Section F.1.8. for calibration standards for lead.

F.1.6 Lead intermediate stock solution - Dilute 15.0 mL of the 1000 mg/L Pb stock to 50 mL with 0.5 mL HNO_3 and deionized water. The final concentration of the intermediate stock solution is 300 mg/L. The solution is good for 1 month. Store at room temperature.

F.1.7 Lead calibration stock solution - Dilute 3.0 mL of the 300 mg/L lead intermediate stock solution to 100 mL with 5.0 mL of HNO_3 and deionized water. The final concentration of the lead calibration stock solution is 9.0 mg/L. This standard is good for 1 month. Store at room temperature.

F.1.8 Lead calibration standard - Dilute 1.0 mL of the lead calibration stock solution to 100 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the lead calibration standard is 90 µg/L. This standard is made daily. Store at room temperature.

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F.1.9 Silver calibration stock solution - Dilute 0.1 ml of 1000 mg/L Ag stock to 100 mL with 5.0 mL of concentrated HNO_3 and deionized water. The final concentration of the silver calibration stock solution is 1.0 mg/L. This solution is made daily. Store at room temperature.

F.1.10 Silver calibration standard - Dilute 0.5 mL of the silver calibration stock solution to 100 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the silver calibration standard is 5 μg/L. This solution is made daily. Store at room temperature.

F.1.11 Thallium potable waters calibration standard - Dilute 2.0 mL of the calibration standard solution to 10 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the thallium potable waters calibration standard is 20 μg/L. This standard is made daily. Store at room temperature.

F.2 Control solutions

F.2.1 Initial calibration verification stock solution (ICV) - This is a custom mixed solution purchased from an independent source.

The concentrations are:

As/Sb/Tl	5.00 mg/L
Pb/Ni/Cu/Se	2.00 mg/L
Cr	1.00 mg/L
Be	0.20 mg/L
Cd	0.25 mg/L

This standard is good for 1 year unless specified by the manufacturer. Store at room temperature.

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F.2.2 Initial calibration verification standard (ICV) - Dilute 0.50 mL of the initial calibration verification stock solution to 50 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentrations are:

As/Sb/Tl	50.0 µg/L
Pb/Ni/Cu/Se	20.0 µg/L
Cr	10.0 µg/L
Be	2.0 µg/L
Cd	2.5 µg/L

This standard should be made daily. Store at room temperature.

F.2.3 Thallium potable waters initial calibration verification standard (ICV) - Dilute 2.0 mL of the initial calibration verification standard to 10 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the thallium initial calibration verification standard is 8.0 µg/L. This standard is made up daily. Store at room temperature.

F.2.4 Arsenic, antimony, and thallium intermediate (CCV) stock solution - Dilute 1.0 mL of each of the 1000 mg/L stock solutions for As, Sb, and Tl to 5 mL with deionized water. The final concentration is 200 mg/L for As, Sb, and Tl. This solution is good for 1 month. Store at room temperature.

F.2.5 Beryllium and cadmium intermediate (CCV) stock solution - Dilute 1 mL of both the Be and Cd 1000 mg/L standard to 10 mL with deionized water. The final concentration of this intermediate solution is 100 mg/L Be and Cd. This solution is good for 1 month. Store at room temperature.

F.2.6 Continuing calibration verification (CCV) stock solution - Pipet the following volumes (in mL) of 1000 mg/L stock solutions into a 50-mL volumetirc flask containing approximately 10 mL of deionized water except where noted:

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Analyte	Volume of Stock Soln. (mL)	Concentration of Standard (mg/L)	Final Volume (mL)	***Final Concentration (mg/L)
As/Tl/Sb*	2.00	200	50	8.0
Se	0.25	1000	50	5.0
Pb	0.25	1000	50	5.0
Cu	0.25	1000	50	5.0
Ni	0.25	1000	50	5.0
Cr	0.10	1000	50	2.0
Be/Cd**	0.25	100	50	0.5

*Use the arsenic, antimony, and thallium intermediate (CCV) solution.

**Use the beryllium and cadmium intermediate (CCV) solution.

***After pipetting the standards into the 50-L volumetric flask, add 2.5 mL of concentrated HNO_3 and bring up to volume with deionized water. This solution is good for 1 month. Store at room temperature.

F.2.7 Continuing calibration verification standard (CCV) - Dilute 0.25 mL of the continuing calibration verification stock to 50 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentrations are:

As/Sb/Tl	40.0 µg/L
Pb/Ni/Cu/Se	25.0 µg/L
Cr	10.0 µg/L
Be	2.5 µg/L
Cd	2.5 µg/L

This standard should be made daily. Store at room temperature.

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F.2.8 Silver calibration verification stock - To properly verify the calibration solution this stock must be prepared from an alternate source of equal analytical quality. Dilute 0.1 mL of the 1000-mg/L stock solution to 100 mL with 5.0 mL of HNO_3 and deionized water. The concentration of the silver calibration verification stock is 1.0 mg/L. This solution is made up daily. Store at room temperature.

F.2.9 Silver calibration verification standard (CCV) - Dilute 0.25 mL of the silver calibration verification stock to 100 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the silver calibration verification standard is 2.5 μg/L. This standard is made up daily. Store at room temperature.

F.2.10 Thallium potable waters continuing calibration verification standard (CCV) - Dilute 2.0 mL of the continuing calibration verification standard to 10 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the thallium continuing calibration verification standard is 10.0 μg/L. This standard is made up daily. Store at room temperature.

F.2.11 Contract required detection limit check (CRA) - Dilute 0.05 mL of the calibration stock solution to 50 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentrations are:

As/Sb/Tl	10.0 μg/L
Ni/Cu/Se	5.0 μg/L
Cr	2.5 μg/L
Be	0.5 μg/L
Cd	0.5 μg/L

This solution should be made daily. Store at room temperature.

F.2.12 Lead contract required detection limit check (CRA) - Dilute 3.0 mL of the calibration standard solution to 50 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the lead CRA is 3.0 μg/L. This solution is made up daily. Store at room temperature.

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F.2.13 Silver contract required detection limit check (CRA) - Dilute 1.0 mL of the silver calibration standard solution to 10 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the silver CRA is 0.5 μg/L. This solution is made up daily. Store at room temperature.

F.2.14 Thallium potable water required detection limit check (CRA) - Dilute 2.0 mL of the contract required detection limit check standard to 10 mL with 1% HNO_3 and 2% H_2O_2 in deionized water. The final concentration of the silver CRA is 0.5 μg/L. This solution is made up daily. Store at room temperature.

F.3 Modifiers

F.3.1 Ammonium phosphate - magnesium nitrate solution - Dissolve approximately 0.8 grams ammonium phosphate [$(HN_4)H_2PO_4$] and approximately 0.07 grams magnesium nitrate [$Mg(NO_3)_2$] in deionized water, dilute to 100 mL. This solution is good for 3 months. Store at room temperature.

F.3.2 Ammonium phosphate - magnesium nitrate - ascorbic acid solution - Dissolve approximately 0.8 grams ammonium phosphate [$(HN_4)H_2PO_4$], approximately 0.07 grams magnesium nitrate [$Mg(NO_3)_2$] and approximately 1.0 grams ascorbic acid ($C_6H_8O_6$) in deionized water, dilute to 100 mL. This solution is made up daily. Store at room temperature.

F.3.3 Palladium nitrate solution - Dilute Perkin Elmer 1% $Pd(NO_3)_2$ modifier or equivalent in a 1 to 1 ratio with 1% HNO_3 in deionized water. The final concentration is 0.5% $Pd(NO_3)_2$. This solution is good for 1 month. Store at room temperature.

F.4 Silver spike solution for graphite furnace

Ag intermediate standard (5 mg/L) - Pipet 0.5 mL of 1000 mg/L Ag standard into a 100-mL volumetric flask containing approximately 20-mL water and 1mL HNO_3 and dilute to volume with water. Prepare daily.

Ag spike solution for graphite furnace (0.25 mg/L) - Pipet 0.5 mL of 5 mg/L Ag intermediate standard into a 10-mL volumetric flask, add 0.1 mL HNO_3, and dilute to volume with water. Prepare daily. Pipet 1.0 mL of this solution for sample spike (for final sample volume of 100 mL).

NOTE: Theoretical recovery for spiked sample is a spike concentration of 0.0025 mg/L Ag.

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Prepared by: 744 Date: 11/8/95

Approved by: 383 Date: 11-8-95

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G. Prep room solutions (waters)

G.1 CLP spike solutions

G.1.1 Solution 1

Pipet the following volumes of 1000 mg/L standard solution into a 100-mL volumetric flask.

Element	Volume (mL)	Final Concentration (mg/L)
Ca	20.0	200
Mg	10.0	100
K	20.0	200
Na	20.0	200
Li	10.0	100

Add 5 mL HNO_3, 3 mL HCl, and dilute to volume with water. The holding time for this solution is 6 months.

G.1.2 Solution 2

Place approximately 20 mL water in a 100-mL volumetric flask. Add 20 mL HCl and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
Ag	0.25	2.5
Be	0.25	2.5
Cd	0.25	2.5

Dilute to volume with water. Store in a dark bottle. Prepare monthly.

G.1.3 Solution 3

Place approximately 50 mL water in a 100-mL volumetric flask. Add 5 mL HNO_3, 3 mL HCl, and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
Cr	1.0	10
Cu	1.25	12.5
Fe	5.0	50
Mn	2.5	25
Ni	2.5	25
Tl	10.0	100
Zn	2.5	25

Dilute to volume with water. The holding time for this solution is 6 months.

G.1.4 Solution 4

Place approximately 20 mL water in a 100-mL volumetric flask. Add 5 mL HNO_3, 3 mL HCl and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
Al	10.0	100
Ba	10.0	100
Pb	2.5	25
Mo	10.0	100
Sn	20.0	200
V	2.5	25
B	10.0	100

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Dilute to volume with water. The holding time for this solution is 6 months.

G.1.5 Solution 5

Place approximately 20 mL water in a 100-mL volumetric flask. Add 5 mL HNO_3, 3 mL HCl, and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
Si	25.0	250
Sr	5.0	50
Ti	5.0	50
Co	2.5	25
Sb	2.5	25
As	10.0	100
Se	10.0	100

Dilute to volume with water. The holding time for this solution is 6 months.

G.1.6 Solution 6

Pipet 1.0 mL of 1000 mg/L Hg standard into a 100-mL volumetric flask. Add 25 mL water, 1 mL HNO_3, and 0.01 g solid potassium dichromate ($K_2Cr_2O_7$). Swirl to dissolve the dichromate. Dilute to volume with water. Store in a polyethylene container. The holding time for this solution is 6 months. The final concentration is 10 mg/L Hg.

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G.1.7 Solution 7

Place approximately 10 mL water in a 100-mL volumetric flask. Add 10 mL HNO_3, and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
As	2.5	25
Se	2.5	25

Dilute to volume with water. The holding time for this solution is 6 months.

G.1.8 Solution 8

Place approximately 50 mL water in a 1000-mL volumetric flask. Add 50 mL HNO_3, and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
As	4.0	4
Cd	0.25	0.25
Pb	2.0	2.0
Se	1.0	1.0
Tl	5.0	5.0
Sb	5.0	5.0
Cu	2.0	2.0
Ni	2.0	2.0
Cr	1.0	1.0
Be	0.25	0.25

Dilute to volume with water. The holding time for this

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G.1.9 Solution 10

Place approximately 50 mL deionized water in a 1000-mL volumetric flask. Add 50 mL HNO_3. Add the following volumes of 1000 mg/L standard solutions.

Element	Volume (mL)	Final Concentration (mg/L)
Cu	25.0	25.0
Pb	1.0	1.0
Tl	2.0	2.0

Dilute to volume with deionized water. The holding time for this solution is 1 month.

G.1.10 CLP spike Solution 11

Transfer 500 mL of deionized water, 50 mL HNO_3, and 30 mL HCl into a 1000-mL volumetric flask.

Pipet the following volumes (mL) of 1000 mg/L standard solutions into the flask:

Cr	10
Cu	12.5
Fe	50
Mn	25
Ni	25
Tl	2.5
Zn	25
Pb	1
As	2
Se	0.5

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Dilute to volume with deionized water and **mix well.** Final concentration in mg/L is the same value as mL pipetted. The holding time for this solution is 6 months.

G.1.11 CLP spike Solution 12

Transfer 200 mL of deionized water, 50 mL HNO_3, and 30 mL HCl into a 1000-mL volumetric flask.

Pipet the following volumes (mL) of 1000 mg/L standard solutions into the flask:

Al	100
Ba	100
Mo	100
Sn	200
V	25
B	100

Dilute to volume with deionized water and **mix well.** Final concentration in mg/L is the same value as mL pipetted. The holding time for this solution is 6 months.

G.1.12 CLP spike Solution 13

Transfer 200 mL of deionized water, 50 mL HNO_3, and 30 mL HCl into a 1000-mL volumetric flask.

Pipet the following volumes (mL) of 1000 mg/L standard solutions into the flask:

Si	250
Sr	50

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Co	25
Sb	25

Dilute to volume with deionized water and mix well. Final concentration in mg/L is the same value as mL pipetted. The holding time for this solution is 6 months.

G.2 CLP spike solution addition/theoretical recovery for spike samples

Solution	Element	Volume of CLP Spike Solution Added (mL) Waters*	Solids**	Spike Concentration (mg/L)
1	Na	2.0	4.0	4.0
	K			4.0
	Ca			4.0
	Mg			2.0
	Li			2.0
2	Be	2.0	4.0	0.05
	Cd			0.05
	Ag			0.05
3	Fe	2.0	4.0	1.0
	Cr			0.2
	Cu			0.25
	Ni			0.50
	Mn			0.50
	Tl			2.0
	Zn			0.5
4	Pb	2.0	4.0	0.5
	V			0.5
	Al			2.0
	B			2.0
	Ba			2.0
	Mo			2.0
	Sn			4.0

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Solution	Element	Volume of CLP Spike Solution Added (mL) Waters*	Solids**	Spike Concentration (mg/L)
5	Co	2.0	4.0	0.5
	Sb			0.5
	Ti			1.0
	Si		***	5.0
	Sr			1.0
	As			2.0
	Se			2.0

*Final volume is 100 mL.
**Final volume is 200 mL.
***For solid LCS, add 2.0 mL of 1000 mg/L Si standard to 100 mL final volume. The spike concentration is 20 mg/L.

Solution	Element	Volume of CLP Spike Solution Added (mL) Waters[1]	Solids[2]	Spike Concentration (mg/L)
6	Hg	0.1*	0.1*	0.0010
7	As	.05[3]	0.5**	0.025
	Se	.05[3]	0.5**	0.025
8 (GFAA)	As	1.0	2.0	0.04
	Cd			0.0025
	Pb			0.02
	Se			0.01
	Tl			0.05
	Sb			0.05
	Cu			0.02
	Ni			0.02
	Cr			0.01
	Be			0.0025

*Prepare a 1 mg/L Hg spike solution weekly from CLP Spike Solution 6 and use it to spike samples.

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[1,2]Final volume for Hg in waters and solids is 100 mL.

[3]Final volume for As, Se in waters is 50 mL.

[1,2]Final volume for GFAA metals in waters is 100 mL and in solids is 200 mL.

Solution	Element	Volume of CLP Spike Solution Added (mL) Waters*	Solids**	Spike Concentration (mg/L)
10	Cu	1.0	N/A	0.25
	Pb			0.01
	Tl			0.02
11	Cr	2.0	4.0	0.2
	Cu			0.25
	Fe			1.0
	Mn			0.5
	Ni			0.5
	Tl			0.05
	Zn			0.5
	Pb			0.02
	As			0.04
	Se			0.01
12	Al	2.0	4.0	2.0
	Ba			2.0
	Mo			2.0
	Sn			4.0
	V			0.5
	B			2.0
13	Si	2.0	4.0	5.0
	Sr			1.0
	Ti			1.0
	Co			0.5
	Sb			0.5

*Final volume is 100 mL.

**Final volume is 200 mL.

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G.3 Silver spike solution for graphite furnace

Ag intermediate standard (5 mg/L) - Into a 100-mL volumetric flask, place about 20 mL water and 1 mL HNO_3. Pipet 0.5 mL of 1000 mg/L Ag standard into the flask and dilute to volume with water. Prepare weekly.

Ag spike solution for graphite furnace (0.25 mg/L) - Pipet 0.5 mL of 5 mg/L Ag intermediate standard into a 10-mL volumetric flask, add 0.1 mL HNO_3, and dilute to volume with water. Prepare daily. Pipet 1.0 mL of this solution for sample spike (for final sample volume of 100 mL).

NOTE: Theoretical recovery for spiked sample is a spike concentration of 0.0025 mg/L Ag.

G.4 General solutions

G.4.1 Methyl orange indicator solution - Dissolve approximately 25 mg of methyl orange in 100 mL of water.

G.4.2 Sodium hydroxide solution (8 g/L) - Weigh approximately 4 g of sodium hydroxide beads (NaOH) into a 250-mL beaker. Add about 100 mL water and swirl to dissolve. Cool. Transfer to a 500-mL volumetric flask and dilute to volume with water.

G.4.3 Potassium permanganate solution (5%) - Weigh approximately 50 g of potassium permanganate ($KMnO_4$) into a 600-mL beaker. Transfer the $KMnO_4$ into a 1000-mL volumetric flask using water. Dilute to approximately 950 mL with water. Using a stir plate, stir until the $KMnO_4$ is dissolved. Remove spin bar and dilute to volume with water.

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G.4.4 Calcium chloride solution (15 g/L) - Weigh approximately 7.5 g of calcium chloride ($CaCl_2 \cdot 2H_2O$) into a 150-mL beaker. Transfer the calcium chloride into a 500-mL volumetric flask using water, add 2.5 mL HCl, swirl to dissolve, and dilute to volume with water.

G.4.5 Nitric acid (1:1) - Add 500 ml of HNO_3 to 500 mL of water.

G.4.6 Hydrochloric acid (1:1) - Add 500 mL of HCl to 500 mL of water.

G.4.7 Chromium spike solution (100 mg/L Cr) - Transfer 50 mL of deionized water, 5 mL HNO_3, and 3 mL HCl to a 100-mL volumetric flask. Pipet 10 mL of 1000 mg/L Cr standard solution into the flask. Dilute to volume with deionized water and mix well. Holding time for this solution is 6 months.

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Prepared by: 383 Date: 10-3-95

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Approved by: 972 Date: 10/4/95

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H. Prep room solutions (solids)

H.1 CLP spike solutions

H.1.1 Solution 1

Pipet the following volumes of 1000 mg/L standard solution into a 100-mL volumetric flask.

Element	Volume (mL)	Final Concentration (mg/L)
Ca	20.0	200
Mg	10.0	100
K	20.0	200
Na	20.0	200
Li	10.0	100

Add 5 mL HNO_3, 3 mL HCl, and dilute to volume with water. The holding time for this solution is 6 months.

H.1.2 Solution 2

Place approximately 20 mL water in a 100-mL volumetric flask. Add 20 mL HCl and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
Ag	0.25	2.5
Be	0.25	2.5
Cd	0.25	2.5

Dilute to volume with water. Store in a dark bottle. Prepare monthly.

H.1.3 Solution 3

Place approximately 50 mL water in a 100-mL volumetric flask. Add 5 mL HNO_3, 3 mL HCl, and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
Cr	1.0	10
Cu	1.25	12.5
Fe	5.0	50
Mn	2.5	25
Ni	2.5	25
Tl	10.0	100
Zn	2.5	25

Dilute to volume with water. The holding time for this solution is 6 months.

H.1.4 Solution 4

Place approximately 20 mL water in a 100-mL volumetric flask. Add 5 mL HNO_3, 3 mL HCl and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
Al	10.0	100
Ba	10.0	100
Pb	2.5	25
Mo	10.0	100
Sn	20.0	200
V	2.5	25
B	10.0	100

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Dilute to volume with water. The holding time for this solution is 6 months.

H.1.5 Solution 5

Place approximately 20 mL water in a 100-mL volumetric flask. Add 5 mL HNO_3, 3 mL HCl, and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
Si	25.0	250
Sr	5.0	50
Ti	5.0	50
Co	2.5	25
Sb	2.5	25
As	10.0	100
Se	10.0	100

Dilute to volume with water. The holding time for this solution is 6 months.

H.1.6 Solution 6

Pipet 1.0 mL of 1000 mg/L Hg standard into a 100-mL volumetric flask. Add 25 mL water, 1 mL HNO_3, and 0.01 g solid potassium dichromate ($K_2Cr_2O_7$). Swirl to dissolve the dichromate. Dilute to volume with water. Store in a polyethylene container. The holding time for this solution is 6 months. The final concentration is 10 mg/L Hg. (See Section H.7 for mercury general solutions.)

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H.1.7 Solution 7

Place approximately 10 mL water in a 100-mL volumetric flask. Add 10 mL HNO_3, and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
As	2.5	25
Se	2.5	25

Dilute to volume with water. The holding time for this solution is 6 months.

H.1.8 Solution 8

Place approximately 50 mL water in a 1000-mL volumetric flask. Add 50 mL HNO_3, and the following volumes of 1000 mg/L standard solution.

Element	Volume (mL)	Final Concentration (mg/L)
As	4.0	4
Cd	0.25	0.25
Pb	2.0	2.0
Se	1.0	1.0
Tl	5.0	5.0
Sb	5.0	5.0
Cu	2.0	2.0
Ni	2.0	2.0
Cr	1.0	1.0
Be	0.25	0.25

Dilute to volume with water. The holding time for this

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H.1.9 CLP spike Solution 11

Transfer 500 mL of deionized water, 50 mL HNO_3, and 30 mL HCl into a 1000-mL volumetric flask.

Pipet the following volumes (mL) of 1000 mg/L standard solutions into the flask:

Cr	10
Cu	12.5
Fe	50
Mn	25
Ni	25
Tl	2.5
Zn	25
Pb	1
As	2
Se	0.5

Dilute to volume with deionized water and mix well. Final concentration in mg/L is the same value as mL pipetted. The holding time for this solution is 6 months.

H.1.10 CLP spike Solution 12

Transfer 200 mL of deionized water, 50 mL HNO_3, and 30 mL HCl into a 1000-mL volumetric flask.

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Pipet the following volumes (mL) of 1000 mg/L standard solutions into the flask:

Al	100
Ba	100
Mo	100
Sn	200
V	25
B	100

Dilute to volume with deionized water and mix well. Final concentration in mg/L is the same value as mL pipetted. The holding time for this solution is 6 months.

H.1.11 CLP spike Solution 13

Transfer 200 mL of deionized water, 50 mL HNO_3, and 30 mL HCl into a 1000-mL volumetric flask.

Pipet the following volumes (mL) of 1000 mg/L standard solutions into the flask:

Si	250
Sr	50
Ti	50
Co	25
Sb	25

Dilute to volume with deionized water and mix well. Final concentration in mg/L is the same value as mL pipetted. The

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H.2 CLP spike solution addition/theoretical recovery for spike samples

Solution	Element	Volume of CLP Spike Solution Added (mL) Waters*	Solids**	Spike Concentration (mg/L)
1	Na	2.0	4.0	4.0
	K			4.0
	Ca			4.0
	Mg			2.0
	Li			2.0
2	Be	2.0	4.0	0.05
	Cd			0.05
	Ag			0.05
3	Fe	2.0	4.0	1.0
	Cr			0.2
	Cu			0.25
	Ni			0.50
	Mn			0.50
	Tl			2.0
	Zn			0.5
4	Pb	2.0	4.0	0.5
	V			0.5
	Al			2.0
	B			2.0
	Ba			2.0
	Mo			2.0
	Sn			4.0
5	Co	2.0	4.0	0.5
	Sb			0.5
	Ti			1.0
	Si		***	5.0
	Sr			1.0
	As			2.0
	Se			2.0

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*Final volume is 100 mL.
**Final volume is 200 mL.
***For solid LCS, add 2.0 mL of 1000 mg/L Si standard to 100 mL final volume. The spike concentration is 20 mg/L.

Solution	Element	Volume of CLP Spike Solution Added (mL) Waters[1]	Solids[2]	Spike Concentration (mg/L)
6	Hg	0.1*	0.1*	0.0010
7	As	.05[3]	0.5**	0.025
	Se	.05[3]	0.5**	0.025
8 (GFAA)	As	1.0	2.0	0.04
	Cd			0.0025
	Pb			0.02
	Se			0.01
	Tl			0.05
	Sb			0.05
	Cu			0.02
	Ni			0.02
	Cr			0.01
	Be			0.0025

*Prepare a 1 mg/L Hg spike solution weekly from CLP spike Solution 6 and use it to spike samples.

**During the digestion procedure, an additional 10 times dilution is performed (2 g/50 mL x 5 mL/50 mL).

[1,2]Final volume for Hg in waters and solids is 100 mL.
[3]Final volume for As, Se in waters is 50 mL.
[1,2]Final volume for GFAA metals in waters is 100 mL and in solids is 200 mL.

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Solution	Element	Volume of CLP Spike Solution Added (mL) Waters*	Solids**	Spike Concentration (mg/L)
11	Cr	2.0	4.0	0.2
	Cu			0.25
	Fe			1.0
	Mn			0.5
	Ni			0.5
	Tl			0.05
	Zn			0.5
	Pb			0.02
	As			0.04
	Se			0.01
12	Al	2.0	4.0	2.0
	Ba			2.0
	Mo			2.0
	Sn			4.0
	V			0.5
	B			2.0
13	Si	2.0	4.0	5.0
	Sr			1.0
	Ti			1.0
	Co			0.5
	Sb			0.5

*Final volume is 100 mL.
**Final volume is 200 mL.

H.3 Silver spike solution for graphite furnace

Ag intermediate standard (5 mg/L) - Into a 100-mL volumetric flask, place about 20 mL water and 1 mL HNO3. Pipet 0.5 mL of 1000 mg/L Ag standard into the flask and dilute to volume with water. Prepare weekly.

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Ag spike solution for graphite furnace (0.25 mg/L) - Pipet 0.5 mL of 5 mg/L Ag intermediate standard into a 10-mL volumetric flask, add 0.1 mL HNO_3, and dilute to volume with water. Prepare daily. Pipet 2.0 mL of this solution for sample spike (for final sample volume of 200 mL).

NOTE: Theoretical recovery for spiked sample is a spike concentration of 0.0025 mg/L Ag.

H.4 General solutions

H.4.1 Acetic acid (4%) - Add 4 mL of glacial acetic acid ($HC_2H_3O_2$) to 96 mL of water.

H.4.2 Nitric acid, bottle rinse (2N) - Add 142 mL of HNO_3 to 858 mL of water.

H.4.3 Nitric acid (1:1) - Add 500 mL of HNO_3 to 500 mL of water.

H.4.4 Hydrochloric acid (0.07N) - Pipet 5.8 mL HCl into a 1000-mL volumetric flask and dilute to volume with water.

H.4.5 Hydrochloric acid (2N) - Add 166 mL HCl to 834 mL of water.

H.4.6 Glassware cleaning solution - Add 200 mL of HNO_3 and 200 mL of HCl to 1600 mL of water.

H.4.7 Aqua regia - Mix 30 mL of HCl with 10 mL of HNO_3.

H.4.8 Air filter acid cocktail - Mix 1200 mL of HNO_3 with 300 mL of $HClO_4$ (60%).

H.4.9 Hydride acid cocktail - Into a 2.5 l bottle, add 1000 mL of water, 400 mL HCl, and then an additional 250 mL of water. Mix. Slowly add 100 mL H_2SO_4, 250 mL of water, and mix.

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H.4.10 Chromium spike solution (100 mg/L Cr) - Transfer 50 mL of deionized water, 5 mL HNO_3, and 3 mL HCl to a 100-mL volumetric flask. Pipet 10 mL of 1000 mg/L Cr standard solution into the flask. Dilute to volume with deionized water and mix well. Holding time for this solution is 6 months.

H.5 Mercury general solutions

H.5.1 Potassium permanganate solution (5%) - Weigh approximately 50 g of potassium permanganate ($KMnO_4$) into a 600-mL beaker. Transfer the $KMnO_4$ into a 1000-mL volumetric flask using water. Dilute to approximately 950 mL with water. Using a stir plate, stir until the $KMnO_4$ is dissolved. Remove the spin bar and dilute to volume with water.

H.5.2 Potassium persulfate solution (5%) - Weigh approximately 25 g potassium persulfate ($K_2S_2O_8$) into a small beaker. Transfer the $K_2S_2O_8$ into a 500-mL volumetric flask using water. Add approximately 250 mL water. Swirl to dissolve the $K_2S_2O_8$. (Gentle heat may be necessary.) Dilute to volume with water.

H.5.3 Sodium chloride/hydroxylamine hydrochloride solution - Weigh approximately 120 g of sodium chloride (NaCl) into a 400-mL beaker. Transfer, using water, to a 1000-mL volumetric flask. Weigh approximately 120 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) into a 400-mL beaker. Transfer, using water, to the 1000-mL volumetric flask containing the NaCl. Add water and swirl to dissolve solids and dilute to volume with water.

H.5.4 Stannous chloride solution (25%) Varian - Weigh approximately 125 g of stannous chloride ($SnCl_2$) into a 250-mL Erlenmeyer flask. Add 100 mL of water and 100 mL HCl. Heat gently with swirling to dissolve the solid material. Cool. Dilute to a final volume of 500 mL with water. Prepare daily.

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H.5.5 Stannous chloride solution (10%) Leeman Labs PS200 - Weigh approximately 100 g of stannous chloride ($SnCl_2$) into a 250-mL beaker. Transfer using water to a 1000-mL volumetric flask. Add 100 mL of HCl and dilute to volume with deionized water.

H.5.6 Hg intermediate standard (10 mg/L) - Prepare two solutions from separate sources, one from SPEX Industries, Inc. 1000 mg/L Hg or equivalent and one from VWR Scientific 1000 mg/L Hg or equivalent. Pipet 1.0 mL of 1000 mg/L Hg standard into a 100-mL volumetric flask. Add 25 mL water, 1 mL HNO_3, and 0.01 g of solid potassium dichromate ($K_2Cr_2O_7$). Swirl to dissolve the dichromate. Dilute to volume with water. Store in a polyethylene bottle. Identify one as "CAL" (Calibration) and the other as "CONTROL" (Calibration Verification). The holding time for this solution is 6 months.

H.5.7 Hg intermediate standard (1.0 mg/L) - Prepare one from the CAL and one from the CONTROL 10 mg/L intermediate standards. Pipet 1.0 mL of 10 mg/L Hg into a 10-mL volumetric flask. Dilute to volume with water. Mark CAL and CONTROL, respectively. Prepare daily.

H.5.8 Hg intermediate (0.1 mg/L) - Prepare one from the CAL and one from the CONTROL 10 mg/L intermediate standards. Pipet 0.1 mL of 10 mg/L Hg into a 10-mL volumetric flask. Dilute to volume with water. mark CAL and CONTROL, respectively. Prepare daily.

H.5.9 Hg calibration standards - Prepare the calibration standards daily by pipetting the following CAL Intermediate Standard volumes into 100 mL of water:

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Quantity	Calibration Standard Concentration (mg/L)	Volume of Intermediate Standard Added (mL)	Intermediate Standard Concentration (mg/L)
2	Blank	---	---
1	.0002	0.2	0.1
1	.0005	0.5	0.1
2	.0010	0.1	1.0
1	.0025	0.25	1.0
1	.0050	0.5	1.0

Digest the standards and controls using digestion Method 494 for CLP solid samples. See the digestion method for details.

[2.5 mL HNO_3, 5 mL H_2SO_4, 5 mL $KMnO_4$(5%), 2.5 mL $K_2S_2O_8$(5%)]

Digest the standards and controls using digestion Method 5711 for SW-846 solid samples. See the digestion method for details.

[5 mL deionized water, 5 mL Agua Regia, 50 mL deionized water, 15 mL $KMnO_4$ (5%)]

H.5.10 Hg initial calibration verification (ICV) standard (0.0020 mg/L) - Pour 100 mL of water into a 250-mL Erlenmeyer flask. Pipet 0.20 mL of CONTROL intermediate standard (1.0 mg/L Hg) into the flask. Continue as described in Section H.5.9. Transfer to a 100-mL volumetric flask, dilute to volume with water, and reserve for analysis. Prepare daily.

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H.5.11 Hg low-level check (CRA) standard (0.0002 mg/L) - Pour 100 mL of water into a 250-mL Erlenmeyer flask. Pipet 0.2 mL of CONTROL Intermediate Standard (0.1 mg/L Hg) into the flask. Continue as described in section H.5.9.

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Prepared by: 383 Date: 9/21/95

Approved by: Clayman Date: 10/3/95

Approved by: 972 Date: 10/3/95

Lancaster Laboratories
Where quality is a science.

SOP-IO-011
Initiated Date: 07/13/89
Effective Date: JUL 17 1995

Inorganic Analysis Safety Procedures

Purpose:

To maintain the health and welfare of the employees working in the inorganic analysis departments.

Scope:

This SOP will cover those safety practices that are essential in maintaining the health and welfare of the employees working in the inorganic analysis departments.

Procedure:

In order to maintain a safe mode of laboratory operation, the following procedures should be performed.

1. Safety glasses must be worn at all times within the area designated by the yellow and black tape on the floor.

2. Gloves must be worn when a potential skin exposure exists.

   a. Natural rubber, neoprene, or nitrile gloves are used when handling concentrated acids or unknown substances.

      NOTE: Always wear gloves when handling hydrofluoric acid (HF).

   b. Gloves or finger cots made of heat resistant materials are used for handling hot objects. These gloves are usually kept near the muffle furnaces or near the hoods.

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3. Safety bulbs are provided for pipetting purposes. Mouth pipetting is never performed.

4. Hoods are required for performing acid digestions. They must be turned on at the beginning of the digestion procedure. The hood alarms must also be on. If the alarm goes off or the hood appears to be working improperly, immediately inform your coordinator or group leader.

5. An approved acid bottle carrier or cart must be used when bringing large acid bottles in from the storage shed. The person bringing in the acid must be accompanied by a co-worker.

6. Transport gas cylinders (full or empty) with a hand truck.

7. Gas cylinders must be chained to some form of solid support.

8. All containers that contain chemical solutions must be labeled with the following information: name and concentration of solution, preparation date, expiration date, storage conditions, and name of the individual who prepared the solution.

9. Dispose of acid waste properly. All acid digestions, waste solutions, and expired reagent solutions should be collected in waste containers. When the large acid waste containers are full, a designated acid waste handler will transfer the waste to the acid neutralization tank.

10. Promptly clean up chemical spills.

a. Small acid spills may be cleaned up with wet paper towels. These towels should be rinsed in the sink with water prior to discarding them in the wastebasket. Use extra caution with perchloric acid by using large amounts of water on spills and on the paper used for wiping up the spill area. See Section 15e of this SOP for more about perchloric acid.

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b. For large spills, immediately assist or get assistance for any employee who may have been exposed to the spilled material and suffered injury and inform your supervisor, group leader, or a Chemical Hygiene Officer/Safety Specialist. There is a safety shower outside the prep area and eye wash bottles are available in each room.

Large spills are cleaned up with spill pillows. (They are located in yellow plastic bags in the first floor coffee room on the floor under the coat rack.) Neutralize the remaining acid with sodium bicarbonate (baking soda) and rinse the area with water. The baking soda is on the shelf in the solids prep area. Do not use spill pillows for hydrofluoric acid - use boric acid followed by a copious water rinse.

For further information on clean-ups see Section 7.7.4, Spills, in the Lancaster Laboratories Chemical Hygiene Plan.

11. Cracked glassware should not be used. Cracked glassware should be either repaired or discarded. For additional information, contact your supervisor or group leader.

12. Electrical equipment should be frequently checked (minimum: once a week) for cord fraying, cracked insulation, or other damage. Do not use damaged electrical equipment. Immediately report all damaged electrical equipment to your group leader.

13. **Always unplug electrical equipment before performing maintenance activities.**

14. When using chemicals, read the labels carefully. See your group leader or the safety director with any questions concerning the safety of chemicals. Material safety data sheets (MSDS) are on file in the office of the Safety Director. For second or third shift personnel, security will aid you in locating them.

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15. Preparing samples for inorganic analysis involves working with concentrated acids. Acids can be dangerous if not handled cautiously.

    If acid comes in contact with skin, flush the contaminated area with plenty of water and notify a co-worker to alert a first-aid provider. If acid comes in contact with the eyes, flush with water for at least 15 minutes and get medical attention immediately. Notify your supervisor or group leader about all injuries and/or accidents.

    The following precautions apply to specific acids and chemicals that are frequently encountered with inorganic analyses. Additional information may be found in the MSDS for the specific chemical.

    a. Hydrofluoric acid (HF): This acid is very toxic and absorbs through the skin without pain. Wear rubber gloves and handle the solution in a fume hood with assistance from your supervisor.

    b. Nitric acid (HNO_3): This acid causes burns on skin. Add nitric acid to samples in a hood because toxic fumes may be given off.

    c. Sulfuric acid (H_2SO_4): This acid is a strong oxidizing agent and causes severe burns. Sulfuric acid spills are extremely slippery, adding to the danger. Always use in a fume hood. Never mix with concentrated HCl or concentrated $KMNO_4$ as a violent reaction (explosive splattering and extreme heat) will occur.

    d. Hydrochloric acid (HCl): This acid causes burns on skin. Never mix with concentrated H_2SO_4 as a violent reaction will occur. Always use in a fume hood.

    e. Perchloric acid ($HClO_4$): This acid is a very strong oxidizing agent. Use only with H_2SO_4 and in a perchloric acid hood. This acid may be explosive under certain conditions.

    f. When working with hydrogen peroxide (H_2O_2) avoid contact with skin. This is a strong oxidizing agent and will cause severe burns.

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16. When diluting strong acids, never add water to acid; always add acid to water.

17. Store concentrated acids in the prep room acid lockers. Only acids are to be stored in these lockers. Solvents, bases, and other chemicals must be stored away from acids. Small amounts of the concentrated acids are kept in the acid reagent bottles on the prep room counters. These reagent bottles should be filled in an operating fume hood using caution to avoid spills.

18. Any sample that may contain cyanide is potentially hazardous. See your supervisor or group leader before adding any acid.

19. Samples which contain dust may be hazardous. Handle in a fume hood or wear a dust mask.

20. Food and beverages should not be consumed in any area designated as requiring safety glasses. In addition to protecting the employee from any chance of chemical contamination, this policy prevents any contamination of samples or spills onto instruments or computers. Hands must be washed following the handling of any chemical or sample before consuming any food.

21. For additional safety information, please consult the current Lancaster Laboratories Chemical Hygiene Plan.

22. Communicate any safety concerns or injuries to your coordinator or group leader as soon as possible.

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Prepared by: Ramona Layman Date: 7/14/95

Approved by: 383 Date: 7/14/95

Approved by: 972 Date: 7/14/95

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Analysis #:
Initiated Date: 10/10/96
Effective Date:

Title: Prescreening of Water and Soil Samples for Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) and Volatile Organic Content (VOC) Using Headspace Solid Phase Microextraction (SPME) and Gas-Chromatography with Flame Ionization Detection (GC/FID).

Reference:
"Rapid Analysis of BTEX and TPH in Water Using Solid Phase Microextraction (SPME) and "FastGC"", Jennison & Jennison, Varian GC Application Note # 10.

Scope:
This prescreening method was developed to provide purge and trap operators with an estimate of BTEX/VOC contamination in water and soil samples scheduled for purge and trap analysis. The prescreen estimates are then used to determine the dilution necessary (if any) to avoid purge and trap overload (often causing system contamination and instrument down time).

This method applies to but is not limited to prescreening samples for the analytes listed below. It is not necessarily pertinent to speak in terms LOQs for this prescreen analysis. But, for information purposes an estimated quantitation limit (EQL) is listed below. This value is an estimate of the lowest sample concentration which can be detected. Realistically values >/= 10 times this amount will give more accurate estimates. The linear range of the prescreening system is very broad and system saturation/overload occurs only for a very small percentage of samples. Sample amounts ranging up to 200,000 ug/l for water samples have been accurately estimated to within a factor of 2 using this prescreen technique . This method is not an EPA approved method and is not intended to be used to report analytical data.

A single technician can prepare approximately 40 water samples or 20 soils in one hour. Each sample requires between 4 and 5 minutes from injection to injection. Samples are loaded on autosampler trays 48 at a time. The full capacity of the SPME/GC/FID system is 300 injections in 24 hours.

Analyte	Water EQL ug/l	Soil EQL mg/kg
Acetone	6000.	600
Methylene Chloride (MeCl2)	600.	60.
Methyl tertiary-Butyl Ether (MTBE)	60.	6.
Cis-1,2-Dichloroethene (Cis-1,2-DCE)	100.	10.
1,1,1-Trichloroethane (1,1,1-TCA)	50.	5.
Benzene	20.	2.
Trichloroethene (TCE)	50.	5.
Toluene	10.	1.
Tetrachloroethene (PCE)	20.	2.
Chlorobenzene	5.	0.5
Ethylbenzene	2.	0.2
M,P-Xylene	2.	0.2
O-Xylene	2.	0.2
Cumene	2.	0.2
Naphthalene	5.	0.5
Tertiary butyl-Alcohol (TBA)	3000.	300.
Methylethylketone (MEK)	2000.	200.
Chloroform	700.	70.
1,2-Dichloroethane (1,2-DCA)	300.	30.

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Carbon Tetrachloride (CCl4)	300.	30.
Methylisobutylketone (MIBK)	100.	10.
Styrene	3.	0.3
1,4-Dichlorobenzene (1,4-DCB)	3.	0.3

Basic Principles:

A water sample is saturated with sodium chloride in order to favor analyte partitioning into the sample headspace. An SPME fiber coated with 30um of polydimethylsilicone (PDMS) is introduced into the headspace and the analytes are adsorbed onto the fiber. The fiber is thermally desorbed by placing it into the hot injection port of a GC/FID system equipped with a capillary column.

Apparatus and Reagents:

1. Sodium Chloride, NaCl - ACS Reagent Grade
2. Vortex
3. 30um PDMS SPME fibers, Supelco Cat. # 5-7309, or equivalent
4. Varian 8200 Autosampler with SPME upgrade kit and PC control software
5. PC, 486 or better, a serial port, Windows 3.1, and at least 8 meg free memory
6. GC/FID system with a capillary or packed injection port
7. Supelco SPB-1 capillary column; 5M x .20mm x 1.2um or equivalent, alternatively a 10M column could be used.
8. Reduced volume inlet liners having in internal diameter </= 1 mm.
9. GC autosampler vials, Shamrock Cat. # 775170ASM, or equivalent.

Standards:

1. Stock standard solutions of the desired analytes are prepared in methanol at concentrations high enough to allow standard mix preparation at the desired levels.

2. A primary calibration spiking mix is prepared to include the first 15 analytes listed above in addition to 1,4-DCB-d4 which is used as a surrogate. The spiking solution concentrations are listed in Table 1. 4 ul of this spike is added to 0.7 mls of DI water to produce the final aqueous concentrations listed in Table 1. The soil equivalent concentrations are also listed.

3. A Secondary calibration spiking mix is prepared to include the last 8 analytes listed above. The concentrations of these analytes are also listed in Table 1.

4. Surrogate spiking solution - 1,4-Dichlorobenzene d4 surrogate spike is prepared at approximately 5.25 ug/ml in methanol. 4 ul of this spike is added to 0.7 mls of sample to produce an final aqueous concentration of 30. ug/l.

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Sample Preservation:

Since this is only a prescreen method and not an analytical quantitative method the sample preservation is perfomed according to the purge and trap method associated with the sample. This is typically HCl preservation to a pH of 2 or less.

Sample and Extract Hold Time and Storage Conditions:

Samples are refrigerated or packed on ice after collection and during transit to the laboratory. Once they are received at the laboratory they are kept chilled at 4 +/- 2C. Samples must be analyzed within 14 days of collection.

Personnel Training and Qualifications:

No special "formal training" is required beyond training and/or familiarity with GC/FID operation, data handling, and general analytical procedures.

Safety Precautions:

When handling standard materials use gloves and protective clothing including protective eye wear. Avoid breathing standards or getting them on the skin. Samples which have been prescreened are disposed of as standard laboratory waste.

Preparation Procedure:

A. Autosampler Salt Vial Preparation

1. The choice of GC autosampler vials (1.5 ml capacity) to be used is an important one. Trial and error has indicated that some autosampler vials create autosampler problems/downtime because of the rigidity and resistence to puncture of the septa materials. Experience has shown that single Teflon faced (0.005 ") septa with an overall thickness of 0.07 " as supplied by Shamrock (Cat # 775170ASM) work well. Other brands may be used provided that do not cause problems.

2. The GC vials are prepared by placing approximately 3 mm of NaCl in the bottom of each vial. As long as a saturated salt solution is formed upon aqueous sample addition, the exact amount of salt is not critical. Typically between 2 and 4 mm of salt will ensure a saturated salt solution. A saturated salt solution is evident by undissolved salt remaining after sample agitation.

3. To save time salt vial can be prepared in bulk by placing 60 empty, uncapped vials in the middle sections of a cardboard vial file separator. Salt is added to all vials at once using an ASTM E-11 No. 30 sieve (600 um) available from suppliers such as VWR.

4. The salt vials can be prepared well in advance. They do not need to be recapped, after salt addition, but should be stored covered by foil or a vial file lid.

B. Aqueous Standard Preparation

1. Using an autopipetor place 0.7 mls of deionized water in a salt vial as prepared above. For operational efficiency, prepare all the standards needed to set up the samples which you will be prepping at the same time. Refer to Appendix A for instruction on how to set up an autosampler sequence and the number of standards needed to do so. The samples that a given analyst prepares must be bracketed with standards which that same analyst has prepared in the same 4-

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8 hour shift. Do not prepare standards ahead or save leftovers for the next analyst or the next day. If you have leftover standards, put them on the end of your sample sequence.

2. Add 4 ul of Primary Spiking Solution using a 10 ul syringe. The spike should be added to the approximate mid-point of the water. The syringe plunger is depressed smoothly and the needle is withdrawn rapidly after the plunger if fully depressed. Each standard vial is capped very tightly immediately after spike addition.

3. The vial is then vortexed for approximately 5 seconds to adequately dissolve the salt and drive the analytes into the headspace.

4. Care should be taken never to drop the vial or tilt it on its side after vortexing. This causes water to lodge in the neck of the vial and true headspace work is no longer being performed. If a vial is dropped or tilted it must be re-vortexed to pull the water out of the neck of the vial.

C. Aqueous Sample Preparation

1. For operational consistency and best results, samples should be prepared in sets of 10. Hence, 10 40-ml VOA vials containing samples are lined up in a row. The "C" vial is used for prescreening whenever possible. Also line up and label 10 dry salt vials in front of the sample VOA vials. The GC vials must be labeled clearly and legibly with the LL sample #, an analysis code (see note below), and any pH's that are > 2 (see 4 below).

Note - The analysis group type is recorded on the GC vials according to the following code: B = BTEX; G = GRO; N = Naphthalene; M = MTBE, etc. This will also be typed into the autosampler sequence at a later time.

2. Add 4 ul of Surrogate Spike to a each dry salt vial using a 10 ul syringe. The vials do not have to be capped after surrogate addition, but the analyst should work without interruption so that the surrogate does not volatilize before sample addition. The tip of the syringe needle should be place approximately 2-4 mm higher that the surface of the salt. This distance helps keep the syringe free of salt and in good working order. The syringe needle should be held against the glass while adding the surrogate spike. The analyst must watch surrogate addition into each vial to ensure that the syringe has not become clogged. Only samples and blanks require surrogate addition to the dry salt vials. The aqueous standards receive surrogate from the standard spiking mix.

3. Using an autopipetor, 0.7 mls of sample is added. The GC vial and the 40-ml VOA vial are recapped immediately following each sample preparation.

4. After a batch of ten samples is prepped and capped tightly, the pHs of all applicable samples should be determined with pH paper. The pH should be </= 2. If it is not, the pH must be documented in the pH log, the non-complient pHs are also recorded on the GC autosampler vial and must be typed into the autosampling sequence at a later time. The non-complient pH's are also brought to the attention of the departmental coordinator.

5. After the pH's are taken, any necessary rebottling must be performed.

6. Once all ten samples are prepped they are vortexed for approximately 5 seconds and placed in a vial file in the same order as they will be run on the autosampler sequence (including blanks and standards - see Appendix A for more information on setting up a sequence).

7. The next ten samples are prepared in the same fashion.

8. An experienced and efficient analyst can prep on the order of 40 samples in an hour.

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D. Soil Sample Preparation:

1. 2 grams of soil is placed in a 15 ml screw cap vial with a Teflon lined lid. The gram weight must fall between 1.5 and 2.5 grams. The exact weight is not recorded unless it does not fall between 1.5 and 2.5 grams. For operational efficiency, many soils can be weighed out before proceeding to step 2, however, each one must be capped tightly to avoid volatile loss.

2. 2 mls of methanol is added to each vial and the vials are re-capped tightly, immediately following methanol addition.

3. The sample is shaken by hand or with a wrist action shaker for approximately 2 minutes.

4. Allow 30 minutes to an hour for the sediment to settle. If a somewhat clear methanol layer does not form, the sample will need cetrifugation. Centrifugation can be performed immediately after shaking if it is more time efficient to do so.

5. Next, the methanolic extract must be diluted into salt water in order for the analytes to partition into the headspace prior to SPME analysis. In order to reduce the methanolic content of the aqueous dilution without compromising sensitivity, no surrogate is added to soil samples. Using a 10ul syringe, add 7 ul of methanolic extract to a salt vial which already contains 0.7 mls of DI water. Cap the sample immediately. This soil sample preparation has a net effect of a DF100 on the sample. It is critical, therefore, that a dilution factor of 100 be typed into the autosampling sequence (see Appendix A for further instructions).

6. Vortex the aqueous dilution as usual for approximately 5 seconds.

7. Place the samples in a vial file in the order that they will be typed into the autosampling sequence (See Appendix A).

SPME Procedure:

SPME Fiber - 30um Polydimethysiloxane (PDMS) Coating for Varian Autosampler (Supelco Cat.# 5-7309)

Autosampling Method Configuration:

Carrousel Type - 48 vials
GC Cycle Time - 0.00
No Prep Ahead
SPME Sampling Mode ON
SPME Adsorb Time - 0.2 min
SPME Desorb Time - 2.8 min
Headspace Sample Mode ON

Gas Chromatographic Procedure:

1. GC Columns
   a. Retention Gap/Guard Column (optional) - 1-2 ft of .32mm ID Deactivated Fused Silica
   b. Analytical Column - SPB1 10M x .20mm x 1.2um or equivalent

2. Injection Port Liner - A glass liner with an ID <= 1.0 mm must be used for acceptably sharp peak shape. Restek 0.75mm low dead volume Uniliners and Supelco 0.75mm straight capillary liner have both been shown to work well. Example chromatograms are shown in Figures 1 and 2.

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3. GC Conditions

a. Carrier Gas - Hydrogen for optimum resolution at approximately 12 psi measured at 70C.
b. Temperature Program - 70C hold for 0.2 min; program to 180C @ 50C/min
c. FID Temp. - 250 C
d. FID Range - 8 (Using an OI FID mounted on an HP5890)
e. FID Make-up Gas - Nitrogen or helium at approximately 30 mls/min
f. Injector Temp. - 250 C

Note: GC columns and/or conditions can be modified as long as all of the QC criteria can still be met and comparable or better chromatographic performance is demonstrated.

4. Single point external standard calibration is used. Example chromatograms are shown in Figures 1 and 2. The system calibration is updated as needed at the discretion of the analyst. Although there are no hard and fast criteria for evaluation, as a general rule as long as the system maintains consistency of response within +/- 30 % recalibrating is not necessary. Alternatively, the calibration can be updated with every standard.

5. Once the system is calibrated, a calibration check standard is injected after approximately every twenty injections and after the last sample has been analyzed. Since this is a screening method used to derive estimate concentrations there are no absolute criteria for evaluating the check standards. However, as a general rule the system is easily capable of staying within a +/- 30% window. When the responses vary more than this, the possible cause(s) should be investigated. If no systematic problems are detected and the system is consistently running high or low, then the calibration should be updated. Possible systematic problems may include but are not limited to those listed in Appendix B.

6. SPME fibers used in the headspace sampling mode have lasted well over 500 injections. Theoretically they may last forever in the headspace mode, but they usually expire due to mechanical problems such as bending or breaking. Some SPME fiber handling instructions are listed in Appendix C.

7. Department specific data interpretation guidelines are listed in Appendix D.

8. Common, routine mainainance procedures for the autosampler, GC/FID, and data acquisition system are listed in Appendix E.

Calculations:

A single point calibration "curve" is used for all compounds.

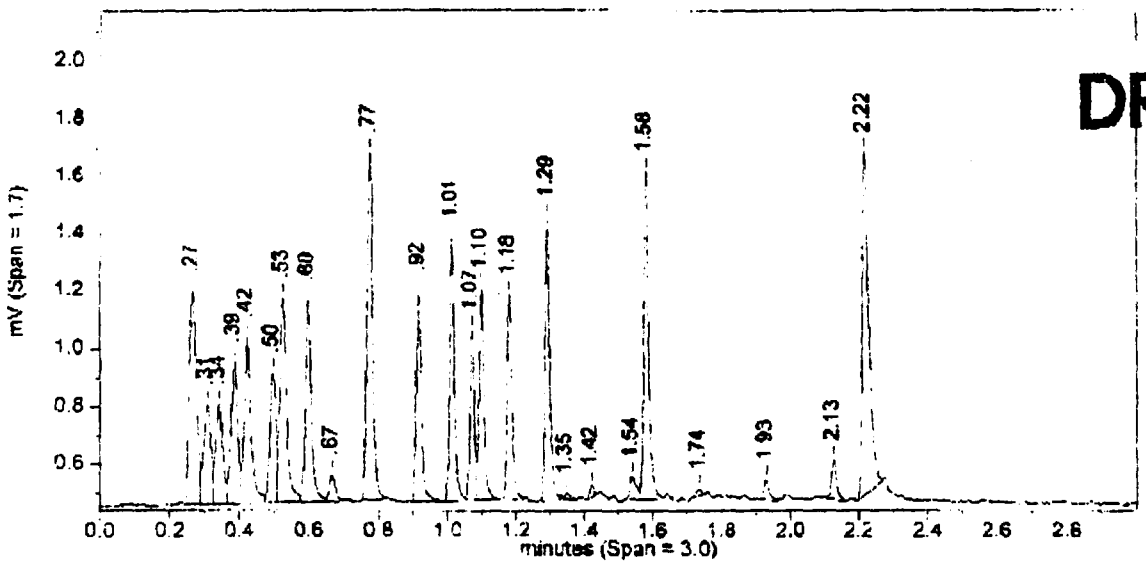
X = Ht.Sam/Ht.Std * Conc.Std = Water Sample concentration in ug/l
and
X = Ht.Sam/Ht.Std * Conc.Std * EFV/EIV * SFV/SIW * 1/1000 (to convert ppb to ppm)
= Soil Sample concentration in mg/kg

Where:

Ht.Sam = Peak height of analyte found in sample
Ht.Std = Peak height of analyte in standard
Conc.Std = Standard concentration in ug/l
EFV = Extract final volume (aqueous) = 0.7 mls
EIV = Extract initial volume (methanolic) = 0.007 mls
SFV = Sample final volume of methanolic extract = 2 mls
SIW = Sample initial weight = 2 grams

Figure 1

VOA711 C:\CPWIN\DATA1\F21816.04R



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Lancaster Laboratories VOA Prescreen by SPME-GC

METHOD FILE: C:\CPWIN\DATA1\EXT21.MET
CAL FILE: C:\CPWIN\DATA1\EXT21.CAL (Version 112)

VOA711 Date Taken: 08-16-1996 11:54:12

Column: SPB-1 10M X .2MM X 1.2UM; H2 12 PSI; FID RNG 6
Conditions: 70C .2M TO 180C @ 50C/M: 30UM PDMS/AMB/12SEC

HP5890--FID DF=1 Operator: SC523

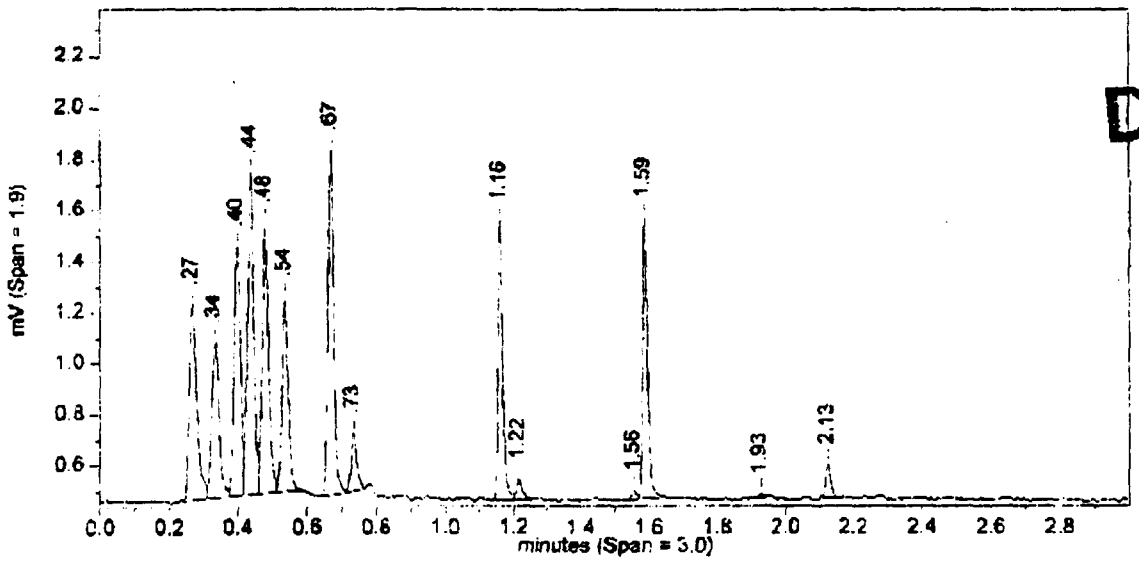
Expected RT	Ret Time (min)	Peak Name	Peak Height	Peak Area	Pk Width (min)	Amount ug/l
0.266	0.266	Methanol	738	1049	0.0226	1.0
0.309	0.309	Acetone	347	498	0.0177	59568.0
0.342	0.342	MeCl2	346	511	0.0201	5684.0
0.386	0.386	MTBE	493	644	0.0184	605.7
0.424	0.424	Cis1,2-DCE	577	810	0.0189	1140.0
0.497	0.497	111TCA	450	518	0.0192	575.0
0.526	0.526	Benzene	708	947	0.0181	172.9
0.599	0.599	TCE	696	822	0.0166	532.8
0.775	0.775	Toluene	1208	1230	0.0151	84.6
0.916	0.916	PCE	731	745	0.0149	188.1
1.012	1.012	Chlorobenzene	912	881	0.0142	52.8
1.071	1.071	Ethylbenzene	590	534	0.0140	16.3
1.098	1.098	M,P-Xylene	735	726	0.0143	19.4
1.180	1.180	O-Xylene	707	661	0.0139	18.5
1.291	1.291	Cumene	987	936	0.0140	19.6
1.580	1.580	1,4-DCB-d4 SURSTD	140	1129	0.0143	1.0
2.217	2.217	Naphthalene	1191	1621	0.0200	57.7

Recommended DF(s): _____ pH_____

Checked by _____ Date _____
Chrom Perfect for Windows Version 2.06 (S/N 21406)

Figure 2

VOASEC C:\CPWIN\DATA1\E21816.06R



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Lancaster Laboratories VOA Prescreen by SPME-GC

METHOD FILE: C:\CPWIN\DATA1\SEC21.MET
CAL FILE: C:\CPWIN\DATA1\SEC21.CAL (Version 31)

VOASEC Date Taken: 08-16-1996 12:12:20

Column: SPB-1 10M X .2MM X 1.2UM; H2 12 PSI; FID RNG 6
Conditions: 70C .2M TO 180C @ 50C/M; 30UM PDMS/AMB/12SEC

HP5890--FID DF=1 Operator: SC523

Expected RT	Ret Time (min)	Peak Name	Peak Height	Peak Area	Pk Width (min)	Amount ug/l
0.262	0.267	METHANOL	766	1190	0.0230	0.6
0.329	0.335	TBA	607	901	0.0217	43089.5
0.394	0.399	MEK	976	1226	0.0197	26190.1
0.434	0.437	CHLOROFORM	1259	1591	0.0174	12620.7
0.475	0.479	1,2 DCA	1055	1348	0.0179	5232.4
0.533	0.536	CCl4	761	921	0.0177	4593.6
0.665	0.668	MIBK	1350	1522	0.0168	2237.6
1.157	1.160	STYRENE	1091	1040	0.0139	57.4
1.584	1.587	1,4 DCB	1103	1085	0.0142	65.7

Recommended DF(s): _____ pH_____

Checked by _____ Date _____
Chrom Perfect for Windows Version 2.06 (S/N 21406)

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Quality Assurance:

This is a prescreening method used to generate estimate concentrations to help prevent future purge and trap overload/contamination problems. For this reason, only a minimum of QC requirements have been instituted.

The main QC requirement is that a check standard is run after approximately every 20 injections. The purpose of this check is two-fold. It provides information and traceability as to whether or not the autosampling sequence was typed and run accurately. It also gives the analyst an indication if the system is running properly. Refer to Appendix B for more information on system performance issues. As a general rule the check standards should agree within +/- 30% as compared to the current calibration value. However, since this is only a prescreening technique, sample repeats are left to the discretion of an experienced analyst.

Surrogate standard is added to water samples. Ideally the surrogate recovery should fall between 50 and 150%. Experience has shown, however, that the surrogate recovery is not necessarily representative of some and/or all of the analytes being screening. Therefore, sample repeats are left to the discretion of the analyst.

Please Note Appendices A-E and Table 1 are in progress and not complete at this time.

tls/draft
10/10/96

Lancaster Laboratories
A division of Thermo Analytical Inc.
Where quality is a science.

Analysis #0374
Initiated Date: 08/21/89
Effective Date: NOV 14 1996

Solid Matrix Sample Preparation

Reference:

1. *USEPA Contract Laboratory Program Statement of Work for Organic Analysis*, OLM01.8, 3/90.

2. Method #8240B, Rev 2, USEPA SW-846, September 1994.

3. Method #8260A, Rev 1, USEPA SW-846, September 1994.

4. *USEPA Contract Laboratory Program Statement of Work for Organics Analysis*, OLM03.1, 8/94.

Scope:

This method is suitable for preparation of solid samples for analysis using GC/MS purge and trap techniques. Care must be exercised to prevent sample cross-contamination of glassware, solvents, and other equipment.

Basic Principles:

A determination of the level of volatile organics present is made based on prescreen data or best assessment of the sample's history. Samples expected to contain less than 1000 to 1500 µg/kg volatile organics are prepared for analysis by the low-level method. Samples expected to contain greater than 1000 to 1500 µg/kg volatile organics are prepared for analysis by the medium-level method.

The low-level sample preparation consists of weighing 1 to 5 g solid material (weighing 0.5 to 5 g solid material for OLM03.1) into a special low-soils impinger (Figure 1), adding 5 mL reagent water that has been spiked with surrogate and internal standards, and assembling the impinger on the purge and trap system.

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The medium-level extraction consists of weighing 4 g of solid into a 15-mL vial. 9 mL of methanol and 1 mL of surrogate spiking solution are added to the vial. The mixture is shaken for approximately 2 minutes, then left to stand for about 10 minutes to allow for separation of phases. Approximately 1 mL of the extract is removed and stored in a 1.5-mL screw-cap vial. A portion, not exceeding 100 µL, of the methanol extraction is spiked into 5 mL of reagent water containing internal standards. The 5 mL of reagent water is then analyzed using a water purge vessel on the purge and trap system.

Apparatus:

1. Micro syringes, 10 µL and larger
2. Syringe, 5 mL gastight
3. Top-loading balance capable of weighing ± 0.1 g
4. Glassware
   a. Bottle, 15 mL screw cap with Teflon cap liner
   b. Volumetric flasks, Class A
   c. Vial, 1.5 mL screw cap, with Teflon/silicone septum

Reagents:

1. Reagent water
2. Methanol, pesticide quality or equivalent
3. Surrogate standard spiking solution (8240B and OLM01.8) - Prepare stock standard solutions for toluene-d8, *p*-bromofluorobenzene, and 1,2-dichloroethane-d4 in methanol. Prepare the surrogate standard spiking solution from the stock standards at a concentration of 25 µg/mL in methanol.

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4. 8260A Surrogate standard spiking solution - Prepare stock standard solutions for toluene-d8, *p*-bromofluorobenzene, dibromofluoromethane and ~~1,2~~-dichloroethane-d4 in methanol. Prepare the surrogate standard spiking solution from the stock standards at a concentration of 25 µg/mL in methanol. 11/14/96

5. TCL matrix spiking solution - Prepare a solution in methanol that contains all the analytes of interest at a concentration of 25 µg/mL. Matrix spikes also serve as duplicates, therefore, two aliquots of the same sample need to be spiked for analysis with this solution.

6. 8000 Series matrix spiking solution(s) - Prepare solution(s) in methanol that contain all the analytes of interest at appropriate concentrations. Matrix spikes also serve as duplicates, therefore, two aliquots of the same sample need to be spiked for analysis with this solution.

7. Store all standard solutions at -10 to -20°C.

8. Replace reagents and solutions every 6 months.

Preparation of Glassware:

All glassware is washed with soapy water, rinsed with tap water, then rinsed with deionized water and dried in a drying oven at 100°C for at least 4 hours in accordance with SOP-MS-001 "Glassware Cleaning."

Safety Precautions:

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined, therefore, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available, such as the use of fume hoods, lab coats, safety glasses, and gloves.

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Training and Qualification Requirements:

Analysts must be trained in the proper method of volatile organic sample preparation as indicated on the GC/MS volatile analyst training checklist and as determined by the supervisor(s). All training and education relating to volatile organic sample preparation and analysis shall be documented by each analyst in their training record.

Waste Generation and Disposal:

Neat compound sources and stock solutions shall be collected in a lab pack upon expiration. The lab pack is delivered to safety personnel for appropriate disposal. Expired secondary standard solutions in methanol shall be disposed of as solvent waste. Pour expired secondary standard solutions into appropriate waste collection container.

Procedure:

1. Decide which soil preparation method is most appropriate for the samples using prescreening information or information supplied with the samples. Samples believed to contain contaminates at less than 1000 to 1500 µg/kg or of unknown origin should be prepared using the low-level method. Samples expected to contain greater than 1000 to 1500 µg/kg should be prepared using the medium-level method. For holding times, the specific analysis method being used should be referenced.

2. Low-level method

   To prepare reagent water, remove the plunger from a 5-mL glass Luer-Lok syringe and fill to overflowing with reagent water. Replace the plunger and compress the water such that no air is trapped in the syringe. Adjust the syringe volume to 5.0 mL. Add 10 µL of the surrogate spiking solution and the internal standard solution to the syringe through the syringe tip.

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b. The sample consists of the entire contents of the sample container. Do not discard any liquids. Mix the contents of the sample using a metal spatula. Weigh 1.0 to 5.0 g of sample (weigh 0.5 to 5 g of sample for OLM03.1) into a tared low-soils impinger tube (Figure 1) using the top loading balance. 5 g of sample yields the lowest limit of quantitation for this preparation. Record the actual mass used in the GC/MS VOA Solids Preparation Log to the nearest .01 g.

c. For USEPA CLP Statement of Work for Organics Analysis, 3/90, an approved solid matrix must be used in the preparation of the method blank. Weigh 5.0 g of the approved solid matrix into a tared vial using the top-loading balance. Record the actual mass used in the GC/MS VOA Solids Preparation Log to the nearest .01 g.

d. Assemble the low-soils impinging tube on the purge and trap device. Add the spiked reagent water to the impinging tube through the Luer-Lok assembly attached to the impinging assembly. Do these steps quickly to minimize the loss of volatiles from the sample and to minimize the possibility of airborne contamination of the sample.

e. Heat the sample to the temperature required by the method. Begin the normal purge and trap analysis as described in the particular analytical methodology to be followed.

f. For matrix spikes, add appropriate amounts of the TCL-matrix spiking solution or the 8000 Series spiking solutions to the 5 mL of reagent water in the syringe which is added to the 5 g of soil.

3. Medium-level method

a. The medium-level sample preparation method is used for the following situations:

(1) when target compounds are detected at a concentration beyond the calibration range of the analysis

(2) when high levels on nontarget peaks are detected after using the low-level method with a 1-g sample mass

(3) when prescreen results indicate a medium-level method is required

The sample consists of the entire contents of the sample container. Do not discard any free liquids. Mix the contents of the sample container using a metal spatula. Weigh 4.0 g of sample into a tared vial using a top-loading balance. Record the actual mass in the GC/MS VOA Solids Preparation Log to the nearest .01 g.

b. Quickly add 9.0 mL of methanol and 1.0 mL surrogate spiking solution to the vial. Cap the vial with the Teflon seal and cap, and shake for 2 minutes. The mixture is then left to stand for 10 minutes to allow for sufficient separation of phases. Do these steps quickly to minimize the loss of volatile organics. Record the amount of methanol and surrogate spiking solution used and information concerning their origin. For example, record the lot number for methanol and the preparation date of the standard.

c. For USEPA CLP SOW for Organic Analysis, 3/90, an approved solid matrix must be used in the preparation of the method blank. Weigh 4.0 g of solid matrix into a tared vial using a top-loading balance. Record the actual mass in the GC/MS VOA Solids Preparation Log to the nearest .01 g. Add 9.0 mL of methanol and 1.0 mL surrogate spiking solution to the vial. Record the amount added and the lot number of the methanol. Mix as in 3.b.

d. Transfer approximately 1.0 mL of the methanol solution to a GC vial for storage. Dispose of the remaining methanol in the waste solvent can.

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e. Remove the plunger from a 5-mL Luer-Lok syringe. Fill the barrel of the syringe to overflowing with reagent water. Replace the plunger, compressing the water such that no air is present in the syringe. Adjust the syringe volume to 4.9 mL. Add 10 µL internal standards solution through the Luer-Lok tip of the syringe. Add 5 to 100 µL (10 to 100 µL for USEPA CLP SOW Organic Analysis) of the methanol extract in the same manner, as needed, to give peak responses in the top half of the calibration curve. Add enough methanol to bring the total volume of methanol to 100 µL.

f. Attach the syringe to the purge and trap vessel and place the sample in the purge vessel. Begin the normal purge and trap analysis as described in the particular analytical methodology to be followed.

g. For TCL matrix spikes, prepare the extract using 8.0 mL methanol, 1.0 mL surrogate spiking solution, and 1.0 mL matrix spiking solution. Record the surrogate and matrix spiking solution amounts in the GC/MS VOA Solids Preparation Log. Also include information on the lot number for the methanol.

h. For 8000 Series matrix spikes, prepare the extract using 1.0 mL of surrogate spiking solution, an appropriate amount of matrix spiking solution(s), and add methanol to equal a final volume of 10.0 mL. Record the surrogate and matrix spiking solution amounts in the GC/MS VOA Solids Preparation Log. Also, include information on the lot number for the methanol.

Calculations:

See specific analysis method.

Statistical Information:

See specific analysis method.

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Quality Assurance:

For each set of 20 samples or fewer and for each level of preparation, a method/reagent blank, a matrix spiked sample, and a duplicate of the matrix spiked sample must be prepared and analyzed. If the matrix spike and matrix spike duplicate do not meet method requirements for quality control, a laboratory control sample (LCS) must be prepared without the sample matrix, if required by the method being used to analyze the samples. If more than 20 samples are analyzed in a batch, additional blanks, spiked samples, and spiked duplicate samples must be prepared and analyzed. Surrogate recoveries, spike recoveries, and spike relative percent differences are addressed in the appropriate analysis method.

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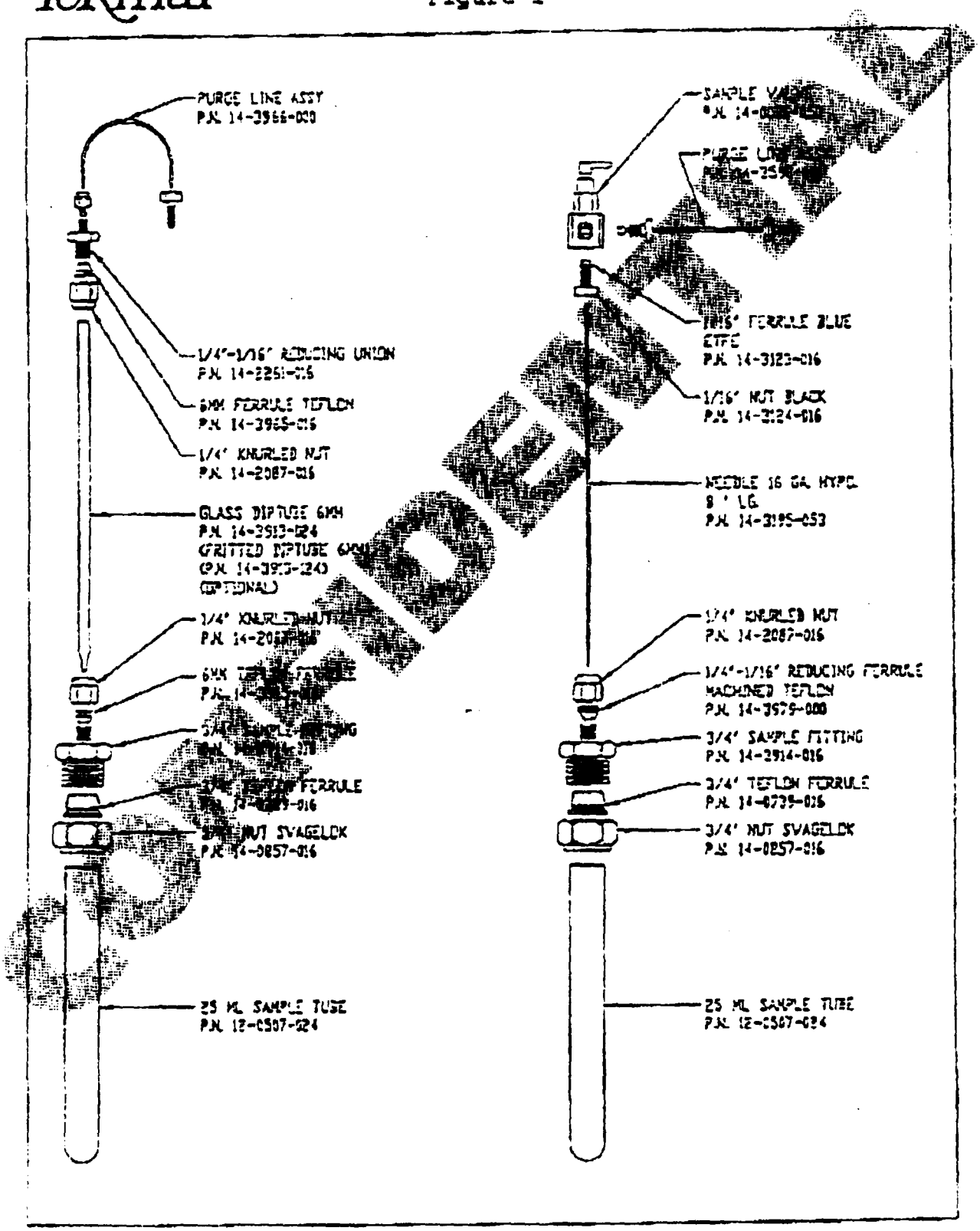
Prepared by: Michele McClain Date: 11/13/96

Approved by: Michele M. McClain Date: 11/13/96

Approved by: Susan G. Shorter Date: 11/13/96

Tekmar

Figure 1



Analysis #1508, 1265, 1266, 1358,
1384, 1131, 3981, 4592,
5121, 5122, 5222, 5243,
5244
Initiated Date: 12/13/89
Effective Date: AUG 08 1995

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Waters and Wastewaters for Priority Pollutant Volatile Target Compounds

Reference:

Method 8240B, USEPA SW-846, Second Revision, September 1994.

Scope:

This method is suitable for the determination of compounds listed in USEPA SW-846 Method 8240B for aqueous matrices. The method also is appropriate for acquiring data files required to perform a search for tentatively identified compounds (TIC) in volatile organics GC/MS analyses. This analysis should be performed by or under the direct supervision of an operator experienced in the analysis of volatile organics by GC/MS purge-and-trap methodologies.

Basic Principles:

A 5-mL sample or a dilution of a sample is placed in a specially designed purge vessel. The sample is purged with an inert gas and the effluent gas passed through a sorbent trap where the volatile organics are trapped. After purging, the sorbent trap is rapidly heated and backflushed onto the head of a gas chromatographic column held at the appropriate initial temperature for the column in use. The gas chromatographic column is temperature programmed to separate the volatile compounds which are subsequently detected and identified using mass spectrometric techniques.

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Apparatus:

1. Gastight micro syringes - 10 μL and larger

2. 5-mL syringe

3. Analytical balance, capable of accurately weighing ±0.001 g

4. Glassware - Volumetric flasks, Class A with ground-glass stopper

5. Purge-and-trap device - Consisting of the sample purger, the trap, and desorber; the Tekmar LSC-2 and LSC 2000 or equivalent meets the requirements of this method

6. GC/MS system - The HP 5970 MSD, Finnigan Incos 50, Finnigan 1020/OWA, or equivalent GC/MS system meets the requirements for this method

Reagents:

1. Reagent water is defined as water in which an interferant is not observed at or above the reporting limit for parameters of interest. In general, the deionized water supplied at the taps in the laboratory will meet this criteria. If the reagent water does not meet the requirements, see your supervisor for further instructions.

2. Methanol and other appropriate solvents (i.e., TGDE, CS_2) - For purge-and-trap analysis or equivalent

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3. Stock standard solutions - Prepared from assayed standard materials or purchased. Stock solutions must be prepared in methanol or an equivalent solvent.

   a. Place about 9.8 mL methanol or an equivalent solvent into a tared 10.0-mL glass-stoppered volumetric flask. Weigh the flask to the nearest 0.1 mg.

   b. Add the liquids using a syringe or pipette by adding two or more drops of the assayed material to the flask being careful that no drop hits the side of the flask. Bring the volume of solvent in the flask to 10.0 mL. Calculate the concentration of the standard.

   c. The gases bromomethane, chloromethane, chloroethane, vinyl chloride, and dichlorodifluoromethane are purchased from an outside vendor and used as received.

   d. The stock standard solutions are stored in Teflon-sealed screw-capped vials at -10° to -20°C. The compound name, concentration, date prepared, and expiration date must appear on the bottle.

   e. Replace stock standard solutions every 6 months.

4. Secondary dilution standards - Using the stock standard solutions, prepare secondary stock solutions in methanol or an equivalent solvent containing the desired compounds. Table I lists the priority pollutant compounds analyzed under Analysis #1508. These standards are prepared by calculating the volume of each stock standard required to produce a given volume of a mixed working standard with a known concentration of each analyte. The working standard is tested according to SOP-MS-006, "GC/MS Volatile Standards Traceability." The verified working standard is pipetted into 1.5-mL Teflon-lined screw-capped GC

vials and is stored at -10° to -20°C. A designator indicating the standard, month, and day of preparation must be on the standard vials. The designator and the calculations for the working standard preparation are to be recorded in the standards logbook. Replace secondary dilution standards every 6 months.

5. Matrix spiking solution - Prepare solutions in methanol or an equivalent solvent that contain the compounds of interest at known concentrations in a similar manner as described above for the secondary dilution standards. These solutions serve as both the matrix spiking solution and the quality control reference stock solution. Matrix spikes also serve as duplicates; therefore, two aliquots of the same sample need to be spiked for analysis with these solutions.

6. Surrogate standard spiking solutions - Prepare stock standard solutions for 1,2-dichloroethane-d4, toluene-d8, and 4-bromofluorobenzene in methanol. Prepare surrogate standard spiking solutions from the stock standards at concentrations of 25 µg/mL and 100 µg/mL in methanol. The 100-µg/mL solution shall be used in initial calibration standards. The 25-µg/mL solution shall be used in initial calibration standards, continuing calibration standards, blanks, and samples. Replace the surrogate standard spiking solutions every 6 months.

7. Internal standards solution - Prepare a solution in methanol or an equivalent solvent containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5 at a concentration of 25 µg/mL using stock standards as described in step 4 above. Replace the internal standards solution every 6 months.

8. 1,4-Bromofluorobenzene (BFB) standard - Prepare a 25-µg/mL solution of BFB in methanol. Replace this solution every 6 months.

9. Store all standard solutions at -10° to -20°C.

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Preparation of Glassware:

All glassware is washed with soapy water, rinsed with tap water, then rinsed with deionized water, and baked in a drying oven at 100°C for at least 4 hours.

Safety Precautions:

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; therefore, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available, such as the use of fume hoods, lab coats, and gloves.

Sample Handling:

The samples to be analyzed using USEPA SW-846 Method 8240B, should be stored in a refrigerator between 2° and 6°C. The samples should be preserved to a pH of less than two in order to prevent degradation of aromatic compounds that may be present in the sample. The recommended preservative is 1 + 1 HCl; however, samples with other preservatives can be analyzed. In addition, all samples must be analyzed within 14 days of collection.

Procedure:

1. Tune the GC/MS system to meet the criteria in Table II following a 2-μL injection of BFB. The chromatographic conditions must be the same as those under which the samples will be analyzed except that the temperature ramp may be increased and the initial temperature may be different. The BFB tune must be verified every 12 hours.

2. The purge-and-trap device should have the trap conditioned for 30 minutes at 180° to 200°C at a flow rate of 20 to 40 mL/minute prior to initial use.

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3. The recommended gas chromatographic operating conditions are listed in the table below:

	Method 8240B Packed Column	Method 8240B Capillary Column
Column packing	SP-1000 on Carbopack B	DB-624
Carrier gas	Helium	Helium
Carrier gas flow	30 mL/minute	9 to 10 mL/minute
Makeup gas flow	----	20 mL/minute
Initial temperature	45°C	35°C
Initial hold time	3 minutes	5 minutes
Temperature ramp	8°C/minute	10°C/minute
Final temperature	220°C	180°C
Final hold time	15 minutes	2.5 minutes

4. The recommended mass spectrometer operating conditions are listed below:

Ions Positive
Electron energy 70 volts
Mass range 35 to 300 amu

Scan time: Packed

INCOS Systems: Total scan time 1.5 sec

H-P Systems: Number A/D samples 2^4 (16)
Integration time/sample 50 microsec
Total time 2.3 sec

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Scan time: Capillary

INCOS Systems: Total scan time 0.7 sec

OWA System: Total scan time 1.0 sec

H-P Systems: Number A/D samples 2^2 (4)
Integration time/sample 50 microsec
Total time 0.6 sec

5. The average RRF value for each analyte is used for method blank and sample calculation. The relative standard deviation of the response factors determine the suitability of the average relative response factor for calculation of the analyte concentration.

   a. All aqueous matrices should be prepared in the following manner. Remove the plunger from a 5-mL glass Luer-Lok syringe and fill the syringe barrel to overflowing with the aqueous matrix. Replace the plunger and compress the aqueous matrix such that no air is trapped in the syringe. Adjust the syringe volume to 5.0 mL. Add an appropriate volume of the surrogate spiking solution and the internal standard solution to the syringe through the syringe tip.

   b. Add the spiked aqueous matrix to the purge vessel through the Luer-Lok assembly at the top of the impinging assembly. Do these steps quickly to minimize the loss of volatiles from the aqueous matrix and to minimize the possibility of airborne contamination of the aqueous matrix.

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c. The suggested purge-and-trap conditions are listed below:

Purge flow	35 mL/minute
Purge temperature	Ambient temperature
Purge time	11 minutes
Desorb temperature	220°C
Desorb time	1 minute
Bake temperature	180°C
Bake time	8 minutes

Purge-and-trap conditions may be changed to optimize instrument operations. A record of actual purge-and-trap conditions for each instrument may be found in the appropriate instrument maintenance log.

d. Empty and rinse the purging chamber twice with reagent water prior to loading another sample into the vessel, to minimize the possibility of carryover contamination.

e. Continue collecting GC/MS data until the end of the GC run.

f. Prepare the calibration standards at appropriate levels; an example of a five-point calibration is listed below:

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Standard Concentration (µg/L)	Gas Mix (µL)	µL Secondary Dilution Stock Standard	Final Volume (mL)
4 (Five times dilution of 20 µg/L standard)			
20	20	4	200
50	25	5	100
100	25	5	50
300	37.5	7.5	25

Due to poor purging efficiency or poor chromatography, certain analytes (Table I) require calibration at higher concentrations. To prevent confusion and assure proper calibration, a Theoretical Standard Concentration (TSC) sheet is completed for each calibration (Figure 2). The TSC sheet contains the theoretical concentration for each analyte in the calibration at each of the five levels.

g. Each level is analyzed as described above by substituting five milliliters of the calibration standard as the aqueous matrix. Next, tabulate the area response of the characteristic ions against concentration for each analyte, surrogate standard,and internal standard and calculate relative response factors (RRF) for each compound using the calculation below:

$$RRF = \frac{Ax}{Ais} \times \frac{Cis}{Cx}$$

Where:

Ax = Area of the characteristic ion for the analyte

Ais = Area of the characteristic ion of the appropriate internal standard

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Cis = Concentration of the internal standard

Cx = Concentration of the analyte to be measured

h. Calculate the average relative response factors for all analytes. Five analytes are checked for minimum average response factors. These compounds are system performance check compounds (SPCCs). The compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. Six additional compounds are evaluated on the basis of the relative standard deviation of the RRF values (%RSD). These compounds are known as calibration check compounds (CCCs). The CCCs are 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride. Minimum average RRF value for each SPCC compound is 0.30 except for bromoform which is 0.10. The %RSD for the CCC compounds must be less than 30%. Failure to meet either of the criteria for the SPCC and CCC compounds invalidates the calibration and the calibration must be redone after proper corrective action to the system is taken.

i. The %RSD for each analyte should be ≤15%. If the %RSD is ≤15%, the average RRF value for each analyte is used for method blank and sample calculations. If the %RSD of any analyte is >15, use a first or second order regression fit of the five calibration points for method blank and sample calculations. The calibration is valid for 12 hours, at which time a new tune check and a calibration check must occur prior to the analysis of additional samples.

j. The calibration check involves analyzing the 50 µg/L standard and calculating the RRF for each compound. Minimum RRF values as described under the calibration section for the SPCC compounds

must be met. Also the percent drift between the standard concentration and the measured concentration for each compound in the 50 μg/L check standard are calculated as follows:

$$\% \ Drift = \frac{C_1 - C_c}{C_1} \times 100.$$

Where:

C_1 = Standard concentration of analyte

C_c = Measured concentration of analyte using selected quantitation method

The percent drift for the CCC compounds must be less than or equal to 20%. If any SPCC or CCC compound fails to meet the criteria listed above, the calibration is considered invalid. Corrective action must be taken and the calibration redone. If the criteria are met, the selected quantitation method from the initial calibration are used for blank and sample calculation for the next 12-hour period.

6. A method blank is then analyzed as described above in steps 5.a. through 5.e. using reagent water as the aqueous matrix. The method blank is examined for interfering peaks. Any target compound peaks are calculated as described under the Calculation section of this procedure. Methylene chloride, acetone, toluene, and 2-butanone must not exceed five times the quantitation limit in the blank. All other compounds may not exceed the quantitation limit. If the blank values exceed these values, corrective action must be taken and the method blank reanalyzed until the criteria are met. Also, all surrogate compound recoveries must meet the criteria listed in Table III.

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7. Sample analysis

   a. Sample analysis for water and wastewater proceeds as described in steps 5.a. to 5.e. above.

   b. For each set of 20 field samples, one sample shall be analyzed in triplicate, spiking each duplicate with each of the quality control reference concentrates. Results of the unspiked and spiked duplicates shall be compared to Table IV.

   c. All samples must also meet the surrogate recoveries listed in Table III. If a sample surrogate recovery falls outside the criteria, the sample shall be reanalyzed. If the reanalysis shows the same surrogate results, the sample matrix is assumed to be interfering and the initial results are reported. If the reanalysis meets the recovery criteria, the first analysis is assumed to have been outside of limits due to a laboratory error and the second analysis is reported.

8. Data analysis

   a. Sample chromatograms are analyzed both qualitatively and quantitatively. First a determination of the identity of a sample peak as a compound on the priority pollutant list (Table I) is made through the use of computerized analysis. Guidelines for the qualitative determination are as follows:

      (1) The relative retention time (RRT) of the sample peak is within 0.06 of the RRT of the most recent check standard.

      (2) Each ion with a relative intensity of greater than 10% of the base ion of the mass spectra of the sample must be present in the sample spectrum produced on the same mass spectrometer.

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(3) The relative intensities of the ions in the sample mass spectrum must be within 20% of the intensities of the standard mass spectrum.

(4) Peaks greater than 10% relative intensity in the sample mass spectrum but not present in the standard mass spectrum from the same mass spectrometer must be accounted for by the analyst.

(5) If a compound fails any of the criteria listed above but in the judgment of the mass spectral interpretation specialist is a correct identification, the identification is used and the quantitation of the peak is performed.

b. Quantitation of identified priority pollutant compounds is performed using the equations listed in the Calculation section of this procedure. All calculations should report concentrations in values of µg/L. Any analyte with a calculated concentration above the highest standard must be reanalyzed at a dilution which will bring the concentration in solution within the calibration curve. It is desirable to have the dilution within the top half of the calibration curve but not required.

Calculation:

$$Concentration\ (\mu g/L) = \frac{(Ax)\ (Is)}{(Ais)\ (RRF)\ (Vo)}$$

Where:

Ax = Area of the quantitation ion peak for the compound to be measured

Ais = Area of the quantitation ion peak for the appropriate internal standard

Is = Amount of internal standard added in nanograms

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Vo = Volume of sample purged

RRF = Relative Response Factor from the initial calibration

Quality Assurance:

1. The GC/MS system must be tuned to meet the criteria in Table II following BFB injection. The chromatographic conditions must be the same as those under which the samples will be analyzed except that the rate of temperature ramping may be increased and the initial temperature may be different. The BFB tune must be verified every 12 hours.

2. Internal standard calibration requires analysis of a minimum of five levels of analyte concentration. Response factors for each compound are calculated. The average response factor and the relative standard deviation of the response factors determine the suitability of the average relative response factor for calculation of the analyte concentration.

   a. Five compounds are checked for minimum average response factors. These compounds are SPCCs. The compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum average RRF value for each SPCC compound is 0.30 except for bromoform which is 0.10. If these values cannot be attained there is a problem with the purge-and-trap or the chromatographic system. Corrective action needs to be taken.

   b. Six additional compounds are evaluated on the basis of the percent standard deviation of the RRF values (%RSD). These compounds are known as CCCs. The CCCs are 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride. %RSD values for these compounds on the initial calibration must be

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less than 30%. For continuing calibration to be valid, the percent drift between the standard concentration and the measured concentration for each CCC compound in the 50-μg/L check standard must be within ±20%.

3. Abundances for the three internal standards must be within +100% and -50% of the abundances of the internal standards of the current calibration check standard (50 μg/L). The retention time for each internal standard must be within 30 seconds of the value for the last calibration check. Values outside these limits indicate a change in system performance or a matrix effect. Samples with internal standard abundances outside of limits are to be reanalyzed. If the reanalysis is within limits, the data from the reanalysis is reported. If the reanalysis confirms the first analysis, the sample matrix is interfering and the data from the first analysis should be reported.

4. Surrogate recoveries are calculated for each sample and blank analyzed. Surrogate recovery limits are listed in Table III. If any surrogate is outside of limits, the sample is to be reanalyzed. If surrogates in the reanalysis are within limits, the reanalysis data are reported. If surrogate recoveries are again outside of limits on the reanalysis, the first analysis is reported.

5. The method blank must meet all the above criteria for internal standard recoveries and surrogate recoveries. In addition, the method blank may not contain any target compound above the quantitation limit except that methylene chloride, acetone, toluene, and 2-butanone may be present up to five times the quantitation limit. All method blanks must meet these criteria. Otherwise, the system is considered out of control and corrective action must be taken.

6. The matrix spike and matrix spike duplicate pair are analyzed for each set of 20 field samples. The recoveries and the percent differences of the recoveries for each spiked compound are calculated and compared to the

values in Table IV or from the statistical results of multiple analysis of the spiked samples. The results of the matrix spike/matrix spike duplicate must be within the windows outlined in Table IV. For samples with results outside the statistical windows, analysis of a quality control reference sample is required. The quality control reference sample is a method blank spiked with each of the matrix spiking solutions. The quality control reference sample must yield recoveries for all analytes within the specification of Table IV. If the quality control reference sample fails to meet the criteria, the analysis must stop and the cause of the problem found. If the analysis meets the values in the table, the results are reported.

7. All data is reviewed by a data review specialist prior to release of the data from the analytical laboratory with respect to quality assurance and data interpretation. The data review specialist will returndata to the analyst for correction as necessary. The specialist will also report the results of the review and corrections on a form to be kept with the raw data. Any noncompliant data that cannot be corrected will be referred to the group leader for further action.

Additional Analyses:

The following methods are also performed using USEPA SW-846 Method 8240B: 1508, 1131, 1265, 1266 1384, 3981, 4592, 5121, 5122, 5222, 5243, and 5244. The target compound lists for each of these analyses are listed in Table V through Table XVI, respectively. Any additional compounds should be added to the theoretical standards concentration sheet when performing these analyses. Standards containing additional analytes should be prepared as described in the reagents section of this document. Both secondary stock solutions and matrix spike solutions should be prepared for use in analyzing for additional compounds.

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Prepared by: [illegible] Date: 7/24/95

Approved by: Michele M. McClain Date: 7/28/95

Approved by: Susan B. Shorter Date: 7/31/95

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Table I

Practical Quantitation Limits (PQL) for Volatile Organics*

Volatiles	PQLs Water/ Wastewater (µg/L)
Acrolein	100
Acrylonitrile	50
Benzene	5
Bromodichloromethane	5
Bromoform	5
Bromomethane	5
Carbon tetrachloride	5
Chlorobenzene	5
Chlorodibromomethane	5
Chloroethane	5
2-Chloroethyl vinyl ether	10
Chloroform	5
Chloromethane	5
1,1-Dichloroethane	5
1,2-Dichloroethane	5
1,1-Dichloroethene	5
cis-1,2-Dichloroethene	5
trans-1,2-Dichloroethene	5
1,2-Dichloropropane	5
cis-1,3-Dichloropropene	5
trans-1,3-Dichloropropene	5
Ethylbenzene	5
Methylene chloride	5
1,1,2,2-Tetrachloroethane	5
Tetrachloroethene	5
Toluene	5
1,1,1-Trichloroethane	5
1,1,2-Trichloroethane	5
Trichloroethene	5
Trichlorofluoromethane	5
Vinyl chloride	5
Xylene (total)	5

*Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be

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Table II

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of mass 95
75	30% to 60% of mass 95
95	Base peak, 100% relative abundance
96	5% to 9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5% to 9% of mass 174
176	Greater than 95%, but less than 101% of mass 174
177	5% to 9% of mass 176

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Table III

Surrogate Spike Recovery Limits for Water and Wastewater Samples

Surrogate Compound	Water/Wastewater
4-Bromofluorobenzene	86-115
1,2-Dichloroethane-d4	76-114
Toluene-d8	88-110

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Table IV

Calibration and QC Acceptance Criteria*

Parameter	Range for Q (μ/L)	Range p,p_2 (%)
Acrolein	Not Defined	Not Defined
Acrylonitrile	Not Defined	Not Defined
Benzene	12.8-27.2	37-151
Bromodichloromethane	13.1-26.9	35-155
Bromoform	14.2-25.8	45-169
Bromomethane	2.8-37.2	D-242
Carbon tetrachloride	14.6-25.4	70-140
Chlorobenzene	13.2-26.8	37-160
Chloroethane	7.6-32.4	14-230
2-Chloroethylvinyl ether	D-44.8	D-305
Chloroform	13.5-26.5	51-138
Chloromethane	D-40.8	D-273
Dibromochloromethane	13.5-26.5	53-149
1,1-Dichloroethane	14.5-25.5	59-155
1,2-Dichloroethane	13.6-26.4	49-155
1,1-Dichloroethene	10.1-29.9	D-234
cis-1,2-Dichloroethene	13.9-26.1	54-156
trans-1,2-Dichloroethene	13.9-26.1	54-156
1,2-Dichloropropane	6.8-33.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	D-227
trans-1,3-Dichloropropene	10.0-30.0	17-183
Ethyl benzene	11.8-28.2	37-162
Methylene chloride	12.1-27.9	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	46-157
Tetrachloroethene	14.7-25-3	64-148
Toluene	14.9-25.1	47-150
1,1,1-Trichloroethane	15.0-25.0	52-162
1,1,2-Trichloroethane	14.2-25.8	52-150
Trichloroethene	13.3-26.7	71-157
Trichlorofluoromethane	9.6-30.4	17-181
Vinyl chloride	0.8-39.2	D-251
Xylenes (total)	Not Defined	Not Defined

Q = Concentration measured in QC check sample, in μg/L.
p,p_2 = Percent recovery measured (20 μg/L spike)
*Criteria from 40 CFR Part 136 for Method 624 and were calculated assuming a QC check sample concentration of 20 μg/L.

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Table V

Analysis #1131

Compound	PQL
Dichlorodifluoromethane	5.
3-Chloro-1-propene	5.
2-Butanone	10.
1,2-Dibromoethane	5.
1,1,1,2-Tetrachloroethane	5.
4-Methyl-2-pentanone	10.
1,2,3-Trichloropropane	5.
1,3-Dichlorobenzene	5.
1,2-Dichlorobenzene	5.
1,4-Dichlorobenzene	5.

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Table VI

Analysis #1265

Compound	PQL
Chloromethane	5.
Bromomethane	5.
Vinyl chloride	5.
Dichlorodifluoromethane	5.
Chloroethane	5.
Methyl iodide	5.
Acrolein	100.
Acrylonitrile	50.
Acetonitrile	100.
Methylene chloride	5.
Acetone	20.
Trichlorofluoromethane	5.
Carbon disulfide	5.
Propionitrile	100.
1,1-Dichloroethene	5.
Allyl chloride	5.
1,1-Dichloroethane	5.
cis-1,2-Dichloroethene	5.
trans-1,2-Dichloroethene	5.
Chloroform	5.
1,2-Dichloroethane	5.
Methacrylonitrole	50.
2-Butanone	10.
Dibromoethane	5.
1,1,1-Trichloroethane	5.
1,4-Dioxane	250.

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Table VII

Analysis #1266

Compound	PQL
Carbon tetrachloride	5.
Isobutyl alcohol	250.
Vinyl acetate	10.
Bromodichloromethane	5.
2-Chloro-1,3-butadiene	5.
1,2-Dichloropropane	5.
trans-1,3-Dichloropropene	5.
Trichloroethene	5.
Dibromochloromethane	5.
1,1,2-Trichloroethane	5.
1,2-Dibromoethane	5.
Benzene	5.
cis-1,3-Dichloropropene	5.
Methyl methacrylate	5.
1,1,1,2-Tetrachloroethane	5.
Bromoform	5.
trans-1,4-Dichloro-2-butene	50.
1,2,3-Trichloropropane	5.
2-Hexanone	10.
4-Methyl-2-pentanone	10.
Tetrachloroethane	5.
1,1,2,2-Tetrachloroethane	5.
Toluene	5.
Ethyl methacrylate	5.
Chlorobenzene	5.
Pentachloroethane	5.
Ethylbenzene	5.
1,2-Dibromo-3-chloropropane	5.
Styrene	5.

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Table VIII

Analysis #1358

Compound	PQL
Benzene	5.
1,2-Dibromoethane	5.
1,1-Dichloroethane	5.
1,1-Dichloroethene	5.
1,2-Dichloroethane	5.
cis-1,2-Dichloroethene	5.
trans-1,2-Dichloroethene	5.
Ethylbenzene	5.
Methylene chloride	5.
Tetrachloroethene	5.
Toluene	5.
1,1,1-Trichloroethane	5.
Trichloroethene	5.
Vinyl chloride	5.
Xylene (total)	5.

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Table IX

Analysis #1384

Compound	PQL
Benzene	5.
1,2-Dibromoethane	5.
1,1-Dichloroethane	5.
1,1-Dichloroethene	5.
1,2-Dichloroethane	5.
cis-1,2-Dichloroethene	5.
trans-1,2-Dichloroethene	5.
Ethylbenzene	5.
Methylene chloride	5.
Tetrachloroethene	5.
Toluene	5.
1,1,1-Trichloroethane	5.
Trichloroethene	5.
Trichlorofluoromethane	5.
Vinyl chloride	5.
Xylene (total)	5.

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Table X

Analysis #3981

Compound	PQL
Benzene	5.
Toluene	5.
Ethylbenzene	5.
Xylene (total)	5.

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Table XI

Analysis #4592

Compound	PQL
Chloromethane	5.
Bromomethane	5.
Vinyl chloride	5.
Chloroethane	5.
Methylene chloride	5.
Acetone	20.
Carbon disulfide	5.
1,1-Dichloroethene	5.
1,1-Dichloroethane	5.
cis-1,2-Dichloroethene	5.
trans-1,2-Dichloroethene	5.
Chloroform	5.
1,2-Dichloroethane	5.
2-Butanone	10.
1,1,1-Trichloroethane	5.
Carbon tetrachloride	5.
Vinyl acetate	10.
Bromodichloromethane	5.
1,2-Dichloropropane	5.
cis-1,3-Dichloropropene	5.
Trichloroethene	5.
Dibromochloromethane	5.
1,1,2-Trichloromethane	5.
Benzene	5.
trans-1,3-Dichloropropene	5.
Bromoform	5.
4-Methyl-2-pentanone	10.
2-Hexanone	10.
Tetrachloroethene	5.
1,1,2,2-Tetrachloroethane	5.
Toluene	5.
Chlorobenzene	5.
Ethylbenzene	5.
Styrene	5.

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Table XII

Analysis #5121

Compound	PQL
Chloromethane	5.
Vinyl chloride	5.
Bromomethane	5.
Chloroethane	5.
Trichlorofluoromethane	5.
Ethyl ether	5.
Acrolein	100.
1,1-Dichloroethene	5.
Acetone	20.
Carbon disulfide	5.
Isopropyl alcohol	250.
Acetonitrile	100.
Methylene chloride	5.
t-Butyl alcohol	100.
Acrylonitrile	50.
Hexane	5.
1,1-Dichloroethane	5.
1,2-Dichloroethene (total)	5.
2-Butanone	10.
Tetrahydrofuran	5.
Chloroform	5.
1,1,1-Trichloroethane	5.
Carbon tetrachloride	5.
Benzene	5.
1,2-Dichloroethane	5.
Heptane	5.
Isopropyl acetate	5.
n-Butanol	250.
Trichloroethene	5.
1,2-Dichloropropane	5.
Bromodichloromethane	5.

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Table XIII

Analysis #5122

Compound	PQL
Monochloroacetone	250.
2-Chloroethyl vinyl ether	10.
cis-1,3-Dichloropropene	5.
Toluene	5.
trans-1,3-Dichloropropene	5.
1,1,2-Trichloroethane	5.
Tetrachloroethane	5.
Dibromochloromethane	5.
Chlorobenzene	5.
Ethylbenzene	5.
Xylene (total)	5.
Bromoform	5.
1,1,2,2-Tetrachloroethane	5.

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Table XIV

Analysis #5222

Compound	PQL
Acetone	20.
n-Pentane	10.
Ethyl ether	5.
1,3-Diethylbenzene	5.
1,4-Diethylbenzene	5.
1,2-Diethylbenzene	5.

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Table XV

Analysis #5243

Compound	PQL
2-Butanone	10.
Allyl chloride	5.
2-Chloro-1,3-butadiene	5.
Bromomethane	5.
Chloromethane	5.
Dibromomethane	5.
Methyl iodide	5.
Trichlorofluoromethane	5.
Vinyl chloride	5.
Dichlorodifluoromethane	5.
Chloroethane	5.
Methylene chloride	5.
Acetone	20.
Carbon disulfide	5.
1,1-Dichloroethene	5.
1,1-Dichloroethane	5.
1,2-Dichloroethene (total)	5.
Chloroform	5.
1,2-Dichloroethane	5.
1,1,1-Trichloroethane	5.
Carbon Tetrachloride	5.
Bromodichloromethane	5.
1,2-Dichloropropane	5.
Trichloroethene	5.
Benzene	5.
2-Chloroethyl vinyl ether	10.
Ethyl ether	5.
Freon 113	10.
Ethyl acetate	5.
2-Nitropropane	10.

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Table XVI

Analysis #5244

Compound	PQL
Cyclohexanone	250.
trans-1,4-Dichloro-2-butene	50.
1,2-Dichlorobenzene	5.
trans-1,3-Dichloropropene	5.
Dibromochloromethane	5.
1,1,2-Trichloroethane	5.
1,2-Dibromomethane	5.
cis-1,3-Dichloropropene	5.
1,1,1,2-Tetrachloroethane	5.
Bromoform	5.
1,2,3-Trichloropropane	5.
4-Methyl-2-pentanone	10.
Tetrachloroethene	5.
1,1,2,2-Tetrachloroethane	5.
Toluene	5.
Chlorobenzene	5.
Ethylbenzene	5.
1,2-Dibromo-3-chloropropane	5.
Xylene (total)	5.

Figure 1

Tekmar

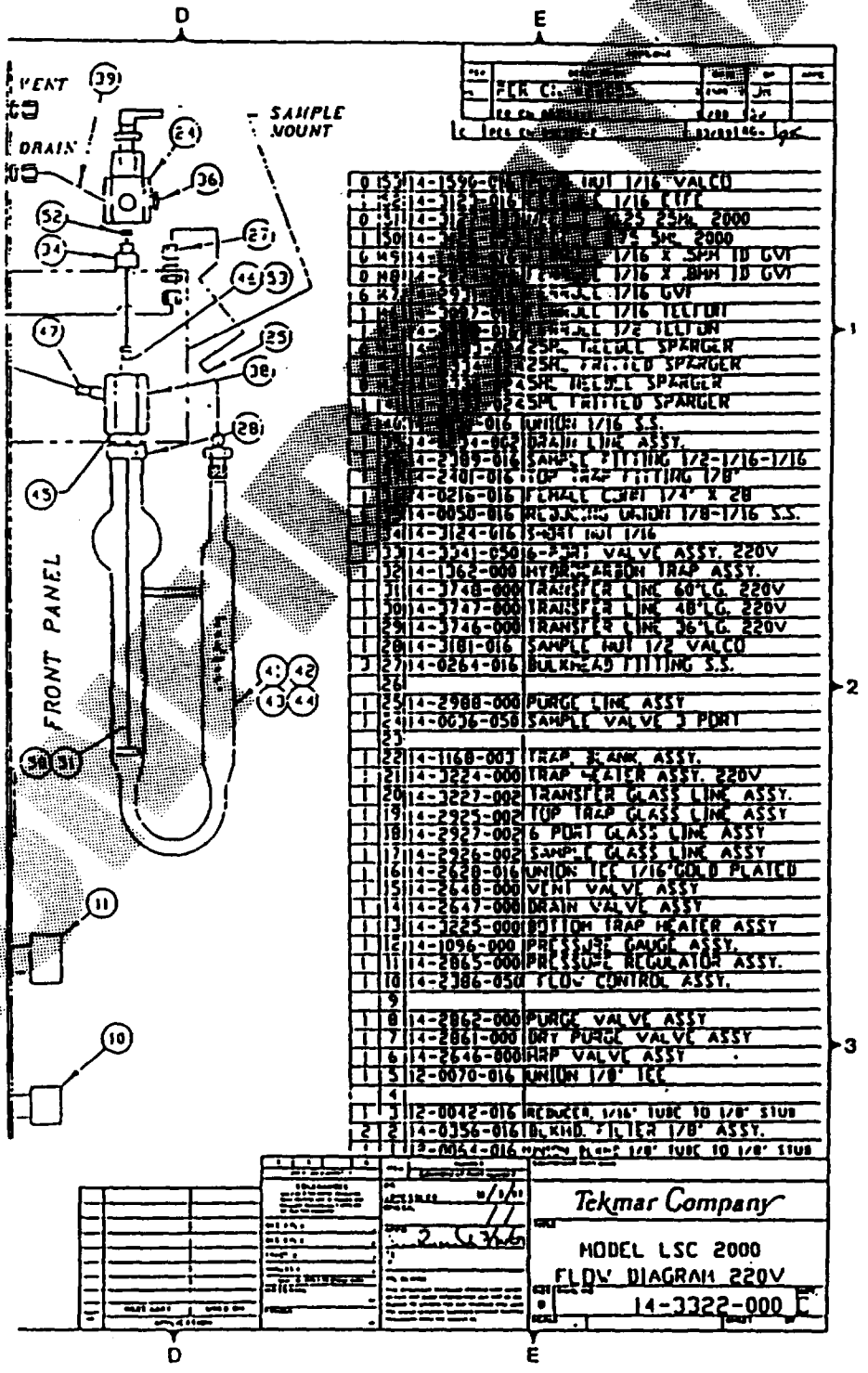

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Figure 2

THEORETICAL STANDARD CONCENTRATIONS
INITIAL CALIBRATION
HP CAPILLARY COLUMN
EPA SW846 METHODS 8240B & APPIX by 8260A (Rev: 07/03/95)

DATE:

INSTRUMENT:

stock mix name	V1	V3	V11	V12		RESTEK GAS MIX Lt#	FLASK ml
	V2	V5					
	V4						
	V6						
	V7						
	V9						
APPIX by 8260A only-->	V10						
	BCM						
300 ppb std	7.5 ul	15 ul	7.5 ul	37.5 ul		37.5 ul	25
100 ppb std	5 ul	10 ul	5 ul	25 ul		25 ul	50
50 ppb std	5 ul	10 ul	5 ul	25 ul		25 ul	100
20 ppb std	2.0 ml of 50 ppb std into 5 ml syringe						
4 ppb std	4 ul	8 ul	16 ul	80 ul		20 ul	200*

*Dilute 1.0 ml of 200 ml flask into 5 ml syringe

compound name	V mix	stock ppm	300 ppb	100 ppb	50 ppb	20 ppb	4 ppb	LOQ ppb
1,1,2-Trichloroethane	V1	1000	300	100	50	20	4	5
1,1-Dichloroethane		1000	300	100	50	20	4	5
1,1-Dichloroethene		1000	300	100	50	20	4	5
1,2-Dichloroethane		1000	300	100	50	20	4	5
1,2-Dichloropropane		1000	300	100	50	20	4	5
Bromodichloromethane		1000	300	100	50	20	4	5
Bromoform		1000	300	100	50	20	4	5
Carbon Tetrachloride		1000	300	100	50	20	4	5
Chlorobenzene		1000	300	100	50	20	4	5
Chloroform		1000	300	100	50	20	4	5
Dibromochloromethane		1000	300	100	50	20	4	5
p-Xylene		1000	300	100	50	20	4	5
Styrene		1000	300	100	50	20	4	5
trans-1,2-Dichloroethene		1000	300	100	50	20	4	5
1,1,1-Trichloroethane	V2	1000	300	100	50	20	4	5
1,1,2,2-Tetrachloroethane		1000	300	100	50	20	4	5
Benzene		1000	300	100	50	20	4	5
cis-1,2-Dichloroethene		1000	300	100	50	20	4	5
cis-1,3-Dichloropropene		1000	300	100	50	20	4	5
Ethylbenzene		1000	300	100	50	20	4	5
m-Xylene		1000	300	100	50	20	4	5
Methylene Chloride		1000	300	100	50	20	4	5
o-Xylene		1000	300	100	50	20	4	5
Tetrachloroethene		1000	300	100	50	20	4	5
Toluene		1000	300	100	50	20	4	5
trans-1,3-Dichloropropene		380	114	38	19	7.6	1.5	5
Trichloroethene		1000	300	100	50	20	4	5
Trichlorofluoromethane		1000	300	100	50	20	4	5

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Figure 2 (Continued)

EPA SW846 METHODS 8240B & APPIX by 8260A (cont'd)

compound name	V MIX	stock ppm	300 ppb	100 ppb	50 ppb	20 ppb	4 ppb	LOQ ppb
2-Chloroethyl Vinyl Ether	V3	1000	600	200	100	40	8	10
Acrolein		5000	3000	1000	500	200	40	100
Acrylonitrile		5000	3000	1000	500	200	40	50
Carbon Disulfide	V4	1000	300	100	50	20	4	5
Vinyl Acetate		1000	300	100	50	20	4	10
Methyl Iodide		1000	300	100	50	20	4	5
Freon 113		2000	600	200	100	40	8	10
2-Butanone	V5	1000	600	200	100	40	8	10
2-Hexanone		1000	600	200	100	40	8	10
4-Methyl-2-Pentanone		1000	600	200	100	40	8	10
Acetone		1000	600	200	100	40	8	20
1,2,3-Trichloropropane	V6	1000	300	100	50	20	4	5
1,2-Dibromoethane (EDB)		1000	300	100	50	20	4	5
1,2-Dichlorobenzene		1000	300	100	50	20	4	5
1,3-Dichlorobenzene		1000	300	100	50	20	4	5
1,4-Dichlorobenzene		1000	300	100	50	20	4	5
Allyl Chloride		1000	300	100	50	20	4	5
Cumene		1000	300	100	50	20	4	5
Methyl t-Butyl Ether		1000	300	100	50	20	4	5
1,1,1,2-Tetrachloroethane	V7	1000	300	100	50	20	4	5
Dibromomethane		1000	300	100	50	20	4	5
Ethyl Methacrylate		1000	300	100	50	20	4	5
Methyl Methacrylate		1000	300	100	50	20	4	5
Pentachloroethane		1000	300	100	50	20	4	5
1,2-Dibromo-3-chloropropane		1000	300	100	50	20	4	5
2-Nitropropane		2000	600	200	100	40	8	10
Cyclohexane	V9	1000	300	100	50	20	4	5
Ethyl Acetate		1000	300	100	50	20	4	5
Ethyl Ether		1000	300	100	50	20	4	5
Isoamyl Acetate		1000	300	100	50	20	4	5
n-Propyl Acetate		1000	300	100	50	20	4	5
Tetrahydrofuran		1000	300	100	50	20	4	5
Benzyl Chloride		1000	300	100	50	20	4	5
Furan		1000	300	100	50	20	4	5
Hexane		1000	300	100	50	20	4	5
Heptane		1000	300	100	50	20	4	5
1,2-Diethylbenzene	V10	1000	300	100	50	20	4	5
1,3-Diethylbenzene		1000	300	100	50	20	4	5
1,4-Diethylbenzene		1000	300	100	50	20	4	5
Methacrylonitrile	V11	2500	750	250	125	50	40	50
t-1,4-Dichloro-2-Butene		2500	750	250	125	50	40	50
t-Butyl Alcohol		5000	1500	500	250	100	80	100
Propionitrile		5000	1500	500	250	100	80	100
2-Propanol		5000	1500	500	250	100	80	100

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Figure 2 (Continued)

EPA SW846 METHODS 8240B & APPIX by 8260A (cont'd)

compound name	V MIX	stock ppm	300 ppb	100 ppb	50 ppb	20 ppb	4 ppb	LOQ ppb
1,4-Dioxane	V12	2500	3750	1250	625	250	200	250
Isobutanol		2500	3750	1250	625	250	200	250
1-Propanol		2500	3750	1250	625	250	200	250
Cyclohexanone		2500	3750	1250	625	250	200	250
n-Butanol		2500	3750	1250	625	250	200	250
Dichlorodifluoromethane	GAS	200	300	100	50	20	4	5
Chloromethane	MIX	200	300	100	50	20	4	5
Vinyl Chloride		200	300	100	50	20	4	5
Bromomethane		200	300	100	50	20	4	5
Chloroethane		200	300	100	50	20	4	5
Bromochloromethane	BCM	1000	300	100	50	20	4	5

ppb of analytical standard = stock ppm x ul stock / flask ml

Calibration Standard Conc. (ppb)	300	100	50	20	4
25 ug/mL Surrogate Spiking Volume (ul)*	# 15	# 5	10	4	0.8

*Spiked directly into 5 ml syringe
#100 ug/mL Surrogate Spiking Solution

ANALYST_____

DATE_____

(saved as file TS824B::DB)

Analyses: 7349,6905,6907,5539

Date acquired: Oct 13, 1996 10:53:31 Dil. Factor: 1
Cycle: 2
Analyst: 421
Raw file: C:\CP\DATA1\17241IAB.02R
Area File: C:\CP\DATA1\17241IAB.02A
Method File: C:\CP\DATA1\17241BB.MET
Instrument: Clewmark #5359--PID
Column Type: J&W DB-VRX 2.5um
Threshold: 0
Run Time: 15 (mins)

Peak table using calibration C:\CP\DATA1\P17241B.CAL(version 2):
Calibration Date: 09/03/96 21:15:04

Ret time (min)	Expected ret time	Peak name	Amount (ug/l)	Peak area	Peak height
5.145	5.150	METHYL T-BUTYL ETHER	15.5377	143090	26937
6.456	6.460	BENZENE	24.4392	142908	53029
6.743	6.740	ISO-OCT/N HEPTANE	88.8655	49153	12520
7.021	7.020	ISTD-TFT	1.0000	178573	68030
8.003	8.000	TOLUENE	73.8869	402363	169300
9.461	9.450	ETHYLBENZENE	26.9227	123640	49337
9.659	9.650	M-, P-XYLENE	110.0655	557361	198675
10.102	10.100	O-XYLENE	55.9041	242245	91549
11.077	11.070	SURR-N-PROPBEN	98.9709	331382	115948
11.945	11.940	1,2,4-TMB	54.5893	239263	97039
		XYLENES (TOTAL)	165.9696		

SURROGATE RECOVERY

Surrogate NPB: 99.0%

Chrom Perfect version 6.07
Report format file: C:\CP\DATA1\BTEXPID.FMT

Internal Standard Calculations from ISTDTRK v. 960910.1443
ISTD-TFT 100.0%

Check standard used in calculating percentage: C:\CP\DATA1\17241IAB.02A

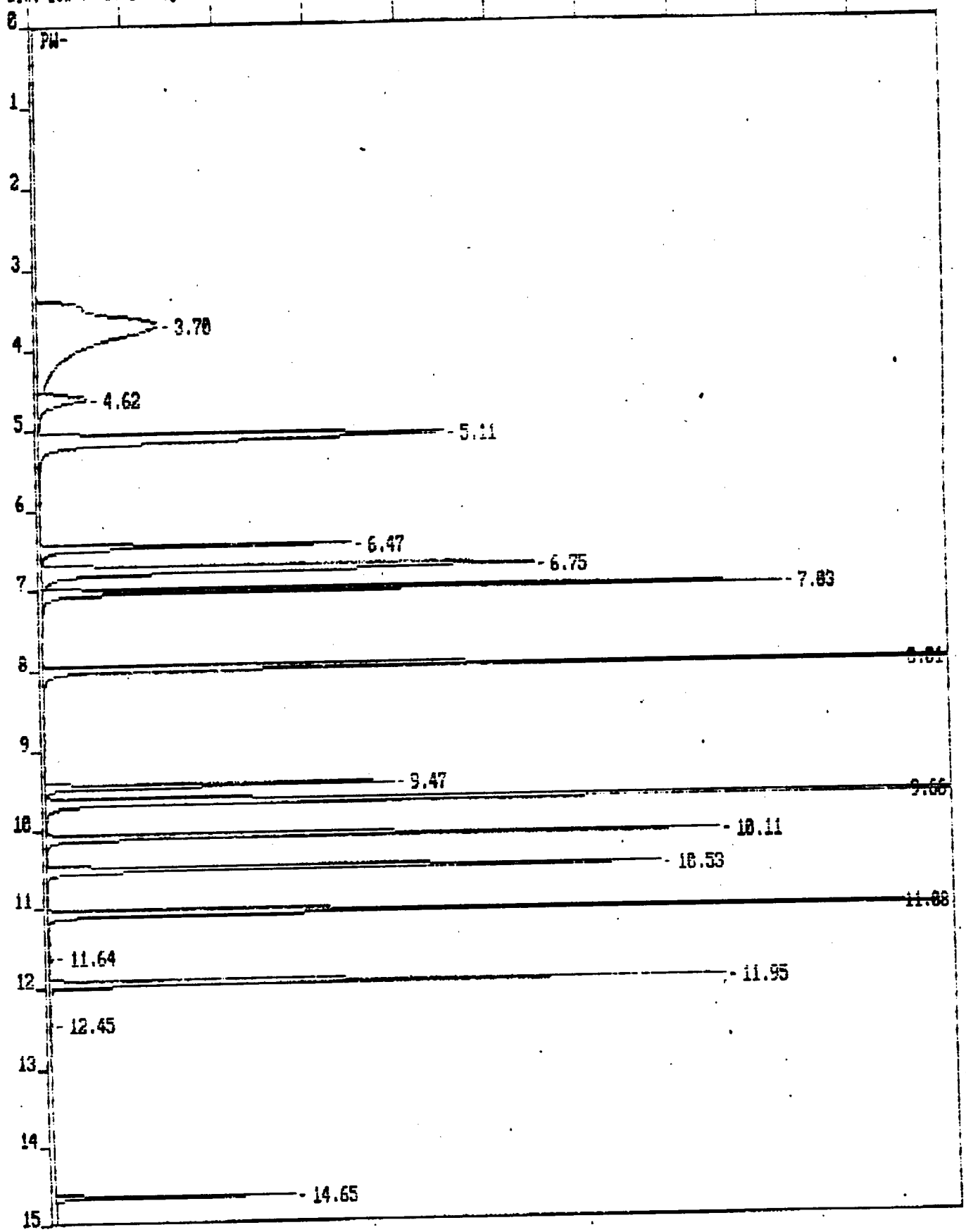
Entered by: DR 421 Date: 10-14-96

Verified by: [illegible] Date: 10-14-96

GRO - FID

Sample Name=CHKSTD 96286B177349,6905,6907,5539

0.0 to 15.0 min. Low Y=-1.724 High Y=98.276 mv Span=100.0



Sample name: CHKSTD 96286817

Analyses: 7349,6905,6907,5539

Date acquired: Oct 13, 1996 19:53:33 Dil. Factor: 1
Cycle: 2
Analyst: 421
Raw file: C:\CP\DATA1\17241IA.02R
Area file: C:\CP\DATA1\17241IA.02A
Method file: C:\CP\DATA1\172418.MET
Instrument: Clewmark #5359--FID
Column Type: J&W DB-VRX 2.5um
Threshold: 4
Run Time: 15 (mins)

Peak table using calibration C:\CP\DATA1\F172418.CAL(version 2):
Calibration Date: 09/03/96 21:15:34

Ret time (min)	Expected ret time	Peak name	Amount (ug/l)	Peak area	Peak height
3.705	0.000		0.0000	369918	13261
4.619	4.661	TBA	245.8753	46775	5404
5.110	5.120	MTBE/2 meth pentane	95.0164	270982	44556
6.471	6.470	BENZENE	22.6382	94691	35083
6.748	6.740	ISO-OCT/N HEPTANE	78.3710	257165	54446
7.020	7.020	SURR-TFT	91.9952	211252	91554
8.008	8.000	TOLUENE	76.8463	291402	124498
9.466	9.460	ETHYLBENZENE	24.9669	96419	38424
9.664	9.660	M-, P-XYLENE	100.1020	385175	138880
10.107	10.100	O-XYLENE	50.4922	195888	74153
10.531	0.000		0.0000	194742	68187
11.082	11.080	SURR-N-PROPBEN	92.8810	278435	97999
11.637	0.000		0.0000	1089	446
11.950	11.950	1,2,4-TMB	50.2039	184068	74257
12.453	0.000		0.0000	626	230
14.654	0.000		0.0000	48606	27622

SURROGATE RECOVERIES

Surrogate TFT: 92.0%
Surrogate NPB: 92.9%

Sample Name: CHKSTD 96286817
Date acquired: Oct 13, 1996 19:53:33
Chrom Perfect version 6.07
Report format file: C:\CP\DATA1\GROFID.FMT

GRO Calculations From GROPCT v. 960918.1007
Amounts and areas of calibration components 2 - 11 were used to calculate the GRO average calibration factor. Surrogate and internal standard components were excluded.

GRO ave. cal. factor: 3,492
Total GRO area: 1,972,321
Total GRO conc. (ppb): 564.855

Analysis #7003
Initiated Date: 08/04/95
Effective Date: DEC 1 1 1995

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Extraction Procedure for the Determination of Diesel Range Organics in Water and Wastewater

Reference:

1. Method 3510, *Separatory Funnel, Liquid/Liquid Extraction*, EPA SW-846.

2. "Method for the Determination of Diesel Range Organics," American Petroleum Institute (EPA Underground Storage Tank Work Group Draft), Revision 4, 08/18/93.

3. Total Petroleum Hydrocarbon Analysis - Diesel Method (modified), California Department of Health Services, LUFT Task Force. Also referred to as the California Modified 8015 Method.

4. Glas-Col 3D Floor Shaker, Model VS5504 and VS550424 User Instructions.

5. N-Evap. Organomation, Model 112 User Instructions.

6. S-Evap. Organomation, Model 120 User Instructions.

Scope:

This procedure is applicable for the extraction of petroleum products from waters and wastewaters. This extraction technique is used as the sample preparation for TPH-DRO (Analysis #5322 or 5553). The analysis method should be consulted for more specific application information.

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Basic Principles:

A measured volume of sample is serially liquid/liquid extracted with methylene chloride in a separatory funnel. Petroleum products present in the sample partition into the extraction solvent. The serial extracts are then combined, dried, and concentrated to 1 mL. The extracts will be analyzed by Gas Chromatography using FID detection (usually by one of the methods listed in the scope).

Apparatus:

1. 2-L separatory funnel
2. Kuderna-Danish - 500 mL, with three-ball Snyder column and 100-mL graduated ampule
3. Chromatographic column - Pyrex 20 mm ID, approximately 400 mm long with 24/40 m inside drip
4. Water or steam bath
5. N-Evap. Organomation, Model 112 or equivalent
6. S-Evap. Organomation, Model 120 or equivalent

Reagent:

1. Methylene chloride - Pesticide quality or equivalent (Optima Grade)
2. Acetone - Pesticide quality or equivalent
3. Carbon disulfide - Glass distilled, HPLC/spectral grade
4. Sodium sulfate - Reagent grade prepared by baking at 400°C for 4 hours prior to use, to remove organic contaminants
5. Nitrogen - Ultra pure carrier grade or equivalent

6. Surrogate standards:

   Chlorobenzene - Standards Grade Chem. Service or equivalent

   o-Terphenyl - 99% Aldrich Chem. Co. or equivalent

   Spiking concentration of surrogate standards:

7. For stock solution - Accurately weigh (to 0.1 mg) 0.5 g *o*-terphenyl and 0.5 g chlorobenzene into a 200-mL volumetric containing several mL of acetone. Bring the flask to volume with acetone. This stock solution is stored in a freezer and is stable for 6 months.

8. For working solution of the surrogate standards make a DF 50 of the above stock in acetone. This solution is stored in a freezer and is stable for 6 months.

9. Spiking solution - For working solution of the spike, make a DF 50 of the stock (see Reagents section of Analysis #4828 and Analysis #4834) in acetone. Unless otherwise instructed, use 1.0 mL of this spiking solution in each sample. This solution is stored in a freezer and is stable for 6 months.

Preparation of Glassware:

All glassware is soaked in dilute Chem-Solv for at least 4 hours, rinsed several times with tap water and rinsed several times with deionized water. Kuderna-Danish glassware is oven dried at 115°C.

Sample Collection:

Samples should be collected in two 1-L glass containers with no headspace and kept cool (4°C) until extraction is performed. Holding time until extraction is 14 days. Samples are acidified to pH <2 with HCl upon receipt at the lab.

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Safety Precautions:

All concentration steps should be carried out in a hood. Direct exposure of skin and respiratory tract to methylene chloride, carbon disulfide, or acetone should be avoided. Many sample materials to be analyzed by this method are "unknowns" and may contain toxic materials. Use good laboratory practice for handling of unknowns.

Extraction Procedure:

NOTE: This procedure assumes that two 1-L bottles of sample are available for analysis and that the sample is one aqueous phase. Consult your supervisor if other conditions exist.

1. Mark the liquid level on the 1-L sample bottle to be used for extraction. If the bottle contains liquid into the neck write *Full* on the bottle instead of marking the level. Transfer the sample to a 2-L separatory funnel.

   Spiking solution, as specified by the analytical method, is added to the separatory funnel at this time. (See Reagent #9.) Use 1.0 mL of the spiking solution unless otherwise instructed.

   Surrogate: Add 1.0 mL of the surrogate working solution at this time. (See Reagent #8.)

   NOTE: While transferring the sample, please record visual and olfactory observations relating to its petroleum/organic content (such as strong gasoline smell, weak oil smell, dark oily film on container walls, solvent-like odor, etc.).

2. Add 100 mL of methylene chloride to the sample bottle and rinse the inner surface by swirling. Then transfer the methylene chloride to the separatory funnel. Retain the sample bottle and at some time during the extraction, fill the bottle with water to the marked level and determine this volume by transfers to a 1-L graduated cylinder. Record this volume.

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3. Hand shake the sample 15 seconds, venting frequently to relieve the excess pressure.

4. Place the separatory funnel on the automatic shaker and shake for 30 seconds at a setting of 65 with the stopcocks open.

5. Close the stopcocks and shake for 1.5 minutes at a setting of 80.

6. Remove the funnels from the shaker and place them on the funnel rack. Allow the layers to separate completely. If an emulsion greater than ⅓ of the solvent volume forms, it must be broken using stirring, filtration, or centrifugation. Consult your supervisor if you are unsure of how to proceed.

7. Rinse the sodium sulfate column with 20 to 30 mL of methylene chloride. Then remove the column, add a glass boiling bead, attach a three-ball Snyder column and wet the column with solvent.

8. Place each K-D apparatus on a steam bath and concentrate the solvent to ~2 mL volume. Do not allow the K-D to go dry. Allow the apparatus to cool for at least 10 minutes. Approximately 1 to 2 mL will condense into the ampule during this time. Remove the Snyder column and flask, rinsing the joints with a small amount of methylene chloride.

9. If high levels of petroleum are not expected, place the ampule on an N-Evap. The bath should be set at 35°C; the supply pressure should be set at 5 psi. N-Evap tips should be 3 to 5 mm from the liquid surface. Adjust tip pressure so the sample does not splatter. With the ampule submerged in water, concentrate the extract to 1 mL. Remove the ampule. If the final volume of the extract is less than 1 mL, it should be adjusted to 1 mL in the ampule using $MeCl_2$.

10. Transfer the entire contents of the ampule to a 2-mL GC vial marked with the appropriate sample number. Put the GC vials in a vial file and place in the GC instrument room.

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11. If high levels of petroleum are expected (based on color), quantitatively transfer the entire contents of the ampule to a 5.0-mL volumetric flask marked with the appropriate sample number and bring to volume with methylene chloride. Mix well and transfer a portion of the solution to a GC vial marked with the appropriate sample number. Transfer the rest of the solution to a 12-mL glass vial also marked with the appropriate sample number. The vial cap used should have a Teflon liner. Store the 12-mL vial in the freezer dated with the prep date and put the GC vials in a vial file and place in the GC instrument room.

    NOTE: If high levels of petroleum are expected, based on preliminary observations, dilutions should also be prepared, bottled, and documented.

12. Also transfer approximately 1 to 2 mL of the working surrogate solution into a labeled GC vial so that it can be run with the batch of samples.

Calculations:

See analysis method.

Statistical Information:

See analysis method.

Quality Assurance:

For each set of samples, a blank must be extracted. Surrogates are monitored in each extract against acceptance criteria in the analytical method. Ideally a matrix spike and matrix spike duplicate sample is prepared for every batch of 20 samples or less along with a lab control sample (deionized water treated as a matrix spike). Duplicate lab control samples can be substituted because insufficient sample is routinely submitted.

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Prepared by: Melissa McDermott Date: 11/1/95

Approved by: Terry Schmidt Date: 11/29/95

Approved by: 972 Date: 12/11/95

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Procedural Amendment #1

Number: Analysis #7003

Title: Extraction Procedure for the Determination of Diesel Range Organics in Water and Wastewater

Effective Date (listed on procedure): 12/11/95

Section(s) affected by change: Extraction Procedure

Reason for addition(s) or change(s): Procedural step omitted in re-write

Change will be effective from (date): 12/27/95

Samples or project affected: All

List change(s) or addition(s) (specify which section):

Extraction Procedure:

Add to #6.

6. Transfer the solvent layer (bottom phase) through a column containing about 100 mm of sodium sulfate into a 500-mL Kuderna-Danish flask fitted with a graduated jacketed ampule. Be sure the ampule is labeled with the sample number using a black marking pen.

   Add a second 100 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure above. Perform a third extraction in the same manner.

7003.W60
122895

Prepared by: _____ Date: 12/28/95

Approved by: _____ Date: 12/28/95

Approved by: _____ 972 Date: 12/28/95

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Procedural Amendment #2

Number: Analysis #7003

Title: Extraction Procedure for the Determination of Diesel Range Organics in Water and Wastewater

Effective Date (listed on procedure): 12/11/95

Section(s) affected by change: Extraction Procedure

Reason for addition(s) or change(s): Authorized use of less reagent for extraction

Change will be effective from (date): 06/27/96

Samples or project affected: All

List change(s) or addition(s) (specify which section):

Extraction Procedure:

2. *Make the following change*

   Change 100 mL of methylene chloride to 60 mL

6. *Make the following change to the second paragraph added in Procedural Amendment #1*

   Change 100 mL volume of methylene chloride to 60 mL

7003.W60
071696

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Prepared by: _____ Date: 8-5-96

Approved by: _____ Date: 8/5/96

Approved by: _____ 972 Date: 8/9/96

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Analysis #7004
Initiated Date: 08/03/95
Effective Date: AUG 08 1995

Extraction Procedure for the Determination of Diesel Range Organics in Soil or Solid Waste Matrices

Reference:

1. Method 3550, *Sonication Extraction*, EPA SW-846.

2. *Sonicator Ultrasonic Processor and Cell Disrupter Operations Manual,* Sound Heat Systems, Inc., 1985.

3. *Method for the Determination of Diesel Range Organics*, American Petroleum Institute (EPA Underground Storage Tank Work Group Draft), Revision 5, 2/5/92.

4. *Total Petroleum Hydrocarbon Analysis - Diesel Method* (modified), California Department of Health Services, LUFT Task Force. Also referred to as the California Modified 8015 Method.

Scope:

This procedure is applicable for extraction of petroleum products from soils or solid wastes for TPH-DRO (Analysis #5321 or #5547). The analysis method should be consulted for more specific information.

Basic Principles:

A measured weight of soil or solid waste sample is blended with anhydrous sodium sulfate. This mixture is then serially extracted with methylene chloride using a sonic probe disrupter. The serial extracts are combined, dried, and concentrated to

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approximately 1 mL, which is brought to a final volume of 5 mL. The extracts are analyzed by gas chromatography using FID detection (by one of the methods listed in the Scope section).

Apparatus:

1. Sonic probe apparatus, Heat Systems-Ultrasonics, Inc. Model W-385, or equivalent

2. Kuderna-Danish - 500 mL, with three-ball Snyder column and 10-mL graduated ampule

3. Chromatographic column - Pyrex 20-mm ID, approximately 400 mm long with a plain stem

4. Water or steam bath

5. 11-cm diameter Buchner funnels

6. 11-cm Whatman 3 filter paper

7. 500-mL filter flasks

Reagents:

1. Methylene chloride - Pesticide quality or equivalent (Optima Grade)

2. Acetone - Pesticide quality or equivalent

3. Carbon disulfide - Glass distilled, HPLC/spectral grade

4. Sodium sulfate - Reagent grade prepared by baking at 400°C for 4 hours prior to use, to remove organic contaminants

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5. Surrogate standards - Chlorobenzene, standards grade - Chem. Service, *o*-Terphenyl, 99% - Aldrich Chem. Co. or equivalent

6. Spiking concentration of surrogate standards -

   For stock solution, accurately weigh (to 0.1 mg) 0.5 g *o*-Terphenyl and 0.5 g chlorobenzene into a 200-mL volumetric containing several mL of acetone. Bring the flask to volume with acetone. This stock solution is stored in a freezer and is stable for 6 months.

   For a working solution of the surrogate standards, make a DF 10 of the above stock in acetone. This solution is stored in a freezer and is stable for 6 months.

7. Spiking solution - See Reagents section of Analysis #4835 and #4703 for the preparation of the spiking solution. Unless otherwise instructed, use 1.0 mL of this spiking solution in each sample.

Preparation of Glassware:

All glassware is soaked in dilute Chem-Solv for at least 4 hours, rinsed several times with tap water, then rinsed several times with deionized water. Kuderna-Danish glassware is oven dried at 115°C.

Sample Collection:

Samples should be collected in 8-oz glass containers with minimal headspace and kept cool (4°C) until extraction is performed. Holding time until extraction is 14 days. The analysis should be performed within 40 days from extraction.

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Safety Precautions:

All concentration steps should be carried out in a hood. Direct exposure of skin and respiratory tract to methylene chloride, carbon disulfide, or acetone should be avoided. Many sample materials to be analyzed by this method are "unknowns" and may contain toxic materials. Use good laboratory practice for handling of unknowns.

Extraction Procedures:

1. Soils and solid wastes are not homogenized before being subsampled for extraction.

2. Weigh 60 g of the solid into a 250-mL beaker. An attempt should be made to get a representative sampling of the contents of the sample container.

   NOTE: While weighing the sample please record visual and olfactory observations relating to its petroleum/organic content (such as strong gasoline smell, weak oil smell, dark oil material present, solvent-like odor, etc.).

3. Add 60.0 g of sodium sulfate to the beaker and stir thoroughly using a clean glass stirring rod. Record the Lancaster Laboratories number, the initial weight, and any comments about the sample in the extraction log. Spiking solution as specified by the analytical method is added to the sample at this time (See Reagent #7). Add 1.0 mL of the surrogate working solution.

4. Add 100 mL of methylene chloride to the beaker.

5. Set up the sonic probe as described in the manual.

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6. Immerse the tip of the sonic probe approximately 1 to 2 cm below the surface of the liquid in the beaker containing the sample.

7. Disrupt the sample.

   a. If using the medium tip, turn to full output (10) for 3 minutes.

   b. If using the large tip, turn to (6) for 3 minutes.

8. Remove the probe from the sample.

9. Decant the liquid from the beaker into a filter funnel setup consisting of a Buchner funnel containing Whatman 3 filter paper. The funnel is connected to a 500-mL filter flask with a 4- to 6-psi vacuum.

   NOTE: Be sure to turn the vacuum off immediately after solvent is no longer observed dripping from the funnel.

10. Repeat steps 4 through 9 using the same beaker, filter paper and Buchner funnel for each sample. Perform a third extraction in the same manner.

11. Before placing the probe into a new sample, rinse with both deionized water and acetone and wipe with a paper towel to remove any soil present from the previous sample.

12. Rinse the filter paper with 10 mL of methylene chloride.

13. Pour collected extracts into a Kuderna-Danish, add a glass boiling bead to the K-D, attach a 3-ball Snyder column and wet the column with methylene chloride.

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14. Place each K-D apparatus on a steam bath and concentrate the solvent to about 1-mL volume. Allow the apparatus to cool for at least 10 minutes. Approximately 1 or 2 mL will condense into the ampule during this time. Remove the Snyder column and flask, rinsing the joints with a small amount of methylene chloride.

15. Quantitatively transfer the entire contents of the ampule to a 5.0-mL volumetric flask marked with the appropriate sample identification. Mix well and transfer a portion of the solution to a GC vial marked with the appropriate sample number. Transfer the rest of the solution to a 12-mL glass vial also marked with the appropriate sample number. The vial cap used should have a Teflon liner. Store the 12-mL vial in the freezer—dated with the prep date, and put the GC vials in a vial file and store them in the GC Instrument Room.

    NOTE: If high levels of petroleum are expected based on preliminary observations, dilutions should also be prepared, bottled, and documented.

16. Prepare a DF 5 of the surrogate working solution with $MeCl_2$. Bottle a portion in a labeled GC vial so that it can be run with the batch of samples. Store the remainder of the solution in a 12-mL vial that has been appropriately labeled with the rest of the vials in the freezer.

Calculations:

See analysis method.

Statistical Information:

See analysis method.

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Quality Assurance:

A blank, a laboratory control sample (LCS), a laboratory control sample duplicate (LCSD), and a matrix spike must be extracted for every batch of 20 samples or less. If a batch is continued from one day to another, a blank must be extracted each day. Surrogates are monitored in each extract against acceptable criteria in the analytical method.

7004.W60
080305

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Prepared by: _____ Date: 8/7/95

Approved by: _____ Date: 8/7/95

~~Approved by:~~ _____ 972 Date: 8/7/95

ATTACHMENT 1
SANBORN FIRE INSURANCE MAPS

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Procedural Amendment #1

Number: Analysis #4833

Title: Extraction Procedure for the Determination of GC Fingerprints on Petroleum Products in Soil or Solid Waste Matrices

Effective Date (listed on procedure): March 1, 1994

Section(s) affected by change: Quality Assurance

Reason for addition(s) or change(s): Change in quality control requirements.

Change will be effective from (date): April 19, 1995

Samples or project affected: All

List change(s) or addition(s) (specify which section):

Quality Assurance:

A blank, a laboratory control sample (LCS), a laboratory control sample duplicate (LCSD), and a matrix spike must be extracted for every batch of 20 samples or less. If a batch is continued from one day to another, a blank must be extracted each day. Surrogates are monitored in each extract against acceptable criteria in the analytical method.

4833.W60
042795

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Prepared by: _____ Date: 5/1/95

Approved by: _____ Date: 5/1/95

Approved by: _____ Date: 5/1/95

Analysis #2376
Initiated Date: 01/14/93
Effective Date: APR 08 1994

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Extraction Procedure for the Determination of GC Fingerprint on Petroleum Products in Water and Wastewater

References:

EPA SW-846, Method 3510, Separatory Funnel, Liquid/Liquid Extraction.

Scope:

This procedure is applicable for petroleum products extraction from waters and wastewaters. This extraction technique is typically used as the sample preparation for TPH by GC/FID (Analysis #4828, 5260, or 5302), Petroleum Fules by GC/FID (Analysis #4834 or 5301), TPH by GC/FID-DRO (Analysis #5322 or 5553), or Qualitative GC Fingerprint (Analysis #2012). The analysis method should be consulted for more specific application information. Many "nonpetroleum" organics are also extracted by this procedure and may interfere with petroleum product characterization and/or quantitation.

Basic Principles:

A measured volume of sample is serially liquid/liquid extracted with methylene chloride in a separatory funnel. Petroleum products present in the sample partition into the extraction solvent. The serial extracts are then combined, dried, and concentrated to 5 ml. The extracts will be analyzed by Gas Chromatography using FID detection (usually by one of the methods listed in the scope).

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Apparatus:

1. 2 liter separatory funnel

2. Kuderna-Danish - 500 ml, with three-ball Snyder column and 10 ml graduated ampule

3. Chromatographic column - Pyrex 20 mm ID, approximately 400 mm long with 24/40 m inside drip

4. Water or steam bath

Reagents:

1. Methylene Chloride - Pesticide quality or equivalent (Optima Grade)

2. Acetone - Pesticide quality or equivalent

3. Carbon Disulfide - Glass distilled, HPLC/spectral grade

4. Sodium Sulfate - Reagent grade prepared by baking at 400°C for 4 hours prior to use, to remove organic contaminants

5. Surrogate Standards:

   Chlorobenzene - Standards Grade Chem. Service or equivalent

   o-Terphenyl - 99% Aldrich Chem. Co. or equivalent

6. Spiking Concentrations of Surrogate Standards:

   For stock solution - Accurately weigh (to 0.1 mg) 0.8 g o-terphenyl and 0.5 g chlorobenzene into a 200 ml volumetric containing several ml of acetone. Bring the flask to volume with acetone. This stock solution is stored in a freezer and is stable for six months.

   For working solution of the surrogate standards make a DF 10 of the above stock in acetone. This solution is stored in a freezer and is stable for six months.

7. Spiking Solution - See Reagents section of Methods #4828 and 4834 for the preparation of the spiking solution. Unless otherwise instructed, use 1.0 ml of this spiking solution in each sample.

Preparation of Glassware:

All glassware is soaked in dilute "Chem-solv" for at least four hours, rinsed several times with tap water and rinsed several times with deionized water. Kuderna-Danish glassware is oven dried at 115°C.

Sample Collection:

Samples should be collected in two 1 liter glass containers with no headspace and kept cool (4°C) until extraction is performed. Holding time until extraction is 14 days. Samples are acidified to pH <2 with HCl upon receipt at the lab.

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Safety Precautions:

All concentration steps should be carried out in a hood. Direct exposure of skin and respiratory tract to methylene chloride, carbon disulfide, or acetone should be avoided. Many sample materials to be analyzed by this method are "unknowns" and may contain toxic materials. Use good laboratory practice for handling of unknowns.

Extraction Procedure:

NOTE: This procedure assumes that two 1 liter bottles of sample are available for analysis and that the sample is one aqueous phase. Consult you supervisor if other conditions exist.

1. Mark the liquid level on the 1 liter sample bottle to be used for extraction. If the bottle contains liquid into the neck write "full" on the bottle instead of marking the level. Transfer the sample to a 2 liter separatory funnel.

   Spiking solution, as specified by the analytical method, is added to the separatory funnel at this time. (See Reagent #9.) Use 1.0 ml of the spiking solution unless otherwise instructed.

   Surrogate: Add 1.0 ml of the surrogate working solution at this time. (See Reagent #8.)

   NOTE: While transferring the sample, please record visual and olfactory observations relating to its petroleum/organic content (such as strong gasoline smell, weak oil smell, dark oily film on container walls, solvent-like odor, etc.).

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2. Add 100 ml of methylene chloride to the sample bottle and rinse the inner surface by swirling. Then transfer the methylene chloride to the separatory funnel. Retain the sample bottle and at some time during the extraction fill the bottle with water to the marked level and determine this volume by transfers to a 1 liter graduated cylinder. Record this volume.

3. Extract the sample by shaking for two minutes with frequent venting to release excess pressure.

   NOTE: Do not use an automatic shaker for this analysis preparation.

4. Allow the layers to separate for at least 10 minutes. If an emulsion forms that is greater than one third of the solvent volume, it must be broken using stirring, filtration, or centrifugation. Consult your supervisor if you are unsure of how to proceed.

5. Transfer the solvent layer (bottom phase) through a column containing about 100 mm sodium sulfate into a 500 ml Kuderna-Danish flask fitted with a graduated ampule. Be sure the ampule is labeled with the sample number using a black marking pen.

6. Add a second 100 ml volume of methylene chloride to the separatory funnel and repeat the extraction procedure in Steps 3 through 5 above. Perform a third extraction in the same manner.

7. Rinse the sodium sulfate column with 20 to 30 ml of methylene chloride. Then remove the column, add a glass boiling bead, attach a three-ball Snyder column and wet the column with solvent.

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8. Place each K-D apparatus on a steam bath and concentrate the solvent to ~1 ml volume. Do not allow the K-D to go dry. Allow the apparatus to cool for at least ten minutes. Approximately 1 to 2 ml will condense into the ampule during this time. Remove the Snyder column and flask, rinsing the joints with a small amount of methylene chloride.

9. Quantitatively transfer the entire contents of the ampule to a 5.0 ml volumetric flask marked with the appropriate sample number and bring to volume with methylene chloride. Mix well and transfer a portion of the solution to a GC vial marked with the appropriate sample number. Transfer the rest of the solution to a 12 ml glass vial also marked with the appropriate sample number. The vial cap used should have a Teflon liner. Store the 12 ml vial in the freezer dated with the prep date and put the GC vials in a vial file and place in the GC instrument room.

   NOTE: If high levels of petroleum are expected, based on preliminary observations, dilutions should also be prepared, bottled, and documented.

10. Also prepare a DF 5 of the surrogate working solution with $MeCl_2$. Bottle some in two labeled GC vials so that they can be run with the batch of samples. Store the remainder of the solution in a 12 ml vial that has been appropriately labeled with the rest of the vials in the freezer.

Calculations:

See analysis method.

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Statistical Information:

See analysis method.

Quality Assurance:

For each set of samples, a blank must be extracted. Surrogates are monitored in each extract against acceptance criteria in the analytical method. Ideally a matrix spike and matrix spike duplicate sample is prepared for every batch of 20 samples or less along with a lab control sample (deionized water treated as a matrix spike). Duplicate lab control samples can be substituted because insufficient sample is routinely submitted.

2376.W60
022494

CONFIDENTIAL

Prepared by: Terry Schrock Date: 3/16/94

Approved by: [signature] Date: ~~4/17/94~~ 4/8/94 3 2 4/8/94

Approved by: Linda L. Saad Date: 4-8-94

lity Assurance:

For each set of samples, a blank and a laboratory control sample (LCS) must be extracted. A matrix spike and matrix spike duplicate must be extracted for every batch of 20 samples or less. Surrogates are monitored in each extract against acceptance criteria in the analytical method.

4833.W60
022194

CONFIDENTIAL

Prepared by: _____ Date: 2/28/94

Approved by: _____ Date: 2/28/94

Approved by: Linda L Saad Date: 2-28-94

GRO-PID

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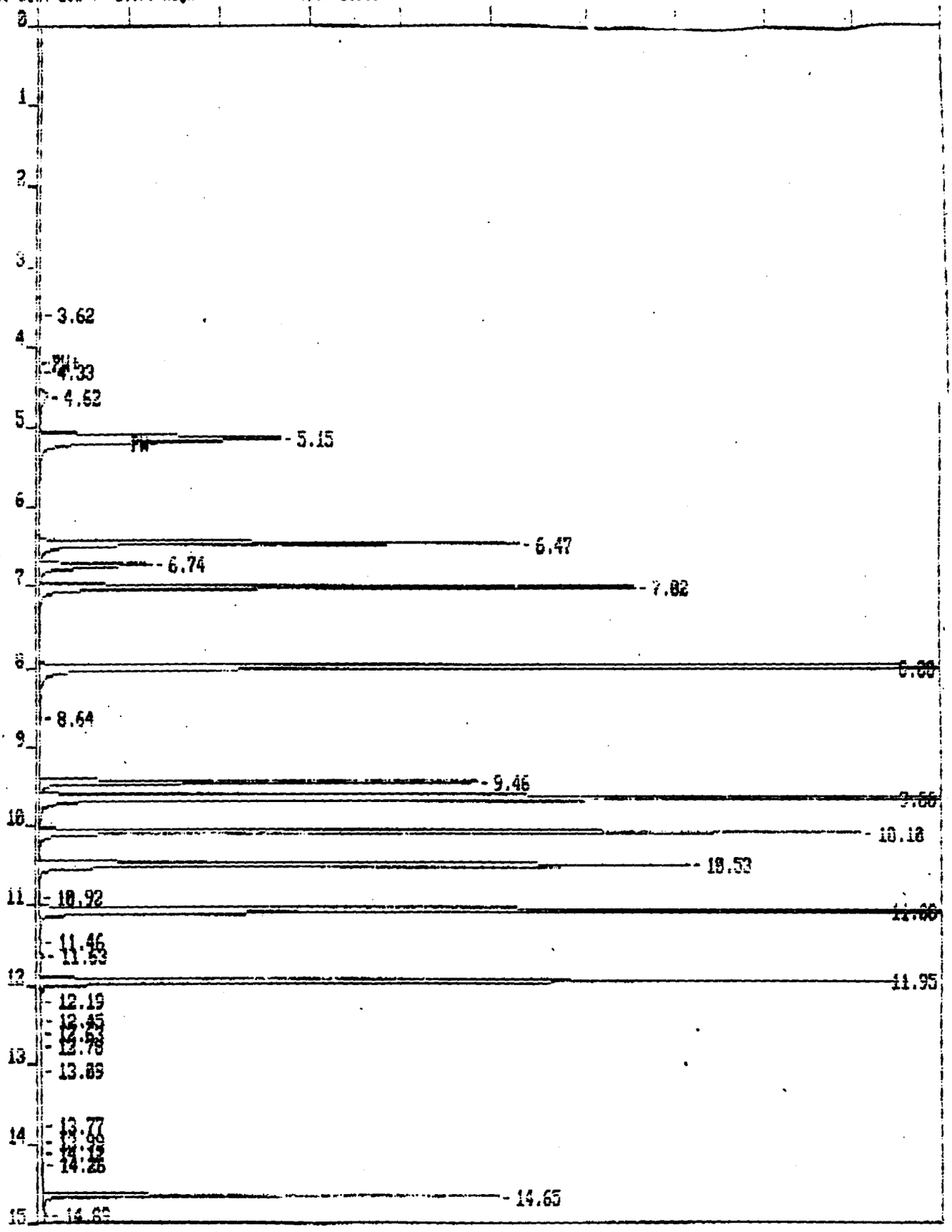

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Procedural Amendment #1

Number: Analysis #2376

Title: Extraction Procedure for the Determination of GC Fingerprint on Petroleum Products in Water and Wastewater

Effective Date (listed on procedure): 04/08/94

Section(s) affected by change: Extraction Procedure

Reason for addition(s) or change(s): Authorized use of less reagent for extraction

Change will be effective from (date): 06/27/96

Samples or project affected: All

List change(s) or addition(s) (specify which section):

Extraction Procedure:

2. *Make the following change*

   Change 100 mL of methylene chloride to 60 mL

6. *Make the following change*

   Change 100 mL volume of methylene chloride to 60 mL

2376.W60
071696

CONFIDENTIAL

Prepared by: _____ Date: 8-5-96

Approved by: _____ Date: 8/8/96

Approved by: _____ 972 Date: 8/9/96

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Analysis #5321, 5322
Initiated Date: 09/23/93
Effective Date: APR 0 2 1996

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TPH-DRO API
(Diesel Range Organics)

Reference:

"Method for Determination of Diesel Range Organics," American Petroleum Institute (EPA Underground Storage Tank Work Group Draft), Revision 4, August 8, 1993.

Related Reference:

1. Total Petroleum Hydrocarbons Analysis – Diesel Method (modified), California Department of Health Services, LUFT Task Force. Also referred to as the California Modified 8015 Method.

2. Method 8015B, EPA SW-846.

Scope:

This method is designed to quantitate mid-range petroleum products in water and soil. This corresponds to a range of C10 normal hydrocarbons through C28 normal hydrocarbons. Distillate fractions less than C10 normal hydrocarbons or greater than C28 normal hydrocarbons (detectable under conditions of this method) will not be reported. Samples are extracted by Analysis #7004 (soils), "Extraction Procedure for the Determination of Diesel Range Organics in Soil or Solid Waste Matrices" and #7003 (waters), "Extraction Procedure for the Determination of Diesel Range Organics in Water and Wastewater." Diesel range organics are reported to a limit of 7 mg/kg or 0.1 mg/L on an "as-received" basis.

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Basic Principles:

Sample extracts in methylene chloride are analyzed by capillary gas chromatography using flame ionization detection. Quantitation is performed by comparing the area of all chromatographic peaks (including resolved and unresolved components) eluting between C10 (*n*-decane) and C28 (*n*-octacosane) with the total area of the ten components in the diesel component standard.

Apparatus:

1. Hewlett-Packard HP 5890 Gas Chromatograph, or equivalent, capable of performing automated direct injection capillary chromatography with temperature programming and flame ionization detection

2. Primary column - 30 meters x 0.53 mm ID fused silica capillary lined with a 1.5-μm film of RTX-5 (or equivalent)

Reagents:

1. Methylene chloride - Pesticide quality or equivalent; store at room temperature

2. Acetone - Pesticide quality or equivalent; store at room temperature

3. Normal hydrocarbon standards C10 through C28 as follows:

   a. *n*-Decane - 99% (Sigma Chemical) or equivalent

   b. *n*-Dodecane - 99% (Sigma Chemical) or equivalent

   c. *n*-Tetradecane - 99% (Sigma Chemical) or equivalent

   d. *n*-Hexadecane - 99% (Sigma Chemical) or equivalent

   e. *n*-Octadecane - 99% (Sigma Chemical) or equivalent

f. *n*-Eicosane - 99% (Sigma Chemical) or equivalent

g. *n*-Docosane - 99% (Sigma Chemical) or equivalent

h. *n*-Tetracosane - 99% (Sigma Chemical) or equivalent

i. *n*-Hexacosane - 99% (Sigma Chemical) or equivalent

j. *n*-Octacosane - 99% (Sigma Chemical) or equivalent

NOTE: Store all of the above at room temperature.

4. Stock diesel component standard (Approximately 5000 ppm total hydrocarbon) - Add approximately 0.05 g (to 1.0 mg) of each neat hydrocarbon standard to a 100-mL volumetric flask. The liquid neats may be added dropwise using capillary pipettes. Dilute to volume with $MeCl_2$. Stable 6 months. Store in freezer.

5. Working diesel component standard (Approximately 100 ppm total hydrocarbon) - Pipette 1 mL of the stock diesel component standard into a 50-mL volumetric flask and dilute to volume with $MeCl_2$. Stable 3 months. Store in freezer.

6. Working linearity check standards - Use the following dilutions as a guideline using the stock diesel component standard:

Approx. Conc. Vol. (ppm)	Vol. Std. (mL)	Final Vol. (mL)
500	1.0	10
100	1.0	50
50	0.1	10
20	0.1	25
Use the 20 ppm linearity check standard for the following:		
2	1.0	10

Store in freezer.

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7. #2 fuel oil neat reference material: This material may not be available as a certified standard. A commercial equivalent may be used if the source is traceable. Store at room temperature.

8. Stock #2 fuel oil reference standard (10,000 ppm): Weigh (to 1.0 mg) 0.5 g of the reference material into a 50-mL volumetric flask containing 5 mL carbon disulfide. Bring the flask to volume with methylene chloride. Stable 6 months. Store in freezer.

9. Working #2 fuel oil reference standard (1000 ppm): Transfer 5.0 mL of the #2 fuel oil stock standard to a 50-mL volumetric flask and bring to volume with methylene chloride. Stable 1 month. Used as an alternate source check standard to verify the working diesel component standard. Store in freezer.

10. No. 2 fuel spiking stock - Weigh (to 1. mg) 2. g of neat No. 2 Fuel into a 50-mL volumetric flask containing 5 mL carbon disulfide. Bring the flask to volume with methylene chloride. Stable 6 months. Store in freezer.

11. No. 2 fuel working solution - Prepare a DF 50 of the above stock and bring to volume with acetone. 1 mL of this solution is added to the sample as directed by the sample preparation method (#7003 or #7004). Store in freezer.

Preparation of Glassware:

All glassware is soaked in dilute Chem-Solv for at least 4 hours, rinsed with tap water, and rinsed several times with deionized water. Kuderna-Danish glassware and all glassware related to dilutions are oven dried at 115°C.

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Sample Collection:

Wastewaters and waters should be collected in two 1-liter containers with no headspace and should be iced or refrigerated (4°C) until extraction is performed. Soils should be collected in a glass container (minimum 150 mL) with minimal headspace and iced or refrigerated until extraction is performed. Extraction #7003 (waters) or #7004 (soils) should be performed within 14 days. Waters are acidified to pH <2 with HCl upon receipt to prevent microbiological digestion of sample.

Safety Precautions:

Direct exposure of skin and respiratory tract to methylene chloride and carbon disulfide should be avoided. Many sample materials to be analyzed by this method are "unknowns" and may contain toxic materials. Use good laboratory practice for handling of unknowns.

Initial Method Setup:

The gas chromatographic system is set to the conditions stated in Appendix I. The working linear range of the system is determined for the diesel component standard by injection of five levels of working diesel component standard (Reagent 6). Linearity is assumed if the percent relative standard deviation (%RSD) is less than 20% over the working range. The injection of the 100-ppm diesel component standard at this time gives the analyst the baseline chromatogram for a properly operating system. Initially, the calibration must be verified by analyzing a midlevel #2 fuel oil reference standard (alternate source check standard). The calibration curve must be verified each day and every ten injections by the injection of a continuing calibration standard (midrange - 100-ppm total hydrocarbon diesel component standard). If these standards are not within acceptance criteria (see QC Acceptance Criteria), maintenance should be performed and a new calibration curve prepared.

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General Procedure:

1. On a gas chromatograph set to the conditions stated (Appendix I), place, in order, a sealed 1.5-mL vial with the following: $MeCl_2$ and a continuing calibration diesel component standard (100 ppm total hydrocarbon). The continuing calibration standard should be run after every ten injections. See QC Acceptance Criteria section.

2. Start and download a sequence in the Chrom Perfect data system on the proper chromatograph number.

3. After the initial standards are run, extraction batches can be added to the autosampler in the following order: surrogate standard, extraction blank, LCS, LCSD, and then samples.

4. If the concentration in the sample exceeds the linearity range of the method (approximately 500 ppm total hydrocarbon), the sample must be diluted and reanalyzed.

5. Calculate surrogate standard recoveries by comparing the areas of each surrogate prepped with the calibration curve to the area of the surrogate added to each sample. Chlorobenzene will be used as an "advisory" surrogate to validate the extraction procedure will not be entered into the Wang system unless the *o*-terphenyl surrogate is out of specification due to matrix interference. If the surrogates are out of spec (See QC Acceptance Criteria), reprocess the chromatogram if the cause is obvious matrix interference. If unsure, check with the coordinator, the sample may need to be reinjected, reextracted, or the limit of quantitation increased. Enter 999 for surrogate recovery if matrix interference exists or the sample was diluted more than 20×.

6. Quantitation of the sample is performed by comparing the area of all chromatographic peaks (including resolved and unresolved components) eluting between, and including, C10 (*n*-decane) and C28 (*n*-octacosane) with the average response factor from the calibration curve.

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Calculation:

NOTE: All calculations and data entry must be performed by or under the direct supervision of a chromatographer with extensive experience in the interpretation of GC chromatograms.

Area comparisons are performed by the Chrom Perfect data system to determine the area under the peak pattern for the chromatograms of the samples. Standard area is determined by the summation of the area of the 10 components as determined by the Chrom Perfect data system.

$$Cs = \frac{Ax}{As} \times \frac{Vt}{Vs} \times Df$$

Where:

Cs = Concentration of diesel range organics (mg/L or mg/kg)

Ax = Response for the diesel range organics in the sample, units in area

As = Average response factor from the calibration curve

Vt = Volume of final extract, in mL

Vs = Volume or weight of sample extracted, in mL or grams

Df = Dilution factor

Quality Assurance:

An extraction blank, duplicate laboratory control samples (prepared as a spiked blanks), and matrix spike (on soil samples) should be extracted at least every 20 samples. If a batch is continued for more than 1 day, a blank must be extracted. A continuing calibration standard must be analyzed every ten injections.

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QC Acceptance Criteria:

1. Blank - Value less than the limit of quantitation

2. Matrix spike - 50% to 150% recovery

3. Laboratory control samples - 60% to 120% recovery

4. Chlorobenzene surrogate - 50% to 150% recovery (Note: Advisory Surrogate)

5. *o*-Terphenyl surrogate - 50% to 150% recovery

6. Continuing calibration standard:

   a. Response ±25% of the average response of the calibration curve

   b. Area of C28 within 15% of the area of C20 (mass discrimination check)

NOTE:

$$\%\ Recovery = \frac{Calculated\ Concentration}{Expected\ Value} \times 100$$

$$Expected\ Value = \frac{Concentration\ of\ Solution}{Amount\ of\ Sample}$$

53215322.W60
111495

Prepared by: Melissa McDermott Date: 11/14/95

Approved by: Terry Schmidt Date: 3/26/96

Approved by: 972 Date: 3/29/96

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Appendix I

Gas Chromatographic Conditions for TPH by GC/FID - DRO

Temperature:

Injector: 300°C
Detector: 320°C
Column: 100°C for 2 minutes, 30°C/min rise to 300°C for 6.7 minutes hold

Flows:

Injector:

Septum Purge Flow	6 mL/min ± 0.5 mL/min

Column Flow:

Hydrogen Carrier Gas	See pressure programming below

Detector:

N_2 Make-up Gas (Auxiliary)	30 mL/min
Hydrogen	30 mL/min
Air	400 mL/min

Pressure programming:

NOTE: The following pressure program is designed so that a constant flow of about 10 mL/min is maintained from the time an injection is made until about 1 minute past the elution of C28. The pressure is then rapidly programmed to 25 psi which yields an approximate flow of 45 mL/min for the remainder of the 15-minute run. The constant flow maintained initially is important for reproducible

retention times. The pressure surge at the end is designed as a column cleanup to purge the column of heavier, more labile components. Since the psi settings will vary with column dimensions, exact psi values and programming rates and times are determined for each chromatographic system as outlined below.

1. Determine the pressure needed in psi to maintain a flow rate of 10 mL/min + 1.0 mL/min at 100°C and at 300°C.

2. Using pressure programming, set the initial pressure to the 100°C psi value determined above. Hold this pressure for 2 minutes (the oven temperature is held at 100°C for 2 minutes).

3. The oven reaches 300°C in 6.7 minutes from the onset of temperature programming (the first 2 minutes at 100°C not included). Calculate the psi/min ramp rate which is required to increase the pressure from its initial psi to the 300°C psi value (determined above) in 6.7 minutes.

4. Hold the pressure at the 300 psi value determined in step 2 for approximately 1 minute beyond the retention time of C28.

5. Increase the pressure to 25 psi at 30 psi/min and hold so that the end of the pressure program corresponds to the end of the temperature program.

   Direct injection of 1 μL.

Data collection is performed on the Chrom Perfect Data System.

NOTE: Gas Chromatographic conditions as listed in Appendix II of the TPH by GC/FID (4834, 4835, 4828, 4703, 5256, and 5260) method is an alternative for this analysis. Data collection is performed on the Nelson System 2600 series.

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Appendix II

PART I

1. Analyze $MeCl_2$ blanks until the system is stable.

2. Start a compensation run according to the HP manual instructions (Chromatogram must be manually started at the data collection system).

3. Program the GC to use the compensation run for background subtraction (see HP manual for instructions).

4. After column maintenance or installation of a new column, run a midlevel 100-ppm DRO and surrogate standard. Update the retention times, split events, and slice area tables as follows:

   a. Update retention times for the surrogate standard and each of the ten components of the DRO standard in all calibration files (DRO* and FUEL*).

   b. Update the split timed events (using the retention times of chlorobenzene, *o*-terphenyl, C10 and C28) in the events section of all methods (DRO*STD, DRO*SUM, DRO*PTP, FUEL*, FUEL*PTP, and REPLOT).

   c. Update the slice area table (using the retention times of C10 and C28) in the miscellaneous section of Report Write Plus - DRO*SUM, DRO*PTP, FUEL*, FUEL*PTP, and REPLOT.

5. Create a sequence using the following methods:

   a. DRO*STD.MET - Point-to-point integration with a plot, use for DRO component.

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b. DRO*SUM.MET - Both the horizontal baseline and point-to-point integrations, only creates a plot of the horizontal baseline integration, use for TPH-API samples and corresponding batch QC.

c. DRO*PTP.MET - Point-to-point integration without a plot, method is automatically pulled by DRO*SUM method, used for surrogate calculations in samples.

d. FUEL*.MET - Both the horizontal baseline and point-to-point integrations, only creates a plot of the horizontal baseline integration, use for TPH-CAI samples and corresponding batch QC.

e. FUEL*PTP.MET - Point-to-point integration without a plot, method is automatically pulled by FUEL*.MET method, used for surrogate calculations in samples.

f. REPLOT - Point-to-point integration with a plot - method is automatically pulled by DRO*SUM method; used for surrogate calculations in samples.

PART II

Using the data from the calibration working surrogate standards:

1. Input the C10-C28 "ten component area" from each level of the DRO*STD.MET report into component 1 (DRO AVG RF) of DRO* calibration file. This will generate a plot, corr. coef., % RSD, and an AVG CF for API samples.

2. Input the AVG CF (from step 1) into CN1 of DRO*.Cal.

3. Enter/confirm summed concentration for the ten components of the 10 ppm standard (CCV) in component two (DRO 10.PPM CONC), CN2 of DRO*.Cal. This is used to calculate the percent different of the continuining calibration standards.

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NOTE: Only needs to be changed when new calibrations stock standards are prepared.

4. Put the chlorobenzene DF5 area in CN3 of DRO*.Cal.

5. Put the *o*-terphenyl DF5 area in CN9 of DRO*.Cal.

6. Input the #2 fuel C10 - C28 slice area for each level of the calibration curve into component 1 (#2 fuel AVG) of FUEL*.Cal. This will give you a plot, corr. coef., % RSD, and an AVG RF for the California method samples.

7. Input the AVG RF (from step 6 above) into CN1 of FUEL*.Cal.

8. Input the chlorobenzene and *o*-terphenyl DF5 area into CN3 and CN4, respectively, of the FUEL*.Cal.

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To: Lee Ann Tracy

Fr: Jenifer Hess 10/15/96

Subject: Response to Inquiry on DRO Data

Example calculation for TPH-DRO usibng SOP 5321 or 5322:

$$\frac{\text{Area of C10-C28}}{\text{RF in ICAL}} \times \frac{\text{Final Volume(ml)}}{\text{Initial Wt or Vol (g or l)}} = \text{mg/kg OR mg/l}$$

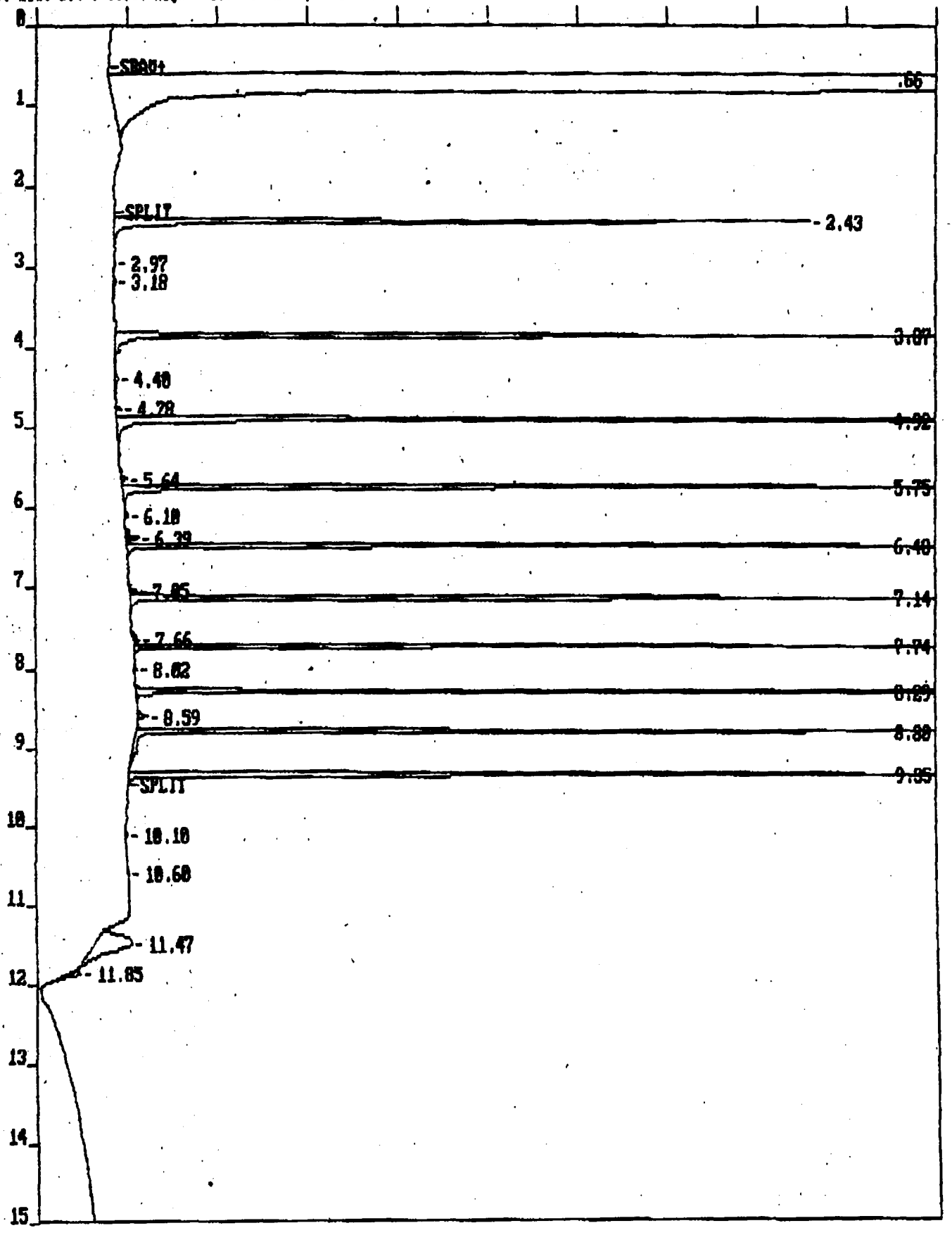
The surrogate and matrix spike concentrations for TPH-DRO are as follows:

	Soil (mg/kg)	Water (mg/l)
Matrix Spike	3.93	0.787
Chlorobenzene (Surr)	4.22	0.051
o-Terphenyl (Surr)	4.22	0.051

I have enclosed copies of chromatograms for TPH-DRO and for TPH-GRO for reference.

FI1 C:\DIRECT6\DATA2\M288.51R Date printed=10-15-1996 Time= 14:19:38
Sam..e Name=105 PPM DRO STD
0.0 to 15.0 min. Low Y=6.304 High Y=156.304 mv Span=150.0

DRO



```
*: ********   Custom Report for DRO by GC-FID   ***********************
*: ***************10-15-199614:19:56*********************************
* SAMPLE NAME:    105 PPM DRO STD                                     *
* RAW DATA FILE NAME:    C:\DIRECT6\DATA2\M288.51R                    *
* DATE TAKEN: Oct 15, 1996  14:18:37              Cycle:  51          *
* METHOD FILE:     C:\DIRECT6\DATA2\DROMSTD.MET  Version  43          *
* CALIBRATION FILE:  C:\DIRECT6\DATA2\DROM.CAL  Version  215          *
* Calibration data can be found on sequence:  M155 & M232             *
* TIME OF LAST MODIFICATION OF CALIBRATION:10/02/96 11:53:02          *
* Clewmark #: 5386 Instrument: CHROM 2--DET 2A OPERATOR:  MAM/856     *
*: ********************************************************************
*: *********************ANALYSIS CONDITIONS***************************
COLUMN:  Rtx-5 30M x .53mm x 1.5um   INJECTOR 300C   FID 320C
GC CONDITIONS:  100C 2min to 300C @ 30C/min hold 6.7min
                CNST.FLOW=10ML/MIN THEN P.PROG.TO 45ML/MIN
*********************************************************************
SAMPLE WEIGHT/VOLUME (GM/ML) = 1        FINAL VOL(ML)*DF  =  1
*: ********************************************************************
```

Peak #	Ret Time (min)	Peak Name	Amount PPM	Peak Area	Peak Width (min)	Peak Height
2	2.432	C-10	11.6177	301291	0.040	116382
[illegible]	3.872	C-12	0.9214	332328	0.033	168856
[illegible]	4.915	C-14	0.9034	329782	0.024	198686
0	5.753	C-16	1.0266	366088	0.027	217518
3	6.485	C-18	0.9380	329885	0.023	213725
15	7.139	C-20	12.0179	361444	0.032	197636
17	7.736	C-22	0.9261	307252	0.027	186295
19	8.285	C-24	1.0279	360569	0.025	220401
21	8.798	C-26	0.8404	341968	0.027	195405
22	9.351	C-28	12.5004	360574	0.032	175666

SLICE REPORT

#	Start Time	Stop Time	Amount	Amount%	Area	Area%
1	2.31	9.45	42.83021	57.94807%	343.0961E+04	23.4333%
2	6.94	6.98	0.00000	0.00000%	0.0000E+00	0.0000%

Total slice amount = 42.83021 Total slice area = 3430961
Total slice amount% = 57.94807 Total slice area% = 23.43328

10 [illegible]MP AREA = 3391180.0

C-10 RF = 30069.0 C-20 RF = 34955.9
C-28 RF = 33263.3

C-10/C-28 Mass Discrimination = -10.62 %
C-20/C-28 Mass Discrimination = 4.84 %

CCV % Recovery
****
%R= 115.28 %
****

O-TERPHENYL % RECOVERY = 0.00 %

Entered by: _____ ___/___/___

Verified by: _____ ___/___/___

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Analysis #5323, 5325, 6175
Initiated Date: 10/20/93
Effective Date: FEB 0 6 1996

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BTEX/Gasoline Range Organics (GRO) - API

Samples will be analyzed for GRO only - Per QAP, P

References:

1. "Method for Determination of Gasoline Range Organics," *EPA Underground Storage Tank Work Group Draft*, American Petroleum Institute, Revision 6, 08/18/93.

2. Methods 8020A, 5030A, 8000A, *Test Methods for Evaluating Solid Waste*, EPA SW-846, Third Edition.

3. Method 602, 40 CFR, Part 136.

Related References:

1. "Total Petroleum Hydrocarbons Analysis—Gasoline Method," LUFT Task Force, California Department of Health Services.

2. Method 8015B (Modified), *Test Methods for Evaluating Solid Waste*, EPA SW-846, Third Edition.

Scope:

This method is based on a purge-and-trap, gas chromatography (GC) procedure and may be used to determine the concentration of gasoline range organics in water and soil. This corresponds to an alkane range of C_6 (methylpentanes) through C_9 (trimethylbenzenes) and a boiling point range between approximately 60° and 170°C. The limit of quantitation (LOQ) for this procedure is 0.05 mg/L for waters and 1 mg/kg for soils. The respective limits for BTEX with separate xylenes are referenced from Lancaster Laboratories' Analysis #2213.

With the use of a photoionization detector (PID) in series, this method can also be extended for the determination of volatile aromatics (BTEX) as specified in EPA Method 8020A, with *o*-, *p*-, and *m*-xylenes being reported as total xylenes.

Summary:

Samples are analyzed using purge-and-trap sample concentration. Water samples are analyzed directly by purge-and-trap extraction and GC. Soil samples are dispersed, according to Lancaster Laboratories' Analysis #2379, "Preparation and Extraction of Soil and Solid Samples for Determination of Purgeable Aromatics and Purgeable Halocarbons," in methanol to dissolve volatile organic constituents and a portion of this methanolic solution is analyzed by purge-and-trap GC following this method as it applies to water samples. Detection is achieved by a flame ionization detector (FID) and, optionally, a PID in series (the PID first in the series). Quantitation is based on FID response to a gasoline component standard.

Apparatus:

1. Gas chromatograph - Any commercially available GC capable of temperature programming and equipped with a PID and FID that provides the proper sensitivity and linearity may be used.

2. GC column - Capillary DB-624 GC column, 75-meters length with 0.53 ID, 3-micron film thickness or equivalent. Equivalent column must be capable of resolving 2-methylpentane from solvent front and resolving ethylbenzene from *p/m*-xylene.

3. Purge and trap - OI Analytical Model 4560 concentrator or equivalent with a 4560 infra-sparge sample heater and the following specifications:

   a. Purging chamber (sparge) is designed to accept 25 mL of sample with a water column at least 12-cm deep. The gaseous headspace of the sparge is <15 mL total volume.

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b. The trap must be at least 25-cm long and have an inside diameter of at least 0.105 inches. The trap is prepacked (Tenax®) purchased from instrument supplies vendor.

c. The desorber should be capable of rapidly heating the trap to 180°C for desorption. The trap should not be heated beyond 180°C, and should not exceed 220°C during the bake cycle.

d. The infra-sparge heater uses unique high intensity infrared heating with direct sample temperature feedback through an inert thermocouple submerged in the sample to heat the sample to 40°C for the purge cycle.

4. Autosampler (optional) - OI Analytical Model 4551 sample cooler or equivalent. This is a 51-position VOA vial multisampler which interfaces to the Model 4560 sample concentrator. The Model 4551 individually transfers the methanol solution from the standard 40-mL VOA vials to the common sparge vessel on the sample concentrator.

5. Standard/surrogate spiker units (optional) - OI Analytical Model 4551 SIM/spiker or equivalent. One or two automated standard/surrogate syringe spikers can be added to the OI Analytical Model 4560 concentrator to automatically introduce internal standard, surrogate standard, and spiking solutions to the samples being transferred to the sparge vessel.

6. Syringes - 25-mL Luer-Lok gastight glass syringe; 5-mL Luer-Lok gastight glass syringe

7. Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1000-μL gastight syringes

8. Volumetric flasks - 10, 25, 50, 100, 200, 500, and 1000 mL, all with ground-glass stoppers

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9. Glass vials - 1.5 mL with screw caps fitted with septa

10. 12-mL glass vials with Teflon-lined screw caps

11. Stainless steel spatula

12. Pasteur pipettes (with long tip)

13. Balances - Mettler analytical balance or equivalent, capable of accurately weighing to the nearest 0.0001 g

14. Mettler toploading balance or equivalent, capable of weighing to the nearest 0.01 g

15. Trap-packing materials - 2,6-diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax®)

Materials:

Laboratory deionized water is used to prepare all sample dilutions and working standards. Purge-and-trap grade (or equivalent) methanol is used to prepare all other calibration and QC standards. Standards can either be prepared in house as stated in the references from neat compounds obtained from suppliers which indicate the purity of the compound or prepurchased from suppliers. No correction for purity is made if the listed purity is >96%. Prepurchased standards must have the concentrations of the solutions documented by the supplier. If the purity of the standard is <96%, a calculation to correct for the standard purity is performed and documented in the standards notebook.

Safety Precautions:

The toxicities of all compounds used in the method have not been established, however, several of the compounds are considered carcinogens. Each compound should be treated as a potential health hazard. The major route of exposure is inhalation during handling of the neat materials while preparing stock standards. These stocks must therefore be prepared in a hood to eliminate the risk of inhaling

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b. 12 individual component stock calibration/check standards prepared in methanol at the concentrations shown in the table below:

Component	Final Individual Component Concentration (µg/mL)	Weight (grams) of Neat Stock to 10 mL Methanol
2-Methylpentane	15000	0.1500
MTBE (Tert-methylbutylether)	10000	0.1000
Benzene	5000	0.0500
Iso-octane (2,2,4-Trimethylpentane)	15000	0.1500
n-Heptane	5000	0.0500
Toluene	15000	0.1500
Ethylbenzene	5000	0.0500
p-Xylene	10000	0.1000
m-Xylene	10000	0.1000
o-Xylene	10000	0.1000
1,2,4-Trimethylbenzene	10000	0.1000
Naphthalene	5000	0.0500

These standards are stored in 12-mL vials with screw-cap lids and Teflon-lined silicone septa (may vary based on availability) at -10° to -20°C (14° to -4°F) for up to 180 days.

NOTE: Indicated weights are targets; actual weights should be within ±10% of the target weight.

c. Surrogate/internal standard - Trifluorotoluene (TFT) is used as the internal standard on the PID and surrogate standard on the FID. 1,2-difluorobenzene is the second surrogate standard on the FID. Bromofluorobenzene (BFB) is the surrogate on the PID. Stock surrogate/internal standards are prepared in methanol by adding

Per Judy Bechtel of Lancaster, the PID surrogate is TFT and the FID surrogate is 1-chloro-3-fluorobenzene

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0.0500 grams of neat compound (±.005 g) to methanol in a 10-mL volumetric flask. These standards are stored in 12-mL vials with screw-cap lids and Teflon-lined silicone septa (may vary based on availability) at -10° to -20°C (14° to -4°F) for up to 180 days.

Secondary dilution standards are prepared by taking the following volumes of individual surrogate stocks to methanol in a 25-mL volumetric flask:

Trifluorotoluene - 0.5 mL
1,4-Difluorobenzene - 0.5 mL
Bromofluorobenzene - 0.25 mL

These standards are stored in 12-mL vials with screw-cap lids and Teflon-lined silicone septa (may vary based on availability) at -10° to -20°C (14° to -4°F) for up to 30 days.

2. Secondary dilution standards

a. 550-ppm BTEX/gasoline working standard is prepared by taking 1 mL of the 5550-ppm BTEX/gasoline stock standard to methanol in a 10-mL volumetric flask. These standards are stored in 12-mL vials with screw-cap lids and Teflon-lined silicone septa (may vary based on availability) at -10° to -20°C (14° to -4°F) for up to 180 days.

b. The BTEX/GRO calibration standard B is prepared by placing 0.5 mL of each individual component stock standard into methanol in a 10-mL volumetric flask. These standards are stored in 12-mL vials with screw-cap lids and Teflon-lined silicone septa (may vary based on availability) at -10° to -20°C (14° to -4°F) for up to 180 days.

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20 µL added to 20 grams of soil (methanol extraction) - 11 mg/kg as gasoline

For BTEX compounds, 20 µL of spike in the appropriate volume/weight of sample yields the values indicated below:

Component	Soil Concentration (µg/kg)	Water Concentration (µg/L)
MTBE	260.5	52.1
Benzene	152.4	30.48
Toluene	974	194.8
Ethylbenzene	204	40.8
p/m-Xylene	878	175.6
o-Xylene	316	63.2
Naphthalene	N/A	N/A

For custom BTEX compounds such as naphthalene, an appropriate single-compound MS standard, prepared as indicated in Analysis #2213, may be used in addition to the above standard.

These standards are stored in 12-mL vials with screw-cap lids and Teflon-lined silicone septa (may vary based on availability) at -10° to -20°C (14° to -4°F) for up to 30 days.

5. Methanol - Purge-and-trap grade or equivalent. Store away from other solvents.

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Sample Collection:

Aqueous samples are to be collected in triplicate without headspace in contaminant-free 40-mL glass vials fitted with Teflon-lined septa in the caps. Samples should be adjusted to pH <2 with approximately .2 mL of 1:1 hydrochloric acid (HCl) as a preservative for aromatic analytes. All samples must be cooled at 2° to 6°C (36° to 43°F) at the time of collection until analysis. All samples must be analyzed within 14 days of collection.

Soil samples are to be collected using the recommended sampling protocol in SW-846. Samples collected according to this protocol should be cooled at 2° to 6°C (36° to 43°F) at the time of collection until analysis. All samples must be analyzed within 14 days of collection.

Instrument Operating Conditions:

1. GC conditions - See Appendix L

2. Purge-and-trap conditions

   The purge cycle should consist of an 8-minute purge followed by an 8-minute dry purge. The desorb cycle should be 4 minutes at 180°C and, if necessary, a desorb preheat should occur at 175°C. The bake cycle should be 9 minutes at a temperature of at least 180°C, with longer bake cycles, whenever necessary, to facilitate baking off heavier compounds that may remain on the trap after desorb.

3. Calibration

   All calibration standards are prepared in the 25-mL syringe, injecting the required amount into the syringe containing reagent water and methanol (25:1 ratio). To this standard is added the 10.0 μL of surrogate/internal standard. Attaching the Luer-Lok end of the syringe to the sparge port, inject this final solution into the purge vessel. Proceed with the purge-and-trap procedure.

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The 12-component BTEX/GRO calibration standards are run at five concentration levels at or above the method detection limit (MDL) through a working range that mimics the normal concentration found in samples. The working calibration standards are prepared by diluting the appropriate volume of secondary dilution standard with a 1:25 proportion of methanol to reagent water in the 25-mL syringe.

Calibration is performed using the external standards method for FID detection and internal standardization for PID detection. In either case, a point-to-point calibration curve is used. The calibration factor (CF; as defined in Department 34 SOP-PA-032, "Manual Calculation of the Analyte Response/Calibration Factors, the Relative Standard Deviation for Analyte Response/Calibration Factors, and the Correlation Coefficient"), is calculated for each analyte in each calibration level. If the relative standard deviation (RSD) of the CFs for any analyte is <20%, the average CFs may be used for the quantitation. If the RSD exceeds 20%, a calibration curve must be utilized. For RSDs >15%, the calibration curve must be reviewed by comparing the individual CFs for each level. any suspect levels are to be repeated to see if a lower %RSD can be achieved. Alternately, a linear least squares fit to the calibration data may be used. For the total petroleum hydrocarbons portion of the analysis, the calibration factor (CF) is calculated for each calibration level for each analyte. If the RSD of the CF is >20%, the calibration for that analyte must be repeated. As defined by Chrom Perfect:

$$\textit{Calibration Response Factor} = \frac{\textit{Total Area Response}}{\textit{Total Amount } (\mu g) \textit{ Purged}}$$

The working calibration curve and CCF are verified every ten samples by injecting a midpoint continuing calibration standard. If the response for this standard is not within 10% relative percent difference (RPD) of the calibration response, or if the PID response for individual components is not within a 15% confidence interval, a new calibration must be performed.

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$$\textit{Relative percent difference} = \frac{CRF - CCF}{\left(\frac{CRF + CCF}{2}\right)} \times 100$$

Where:

CRF = Average calibration factor from the calibration curve

CCF = Calibration factor from the midpoint continuing calibration standard

Procedure (Water Samples):

NOTE: The syringe and syringe plunger should be rinsed at least 3 × with deionized water between samples. All samples, standards, blanks, and spikes should contain 10 µL of the secondary dilution surrogate/PID internal standard solution added prior to purging.

1. Set purge-and-trap and GC conditions as specified under the Apparatus section and Appendix I of this method.

2. Run a deionized water blank as an instrument startup/cleanup blank. Next run a working check standard unless starting a new batch, in which case a laboratory control sample (LCS) and a laboratory control sample duplicate (LCSD) must be run. The LCS will take the place of the initial check standard. Prepare by injecting 10 µL of the GRO check standard solution into the 25-mL syringe filled with 24 mL deionized water and 1 mL of methanol. Inject 10 µL of surrogate standard. Attach the Luer-Lok end of the syringe to the fitting on the purge chamber (sparge) and inject the standard into the sparge. The LCSD is prepared by repeating the same steps as above.

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3. When the program on the concentrator reaches the Desorb cycle, the water in the sparge can be drawn out with the 25-mL syringe (unless the concentrator is fitted with a functional auto-drain mechanism). If the water in the sparge is drawn out manually, any remaining water should be drawn out during the Bake cycle.

4. After the run time has expired, the program on the concentrator will advance to Standby. Once the printout from the data collection software has been reviewed and the possible need for reinjection has been ruled out, the next sample can be prepared and injected into the sparge. See Quality Assurance section of this method for acceptance limits.

5. If starting a new batch, a MeOH blank/surrogate control standard must be run. Fill the 25-mL syringe to the 24-mL mark with deionized water. Inject 1 mL of methanol into the 25-mL syringe followed by 10 μL of surrogate standard. Place this in the sparge and press the Start button.

6. If starting a new batch, a 0.2-ppb detection limit standard must be run. Prepare the 25-mL syringe with 24 mL deionized water and 1 mL of methanol. Inject 10 μL of the BTEX LOQ standard into the 25-mL syringe followed by 10 μL of surrogate standard. Place this into the sparge and press Start.

7. Open the sample vial and carefully pour off the top layer of sample. Fill a 12-mL vial with no headspace (two, if only one 40-mL vial was submitted by client) for repeats. Carefully fill the 5-mL syringe to overflowing with sample. Replace the plunger, vent any residual air, and adjust the volume to 5 mL. Prepare the 25-mL syringe with 19 mL of deionized water, 1 mL of methanol, and 10 μL of surrogate standard. Inject the 5 mL of sample into the sparge first, followed by the contents of the 25-mL syringe and press Start. If the odor of the sample indicates high organics, a dilution should be made.

8. Continue analysis of samples in this manner for ten samples at which time a new CCV must be analyzed.

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9. For every batch of 20 samples analyzed, a BTEX/gasoline MS and matrix spike duplicate (MSD) should be performed. The MSs are 24 mL deionized water + 1 mL MeOH + 20 μL working spike solution + 10 μL surrogate. The sample is placed into the 25-mL syringe, as normal. Inject the sample and spike as in step 8 above.

Procedure (Soils/Solid Wastes):

NOTE: The syringe and syringe plunger should be rinsed at least 3 × with deionized water between samples. All samples, standards, blanks, and spikes should contain 10 μL of the secondary dilution surrogate/PID internal standard solution added prior to purging.

1. Set purge-and-trap and GC conditions as specified under the Apparatus section of this method.

2. Run a deionized water blank as an instrument startup/cleanup blank. Next run a working check standard unless starting a new batch, in which case an LCS and LCSD must be run. The LCS will take the place of the initial check standard. Prepare by injecting 10 μL of the GRO check standard solution into the 25-mL syringe filled with 24 mL deionized water and 1 mL of methanol. Inject 10 μL of surrogate standard. Attach the Luer-Lok end of the syringe to the fitting on the purge chamber (sparge) and inject the standard into the sparge. The LCSD is prepared by repeating the same steps as above.

3. When the program on the concentrator reaches the Desorb cycle, the water in the sparge can be drawn out with the 25-mL syringe (unless the concentrator is fitted with a functional auto-drain mechanism). If the water in the sparge is drawn out manually, any remaining water should be drawn out during the Bake cycle.

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4. After the run time has expired, the program on the concentrator will advance to Standby. Once the printout from the data collection software has been reviewed and the possible need for reinjection has been ruled out, the next sample can be prepared and injected into the sparge. See Quality Assurance section of this method for acceptance limits.

5. If starting a new batch, a MeOH blank/surrogate control standard must be run. Fill the 25-mL syringe to the 24-mL mark with deionized water. Inject 1 mL of methanol into the 25-mL syringe followed by 10 μL of surrogate standard. Place this in the sparge and press the Start button.

6. If analyzing for BTEX and starting a new batch, a 0.2-ppb detection limit standard must be run. Prepare the 25-mL syringe with 24 mL deionized water and 1 mL of methanol followed by 10 μL of surrogate standard. Inject 10 μL of the BTEX LOQ standard into the 25-mL syringe. Place this into the sparge and press Start.

7. Prepare methanol extractions for the samples as per Lancaster Labs' Analysis #2379.

8. Prepare the 25-mL syringe with 24 mL of deionized water, add 1 mL of methanol extract from the sample and 10 μL of surrogate standard. Inject the 25 mL of solution into the sparge and press Start. If the odor of the extract indicates high organics, a dilution should be made.

9. Continue analysis of samples in this manner for ten samples at which time a new CCV must be analyzed.

10. For every batch of 20 samples analyzed, a BTEX/gasoline MS and MSD should be performed. The matrix spikes are 24 mL deionized water + 1 mL MeOH + 20 μL working spike solution + 10 μL surrogate. The sample is placed into the 5-mL syringe, as normal. Inject the sample and spike as in step 8 above.

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Identification of Analytes:

Comparison of sample peak retention times to standard peak retention times is used to tentatively identify compounds. A window of ±3 standard deviations from the average retention time based on five to six previously analyzed QC check standards can also be used as the basis for identification. Further considerations should also include normal vs. abnormal peak shape and the shift in retention times of the surrogates and internal standards. Ultimately, the experience and discretion of the analyst should weigh heavily in the interpretation of the chromatogram.

Dilution of Samples:

Sample which contain levels of analytes above the dynamic range of the method (the highest-level calibration standard) must be reanalyzed. A dilution(s) is performed so that all target analytes can be quantitated and fall within the dynamic range of the method. If the instrument has been running on sequence, the analyst must determine if there is carryover present. It may be necessary to analyze a reagent water blank (cleanup blank) to ascertain all analytes are below the LOQ. If they are not, the cleanup blank is repeated until analyte levels are below the quantitation limit.

Calculations:

The concentration of GRO in the sample is determined by calculating the absolute weight of analyte purged, from a summation of peak area for all peaks eluting in the range of (and including) 2-methylpentane to 1,2,4-trimethylbenzene, using the calibration curve or calibration factor. The concentration of GRO in the sample is calculated as follows:

$$Conc\ (ppm) = \frac{\left(\frac{Ar}{CRF}\right)}{1000} \times \left[\frac{1}{Wt} \times \frac{Vt}{Vp}\right] \times DF$$

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NOTE: The portion of the above equation in [brackets] is for calculating soils only; disregard for waters calculations.

Where:

Conc = Concentration of GRO (in mg/L for waters and mg/kg for soils)

Ar = Area for GRO in the sample, as defined by the gasoline reference pattern, units in area

CRF = Calibration response factor, units in area/μg/L

DF = Dilution factor, normally waters have a default value of 5 and soils have a default value of 25 prior to any dilutions due to sample matrix

Wt = Weight of the sample extracted, units in g. Use wet weight of sample.

Vt = Total volume of extract, units in mL (20-mL default)

Vp = Volume of extract purged, units in mL

Refer to Analysis #2213 for calculation of the concentration of BTEX components in a sample.

Quality Control:

In order to monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix, each sample, blank, standard, and spiked sample is spiked with 10 μL of surrogate/internal standard. Surrogate recoveries should be 75% to 125% for trifluorotoluene, 1,4-difluorobenzene, and bromobenzene. (see note p.6)

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If two or more surrogates are out of specifications, the sample is repeated. If the surrogate(s) is still out of specification, a QC check is analyzed (see below). If the QC check is within specifications, matrix interference is suspected and the analyst can continue. As stated above in the Calibration section, the calibration curves are verified every ten samples by analyzing a QC check standard which contains every analyte of interest. If the recovery of any analyte is outside of the acceptable range (85% to 115% for the PID), the QC check standard is repeated.

If these compounds are within the acceptable range on the repeat, the QC check standard is acceptable. If these compounds are still outside the acceptable range on the repeat, the system is recalibrated. The CCF for the check standard on the FID is calculated using the total area between 2-methylpentane and 1,2,4-trimethylbenzene (minus the areas for the three surrogates) and the total amount (in ppb) of the check standard components.

$$CCF = \frac{Total\ Area}{Total\ Amount}$$

This CCF is then compared to the average CRF from the calibration curve and a RPD is calculated according to the following formula:

$$RPD = \frac{|CCF - CRF|}{\left(\frac{CCF + CRF}{2}\right)} \times 100$$

This RPD must be <20% for the QC check standard. Otherwise, the check standard should be repeated to confirm the results. If the repeat check standard is not within this acceptable range, then recalibration must be performed before any further samples may be analyzed.

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Method blank/surrogate control standard (1 mL of methanol to 24 mL deionized water plus 10 μL of surrogate standard for both soils and waters) - The values should be less than half the LOQ for each component. The values will still be in specification if between this value and the LOQ, but if clean samples are to be run, these levels may be enough to give false reportable values in the samples; therefore, a methanol cleanup should be run, followed by a repeat injection of the method blank/surrogate control standard.

LCS/LCSD - These are performed for every batch of 20 samples analyzed. The LCS and LCSD are prepared by adding 1 mL methanol + 10 μL of the working check standard + 10 μL surrogate standard to 24 mL deionized water. 20 μL of the BTEX/GRO working spike standard, representing levels as indicated in Item 6 of the Reagents section, is added to the 25-mL syringe as described in the Procedure section for each matrix type. The recovery for each analyte of interest (including gasoline) should be between 85% and 115%. The maximum RPD should be 20%. The RPD is calculated as follows:

$$RPD = \frac{|\,LCS\ recovery - LCSD\ recovery\,|}{\left(\frac{LCS\ recovery + LCSD\ recovery}{2}\right)} \times 100$$

Reinject if surrogates appear low or if technique is questioned. If the solution integrity is questioned, pull fresh standard and reinject. If it is still out of spec, new working solution can be prepared from the stock solution and/or new stock and working solutions can be prepared from neats. If it is still out of spec, recalibrate.

MS/MSD - These are performed for every batch of 20 samples analyzed. 20 μL of the BTEX/GRO spiking standard, representing levels as indicated in Item 6 of the Reagents section, is added to the 25-mL syringe as described in the Procedure section for each matrix type. The recovery for each analyte of interest (including gasoline) should be between 75% and 125%. The maximum RPD should be 20%. The RPD is calculated as follows:

$$RPD = \frac{|\,MS\ recovery - MSD\ recovery\,|}{\left(\frac{MS\ recovery + MSD\ recovery}{2}\right)} \times 100$$

MS/MSD - Same as LCS, except calibration is only performed when matrix effect can be eliminated.

The results from the unspiked (BKGD), MS, MSD, LCS, and LCSD duplicate samples are recorded in the Lancaster Laboratories' sample management/QC database referencing each appropriate batch of up to 20 samples in which it was performed. Surrogate standard and blank results are also entered into the database.

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Prepared by: Matthew E Barton Date: 2/5/96

Approved by: Jerry S. Collen Date: 2/6/96

Approved by: [signature] 972 Date: 2/5/96

Appendix I
GC Conditions

Flow Rates
mL/min

Helium	11 ± 2
Hydrogen	*35 ± 4
Air	*160 ± 10
Nitrogen (makeup gas)	20 ± 4

*Settings will vary according to manufacturer's specifications for detectors.

Temperature Program & Ramp Rates

Initial Temp	50°C	for 0.5 minutes
Ramp Rate 1	1.5°C/minute	
Hold Temp 1	65°C	for 0 minutes
Ramp Rate 2	10°C/minute	
Hold Temp 2	210°C	for 0 minutes
Ramp Rate 3	35°C/minute	
Hold Temp 3	240°C	for 2 minutes

Miscellaneous GC Settings

Injector #1 Temp	200°C
Detector #1 Temp*	240°C
Detector #2 Temp*	260°C

*If using "piggyback" detectors installed on a single port, use a temperature of 260°C for that detector port.

NOTE: Conditions may be altered to improve resolution of gasoline range organics or to facilitate column cleanup after samples containing heavier purgeable compounds are run.

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Appendix II

BTEX Calibration Levels for the 12-Component Standard

Component	2.5 µL Level A Std. (µg/L)	5 µL Level A Std. (µg/L)	25 µL Level A Std. (µg/L)	50 µL Level A Std. (µg/L)	10 µL Level B Std. (µg/L)
MTBE	2.00	4.0	20.0	40.0	80
Benzene	1.00	2.0	10.0	20.0	40
Toluene	3.00	6.0	30.0	60.0	120
Ethylbenzene	1.00	2.0	10.0	20.0	40
p/m-Xylene	4.00	8.0	40.0	80.0	160
o-Xylene	2.00	4.0	20.0	40.0	80
Naphthalene	1.00	2.0	10.0	20.0	40

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Appendix II (Continued)

GRO Calibration Levels for the 12-Component Standard

Component	2.5 µL Level A Std. (µg/L)	5 µL Level A Std. (µg/L)	25 µL Level A Std. (µg/L)	50 µL Level A Std. (µg/L)	10 µL Level B Std. (µg/L)
2-Methylpentane	3.00	6.0	30.0	60.0	120
Benzene/Iso-octane	4.00	8.0	40.0	80.0	160
n-Heptane	1.00	2.0	10.0	20.0	40
Toluene	3.00	6.0	30.0	60.0	120
Ethylbenzene	1.00	2.0	10.0	20.0	40
p/m-Xylenes	4.00	8.0	40.0	80.0	160
o-Xylene	2.00	4.0	20.0	40.0	80
1,2,4-Trimethylbenzene	2.00	4.0	20.0	40.0	80

NOTE: The indicated levels for both tables are approximations and will fluctuate with the actual concentration of the individual component stocks.

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Analysis #5441, 5442, 6292
Initiated Date: 06/28/94
Effective Date: OCT 15 1996

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Soils and Solids for Volatile Target Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique

Reference:

1. Method 8260A, USEPA SW-846, Revision 1, September 1994.

2. Lancaster Laboratories Analysis #0374, "Solid Matrix Sample Preparation," Initiated 08/21/89.

Scope:

This method is suitable for the determination of compounds listed in USEPA SW-846, Method 8260A (Tables 1A and 1B) for soil and solid matrices. The method also is appropriate for acquiring data files required to perform a search for tentatively identified compounds (TIC) in volatile organics GC/MS analyses. This analysis should be performed by or under the direct supervision of an operator experienced in the analysis of volatile organics by GC/MS purge and trap methodologies.

Basic Principles:

A 5-gram sample or a dilution of a sample extract, as described in Analysis #0374, "Solid Matrix Sample Preparation," is placed in a specially designed purge vessel. The sample is purged with an inert gas and the effluent gas passed through a sorbent trap where the volatile organics are trapped. After purging, the sorbent trap is rapidly heated and backflushed onto the head of a gas chromatographic column held at the appropriate initial temperature for the column in use. The gas chromatographic column is temperature programmed to separate the volatile compounds which are subsequently detected and identified using mass spectrometric techniques.

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Apparatus:

1. Gastight micro syringes - 10 μl and larger

2. 5-mL gastight syringe

3. Analytical balance capable of accurately weighing ±0.001 g

4. Top-loading balance capable of weighing ±0.01 grams

5. Glassware - Volumetric flasks, Class A with ground-glass stopper

6. Purge and trap device - Consisting of the sample purger, the trap, and desorber; the OI Analytical 4560, Tekmar LSC 2000, or equivalent meets the requirements of this method

7. GC/MS system - The HP 5970 MSD, Finnigan Incos 50, or equivalent GC/MS system meets the requirements for this method

Reagents:

1. Reagent water is defined as water in which an interferant is not observed at or above the reporting limit for parameters of interest. In general, the deionized water supplied at the taps in the laboratory will meet this criteria. If the reagent water does not meet the requirements, see your supervisor for further instructions.

2. Methanol and other appropriate solvents (i.e., TGDE, CS_2) - For purge and trap analysis or equivalent

3. Stock standard solutions - Prepared from assayed standard materials or purchased. Stock solutions must be prepared in methanol or an equivalent solvent.

a. Place about 9.8 mL methanol or an equivalent solvent into a tared 10.0-mL glass-stoppered volumetric flask. Weigh the flask to the nearest 0.1 mg.

b. Add the liquids using a syringe or pipet by adding two or more drops of the assayed material to the flask, being careful that no drop hits the side of the flask. Bring the volume of solvent in the flask to 10.0 mL. Calculate the concentration of the standard.

c. The stock standard solutions are stored in Teflon-sealed screw-capped vials at -10° to -20°C. The compound name, concentration, date prepared, and expiration date must appear on the bottle.

d. Replace stock standard solutions every 6 months.

e. For most of the target compounds, the stock standard solutions are purchased from a vendor as volatile organic compound (VOC) mixes. The VOC mixes are diluted together into one volumetric flask to a known concentration and named VOCXXXZZ, where XXX designates the month and ZZ designates the day that the dilution was made.

f. Also, the target compounds which are gases at room temperature are currently being purchased from a vendor.

4. Secondary dilution standards - Using the stock standard solutions, prepare secondary stock solutions in methanol or an equivalent solvent containing the desired compounds. Tables IA-IB list the compounds analyzed under Analysis #5441, 5442, 6292, "Soils and Solids for Volatile Target Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique." These standards are prepared by calculating the volume of each stock standard required to produce a

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given volume of a mixed working standard with a known concentration of each analyte. The working standard is tested according to SOP-MS-006, "GC/MS Volatile Standards Traceability." The verified working standard is pipetted into 1.5-mL Teflon-lined screw-capped GC vials and is stored at -10° to -20°C. A designator indicating the standard, month, and day of preparation must be on the standard vials. The designator and the calculations for the working standard preparation are to be recorded in the standards logbook. Replace secondary dilution standards every 6 months.

5. Matrix spiking solution - Prepare solutions in methanol or an equivalent solvent that contain the compounds of interest at known concentrations in a similar manner as described above for the secondary dilution standards. These solutions serve as both the matrix spiking solution and the quality control reference stock solution. Matrix spikes also serve as duplicates, therefore, two aliquots of the same sample need to be spiked for analysis with these solutions. Replace the matrix spiking solution every 6 months.

6. Surrogate standard spiking solution - Prepare stock standard solutions for 1,4-dichloroethane-d4, toluene-d8, 4-bromofluorobenzene, and dibromofluoromethane in methanol or an equivalent solvent. Prepare the surrogate standard spiking solution from the stock standard solutions at a concentration of 25 µg/mL in methanol or equivalent solvent. Replace surrogate standard spiking solution every 6 months.

7. Internal standards solution - Prepare a solution in methanol or an equivalent solvent containing fluorobenzene, chlorobenzene-d5, and 1,4-dichlorobenzene-d4 at a concentration of 25 µg/mL using stock standards as described in 4 above. Replace the internal standards solution every 6 months.

8. 1,4-Bromofluorobenzene (BFB) standard - Prepare a 25-µg/mL solution of BFB in methanol. Replace this solution every 6 months.

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9. Store all standard solutions at -10° to -20°C.

Preparation of Glassware:

All glassware is washed with soapy water, rinsed with tap water, then rinsed with deionized water, and baked in a drying oven at 100°C for at least 4 hours.

Safety Precautions:

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; therefore, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available, such as the use of fume hoods, lab coats, safety glasses, and gloves.

Sample Handling:

The samples to be analyzed using USEPA SW-846, Method 8260A, should be stored in a refrigerator between 2° and 6°C. In addition, all samples must be analyzed within 14 days of collection.

Training and Qualification Requirements:

Analysts must be trained in the proper method of volatile organic sample preparation and analysis as determined by the supervisor(s). All training and education relating to volatile organic sample preparation and analysis shall be documented by each analyst in their training record.

Waste Generation and Disposal:

Neat compound sources and stock solutions shall be collected into a lab pack upon expiration. The lab pack is delivered to Safety personnel for appropriate disposal. Expired secondary standard solutions in methanol shall be disposed of as solvent waste. Pour expired secondary standard solutions into the appropriate solvent

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i. The calibration check involves analyzing the 50-μg/kg standard and calculating the RRF for each compound. Minimum RRF values as described under the calibration section for the SPCC compounds must be met. Also, the percent drift between the standard concentration and the measured concentration for each compound in the 50-μg/kg check standard are calculated as follows:

$$\% \ Drift = \frac{C_1 - C_c}{C_1} \times 100$$

Where:

C_1 = Standard concentration of analyte

C_c = Measured concentration of analyte using selected quantitation method

The percent drift for the CCC compounds must be less than or equal to 20%. If any SPCC or CCC compound fails to meet the criteria listed above, the calibration is considered invalid. Corrective action must be taken and the calibration redone. If the criteria are met, the selected quantitation method from the initial calibration are used for blank and sample calculation for the next 12-hour period.

7. A method blank is then analyzed as described above in steps 5.a. through 5.d. using reagent water as the aqueous matrix. The method blank is examined for interfering peaks. Any target compound peaks are calculated as described under the Calculations section of this procedure. The method blank for soils is described in Analysis #0374. All compounds must be less than the quantitation limit. If the blank values exceed these values, corrective action must be taken and the method blank reanalyzed until the criteria are met. Also, all surrogate compound recoveries must meet the criteria listed in Table III.

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8. Sample analysis

   a. Sample analysis for soil, solids, and nonaqueous matrices proceeds as described in steps 6.a. through 6.d. above by adding soil and reagent water or an aliquot of the soil extraction described in Analysis #0374.

   b. For each set of 20 field samples, one sample shall be analyzed in triplicate, spiking each duplicate with each of the quality control reference concentrates. Results of the unspiked and spiked duplicates shall be compared to Table IV. A laboratory control sample, which is reagent water spiked with each of the quality control reference concentrates, must be analyzed when a spike recovery fails the Table IV criteria.

   c. All samples must also meet the surrogate recoveries listed in Table III. If a sample surrogate recovery falls outside the criteria, the sample shall be reanalyzed. If the reanalysis shows the same surrogate results, the sample matrix is assumed to be interfering and the initial results are reported. If the reanalysis meets the recovery criteria, the first analysis is assumed to have been outside of limits due to a laboratory error and the second analysis is reported.

9. Data analysis

   a. Sample chromatograms are analyzed both qualitatively and quantitatively. First, a determination of the identity of a sample peak as a target compound (Table IA or IB) is made through the use of computerized analysis. Guidelines for the qualitative determination are as follows:

      (1) The relative retention time (RRT) of the sample peak is within 0.06 of the RRT of the most recent check standard.

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(2) Each ion with a relative intensity of greater than 10% of the base ion of the mass spectra of the sample must be present in the sample spectrum produced on the same mass spectrometer.

(3) The relative intensities of the ions in the sample mass spectrum must be within 20% of the intensities of the standard mass spectrum.

(4) Peaks greater than 10% relative intensity in the sample mass spectrum but not present in the standard mass spectrum from the same mass spectrometer must be accounted for by the analyst.

(5) If a compound fails any of the criteria listed above but in the judgment of the mass spectral interpretation specialist is a correct identification, the identification is used and the quantitation of the peak is performed.

b. Quantitation of identified priority pollutant compounds is performed using the equations listed in the Calculations section of this procedure. All calculations should report concentrations in values of µg/kg. Any analyte with a calculated concentration above the highest standard must be reanalyzed at a dilution which will bring the concentration in solution within the calibration curve. It is desirable to have the dilution within the top half of the calibration curve, but it is not required.

Calculations:

1. Low level

$$Concentration\ (\mu g/kg) = \frac{(Ax)\ (Is)}{(Ais)\ (RRF)\ (Ws)}$$

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Where:

Ax = Area of the quantitation ion peak for the compound to be measured

Ais = Area of the quantitation ion peak for the appropriate internal standard

Is = Amount of internal standard added in nanograms

Ws = Weight of sample purged

RRF = Relative response factor from the initial calibration

2. Medium level

$$Concentration\ (\mu g/kg) = \frac{(Ax)\ (Is)\ (Vt)}{(Ais)\ (RRF)\ (Ws)\ (Vi)}$$

Where:

Ax = Area of the quantitation ion peak for the compound to be measured

Ais = Area of the quantitation ion peak for the appropriate internal standard

Is = Amount of internal standard added in nanograms

Vt = Volume of the total extract in microliters

Vi = Volume of the extract used for purging in microliters

Ws = Weight of sample extracted

RRF = Relative response factor from the initial calibration

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Table II

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

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Table III

Surrogate Spike Recovery Limits for Soils and Solids Samples

Surrogate Compound	Soils/Solids
4-Bromofluorobenzene	74-121
Dibromofluoromethane	80-120
Toluene-d8	81-117
1,4-Dichloroethane-d4	80-120

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Figure 2 - (Continued)

EPA SW846 METHOD 8260A
INITIAL CALIBRATION
ULTRA STANDARDS (cont'd)

compound name	std mix	stock ppm	300 ppb	100 ppb	50 ppb	20 ppb	4 ppb
Ethylbenzene	VOC	200	300	100	50	20	4
Hexachlorobutadiene	MIX	200	300	100	50	20	4
Isopropylbenzene (Cumene)		200	300	100	50	20	4
p-Isopropyltoluene		200	300	100	50	20	4
Methylene Chloride		200	300	100	50	20	4
Naphthalene		200	300	100	50	20	4
n-Propylbenzene		200	300	100	50	20	4
Styrene		200	300	100	50	20	4
1,1,1,2-Tetrachloroethane		200	300	100	50	20	4
1,1,2,2-Tetrachloroethane		200	300	100	50	20	4
Tetrachloroethene		200	300	100	50	20	4
Toluene		200	300	100	50	20	4
1,2,3-Trichlorobenzene		200	300	100	50	20	4
1,2,4-Trichlorobenzene		200	300	100	50	20	4
1,1,1-Trichloroethane		200	300	100	50	20	4
1,1,2-Trichloroethane		200	300	100	50	20	4
Trichloroethene		200	300	100	50	20	4
1,2,3-Trichloropropane		200	300	100	50	20	4
1,2,4-Trimethylbenzene		200	300	100	50	20	4
1,3,5-Trimethylbenzene		200	300	100	50	20	4
m-Xylene		200	300	100	50	20	4
o-Xylene		200	300	100	50	20	4
p-Xylene		200	300	100	50	20	4
Bromomethane	GAS	200	300	100	50	20	4
Chloroethane	MIX	200	300	100	50	20	4
Chloromethane		200	300	100	50	20	4
Dichlorodifluoromethane		200	300	100	50	20	4
Trichlorofluoromethane		200	300	100	50	20	4
Vinyl Chloride		200	300	100	50	20	4
2-Chloroethyl Vinyl Ether	V3	1000	600	200	100	40	8
Acrolein		5000	3000	1000	500	200	40
Acrylonitrile		5000	3000	1000	500	200	40
Carbon Disulfide	V4	1000	300	100	50	20	4
Vinyl Acetate		1000	300	100	50	20	4
Methyl Iodide		1000	300	100	50	20	4
Freon 113		2000	600	200	100	40	8
2-Butanone	V5	1000	600	200	100	40	8
2-Hexanone		1000	600	200	100	40	8
4-Methyl-2-Pentanone		1000	600	200	100	40	8
Acetone		1000	600	200	100	40	8
Cyclohexane	V9	1000	300	100	50	20	4
Ethyl Acetate		1000	300	100	50	20	4
Ethyl Ether		1000	300	100	50	20	4
Isoamyl Acetate		1000	300	100	50	20	4
n-Propyl Acetate		1000	300	100	50	20	4
Benzyl Chloride		1000	300	100	50	20	4
Furan		1000	300	100	50	20	4
Hexane		1000	300	100	50	20	4
Heptane		1000	300	100	50	20	4

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Figure 2 (Continued)

EPA SW846 METHOD 8260A
INITIAL CALIBRATION
ULTRA STANDARDS (cont'd)

compound name	std mix	stock ppm	300 ppb	100 ppb	50 ppb	20 ppb	4 ppb
Methacrylonitrile	V11	2500	750	250	125	50	40
t-1,4-Dichloro-2-Butene		2500	750	250	125	50	40
t-Butyl Alcohol		5000	1500	500	250	100	80
Propionitrile		5000	1500	500	250	100	80
2-Propanol		5000	1500	500	250	100	80
Methyl t-Butyl Ether	MTBE	1000	300	100	50	20	4

ppb of analytical standard = stock ppm x ul stock / flask ml

Calibration Standard Conc. (ppb)	300	100	50	20	4
Surrogate Spiking Volume (ul)*	60	20	10	4	0.8

*Spiked directly into 5 ml syringe

ANALYST_____

DATE_____

(saved as file TS826A::DB)

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Analysis #0947, 1339
Initiated Date: 04/01/87
Effective Date: AUG 1 2 1996

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Toxicity Characteristic Leaching Procedure
TCLP Nonvolatile Leachates

Reference:

Method 1311, *Test Methods for Evaluating Solid Waste*, SW-846, USEPA, July 1992.

Scope:

This method is designed to determine the mobility of organic and inorganic nonvolatile contaminants in potentially hazardous waste. The extraction is performed over 18 hours.

Method Summary:

For liquid wastes (containing <0.5% solids), the TCLP extract is defined as the filtrate resulting from filtration of the waste through a 0.6- to 0.8-µm glass fiber filter.

For wastes containing ≥0.5% solids (and some liquid), the waste is filtered through a glass fiber filter and the filtrate is stored for later use. The alkalinity of the solid portion is determined and the result indicates which extraction fluid should be used. The solid is then extracted with a volume of extraction fluid 20× the weight of the solid. Following the extraction, the leachate is filtered through a glass fiber filter and the final and initial filtrates are combined.

For wastes which will obviously yield no liquid when subjected to pressure filtration, the sample is analyzed for alkalinity and extracted with a volume of appropriate extraction fluid at 20× the sample weight. The extract is then filtered and the leachate is defined as the filtrate.

3. Extraction Fluid #1

Glacial acetic acid (CH2COOH) ..... 11.4 mL

1 N sodium hydroxide (NaOH) ..... 128.6 mL

Add 11.4 mL of glacial acetic acid (ACS reagent grade) to approximately 500-mL deionized water in a 2000-mL volumetric flask. Add 128.6 mL of 1 N NaOH to this mixture and dilute to 2 L with deionized water. (This solution may be made up in large volumes in a 20-L jug. The ratio of acetic acid and NaOH to final volume must be maintained in that case).

The pH of this fluid must be 4.93 ± 0.05. If not, discard and remake. Record the preparation and the pH of the extraction fluid in the appropriate logbook. Make enough for use each day, and discard any extra.

4. Extraction Fluid #2

Glacial acetic acid (CH2COOH) ..... 11.4 mL

Add 11.4 mL of glacial acetic acid (ACS reagent grade) to approximately 500-mL deionized water in a 2000-mL volumetric flask. Dilute the solution to volume with deionized water. The pH of this fluid must be 2.88 ± 0.05. If not, discard and remake. Record the preparation and the pH in the appropriate logbook. Prepare as needed.

5. 1.0 N nitric acid (HNO_3)

Concentrated nitric acid (ACS reagent grade) ..... 64 mL

Slowly add 64 mL of concentrated HNO_3 to approximately 500-mL deionized water in a 1000-mL volumetric flask. Dilute the solution to volume with deionized water. Remake every 6 months. Store in a glass bottle in the reagent cupboard.

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6. Acid washed filters

The procedure may call for using acid washed filters if the leachate is to be analyzed for metals. Prepare the filter as follows:

a. Assemble the filtration apparatus with the filter in place.

b. Pour enough 1.0 N nitric acid to cover the filter.

c. Apply vacuum or pressure (whichever is appropriate) until the filter is dry.

d. Pour a minimum of 100-mL deionized water into the apparatus.

e. Apply vacuum or pressure until the filter is dry.

f. If a vacuum apparatus was prepared, discard the waste acid/water mixture and rinse the flask several times with deionized water. If a pressure filter was prepared, discard the waste acid/water mixture.

7. 5.0 N nitric acid (HNO_3)

Concentrated nitric acid (ACS reagent grade) ..... 320 mL

Slowly add 320 mL of concentrated HNO_3 to approximately 500-mL deionized water in a 1000-mL volumetric flask. Dilute the solution to volume with deionized water. Remake every 6 months. Store in a glass bottle in the reagent cupboard.

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Safety Precautions:

Follow routine safety steps. Special care must be taken when mixing the acid solution. Wear gloves, lab coat, and safety glasses when preparing the solution and handling samples. Read all lab notes and follow instructions carefully. Avoid skin contact or breathing the vapors from any of the reagents or samples. Use the appropriate ventilation system (bench top or hood) when instructed, if the sample looks suspicious (plating waste contains cyanide), or is particularly odoriferous.

If the sample fumes or reacts in any other way when the acid is added during the extraction procedure, vent the sample periodically until the reaction is no longer evident.

Discard or send for repair any glassware that is chipped, flawed, or broken.

Determining the Amount of Extract to Prepare:

1. Look up the leachate sample in the Wang in-house computer system, under the verification program.

2. Note the analyses requested. Preferred sample aliquots are listed below:

Analysis	# of Bottles	Bottle Code	Type of Bottles	Volume
pH, Hexavalent Chromium	1	04	500 mL plastic, not preserved	500 mL
Phenols (just 434)	2	084	40-mL vials	80 mL (40 in each)
Phenols (434 and 491)	2	03	1000-mL glass	1000 mL
Metals	1	08	500 mL Nalgene	500 mL
BNA	1	45	1000-mL brown glass	1000 mL
Pesticides/ Herbicides	1	30	1000-mL brown glass	500 mL

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If the sample(s) is entered for #4173, see Appendix I for additional information.

3. Add up the sample volume required and divide by 20 to determine how much sample must be extracted.

4. If the amount of extraction fluid generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the leachate from each extraction must be combined and then aliquoted for analysis.

Preliminary Solids Determination:

If the waste appears to be liquid and seems to contain a low percentage of solids, perform the solids determination. The *Federal Register* TCLP method defines percent solids as that fraction of a waste sample from which no liquid may be forced out by an applied pressure.

1. Preweigh the filter and the filtrate collection container to be used and record the weight. If vacuum filtration will be used, preweigh the filter in a gooch crucible.

2. Weigh out a subsample of the waste (minimum 100 g).

   a. Tare a 100-mL graduated cylinder.

   b. Weigh out 100 g of sample (if there is adequate sample for the leachate and other analyses required. If not, use proportionally less) in the graduated cylinder.

   c. Pour the sample into the filter apparatus.

   d. Reweigh the graduated cylinder - Subtract the weight of the sample sticking to the glass from the initial weight of sample to get the weight of the sample filtered.

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4. Add 3.5 mL 1.0 N HCl, stir, cover with a watch glass, and heat to 50°C (and keep the sample at 50°C for 10 minutes).

5. Allow the slurry to cool to room temperature. Measure the pH and record. If the pH is <5, Extraction Fluid #1 will be used for the leaching procedure. If the pH is >5, Extraction Fluid #2 will be used.

6. Quantitatively transfer the rest of the solids or a portion of the solids to an extraction vessel.

7. Slowly add the appropriate extraction fluid at a volume 20× the weight of the solid.

8. Close the extraction bottle tightly and place in a tumbler (rotating 30 ± 2 rpm) for 18 ± 2 hours. Ambient temperature must be maintained at 23° ± 2°C (69.8° to 77°F) during the extraction period.

9. Following the 18 ± 2 hour extraction, filter the solution through a glass fiber filter, again taking care to not exceed 50 psi if using the pressure filter. This filter can be changed if necessary. The filter(s) must be acid washed if the extract is to be analyzed for metals.

10. Add in the appropriate amount of initial filtrate:

$$\textit{Volume of initial filtrate to be added} = \frac{\textit{Volume of leachate collected (mL)}}{\textit{Total volume of leachate (mL)}} \times \frac{\textit{Weight of solid used in leachate (g)}}{\textit{Weight of solid from initial filtration}} \times \textit{mL of initial filtrate}$$

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11. If the initial filtrate does not mix (is not miscible) with the extraction fluid, do not mix the two together. Contact the group leader and technical services. Each phase must be analyzed separately; therefore each phase will be entered as a sample.

12. Determine and record the pH of the leachate.

13. Subsample and preserve the leachate for the appropriate analyses as per SOP-IC-002.

C. If the sample has no free standing liquid.

1. Weigh out 5.0 g of the solid into a 150- or 250-mL beaker.

2. Add 96.5-mL deionized water, cover with a watchglass, and stir for 5 minutes. Measure and record the pH. If the pH is <5, go to step 5 and use Extraction Fluid #1. If the pH is >5 go to step 3.

3. Add 3.5 mL 1.0 N HCL, stir, cover with a watch glass, and heat to 50°C (and keep the sample at 50°C for 10 minutes).

4. Allow the slurry to cool to room temperature. Measure the pH and record. If the pH is <5, use Extraction Fluid #1 in step 6. If the pH is ≥5, use Extraction Fluid #2.

5. Weigh out a minimum of 100 g of the waste (more if a large volume of leachate is required for analysis).

6. Slowly add the appropriate extraction fluid at a volume 20× the weight of the solid.

7. Close the extraction bottle tightly, and place in a tumbler (rotating 30 ± 2 rpm) for 18 ± 2 hours. Ambient temperature must be maintained at 23° ± 2°C (69.8° to 77°F) during the extraction period.

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8. Following the 18 ± 2 hours extraction, filter the solution through a glass fiber filter taking care to not exceed 50 psi if using the pressure filter. This filter can be changed if necessary. The filter(s) must be acid washed if the extract is to be analyzed for metals.

9. Measure and record the pH of the extract.

10. Subsample and preserve the leachate for the appropriate analyses as per SOP-IC-002.

Quality Assurance:

1. A blank will be performed every 20th time an individual extraction vessel is used. A logbook of vessel usage is kept. Each time a vessel is used, record that date. After 20 usages, prepare a blank in that vessel and record the blank number in the logbook.

2. Record all the sample numbers in the batch logbook. One sample in the batch should be designated as the waste type spike and spiked as per the notes in Figure 1. Choose the first sample in the batch that has sufficient volume. Each subsample type in the batch must have a spike. Record the lot number of the spike solution used on the batch sheet. Photocopy the sheet and deliver the photocopies to each department involved in the analyses.

3. The subsamples for BNA must be delivered to that extraction lab as soon as they are finished, along with 1500 mL of the extraction fluid used in the leachate process.

4. Extraction of the solid phase should be initiated as soon as possible after initial filtration.

5. All instruments used in this procedure (i.e., pH meter and balance) should be calibrated according to an approved laboratory plan.

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6. All quality control measures described in the appropriate analytical methods shall be followed.

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Prepared by: Pamona Nayman Date: 8/5/96

Approved by: _____ Date: 8/7/96

Approved by: _____ 972 Date: 8/9/96

Figure 1

Bottle Code	Analysis Type	Preservative	Extraction[a]	Volume for Subsample (mL)	Minimum Subsample (mL)
01	TOC	H_2SO_4	ASTM	125	125
04	pH, solids	—	ASTM	500	100
04	Cr+6	—	TCLP	500	100
06	Oil & Grease	HCL	ASTM	800	500
08	Metals	5N HNO_3	TCLP	500[b]	100
11	COD	H_2SO_4	ASTM	250	150
13	TOX	H_2SO_4+$Na_2S_2O_3$	ASTM	250	250
30	Pest/Herb	$Na_2S_2O_3$	TCLP	500[c]	200
43	Formaldehyde	—	TCLP	500	250
45	BNA	$Na_2S_2O_3$	TCLP	1000[d]	500
81	Ammonia (NH_3-N)	H_2SO_4	ASTM	40 × 2	40
83	Cyanide (CN-)	NaOH	ASTM	40 × 2	40
84	Phenol (O-OH)	H_2SO_4	TCLP	40 × 2	40

[a] The extraction listed is the most commonly requested leachate for the analysis listed. If the analysis is requested on another type of leachate, have the coordinator double check with the client.

[b] If the sample is the waste type spike, prepare a second bottle with 400 mL of sample measured into it and 8 mL of each of the metals spiking solutions added to it.

[c] If the sample is the waste type spike, prepare a second bottle with 500 mL of sample measured into it and 0.5 mL of each of the pest/herb spiking solutions added to it.

[d] If the sample is the waste type spike, prepare a second bottle with 1000 mL of sample measured into it. The BNA prep area will spike the sample.

Appendix I

Leaching Procedure for Formaldehyde (EPA 8315)

Samples which will be analyzed for formaldehyde are extracted using the TCLP protocol with the following modifications:

- Only 25 g of sample is extracted.
- Extraction Fluid #1 is used for all samples (therefore steps 2-5 in Procedure B and 1-4 in Procedure C may be omitted).
- The extract is not preserved in any way at the end of the process.
- An extraction blank is prepared with each set of samples being extracted for formaldehyde.
- If the samples required prefiltration, give the batch sheet **and** a photocopy of the leachate data page(s) to the pesticide prep coordinator.

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Analysis #1055-200.9
Initiated Date: 10/12/92
Effective Date: FEB 25 1993

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Lead in Drinking Water and Wastewater by Graphite Furnace

Purpose:

To describe the procedure for determining lead in drinking water and wastewaters.

References:

1. EPA 600, Method 200.9.

2. EPA 600, Method 239.2.

Scope:

This procedure is applicable to the determination of lead in potable and nonpotable waters. A typical method detection limit is 0.5 ug/l. The limit of quantitation is 1.0 ug/l, and the linear range is to 50 ug/l. Higher concentrations can be determined by dilution.

Basic Principles:

A small volume of acidified sample is deposited onto a L'vov platform in the graphite furnace tube. Chemical modifier is added and the tube is electrically heated through a controlled temperature cycle. The sample is dried, ashed, and atomized. The atomic vapor absorbs light from a hollow cathode lamp. The absorbance is proportional to concentration. The concentration of lead in the solution is calculated from a standard curve. The chemical modifier reduces matrix interferences.

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Reagents:

1. Lead Stock Standard, 1000 mg/l Baker Analyzed atomic absorption standard or equivalent. Store at room temperature.

2. Lead Verification Stock, 1000 mg/l AA Standard from a different manufacturer than the stock standard. Store at room temperature.

3. Nitric Acid, Concentrated, Baker Instra Analyzed or equivalent. Store at room temperature.

4. Magnesium Nitrate, 6 Hydrate, crystal, Baker Analyzed Reagent or equivalent. No storage requirement.

5. Ammonium Phosphate, monobasic crystal, Baker Analyzed Reagent or equivalent. No storage requirement.

6. Ammonium Phosphate/Magnesium Nitate Solution:

   Dissolve 8 grams ammonium phosphate and 0.7 grams magnesium nitrate in deionized water. Dilute to one liter. This solution is stable for one month at room temperature.

7. 100,000 ug/l Intermediate Lead Standard:

   Into a 100 ml volumetric flask containing approximately 50 ml of deionized water add 1 ml concentrated nitric acid. Pipet 10.0 ml of 1000 mg/l lead stock. Bring to volume with deionized water and mix. This solution may be stored at room temperature for six months.

8. 1,000 ug/l Intermediate Lead Standard:

To a 500 ml volumetric flask containing approximately 250 ml of deionized water add 5 ml concentrated nitric acid. Pipet 5.0 ml of 100,000 ug/l lead intermediate standard. Bring to volume with deionized water and mix. This solution may be stored at room temperature for six months.

9. Calibration Standards:

Add approximately 100 ml of deionized water and 2 ml of concentrated nitric acid to each of seven 200 ml volumetric flasks. Add the following volumes of 1,000 ug/l intermediate lead standard to achieve the listed concentrations:

ml of 1,000 ug/l intermediate	Concentration
0.0	Calibration Blank
0.2	1.0 ug/l (CRA)
1.0	5.0 ug/l
2.0	10.0 ug/l
4.0	20.0 ug/l (CCV)
5.0	25.0 ug/l
10.0	50.0 ug/l

NOTE: Only the 5, 10, 25 and 50 ug/l are used in the calibration curve. The 1.0 ug/l is a detection limit check and the 20.0 ug/l is a continuing calibration verification standard. These solutions are stable for one month at room temperature.

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10. Initial Calibration Verification (ICV):

Use a stock standard from a different source than used for the calibration standards. Dilute to 20.0 ug/l in 1% nitric acid. This solution is stable for one month at room temperature.

Proper standard labeling requirements can be found in SOP-QA-110.

Safety Precautions:

Please consult the Inorganics Manual, Safety SOP (SOP-IO-011) for specific safety protocol and procedures.

Procedure:

Sample Preparation:

Sample holding time and storage conditions are documented in SOP-IO-001. If samples have a turbidity of <1 NTU no digestion is needed. 100 ml (or less if sample volume is limited) should be acidified by adding 1 ml concentrated nitric acid per 100 ml of sample. For samples with turbidity ≥1 NTU or wastewaters, prepare by an alternate method. The samples should be batched in groups of 20 or less with one duplicate and one matrix spike (10 ug/l) for each 10 or less samples. Each batch of 20 samples or less should contain one Laboratory Control Sample (LCS) (10 ug/l) and one method blank.

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Suggested GFAA Program Parameters:

The following parameters are for the Hitachi Z-9000. For specific instructions on operating the instrument please refer to the manufacturer's manual and to the appropriate instrument SOP (MC-IO-011).

Lead measured at 283.3 nm

Signal Mode	BKG Corrected
Measurement Mode	Working Curve
Sample Blank	No
Standard Replicates	2
Sample Replicates	2
Statistics	Mean, SD, RSD
Sample Volume	20 ul
Dilution	Off
Conc. Times	1
Modifier Addition	Yes
Cup Position	Depends on # of Samples
Reslope Standard	No
Reslope Interval	1
Cuvette	Pyro
Firings	Depends on number of cycles
Result on Record	Yes (Conc. + Abs.)
Chart Speed	1
Data Communication	Off
Calculation	Peak Area

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Temperature Program:

Number	Stage	Temperature (C) Start	End	Time (sec.)
1	Dry	80	100	3
2	Dry	100	110	20
3	Dry	110	120	25
4	Dry	120	130	15
5	Ash	230	270	4
6	Ash	270	850	3
7	Ash	800	800	10
8	Ash	200	200	3
9	Atomize	2000	2000	3
10	Clean	3000	3000	3

Carrier Gas = 200 ml/min. Interrupt Gas = 6 ml/min.
Gas Type - Argon

Notes:

These parameters are guidelines and may need adjustment to achieve the best performance (sensitivity and reproducibility). With the Hitachi Z-9000 these parameters generally produce a response of between .045 and .055 absorbance for a 10 ug/l lead standard. A series of ten injections of a 10 ug/l standard can be expected to give an RSD of approximately 2 to 3 percent.

Quality Assurance:

Instrument Stability:

A 10 ug/l standard must be run five times before calibration. If an RSD of ≥5% is obtained, adjustments must be made, and the

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stability check rerun. Repeat this procedure until an RSD of <5% is obtained.

NOTE: Set the autosampler for ten injections and calculate the mean of each pair and the RSD. Document on the printout.

Initial Calibration Verification:

After calibration an independent standard (20 ug/l) must be run. The ICV result must be within ± 10% (18 to 22 ug/l). If not, correct the problem and recalibrate. After the ICV, an initial calibration blank (ICB) is run. If this exceeds the LOQ, correct the problem and recalibrate.

Continuing Calibration Verification:

After the ICB and then every ten samples the 20 ug/l calibration standard must be run. The result must be within ± 10% (18 to 22 ug/l). If a CCV is out of the acceptable range, the samples prior to the CCV and since the last good CCV must be reanalyzed. A continuing calibration blank (CCB) must be run after each CCV. If the CCB result is greater than the LOQ or less than the negative LOQ, all samples prior to the CCB and since the last good CCB must be rerun.

CRA:

A standard at the LOQ (1.0 ug/l) must be analyzed following the ICV. There are presently no recovery requirements for this solution.

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Reagent Blank:

A blank of 1% nitric acid (prepared with the samples) must be run for every batch of 20 samples or less. If the Blank reading exceeds the LOQ the samples must be re-analyzed.

Laboratory Fortified Blank (same as an LCS):

This is a reagent blank with 10 ug/l of analyte added. This must be analyzed with each batch of 20 samples or less. Until 30 batches of samples are analyzed the control limit is ± 20% (8 to 12 ug/l). Once 30 fortified blanks have been determined the control limits become the mean ± 3 times the standard deviation. After each ten new batches the control limit is updated to the last 30 data points. All data should be included in calculating the limits unless there is evidence of miss-spiking or other laboratory error. The limit calculations are performed in a Quattro Pro spreadsheet called "Pb in Drinking Water Controls" and must be updated by the analyst.

Duplicate:

One sample in every ten or less should be analyzed in duplicate.

Laboratory Fortified Matrix (same as matrix spike):

One sample in every ten or less should be spiked at 10 ug/l. If this recovery is not within the fortified blank limits and the fortified blank is acceptable, the samples of that type should be run by the method of standard additions.

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Calculations:

The results are reported in ug/l or mg/l (ug/l divided by 1000). If dilutions are made, the final result is the instrument reading multiplied by the dilution factor. Results should be rounded to the tenth of a ug/l.

Statistics:

EPA reports an average recovery of 101.8% and an RSD of 0.7% for samples spiked at 10 ug/l.

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IO METHODS #2
022493

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Prepared by: _____ Date: 2/24/93

Approved by: _____ Date: 2/25/93

Approved by: _____ Date: 2/25/93

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Analysis #1055, 1155
Initiated Date: 03/01/88
Effective Date: AUG 0 3 1995

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Lead by Graphite Furnace

Purpose:

The purpose of this analysis is to detail the methods and procedures used to analyze lead by graphite furnace.

Background Information:

The methods described in this analysis are adopted from the following references:

1. Method 239.2, CLP SOW ILM04.0.
2. Method 239.2, *Methods for Chemical Analysis of Water and Wastes*, EPA 600/4-79-020, June 1991.
3. Method 7421, *Test Methods for Evaluating Solid Waste*, EPA SW-846, September 1986.

The calibration range for this method is 3 to 60 µg/L. The approximate instrument detection limit for this method is 1 µg/L. The following limits of quantitation are used as per the requirements of the governing regulatory agency:

Waters	3. µg/L
CLP Soils	0.6 mg/kg
Soils	1. mg/kg

Scope:

This procedure is applicable to the determination of lead in waters, wastewaters, and leachates (#1055) and soils (#1155).

Basic Principles:

A small amount of digested sample is introduced into a graphite tube. The tube is then heated electrically enabling a precise and accurate heat rise. After a short dry step, the sample is atomized at a high temperature resulting in light absorption at a specific wavelength which can be measured quantitatively. The combination of temperature programming and chemical matrix modification can help eliminate matrix interferences allowing determinations at the parts per billion and parts per trillion ranges.

Reagents:

1. Nitric acid, 70.0% to 71.0%, Baker Instra-Analyzed or equal quality, store at room temperature

2. Hydrogen peroxide, 30%, analytical reagent grade, keep refrigerated

3. Ammonium phosphate, monobasic crystal, Baker Analyzed Reagent or equal quality, no storage restrictions

4. Magnesium nitrate, 6 hydrate, crystal, Baker Analyzed Reagent or equal quality, no storage restrictions

5. Deionized water, type 2 or better

Safety Precautions:

Please consult the Inorganics Manual, Safety SOP (SOP-IO-011, "Inorganic Analysis Safety Procedure") for specific safety protocol and procedures.

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Procedure:

Please consult the Inorganics Manual SOPs regarding sample preservation, holding times, storage conditions (SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses"), and digestion procedures (Analyses #1056, #1156, #5704, #5715, and #5710).

Operations:

1. Preparation of standard solutions

   NOTE: Detailed procedures for preparation of standard solutions are found in the Inorganics Manual SOPs (SOP-IO-007, "Preparation of Standards and Solutions") Sections F, G, and H.

   Proper labeling requirements can be found in SOP-QA-110, "Reagents."

2. Program parameters

   Lead is analyzed using a Varian SpectrAA 400 or 400Z series instrument. Refer to Inorganic Operators Manual GFAA MC-IO-005, "Atomic Absorption Using the Varian SpectrAA 800 Zeeman, Varian SpectrAA 400 Zeeman, and Varian SpectrAA 400 D_2 Graphite Furnaces," for specific instrument operations. The instrument parameters are preset for the program that was developed for lead using the Photron hollow cathode lamp. The parameters for this program are as follows:

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Pb

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Area
Lamp Position	1 to 8
Lamp Current (ma)	2 to 4
Slit Width (nm)	0.5
Slit Height	Normal
Wavelength (nm)	283.3
Sample Introduction	Sampler Automixing
Time Constant	0.05
Measurement Time (sec)	1.0
Replicates	2
Background Correction	Yes

Autosampler Parameters
Volumes (μL)

	Solution (90 μg/L stock)	Blank Solution	Modifier ($[NH_4]H_2PO_4 + Mg[NO_3]_2$)	Concentration (μg/L)
Blank	0	30	4	0
Standard 1	1	29	4	3
Standard 2	3	27	4	9
Standard 3	5	25	4	15
Standard 4	10	20	4	30
Standard 5	20	10	4	60

Hot injection is used at 95°C with an injection rate of 10 (10 μL/15 seconds).

A 30-μL sample aliquot is used with 4 μL of modifier.

Furnace Parameters

Step No.	Temperature (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	120	5.0	3.0	Normal	No
2	120	20.0	3.0	Normal	No
3	220	15.0	3.0	Normal	No
4	220	20.0	3.0	Normal	No
5	350	8.0	3.0	Normal	No
6	900	6.0	3.0	Normal	No
7	900	8.0	3.0	Normal	No
8	2400	0.8	0.0	Normal	Yes
9	2400	2.0	0.0	Normal	Yes
10	2500	0.2	3.0	Normal	No
11	2500	3.0	3.0	Normal	No

3. Notes

The concentration values and instrument conditions are for a Varian SpectrAA 400 spectrophotometer, GTA 96 tube atomizer, GTA programmable sample changer, and IBM PS2 or compatible data station. The analytical range and detection limit were determined using a 30 μL injection volume, purge gas interrupt, and a pyrolytically coated graphite tube with a forked platform.

The use of background correction is required. This program is used with the Varian 400 Zeeman graphite furnace with the IBM PS2 Model 30 computer for analyzing EPA drinking waters and may be used for any other sample matrices.

Changes in furnace programs may be necessary to accommodate the differences in resistivity of the graphite tubes or to achieve better spike recoveries on more complex matrices. Lamp currents may have to be adjusted to comply with the manufacturer's specifications upon

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replacement of hollow cathode source lamps. Changes in turret position may be necessary to accommodate sequenced runs with available lamp turret or lamp socket failure. All changes from the standard analytical program will be documented on the raw data.

Quality Assurance:

Please consult the Graphite Furnace QA section (SOP-IO-004, "QA for Graphite Furnace") in the Inorganic Operators Manual for specific QA protocol and procedures. For other QA requirements not specific to graphite furnace, consult the QA section of this manual (SOP-IO-005, "Department 23 Quality Control Procedures").

Calculation:

Please consult the Graphite Furnace QA section in the Inorganic Operators Manual for the proper equations and analytical flow chart (SOP-IO-004).

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Prepared by: [signature] 744 Date: 8/2/95

Approved by: [signature] 383 Date: 8/2/95

Approved by: [signature] 972 Date: 8/2/95

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Where quality is a science.

Analysis #1056
Initiated Date: 04/21/88
Effective Date: FEB 2 2 1996

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Sample Preparation of Wastewater for Graphite Furnace Analysis of Metals

Reference:

1. USEPA CLP SOW No. ILM02.1, Exhibit D, Section III, Part A.1., Page D-5.

2. USEPA CLP SOW No. ILM04.0, Exhibit D, Section III, Part A, Page D-5.

Scope:

This acid digestion procedure is used to prepare wastewater samples for measurement of metals by graphite furnace following CLP protocol.

Basic Principles:

The samples are digested using nitric acid and 30% hydrogen peroxide to dissolve metals.

Apparatus and Reagents:

For reagent preparation, shelf life, and storage conditions, see SOP-IO-007, "Preparation of Standards and Solutions."

1. 250-mL beakers or other appropriate beakers

2. Watch glasses

3. Nitric Acid, HNO_3, 70.0%-71.0%, Baker Instra-Analyzed reagent, 1.428 g/mL, or equivalent

4. Nitric Acid (1:1) - Add 500 mL of HNO_3 to 500 mL of deionized water

5. Hydrogen peroxide, 30% H_2O_2

6. 100-mL graduated cylinders or other appropriate graduated cylinders

7. 100-mL volumetric flasks or other appropriate Class A volumetric flasks

8. 125-mL Nalgene bottles or other appropriate Nalgene bottles

9. Hot plates

NOTE: As long as the correct ratios are maintained, solutions may be prepared using multiples of indicated weights and volumes.

Safety Precautions:

Refer to SOP-IO-011, "Inorganic Analysis Safety Procedure."

Procedure:

For sample preservation, storage conditions and holding times, see SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses."

Shake sample well. Use a 100-mL graduated cylinder to transfer 100 mL of well-mixed sample into a 250-mL beaker. Add 1 mL of (1:1) HNO_3 and 2 mL of 30%

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H_2O_2. Place the beaker on a hot plate and heat at about 95°C for approximately 2 hours or until the sample volume is reduced to between 25 and 50 mL, making certain that the sample does not boil.

Allow to cool. Transfer the solution to a 100-mL volumetric flask. Adjust volume to the mark with deionized water and mix. Transfer the solution to a Nalgene bottle. The sample is now ready for analysis.

NOTE: For soluble metals analysis, filter unpreserved sample through 0.45-micron filter paper. Adjust the filtered sample to pH 2 or less with nitric acid preserving solution. Measure an appropriate volume of sample and digest as normal.

NOTE: If insufficient sample is submitted to allow using the method-stated volume or the sample contains high solids, one may use a smaller aliquot of the sample. Samples may be concentrated to meet lower than normal limits if approval is obtained from the client. Make appropriate acid, reagent, and spike volume adjustments based on sample final volume.

Quality Assurance:

Perform a method blank, sample duplicate, sample matrix spike, and laboratory control sample with every 1056 (CLP) digestion batch (20 samples or less).

1056.W60
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Prepared by: Eugene K. Abel Date: 2-18-96

Approved by: Ramona Nayman Date: 2/19/96

Approved by: 972 Date: 2/22/96

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Analysis #1156
Initiated Date: 03/01/88
Effective Date: APR 2 5 1996

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Sample Preparation of Soil/Sediment for Graphite Furnace Analysis of Metals

Reference:

1. USEPA CLP SOW No. ILM02.1, Exhibit D, Section III, B.1, D5-8.

2. USEPA CLP SOW No. ILM04.0, Exhibit D, Section III, Part B, D5-7.

Scope:

This acid digestion procedure is used to prepare soil/sediment/sludge samples for measurement of metals by graphite furnace (GF).

Basic Principle:

A representative 1 g (as-received) sample is digested with nitric acid and hydrogen peroxide. The digestate is then refluxed with nitric acid to complete the dissolution of metals for GF analysis.

Apparatus and Reagents:

For reagent preparation, shelf life, and storage conditions, see SOP-IO-007, "Preparation of Standards and Solutions."

1. 250-mL beakers or other appropriate beakers

2. Watch glasses

3. Nitric Acid, HNO_3, 70.0%-71.0%, Baker Instra-Analyzed reagent, 1.428 g/mL, or equivalent

4. Nitric Acid (1:1) - Add 500 mL of HNO_3 to 500 mL of deionized water

5. Hydrogen Peroxide, 30% H_2O_2, Fisher, certified ACS or equivalent

6. Whatman No. 41 filter paper or equivalent

7. Funnels

8. 200-mL volumetric flasks or other appropriate volumetric flasks

9. 250-mL Nalgene bottles or other appropriate Nalgene bottles

10. Hot plates

11. Balance, capable of reading 0.01 g

12. Nitric Acid (2%) - Add 400 mL of concentrated HNO_3 to 16 L (16,000 mL) of deionized water

NOTE: As long as the correct ratios are maintained, solutions may be prepared using multiples of indicated weights and volumes.

Safety Precautions:

Refer to SOP-IO-011, "Inorganic Analysis Safety Procedures."

Procedure:

For sample preservation, storage conditions, and holding times, see SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses."

Weigh 1 g (0.95-1.05 g to the nearest 0.01 g) of a thoroughly homogenized, as-received sample into a 250-mL beaker. Add 10 ml of (1:1) HNO_3, swirl to mix, and cover with a watch glass. Heat the sample to approximately 95°C and reflux for

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about 10 minutes without boiling. Allow the sample to cool somewhat, add 5 mL of concentrated HNO_3, with the watch glass on reflux for about 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

After the second reflux step has been completed and the sample has cooled somewhat, add about 2 mL of deionized water and about 3 mL of 30% H_2O_2. Heat cautiously until effervescence subsides.

Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Add a total of 10 mL of 30% H_2O_2.

Continue heating for approximately 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker. Add about 10 mL of deionized water, then warm the mixture for approximately 10 minutes. Allow to cool somewhat.

Filter through a Whatman No. 41 filter paper into a 200-mL volumetric flask containing 100 mL of 2% HNO_3 solution. Wash the beaker, residue, and paper thoroughly with deionized water. Adjust volume to the mark with deionized water and mix. Transfer the solution to a 250-mL Nalgene bottle. The sample is now ready for analysis.

NOTE: For non-CLP samples when special limits of quantitation are required by the client, use more sample weight.

NOTE: Typically use 5 g for samples of liquid consistency.

NOTE: Dry solvents on a steam bath before digesting.

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Quality Assurance:

Perform a method blank, sample duplicate, sample matrix spike, sample matrix spike duplicate, and laboratory control sample with every digestion batch (20 samples or less).

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Prepared by: Eugene K. Abel Date: 1-23-94

Approved by: [illegible] Date: 1-24-94

Approved by: Kathleen M. [illegible] Date: 1/31/94

Analysis #5715
Initiated Date: 01/04/94
Effective Date: FEB 2 2 1996

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Sample Preparation of Potable Water and NPDES Wastewater for Graphite Furnace Analysis of Total Metals

Reference:

Methods for Chemical Analysis of Water and Wastes, USEPA 600/4-79-020, Section 200.0, Part 4.1.3, Office of R&D, USEPA-EMSL, Cincinnati, Ohio, Revised March 1983.

Scope:

This acid digestion procedure is used to prepare potable water and NPDES wastewater samples for measurement of total metals by graphite furnace.

Basic Principles:

A mixture of nitric acid and the sample is refluxed in a covered beaker at low volume to dissolve metals. It is cooled and brought up to volume with deionized water.

Apparatus and Reagents:

For reagent preparation, shelf life, and storage conditions, see SOP-IO-007, "Preparation of Standards and Solutions."

1. 250-mL beakers or other appropriate beakers

2. Watch glasses

3. Nitric Acid, HNO_3, 70.0%-71.0%, Baker Instra-Analyzed reagent, 1.428 g/mL, or equivalent

4. 50-mL graduated cylinders or other appropriate graduated cylinders

5. 50-mL volumetric flasks or other appropriate Class A volumetric flasks

6. 60-mL Nalgene bottles or other appropriate Nalgene bottles

7. Hot plates

Safety Precautions:

Refer to SOP-IO-011, "Inorganic Analysis Safety Procedures."

Procedure:

For sample preservation, storage conditions, and holding times, see SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses."

Shake sample well. Use a 50-mL graduated cylinder to transfer 50 mL of well-mixed sample into a 250-mL beaker. Add 1.5 mL of HNO_3. Place the beaker on a hot plate and cautiously evaporate to low volume (10 to 20 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 1.5-mL portion of HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

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Continue heating (refluxing) for approximately 15 minutes. Uncover the beaker and evaporate to low volume (10 to 20 mL), not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 5 mL of deionized water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

Allow to cool. Transfer the solution to a 50-mL volumetric flask. Adjust volume to the mark with deionized water and mix. Transfer to a Nalgene bottle. The sample is now ready for analysis.

NOTE: For soluble metals analysis, filter unpreserved sample through 0.45-micron filter paper. Adjust the filtered sample to pH 2 or less with nitric acid preserving solution. Measure an appropriate volume of sample and digest as normal.

NOTE: If insufficient sample is submitted to allow using the method-stated volume or the sample contains high solids, one may use a smaller aliquot of the sample. Samples may be concentrated to meet lower than normal limits if approval is obtained from the client. Make appropriate acid, reagent, and spike volume adjustments based on sample final volume.

Quality Assurance:

Perform a method blank, sample duplicate, sample matrix spike, and laboratory control sample with every digestion batch (10 samples or less).

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Prepared by: Eugene K. Abel Date: 2-16-96

Approved by: Ramona Nayman Date: 2/19/96

Approved by: 972 Date: 2/22/96

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Analysis #2213, 2540, 6868, 6869, 6976, 1837
Initiated Date: 04/03/91
Effective Date: MAY 1 4 1996

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Purgeable Aromatics in Soil Samples

Reference:

Methods 5030A, 8000A, and 8020A, *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition.

Scope:

This method is suitable for analyzing solid samples for the purgeable aromatic compounds listed in Table I. The limit of quantitation for all (BTEX) compounds is 5 µg/kg (ppb) for soils. This method is a modification of 5030A/8020A in that a modified midlevel methanol extraction is used.

Basic Principles:

This method is based on the purge-and-trap gas chromatography method where an inert gas (helium) is bubbled through 25 mL of methanol sample extract/deionized water solution. The volatile aromatics are purged from the solution and trapped on a sorbent trap. The trap is then heated and backflushed with gas to desorb the trapped aromatics onto a suitable gas chromatographic column. The gas chromatograph is then temperature programmed to separate the aromatics which are then detected and quantified by a photoionization detector (PID).

Interferences:

Samples with petroleum fractions that are less volatile than gasoline (i.e., kerosene, #2 fuel oil) may cause baseline ramping and may affect surrogate recoveries. In addition, samples with high organic contents may cause foaming of the methanolic (sample) extract in the sparge vessel. These interferences can be minimized by increasing the methanolic dilution (from 25x). Limits of quantitation must be raised to reflect the final dilution.

(2) Level 2 - 20 µL (working calibration solution "A") to methanol blank (4 ppb)

(3) Level 3 - 50 µL (working calibration solution "A") to methanol blank (10 ppb)

(4) Level 4 - 10 µL (working calibration solution "B") to methanol blank (20 ppb)

(5) Level 5 - 20 µL (working calibration solution "B") to methanol blank (40 ppb)

2. Spike stock solution (5000 ppm)

   a. Follow steps 1.a. through 1.d. of calibration stock preparation.

   b. Working spike solution (10 ppm) - 20 µL spike stock to 10 mL methanol

   c. Add 20 µl of working spike solution to the sample syringe prior to injection for matrix spike and matrix spike duplicates. This is approximately 8 ppb in solution or 200 ppb in a soil sample.

3. Check standard stock solution (5000 ppm)

   a. Follow steps 1.a. through 1.d. of calibration stock preparation

   b. Intermediate check standard solution (250 ppm) - 0.50 mL check standard stock to 10 mL methanol

   c. Working check standard solution (25 ppm) - 1 mL intermediate solution to 10 mL methanol

   d. LOQ/MDL solution

      0.1 mL working check standard to 10 mL MeOH

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e. Add 10 µL of working solution (3.c.) to the sample syringe prior to injection yielding an approximate concentration of 10 ppb.

4. Alternate source check standard

This will be left to the analyst's discretion. The stock solution (and respective intermediate and working solutions) should either be prepared from neats with a different lot number from the same vendor, or may be purchased as a prepared working standard of known concentration(s).

5. Surrogate stock solutions (5000 ppm)

a. Trifluorotoluene (surr #1) - Weigh between 0.045 and 0.055 grams into a 10-mL volumetric flask and bring to final volume with methanol as described above.

b. *n*-Propylbenzene (surr #2) - Follow above procedure.

c. Fluorobenzene (surr #3) - Follow above procedure.

d. Working surrogate solution (100 ppm) - 0.5 mL of each surrogate stock solution to 25 mL methanol. Add 5 µL of working surrogate to each injection yielding an approximate concentration of 20 ppb in solution.

e. Alternate surrogate solutions, may be used to minimize interference. The solution preparation is as described above.

Sample Collection/Preparation:

A methanolic extract is diluted in deionized water before analysis. The methanol concentration is constant for all standards, blanks, and samples. See Analysis #2379, 5899, "Preparation and Extraction of Soil and Solid Samples for Determination of Purgeable Aromatics, Purgeable Halocarbons, and Gasoline Range Organics."

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Table I

Compounds Analyzed as Part of the Purgeable Aromatic Scan or as Individuals

Compound	Analysis #
Methyl tertiary-butyl ether (MTBE)*	1837, 2464
Benzene	2540
Cumene*	6868
Toluene	--
Styrene*	6869
Ethylbenzene	--
p-Xylene	--
m-Xylene	--
o-Xylene	--

*These compounds are not normally reported but can be reported upon client request.

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Table II

Purge-and-Trap Conditions

Trap Type	T*	CPB/CSS*
Purge Flow (mL/min)	40	40
Purge Time (min)	8	8
Dry Purge (min)	8	8
Desorb Preheat (°C)	170	245
Desorb Temp (°C)	180	250
Desorb Time (min)	4	4
Bake Temp (°C)	220	260
Bake Time (min)	9	9
Heated Value and Line Temps (°C)	100 to 130	100 to 130

*T = Tenax CBP = Carbopack B CSS = Carbosieve S-III

NOTE: Higher bake temperatures and times may be used to remove analytes which may carryover after the analysis of samples containing high levels of volatiles.

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Apparatus:

1. 40 mL screw-capped vials

2. Top-loading balance capable of weighing to 0.01 g with 100-g capacity.

3. Spatula

Safety Precautions:

Due to the potentially toxic nature of samples submitted by clients, safety precautions must be observed when handling samples. Protective eyewear and lab coats are required while subsampling. Gloves are optional, but recommended. Samples may also be subsampled in a fume hood if a strong odor is detected.

Procedure:

1. Each sample to be analyzed shall be received, unhomogenized, in a "zero-headspace" container to preserve any aromatics, and to ensure accuracy of the method. When one or both of the previous criteria cannot be achieved, an analysis comment shall be utilized to outline any inadequacies.

2. Weigh 20 g ± 0.1 g into a tared, 40-mL screw-capped vial. Record the sample number and the weight in the appropriate extraction notebook. Be sure the sample number is also written on the vial before setting the sample aside. Other information to be written into the extraction note includes: MeOH number, MeOH lot number, and batch number where MeOH was checked (see below). When it is not possible to use 20 g of sample due to the nature of the sample's matrix or limited sample volume, then smaller sample weights may be used. However, a minimum of 5 g must be utilized.

3. Add 20 mL of reagent methanol, which has been previously analyzed and found to be free of any volatile organics, to the vial containing the weighed

sample. Seal the screw cap on the vial to prevent leakage. If the sample is not dense enough to be covered by 20 mL of methanol, or if the sample absorbs the full 20 mL, a smaller sample weight may be used (see above).

NOTE: If less than 20 g of sample is available, maintain a 1:1 sample to MeOH ratio if possible.

4. Once the methanol has been added, shake the sample vigorously for 2 minutes. After the sample has settled for at least 1 hour, or until a sufficient MeOH layer has formed, decant the methanol into a 12-mL screw-capped vial. Be sure to record the sample number on the side of this vial also.

   NOTE: The MeOH may be left on the sample for a maximum of 24 hours before decanting is required. Centrifuging may be required to remove suspended particles from the MeOH layer.

5. Samples shall be stored in an explosion-proof refrigerator until analyzed. After analysis, decant the separated MeOH back into the original 40-mL vial and discard as hazardous waste. A sample shall not be discarded until after 30 days from submittal, or as per client requirements.

6. See specific analytical method for dilution information.

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Prepared by: Matthew E Dat[illegible] Date: 2/26/96

Approved by: [illegible] Date: 2/26/96

Approved by: [illegible] 972 Date: 2/26/96

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Analysis #4833
Initiated Date: 01/15/93
Effective Date: MAR 0 1 1994

Extraction Procedure for the Determination of GC Fingerprint on Petroleum Products in Soil or Solid Waste Matrices

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References:

1. EPA SW-846, Method 3550, Sonication Extraction.

2. Sonicator Ultrasonic Processor and Cell Disruptor Operations Manual, Sound Heat Systems, Inc., 1985.

Scope:

This procedure is applicable for petroleum products extraction from soils or solid wastes for TPH by GC/FID (Analysis #4703, 5256, and 5300), Petroleum Fuels by GC/FID (Analysis #4835), Qualitative GC Fingerprint (Analysis #2012), or TPH by GC/FID - DRO (Analysis #5321 or 5547).

The analysis method should be consulted for more specific application information. Many "nonpetroleum" organics are also extracted by this procedure and may interfere with petroleum product characterization and/or quantitation.

Basic Principles:

A measured weight of soil or solid waste sample is blended with anhydrous sodium sulfate. This mixture is then serially extracted with methylene chloride using a sonic probe disrupter. The serial extracts are combined, dried, and concentrated to

approximately 1 ml, which is brought to a final volume of 5 ml. The extracts are analyzed by Gas Chromatography using FID detection (by one of the methods listed in the Scope section).

Apparatus:

1. Sonic probe apparatus, Heat Systems-Ultrasonics, Inc. Model W-385, or equivalent

2. Kuderna-Danish - 500 ml, with three-ball Snyder column and 10 ml graduated ampule

3. Chromatographic column: Pyrex 20 mm ID, approximately 400 mm long with a plain stem

4. Water or steam bath

5. 11 cm diameter Buchner funnels

6. 11 cm Whatman 3 filter paper

7. 500 ml Filters flasks

Reagents:

1. Methylene Chloride - Pesticide quality or equivalent (Optima Grade)

2. Acetone - Pesticide quality or equivalent

3. Carbon Disulfide - Glass distilled, HPLC/spectral grade

4. Sodium Sulfate - Reagent grade prepared by baking at 400°C for 4 hours prior to use, to remove organic contaminants

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5. Surrogate Standards - Chlorobenzene, Standards Grade - Chem. Service, o-Terphenyl, 99% - Aldrich Chem. Co. or equivalent

6. Spiking concentration of surrogate standards:

   For stock solution, accurately weigh (to 0.1 mg) 0.8 g o-Terphenyl and 0.5 g chlorobenzene into a 200 ml volumetric containing several ml of acetone. Bring the flask to volume with acetone. This stock solution is stored in a freezer and is stable for six months.

   For a working solution of the surrogate standards, make a DF 10 of the above stock in acetone. This solution is stored in a freezer and is stable for six months.

7. Spiking Solution: See Reagents section of Methods 4835 and 4703 for the preparation of the spiking solution. Unless otherwise instructed, use 1.0 ml of this spiking solution in each sample.

Preparation of Glassware:

All glassware is soaked in dilute "Chem-solv" for at least four hours, rinsed several times with tap water, rinsed several times with deionized water. Kuderna-Danish glassware is oven dried at 115°C.

Sample Collection:

Samples should be collected in 8 oz glass containers with minimal headspace and kept cool (4°C) until extraction is performed. Holding time until extraction is 14 days. The analysis should be performed within 40 days from extraction.

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Safety Precautions:

All concentration steps should be carried out in a hood. Direct exposure of skin and respiratory tract to methylene chloride, carbon disulfide, or acetone should be avoided. Many sample materials to be analyzed by this method are "unknowns" and may contain toxic materials. Use good laboratory practice for handling of unknowns.

Extraction Procedures:

1. Soils and solid wastes are not homogenized before being subsampled for extraction.

2. Weigh 60 g of the solid into a 250 ml beaker. An attempt should be made to get a representative sampling of the contents of the sample container.

   NOTE: While weighing the sample please record visual and olfactory observations relating to its petroleum/organic content (such as strong gasoline smell, weak oil smell, dark oil material present, solvent-like odor, etc.).

3. Add 60.0 g of sodium sulfate to the beaker and stir thoroughly using a clean glass stirring rod. Record the LLI number, the initial weight, and any comments about the sample in the extraction log. Spiking solution as specified by the analytical method is added to the sample at this time (See Reagent #7). Add 1.0 ml of the surrogate working solution.

4. Add 100 ml of methylene chloride to the beaker.

5. Set up the sonic probe as described in the manual.

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6. Immerse the tip of the sonic probe approximately 1 to 2 cm below the surface of the liquid in the beaker containing the sample.

7. Disrupt the sample:

   a. If using the medium tip, turn to full output (10) for 3 minutes.

   b. If using the large tip, turn to (6) for 3 minutes.

8. Remove the probe from the sample.

9. Decant the liquid from the beaker into a filter funnel setup consisting of a Buchner funnel containing Whatman 3 filter paper. The funnel is connected to a 500 ml filter flask with a 4 to 6 psi vacuum.

   NOTE: Be sure to turn the vacuum off immediately after solvent is no longer observed dripping from the funnel.

10. Repeat Steps 4 through 9 using the same beaker, filter paper and Buchner funnel for each sample. Perform a third extraction in the same manner.

11. Before placing the probe into a new sample, rinse with both deionized water and acetone and wipe with a papertowel to remove any soil present from the previous sample.

12. Rinse the filter paper with 10 ml of methylene chloride.

13. Pour collected extracts into a Kuderna-Danish, add a glass boiling bead to the K-D, attach a 3-ball Snyder column and wet the column with methylene chloride.

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14. Place each K-D apparatus on a steam bath and concentrate the solvent to about 1 ml volume. Allow the apparatus to cool for at least ten minutes. Approximately 1 or 2 ml will condense into the ampule during this time. Remove the Snyder column and flask, rinsing the joints with a small amount of methylene chloride.

15. Quantitatively transfer the entire contents of the ampule to a 5.0 ml volumetric flask marked with the appropriate sample identification. Mix well and transfer a portion of the solution to a GC vial marked with the appropriate sample number. Transfer the rest of the solution to a 12 ml glass vial also marked with the appropriate sample number. The vial cap used should have a teflon liner. Store the 12 ml vial in the freezer--dated with the prep date, and put the GC vials in a vial file and store them in the GC Instrument Room.

    NOTE: If high levels of petroleum are expected based on preliminary observations, dilutions should also be prepared, bottled, and documented.

16. Prepare a DF 5 of the surrogate working solution with $MeCl_2$. Bottle a portion in a labeled GC vial so that it can be run with the batch of samples. Store the remainder of the solution in a 12 ml vial that has been appropriately labeled with the rest of the vials in the freezer.

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Calculations:

See analysis method.

Statistical Information:

See analysis method.

Table III

Surrogate Spike Recovery Limits for Soils and Solids Samples

Surrogate Compound	Soils/Solids
4-Bromofluorobenzene	74-121
Dibromofluoromethane	80-120
Toluene-d8	81-117
1,4-Dichloroethane-d4	80-120

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Figure 2 - (Continued)

EPA SW846 METHOD 8260A
INITIAL CALIBRATION
ULTRA STANDARDS (cont'd)

compound name	std mix	stock ppm	300 ppb	100 ppb	50 ppb	20 ppb	4 ppb
Ethylbenzene	VOC	200	300	100	50	20	4
Hexachlorobutadiene	MIX	200	300	100	50	20	4
Isopropylbenzene (Cumene)		200	300	100	50	20	4
p-Isopropyltoluene		200	300	100	50	20	4
Methylene Chloride		200	300	100	50	20	4
Naphthalene		200	300	100	50	20	4
n-Propylbenzene		200	300	100	50	20	4
Styrene		200	300	100	50	20	4
1,1,1,2-Tetrachloroethane		200	300	100	50	20	4
1,1,2,2-Tetrachloroethane		200	300	100	50	20	4
Tetrachloroethene		200	300	100	50	20	4
Toluene		200	300	100	50	20	4
1,2,3-Trichlorobenzene		200	300	100	50	20	4
1,2,4-Trichlorobenzene		200	300	100	50	20	4
1,1,1-Trichloroethane		200	300	100	50	20	4
1,1,2-Trichloroethane		200	300	100	50	20	4
Trichloroethene		200	300	100	50	20	4
1,2,3-Trichloropropane		200	300	100	50	20	4
1,2,4-Trimethylbenzene		200	300	100	50	20	4
1,3,5-Trimethylbenzene		200	300	100	50	20	4
m-Xylene		200	300	100	50	20	4
o-Xylene		200	300	100	50	20	4
p-Xylene		200	300	100	50	20	4
Bromomethane	GAS	200	300	100	50	20	4
Chloroethane	MIX	200	300	100	50	20	4
Chloromethane		200	300	100	50	20	4
Dichlorodifluoromethane		200	300	100	50	20	4
Trichlorofluoromethane		200	300	100	50	20	4
Vinyl Chloride		200	300	100	50	20	4
2-Chloroethyl Vinyl Ether	V3	1000	600	200	100	40	8
Acrolein		5000	3000	1000	500	200	40
Acrylonitrile		5000	3000	1000	500	200	40
Carbon Disulfide	V4	1000	300	100	50	20	4
Vinyl Acetate		1000	300	100	50	20	4
Methyl Iodide		1000	300	100	50	20	4
Freon 113		2000	600	200	100	40	8
2-Butanone	V5	1000	600	200	100	40	8
2-Hexanone		1000	600	200	100	40	8
4-Methyl-2-Pentanone		1000	600	200	100	40	8
Acetone		1000	600	200	100	40	8
Cyclohexane	V9	1000	300	100	50	20	4
Ethyl Acetate		1000	300	100	50	20	4
Ethyl Ether		1000	300	100	50	20	4
Isoamyl Acetate		1000	300	100	50	20	4
n-Propyl Acetate		1000	300	100	50	20	4
Benzyl Chloride		1000	300	100	50	20	4
Furan		1000	300	100	50	20	4
Hexane		1000	300	100	50	20	4
Heptane		1000	300	100	50	20	4

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Figure 2 (Continued)

EPA SW846 METHOD 8260A
INITIAL CALIBRATION
ULTRA STANDARDS (cont'd)

compound name	std mix	stock ppm	300 ppb	100 ppb	50 ppb	20 ppb	4 ppb
Methacrylonitrile	V11	2500	750	250	125	50	40
t-1,4-Dichloro-2-Butene		2500	750	250	125	50	40
t-Butyl Alcohol		5000	1500	500	250	100	80
Propionitrile		5000	1500	500	250	100	80
2-Propanol		5000	1500	500	250	100	80
Methyl t-Butyl Ether	MTBE	1000	300	100	50	20	4

ppb of analytical standard = stock ppm x ul stock / flask ml

Calibration Standard Conc. (ppb)	300	100	50	20	4
Surrogate Spiking Volume (ul)*	60	20	10	4	0.8

*Spiked directly into 5 ml syringe

ANALYST_____

DATE_____

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(saved as file TS826A::DB)

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Analysis #0947, 1339
Initiated Date: 04/01/87
Effective Date: AUG 1 2 1996

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Toxicity Characteristic Leaching Procedure
TCLP Nonvolatile Leachates

Reference:

Method 1311, *Test Methods for Evaluating Solid Waste*, SW-846, USEPA, July 1992.

Scope:

This method is designed to determine the mobility of organic and inorganic nonvolatile contaminants in potentially hazardous waste. The extraction is performed over 18 hours.

Method Summary:

For liquid wastes (containing <0.5% solids), the TCLP extract is defined as the filtrate resulting from filtration of the waste through a 0.6- to 0.8-µm glass fiber filter.

For wastes containing ≥0.5% solids (and some liquid), the waste is filtered through a glass fiber filter and the filtrate is stored for later use. The alkalinity of the solid portion is determined and the result indicates which extraction fluid should be used. The solid is then extracted with a volume of extraction fluid 20× the weight of the solid. Following the extraction, the leachate is filtered through a glass fiber filter and the final and initial filtrates are combined.

For wastes which will obviously yield no liquid when subjected to pressure filtration, the sample is analyzed for alkalinity and extracted with a volume of appropriate extraction fluid at 20× the sample weight. The extract is then filtered and the leachate is defined as the filtrate.

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Sample Handling and Preservation:

Samples should not be preserved and should be stored at 4°C. The holding time for performing the leachate extraction is 14 days from the time of collection to the day the extraction is begun. (If semivolatiles or pesticides/herbicides are to be determined.) The holding time is 28 days if the leachate is to be analyzed for mercury and 180 days for other metals.

Evaluate the solid waste for particle size. The material should be capable of passing through a 9.5-mm sieve or have a diameter of <1 cm with visual inspection. If the particle size does not meet this criteria, have the sample subcontracted for pulverization (if it is a stone-like material) or cut the material into smaller pieces if possible.

Interferences:

Any potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

Apparatus:

1. Agitation apparatus (tumbler) - This must be an EPA-approved device which is capable of rotating the extraction vessels at 30 ± 2 rpm in an end-over-end manner.

2. Extraction vessel - The extraction vessel should be a jar large enough to contain the volume of extraction fluid required (within the limitation of tumbler space). The vessel should be made of Borosilicate glass, preferably, or Teflon, optionally.

3. Filtration device - The Millipore Hazardous Waste Filtration system is suitable (also known as pressure filters)

4. Vacuum filtration system - Consisting of a vacuum flask, filter holder, and hose

5. Glass fiber filters (0.6- to 0.8-µm pore size) - 55- and 150-mm diameter

6. Beakers - 150 to 250 mL capacity and 1000 mL capacity

7. Stirring hot plates

8. Thermometer

9. pH meter

10. Watch glasses

Reagents:

All reagents must be labeled and documented as per SOP-QA-109, "Laboratory Notebooks and Documentation," and SOP-QA-110, "Reagents."

1. 1.0 N hydrochloric acid (HCl)

   Concentrated hydrochloric acid (ACS reagent grade) ..... 83 mL

   Slowly add 83 mL of concentrated HCl to approximately 500-mL deionized water in a 1000-mL volumetric flask.

   Dilute the solution to volume with deionized water. Remake every 6 months. Store in a glass bottle in the reagent cupboard.

2. 1.0 N sodium hydroxide (NaOH)

   Sodium hydroxide pellets (ACS reagent grade)..... 40 g

   Measure out 40 g of NaOH pellets and add them to approximately 500-mL deionized water in a 1000-mL volumetric flask. Using caution, mix thoroughly and dilute to 1 L with deionized water. Remake every 6 months. Store in a plastic container in the reagent cupboard.

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3. Extraction Fluid #1

Glacial acetic acid (CH2COOH) ..... 11.4 mL

1 N sodium hydroxide (NaOH) ..... 128.6 mL

Add 11.4 mL of glacial acetic acid (ACS reagent grade) to approximately 500-mL deionized water in a 2000-mL volumetric flask. Add 128.6 mL of 1 N NaOH to this mixture and dilute to 2 L with deionized water. (This solution may be made up in large volumes in a 20-L jug. The ratio of acetic acid and NaOH to final volume must be maintained in that case).

The pH of this fluid must be 4.93 ± 0.05. If not, discard and remake. Record the preparation and the pH of the extraction fluid in the appropriate logbook. Make enough for use each day, and discard any extra.

4. Extraction Fluid #2

Glacial acetic acid (CH2COOH) ..... 11.4 mL

Add 11.4 mL of glacial acetic acid (ACS reagent grade) to approximately 500-mL deionized water in a 2000-mL volumetric flask. Dilute the solution to volume with deionized water. The pH of this fluid must be 2.88 ± 0.05. If not, discard and remake. Record the preparation and the pH in the appropriate logbook. Prepare as needed.

5. 1.0 N nitric acid (HNO_3)

Concentrated nitric acid (ACS reagent grade) ..... 64 mL

Slowly add 64 mL of concentrated HNO_3 to approximately 500-mL deionized water in a 1000-mL volumetric flask. Dilute the solution to volume with deionized water. Remake every 6 months. Store in a glass bottle in the reagent cupboard.

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6. Acid washed filters

The procedure may call for using acid washed filters if the leachate is to be analyzed for metals. Prepare the filter as follows:

a. Assemble the filtration apparatus with the filter in place.

b. Pour enough 1.0 N nitric acid to cover the filter.

c. Apply vacuum or pressure (whichever is appropriate) until the filter is dry.

d. Pour a minimum of 100-mL deionized water into the apparatus.

e. Apply vacuum or pressure until the filter is dry.

f. If a vacuum apparatus was prepared, discard the waste acid/water mixture and rinse the flask several times with deionized water. If a pressure filter was prepared, discard the waste acid/water mixture.

7. 5.0 N nitric acid (HNO_3)

Concentrated nitric acid (ACS reagent grade) ..... 320 mL

Slowly add 320 mL of concentrated HNO_3 to approximately 500-mL deionized water in a 1000-mL volumetric flask. Dilute the solution to volume with deionized water. Remake every 6 months. Store in a glass bottle in the reagent cupboard.

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Safety Precautions:

Follow routine safety steps. Special care must be taken when mixing the acid solution. Wear gloves, lab coat, and safety glasses when preparing the solution and handling samples. Read all lab notes and follow instructions carefully. Avoid skin contact or breathing the vapors from any of the reagents or samples. Use the appropriate ventilation system (bench top or hood) when instructed, if the sample looks suspicious (plating waste contains cyanide), or is particularly odoriferous.

If the sample fumes or reacts in any other way when the acid is added during the extraction procedure, vent the sample periodically until the reaction is no longer evident.

Discard or send for repair any glassware that is chipped, flawed, or broken.

Determining the Amount of Extract to Prepare:

1. Look up the leachate sample in the Wang in-house computer system, under the verification program.

2. Note the analyses requested. Preferred sample aliquots are listed below:

Analysis	# of Bottles	Bottle Code	Type of Bottles	Volume
pH, Hexavalent Chromium	1	04	500 mL plastic, not preserved	500 mL
Phenols (just 434)	2	084	40-mL vials	80 mL (40 in each)
Phenols (434 and 491)	2	03	1000-mL glass	1000 mL
Metals	1	08	500 mL Nalgene	500 mL
BNA	1	45	1000-mL brown glass	1000 mL
Pesticides/ Herbicides	1	30	1000-mL brown glass	500 mL

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If the sample(s) is entered for #4173, see Appendix I for additional information.

3. Add up the sample volume required and divide by 20 to determine how much sample must be extracted.

4. If the amount of extraction fluid generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the leachate from each extraction must be combined and then aliquoted for analysis.

Preliminary Solids Determination:

If the waste appears to be liquid and seems to contain a low percentage of solids, perform the solids determination. The *Federal Register* TCLP method defines percent solids as that fraction of a waste sample from which no liquid may be forced out by an applied pressure.

1. Preweigh the filter and the filtrate collection container to be used and record the weight. If vacuum filtration will be used, preweigh the filter in a gooch crucible.

2. Weigh out a subsample of the waste (minimum 100 g).

   a. Tare a 100-mL graduated cylinder.

   b. Weigh out 100 g of sample (if there is adequate sample for the leachate and other analyses required. If not, use proportionally less) in the graduated cylinder.

   c. Pour the sample into the filter apparatus.

   d. Reweigh the graduated cylinder - Subtract the weight of the sample sticking to the glass from the initial weight of sample to get the weight of the sample filtered.

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3. Spread the waste evenly over the filter.

4. Slowly apply vacuum or gentle pressure. Apply 10 psi of pressure (if using the pressure filter) until no filtrate appears over a 2-minute interval. Increase the pressure to 20 psi until no filtrate appears for 2 minutes. Continue to increase the pressure to a **maximum of 50 psi**. When no filtrate flows after 2 minutes, or air is being forced through the filter, stop the filtration.

5. The material in the filter holder is defined as the solid phase of the waste and the filtrate is the liquid phase.

6. Weigh the filtrate and the collection container. Subtract the weight of the container from the weight of the filtrate and container. Determine the percent solids:

$$\%\ Solids = \frac{Total\ Weight\ of\ Waste\ -\ Weight\ of\ Filtrate}{Total\ Weight\ of\ Waste} \times 100$$

7. If the percent solids is <0.5%, go to Procedure A.

8. If the percent solids is ≥0.5%, and it appears that a small amount of filtrate is trapped in the filter, dry the filter and solid at 100° ± 20°C until two successive weighings yield the same value within ± 1%. Record this weight, and determine the percent dry solids.

$$\%\ Dry\ Solids = \frac{Weight\ Dry\ Waste\ and\ Filter\ -\ Tared\ Weight\ of\ Filter}{Initial\ Weight\ of\ Waste} \times 100$$

9. If the percent dry solids is <0.5%, go to Procedure A. If the percent dry solids is ≥0.5%, go to Procedure B.

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Procedure:

A. If the sample contains <0.5% solids

1. Filter the waste through glass fiber filter (6.0 to 0.8 μm). The filter must be acid washed if the leachate will be analyzed for metals. The filtrate is defined as the TCLP extract.

2. Determine and record the pH of this extract.

3. Make up a change form to delete Analysis #0947 or #2947 and add #1339. Submit the change form to the administrator responsible for sample entry charges. Enter the appropriate comments and preserve the subsamples as per SOP-IC-002, "Subsampling and Preservation of Leachates."

B. If the sample contains ≥0.5% solids and has a standing liquid phase

1. Prefilter a minimum of 100 g of the sample through the pressure filter apparatus using a glass fiber filter.

   a. If the filter gets clogged after reaching 50 psi, **do not** change it. Any waste left in the filter is considered to be the solid phase.

   b. If the layer of liquid in the solid is organic and does not mix with water, a large quantity of the sample will need to be filtered. This is because each layer of the final leachate (Procedure B, step 11) will be analyzed separately, and enough solids will need to be collected to generate enough extraction fluid for the analyses.

2. Transfer 5.0 g of the solid phase to a 150- or 250-mL beaker.

3. Add 96.5 mL deionized water, cover with a watchglass, and stir for 5 minutes. Measure and record the pH. If the pH is <5, go to step 6 and use Extraction Fluid #1. If the pH is ≥5 go to step 4.

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4. Add 3.5 mL 1.0 N HCl, stir, cover with a watch glass, and heat to 50°C (and keep the sample at 50°C for 10 minutes).

5. Allow the slurry to cool to room temperature. Measure the pH and record. If the pH is <5, Extraction Fluid #1 will be used for the leaching procedure. If the pH is >5, Extraction Fluid #2 will be used.

6. Quantitatively transfer the rest of the solids or a portion of the solids to an extraction vessel.

7. Slowly add the appropriate extraction fluid at a volume 20× the weight of the solid.

8. Close the extraction bottle tightly and place in a tumbler (rotating 30 ± 2 rpm) for 18 ± 2 hours. Ambient temperature must be maintained at 23° ± 2°C (69.8° to 77°F) during the extraction period.

9. Following the 18 ± 2 hour extraction, filter the solution through a glass fiber filter, again taking care to not exceed 50 psi if using the pressure filter. This filter can be changed if necessary. The filter(s) must be acid washed if the extract is to be analyzed for metals.

10. Add in the appropriate amount of initial filtrate:

$$\textit{Volume of initial filtrate to be added} = \frac{\textit{Volume of leachate collected (mL)}}{\textit{Total volume of leachate (mL)}} \times \frac{\textit{Weight of solid used in leachate (g)}}{\textit{Weight of solid from initial filtration}} \times \textit{mL of initial filtrate}$$

11. If the initial filtrate does not mix (is not miscible) with the extraction fluid, do not mix the two together. Contact the group leader and technical services. Each phase must be analyzed separately; therefore each phase will be entered as a sample.

12. Determine and record the pH of the leachate.

13. Subsample and preserve the leachate for the appropriate analyses as per SOP-IC-002.

C. If the sample has no free standing liquid.

1. Weigh out 5.0 g of the solid into a 150- or 250-mL beaker.

2. Add 96.5-mL deionized water, cover with a watchglass, and stir for 5 minutes. Measure and record the pH. If the pH is <5, go to step 5 and use Extraction Fluid #1. If the pH is >5 go to step 3.

3. Add 3.5 mL 1.0 N HCL, stir, cover with a watch glass, and heat to 50°C (and keep the sample at 50°C for 10 minutes).

4. Allow the slurry to cool to room temperature. Measure the pH and record. If the pH is <5, use Extraction Fluid #1 in step 6. If the pH is ≥5, use Extraction Fluid #2.

5. Weigh out a minimum of 100 g of the waste (more if a large volume of leachate is required for analysis).

6. Slowly add the appropriate extraction fluid at a volume 20× the weight of the solid.

7. Close the extraction bottle tightly, and place in a tumbler (rotating 30 ± 2 rpm) for 18 ± 2 hours. Ambient temperature must be maintained at 23° ± 2°C (69.8° to 77°F) during the extraction period.

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8. Following the 18 ± 2 hours extraction, filter the solution through a glass fiber filter taking care to not exceed 50 psi if using the pressure filter. This filter can be changed if necessary. The filter(s) must be acid washed if the extract is to be analyzed for metals.

9. Measure and record the pH of the extract.

10. Subsample and preserve the leachate for the appropriate analyses as per SOP-IC-002.

Quality Assurance:

1. A blank will be performed every 20th time an individual extraction vessel is used. A logbook of vessel usage is kept. Each time a vessel is used, record that date. After 20 usages, prepare a blank in that vessel and record the blank number in the logbook.

2. Record all the sample numbers in the batch logbook. One sample in the batch should be designated as the waste type spike and spiked as per the notes in Figure 1. Choose the first sample in the batch that has sufficient volume. Each subsample type in the batch must have a spike. Record the lot number of the spike solution used on the batch sheet. Photocopy the sheet and deliver the photocopies to each department involved in the analyses.

3. The subsamples for BNA must be delivered to that extraction lab as soon as they are finished, along with 1500 mL of the extraction fluid used in the leachate process.

4. Extraction of the solid phase should be initiated as soon as possible after initial filtration.

5. All instruments used in this procedure (i.e., pH meter and balance) should be calibrated according to an approved laboratory plan.

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6. All quality control measures described in the appropriate analytical methods shall be followed.

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Prepared by: Pamona Nayman Date: 8/5/96

Approved by: _____ Date: 8/7/96

Approved by: _____ 972 Date: 8/9/96

Figure 1

Bottle Code	Analysis Type	Preservative	Extraction[a]	Volume for Subsample (mL)	Minimum Subsample (mL)
01	TOC	H_2SO_4	ASTM	125	125
04	pH, solids	—	ASTM	500	100
04	Cr+6	—	TCLP	500	100
06	Oil & Grease	HCL	ASTM	800	500
08	Metals	5N HNO_3	TCLP	500[b]	100
11	COD	H_2SO_4	ASTM	250	150
13	TOX	H_2SO_4+$Na_2S_2O_3$	ASTM	250	250
30	Pest/Herb	$Na_2S_2O_3$	TCLP	500[c]	200
43	Formaldehyde	—	TCLP	500	250
45	BNA	$Na_2S_2O_3$	TCLP	1000[d]	500
81	Ammonia (NH_3-N)	H_2SO_4	ASTM	40 × 2	40
83	Cyanide (CN-)	NaOH	ASTM	40 × 2	40
84	Phenol (O-OH)	H_2SO_4	TCLP	40 × 2	40

[a] The extraction listed is the most commonly requested leachate for the analysis listed. If the analysis is requested on another type of leachate, have the coordinator double check with the client.

[b] If the sample is the waste type spike, prepare a second bottle with 400 mL of sample measured into it and 8 mL of each of the metals spiking solutions added to it.

[c] If the sample is the waste type spike, prepare a second bottle with 500 mL of sample measured into it and 0.5 mL of each of the pest/herb spiking solutions added to it.

[d] If the sample is the waste type spike, prepare a second bottle with 1000 mL of sample measured into it. The BNA prep area will spike the sample.

Appendix I

Leaching Procedure for Formaldehyde (EPA 8315)

Samples which will be analyzed for formaldehyde are extracted using the TCLP protocol with the following modifications:

- Only 25 g of sample is extracted.
- Extraction Fluid #1 is used for all samples (therefore steps 2-5 in Procedure B and 1-4 in Procedure C may be omitted).
- The extract is not preserved in any way at the end of the process.
- An extraction blank is prepared with each set of samples being extracted for formaldehyde.
- If the samples required prefiltration, give the batch sheet **and** a photocopy of the leachate data page(s) to the pesticide prep coordinator.

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Analysis #1055-200.9
Initiated Date: 10/12/92
Effective Date: FEB 25 1993

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Lead in Drinking Water and Wastewater by Graphite Furnace

Purpose:

To describe the procedure for determining lead in drinking water and wastewaters.

References:

1. EPA 600, Method 200.9.

2. EPA 600, Method 239.2.

Scope:

This procedure is applicable to the determination of lead in potable and nonpotable waters. A typical method detection limit is 0.5 ug/l. The limit of quantitation is 1.0 ug/l, and the linear range is to 50 ug/l. Higher concentrations can be determined by dilution.

Basic Principles:

A small volume of acidified sample is deposited onto a L'vov platform in the graphite furnace tube. Chemical modifier is added and the tube is electrically heated through a controlled temperature cycle. The sample is dried, ashed, and atomized. The atomic vapor absorbs light from a hollow cathode lamp. The absorbance is proportional to concentration. The concentration of lead in the solution is calculated from a standard curve. The chemical modifier reduces matrix interferences.

Reagents:

1. Lead Stock Standard, 1000 mg/l Baker Analyzed atomic absorption standard or equivalent. Store at room temperature.

2. Lead Verification Stock, 1000 mg/l AA Standard from a different manufacturer than the stock standard. Store at room temperature.

3. Nitric Acid, Concentrated, Baker Instra Analyzed or equivalent. Store at room temperature.

4. Magnesium Nitrate, 6 Hydrate, crystal, Baker Analyzed Reagent or equivalent. No storage requirement.

5. Ammonium Phosphate, monobasic crystal, Baker Analyzed Reagent or equivalent. No storage requirement.

6. Ammonium Phosphate/Magnesium Nitate Solution:

   Dissolve 8 grams ammonium phosphate and 0.7 grams magnesium nitrate in deionized water. Dilute to one liter. This solution is stable for one month at room temperature.

7. 100,000 ug/l Intermediate Lead Standard:

   Into a 100 ml volumetric flask containing approximately 50 ml of deionized water add 1 ml concentrated nitric acid. Pipet 10.0 ml of 1000 mg/l lead stock. Bring to volume with deionized water and mix. This solution may be stored at room temperature for six months.

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8. 1,000 ug/l Intermediate Lead Standard:

To a 500 ml volumetric flask containing approximately 250 ml of deionized water add 5 ml concentrated nitric acid. Pipet 5.0 ml of 100,000 ug/l lead intermediate standard. Bring to volume with deionized water and mix. This solution may be stored at room temperature for six months.

9. Calibration Standards:

Add approximately 100 ml of deionized water and 2 ml of concentrated nitric acid to each of seven 200 ml volumetric flasks. Add the following volumes of 1,000 ug/l intermediate lead standard to achieve the listed concentrations:

ml of 1,000 ug/l intermediate	Concentration
0.0	Calibration Blank
0.2	1.0 ug/l (CRA)
1.0	5.0 ug/l
2.0	10.0 ug/l
4.0	20.0 ug/l (CCV)
5.0	25.0 ug/l
10.0	50.0 ug/l

NOTE: Only the 5, 10, 25 and 50 ug/l are used in the calibration curve. The 1.0 ug/l is a detection limit check and the 20.0 ug/l is a continuing calibration verification standard. These solutions are stable for one month at room temperature.

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10. Initial Calibration Verification (ICV):

Use a stock standard from a different source than used for the calibration standards. Dilute to 20.0 ug/l in 1% nitric acid. This solution is stable for one month at room temperature.

Proper standard labeling requirements can be found in SOP-QA-110.

Safety Precautions:

Please consult the Inorganics Manual, Safety SOP (SOP-IO-011) for specific safety protocol and procedures.

Procedure:

Sample Preparation:

Sample holding time and storage conditions are documented in SOP-IO-001. If samples have a turbidity of <1 NTU no digestion is needed. 100 ml (or less if sample volume is limited) should be acidified by adding 1 ml concentrated nitric acid per 100 ml of sample. For samples with turbidity ≥1 NTU or wastewaters, prepare by an alternate method. The samples should be batched in groups of 20 or less with one duplicate and one matrix spike (10 ug/l) for each 10 or less samples. Each batch of 20 samples or less should contain one Laboratory Control Sample (LCS) (10 ug/l) and one method blank.

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Suggested GFAA Program Parameters:

The following parameters are for the Hitachi Z-9000. For specific instructions on operating the instrument please refer to the manufacturer's manual and to the appropriate instrument SOP (MC-IO-011).

Lead measured at 283.3 nm

Signal Mode	BKG Corrected
Measurement Mode	Working Curve
Sample Blank	No
Standard Replicates	2
Sample Replicates	2
Statistics	Mean, SD, RSD
Sample Volume	20 ul
Dilution	Off
Conc. Times	1
Modifier Addition	Yes
Cup Position	Depends on # of Samples
Reslope Standard	No
Reslope Interval	1
Cuvette	Pyro
Firings	Depends on number of cycles
Result on Record	Yes (Conc. + Abs.)
Chart Speed	1
Data Communication	Off
Calculation	Peak Area

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Temperature Program:

Number	Stage	Temperature (C) Start	End	Time (sec.)
1	Dry	80	100	3
2	Dry	100	110	20
3	Dry	110	120	25
4	Dry	120	130	15
5	Ash	230	270	4
6	Ash	270	850	3
7	Ash	800	800	10
8	Ash	200	200	3
9	Atomize	2000	2000	3
10	Clean	3000	3000	3

Carrier Gas = 200 ml/min. Interrupt Gas = 6 ml/min.
Gas Type - Argon

Notes:

These parameters are guidelines and may need adjustment to achieve the best performance (sensitivity and reproducibility). With the Hitachi Z-9000 these parameters generally produce a response of between .045 and .055 absorbance for a 10 ug/l lead standard. A series of ten injections of a 10 ug/l standard can be expected to give an RSD of approximately 2 to 3 percent.

Quality Assurance:

Instrument Stability:

A 10 ug/l standard must be run five times before calibration. If an RSD of ≥5% is obtained, adjustments must be made, and the

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stability check rerun. Repeat this procedure until an RSD of <5% is obtained.

NOTE: Set the autosampler for ten injections and calculate the mean of each pair and the RSD. Document on the printout.

Initial Calibration Verification:

After calibration an independent standard (20 ug/l) must be run. The ICV result must be within ± 10% (18 to 22 ug/l). If not, correct the problem and recalibrate. After the ICV, an initial calibration blank (ICB) is run. If this exceeds the LOQ, correct the problem and recalibrate.

Continuing Calibration Verification:

After the ICB and then every ten samples the 20 ug/l calibration standard must be run. The result must be within ± 10% (18 to 22 ug/l). If a CCV is out of the acceptable range, the samples prior to the CCV and since the last good CCV must be reanalyzed. A continuing calibration blank (CCB) must be run after each CCV. If the CCB result is greater than the LOQ or less than the negative LOQ, all samples prior to the CCB and since the last good CCB must be rerun.

CRA:

A standard at the LOQ (1.0 ug/l) must be analyzed following the ICV. There are presently no recovery requirements for this solution.

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Reagent Blank:

A blank of 1% nitric acid (prepared with the samples) must be run for every batch of 20 samples or less. If the Blank reading exceeds the LOQ the samples must be re-analyzed.

Laboratory Fortified Blank (same as an LCS):

This is a reagent blank with 10 ug/l of analyte added. This must be analyzed with each batch of 20 samples or less. Until 30 batches of samples are analyzed the control limit is ± 20% (8 to 12 ug/l). Once 30 fortified blanks have been determined the control limits become the mean ± 3 times the standard deviation. After each ten new batches the control limit is updated to the last 30 data points. All data should be included in calculating the limits unless there is evidence of miss-spiking or other laboratory error. The limit calculations are performed in a Quattro Pro spreadsheet called "Pb in Drinking Water Controls" and must be updated by the analyst.

Duplicate:

One sample in every ten or less should be analyzed in duplicate.

Laboratory Fortified Matrix (same as matrix spike):

One sample in every ten or less should be spiked at 10 ug/l. If this recovery is not within the fortified blank limits and the fortified blank is acceptable, the samples of that type should be run by the method of standard additions.

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FEB 25 1993

Calculations:

The results are reported in ug/l or mg/l (ug/l divided by 1000). If dilutions are made, the final result is the instrument reading multiplied by the dilution factor. Results should be rounded to the tenth of a ug/l.

Statistics:

EPA reports an average recovery of 101.8% and an RSD of 0.7% for samples spiked at 10 ug/l.

1055200.W51
IO METHODS #2
022493

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Prepared by: _____ Date: 2/24/93

Approved by: _____ Date: 2/25/93

Approved by: _____ Date: 2/25/93

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Where quality is a science.

Analysis #1055, 1155
Initiated Date: 03/01/88
Effective Date: AUG 0 3 1995

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Lead by Graphite Furnace

Purpose:

The purpose of this analysis is to detail the methods and procedures used to analyze lead by graphite furnace.

Background Information:

The methods described in this analysis are adopted from the following references:

1. Method 239.2, CLP SOW ILM04.0.
2. Method 239.2, *Methods for Chemical Analysis of Water and Wastes*, EPA 600/4-79-020, June 1991.
3. Method 7421, *Test Methods for Evaluating Solid Waste*, EPA SW-846, September 1986.

The calibration range for this method is 3 to 60 µg/L. The approximate instrument detection limit for this method is 1 µg/L. The following limits of quantitation are used as per the requirements of the governing regulatory agency:

Waters	3. µg/L
CLP Soils	0.6 mg/kg
Soils	1. mg/kg

Scope:

This procedure is applicable to the determination of lead in waters, wastewaters, and leachates (#1055) and soils (#1155).

Basic Principles:

A small amount of digested sample is introduced into a graphite tube. The tube is then heated electrically enabling a precise and accurate heat rise. After a short dry step, the sample is atomized at a high temperature resulting in light absorption at a specific wavelength which can be measured quantitatively. The combination of temperature programming and chemical matrix modification can help eliminate matrix interferences allowing determinations at the parts per billion and parts per trillion ranges.

Reagents:

1. Nitric acid, 70.0% to 71.0%, Baker Instra-Analyzed or equal quality, store at room temperature

2. Hydrogen peroxide, 30%, analytical reagent grade, keep refrigerated

3. Ammonium phosphate, monobasic crystal, Baker Analyzed Reagent or equal quality, no storage restrictions

4. Magnesium nitrate, 6 hydrate, crystal, Baker Analyzed Reagent or equal quality, no storage restrictions

5. Deionized water, type 2 or better

Safety Precautions:

Please consult the Inorganics Manual, Safety SOP (SOP-IO-011, "Inorganic Analysis Safety Procedure") for specific safety protocol and procedures.

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Procedure:

Please consult the Inorganics Manual SOPs regarding sample preservation, holding times, storage conditions (SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses"), and digestion procedures (Analyses #1056, #1156, #5704, #5715, and #5710).

Operations:

1. Preparation of standard solutions

   NOTE: Detailed procedures for preparation of standard solutions are found in the Inorganics Manual SOPs (SOP-IO-007, "Preparation of Standards and Solutions") Sections F, G, and H.

   Proper labeling requirements can be found in SOP-QA-110, "Reagents."

2. Program parameters

   Lead is analyzed using a Varian SpectrAA 400 or 400Z series instrument. Refer to Inorganic Operators Manual GFAA MC-IO-005, "Atomic Absorption Using the Varian SpectrAA 800 Zeeman, Varian SpectrAA 400 Zeeman, and Varian SpectrAA 400 D_2 Graphite Furnaces," for specific instrument operations. The instrument parameters are preset for the program that was developed for lead using the Photron hollow cathode lamp. The parameters for this program are as follows:

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Pb

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Area
Lamp Position	1 to 8
Lamp Current (ma)	2 to 4
Slit Width (nm)	0.5
Slit Height	Normal
Wavelength (nm)	283.3
Sample Introduction	Sampler Automixing
Time Constant	0.05
Measurement Time (sec)	1.0
Replicates	2
Background Correction	Yes

Autosampler Parameters
Volumes (μL)

	Solution (90 μg/L stock)	Blank Solution	Modifier ($[NH_4]H_2PO_4 + Mg[NO_3]_2$)	Concentration (μg/L)
Blank	0	30	4	0
Standard 1	1	29	4	3
Standard 2	3	27	4	9
Standard 3	5	25	4	15
Standard 4	10	20	4	30
Standard 5	20	10	4	60

Hot injection is used at 95°C with an injection rate of 10 (10 μL/15 seconds).

A 30-μL sample aliquot is used with 4 μL of modifier.

Furnace Parameters

Step No.	Temperature (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	120	5.0	3.0	Normal	No
2	120	20.0	3.0	Normal	No
3	220	15.0	3.0	Normal	No
4	220	20.0	3.0	Normal	No
5	350	8.0	3.0	Normal	No
6	900	6.0	3.0	Normal	No
7	900	8.0	3.0	Normal	No
8	2400	0.8	0.0	Normal	Yes
9	2400	2.0	0.0	Normal	Yes
10	2500	0.2	3.0	Normal	No
11	2500	3.0	3.0	Normal	No

3. Notes

The concentration values and instrument conditions are for a Varian SpectrAA 400 spectrophotometer, GTA 96 tube atomizer, GTA programmable sample changer, and IBM PS2 or compatible data station. The analytical range and detection limit were determined using a 30 μL injection volume, purge gas interrupt, and a pyrolytically coated graphite tube with a forked platform.

The use of background correction is required. This program is used with the Varian 400 Zeeman graphite furnace with the IBM PS2 Model 30 computer for analyzing EPA drinking waters and may be used for any other sample matrices.

Changes in furnace programs may be necessary to accommodate the differences in resistivity of the graphite tubes or to achieve better spike recoveries on more complex matrices. Lamp currents may have to be adjusted to comply with the manufacturer's specifications upon

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replacement of hollow cathode source lamps. Changes in turret position may be necessary to accommodate sequenced runs with available lamp turret or lamp socket failure. All changes from the standard analytical program will be documented on the raw data.

Quality Assurance:

Please consult the Graphite Furnace QA section (SOP-IO-004, "QA for Graphite Furnace") in the Inorganic Operators Manual for specific QA protocol and procedures. For other QA requirements not specific to graphite furnace, consult the QA section of this manual (SOP-IO-005, "Department 23 Quality Control Procedures").

Calculation:

Please consult the Graphite Furnace QA section in the Inorganic Operators Manual for the proper equations and analytical flow chart (SOP-IO-004).

10551155.W60
071795

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Prepared by: [signature] 744 Date: 8/2/95

Approved by: [signature] 383 Date: 8/2/95

Approved by: [signature] 972 Date: 8/2/95

Analysis #1056
Initiated Date: 04/21/88
Effective Date: FEB 2 2 1996

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Sample Preparation of Wastewater for Graphite Furnace Analysis of Metals

Reference:

1. USEPA CLP SOW No. ILM02.1, Exhibit D, Section III, Part A.1., Page D-5.

2. USEPA CLP SOW No. ILM04.0, Exhibit D, Section III, Part A, Page D-5.

Scope:

This acid digestion procedure is used to prepare wastewater samples for measurement of metals by graphite furnace following CLP protocol.

Basic Principles:

The samples are digested using nitric acid and 30% hydrogen peroxide to dissolve metals.

Apparatus and Reagents:

For reagent preparation, shelf life, and storage conditions, see SOP-IO-007, "Preparation of Standards and Solutions."

1. 250-mL beakers or other appropriate beakers

2. Watch glasses

3. Nitric Acid, HNO_3, 70.0%-71.0%, Baker Instra-Analyzed reagent, 1.428 g/mL, or equivalent

4. Nitric Acid (1:1) - Add 500 mL of HNO_3 to 500 mL of deionized water

5. Hydrogen peroxide, 30% H_2O_2

6. 100-mL graduated cylinders or other appropriate graduated cylinders

7. 100-mL volumetric flasks or other appropriate Class A volumetric flasks

8. 125-mL Nalgene bottles or other appropriate Nalgene bottles

9. Hot plates

NOTE: As long as the correct ratios are maintained, solutions may be prepared using multiples of indicated weights and volumes.

Safety Precautions:

Refer to SOP-IO-011, "Inorganic Analysis Safety Procedure."

Procedure:

For sample preservation, storage conditions and holding times, see SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses."

Shake sample well. Use a 100-mL graduated cylinder to transfer 100 mL of well-mixed sample into a 250-mL beaker. Add 1 mL of (1:1) HNO_3 and 2 mL of 30%

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H_2O_2. Place the beaker on a hot plate and heat at about 95°C for approximately 2 hours or until the sample volume is reduced to between 25 and 50 mL, making certain that the sample does not boil.

Allow to cool. Transfer the solution to a 100-mL volumetric flask. Adjust volume to the mark with deionized water and mix. Transfer the solution to a Nalgene bottle. The sample is now ready for analysis.

NOTE: For soluble metals analysis, filter unpreserved sample through 0.45-micron filter paper. Adjust the filtered sample to pH 2 or less with nitric acid preserving solution. Measure an appropriate volume of sample and digest as normal.

NOTE: If insufficient sample is submitted to allow using the method-stated volume or the sample contains high solids, one may use a smaller aliquot of the sample. Samples may be concentrated to meet lower than normal limits if approval is obtained from the client. Make appropriate acid, reagent, and spike volume adjustments based on sample final volume.

Quality Assurance:

Perform a method blank, sample duplicate, sample matrix spike, and laboratory control sample with every 1056 (CLP) digestion batch (20 samples or less).

1056.W60
021296

Prepared by: Eugene K. Abel Date: 2-18-96

Approved by: Ramona Nauman Date: 2/19/96

Approved by: 972 Date: 2/22/96

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Analysis #1156
Initiated Date: 03/01/88
Effective Date: APR 2 5 1996

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Sample Preparation of Soil/Sediment for Graphite Furnace Analysis of Metals

Reference:

1. USEPA CLP SOW No. ILM02.1, Exhibit D, Section III, B.1, D5-8.

2. USEPA CLP SOW No. ILM04.0, Exhibit D, Section III, Part B, D5-7.

Scope:

This acid digestion procedure is used to prepare soil/sediment/sludge samples for measurement of metals by graphite furnace (GF).

Basic Principle:

A representative 1 g (as-received) sample is digested with nitric acid and hydrogen peroxide. The digestate is then refluxed with nitric acid to complete the dissolution of metals for GF analysis.

Apparatus and Reagents:

For reagent preparation, shelf life, and storage conditions, see SOP-IO-007, "Preparation of Standards and Solutions."

1. 250-mL beakers or other appropriate beakers

2. Watch glasses

3. Nitric Acid, HNO_3, 70.0%-71.0%, Baker Instra-Analyzed reagent, 1.428 g/mL, or equivalent

4. Nitric Acid (1:1) - Add 500 mL of HNO_3 to 500 mL of deionized water

5. Hydrogen Peroxide, 30% H_2O_2, Fisher, certified ACS or equivalent

6. Whatman No. 41 filter paper or equivalent

7. Funnels

8. 200-mL volumetric flasks or other appropriate volumetric flasks

9. 250-mL Nalgene bottles or other appropriate Nalgene bottles

10. Hot plates

11. Balance, capable of reading 0.01 g

12. Nitric Acid (2%) - Add 400 mL of concentrated HNO_3 to 16 L (16,000 mL) of deionized water

NOTE: As long as the correct ratios are maintained, solutions may be prepared using multiples of indicated weights and volumes.

Safety Precautions:

Refer to SOP-IO-011, "Inorganic Analysis Safety Procedures."

Procedure:

For sample preservation, storage conditions, and holding times, see SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses."

Weigh 1 g (0.95-1.05 g to the nearest 0.01 g) of a thoroughly homogenized, as-received sample into a 250-mL beaker. Add 10 ml of (1:1) HNO_3, swirl to mix, and cover with a watch glass. Heat the sample to approximately 95°C and reflux for

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about 10 minutes without boiling. Allow the sample to cool somewhat, add 5 mL of concentrated HNO_3, with the watch glass on reflux for about 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

After the second reflux step has been completed and the sample has cooled somewhat, add about 2 mL of deionized water and about 3 mL of 30% H_2O_2. Heat cautiously until effervescence subsides.

Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Add a total of 10 mL of 30% H_2O_2.

Continue heating for approximately 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker. Add about 10 mL of deionized water, then warm the mixture for approximately 10 minutes. Allow to cool somewhat.

Filter through a Whatman No. 41 filter paper into a 200-mL volumetric flask containing 100 mL of 2% HNO_3 solution. Wash the beaker, residue, and paper thoroughly with deionized water. Adjust volume to the mark with deionized water and mix. Transfer the solution to a 250-mL Nalgene bottle. The sample is now ready for analysis.

NOTE: For non-CLP samples when special limits of quantitation are required by the client, use more sample weight.

NOTE: Typically use 5 g for samples of liquid consistency.

NOTE: Dry solvents on a steam bath before digesting.

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Quality Assurance:

Perform a method blank, sample duplicate, sample matrix spike, and laboratory control sample with every digestion batch (20 samples or less).

1156.W60
041896

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Prepared by: Eugene K. Abel Date: 4-19-96

Approved by: Ramona Nayman Date: 4/19/96

Approved by: 972 Date: 4/24/96

Analysis #5704
Initiated Date: 01/04/94
Effective Date: FEB 2 2 1996

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Sample Preparation of Extracts and Other Wastewater for Graphite Furnace Analysis of Total Metals

Reference:

Method 3020A, *Test Methods for Evaluating Solid Waste*, USEPA SW-846, Third Edition, Office of Solid Waste and Emergency Response, Washington, DC 20460, Revision 1, Part I, Chapter 3, July 1992.

Scope:

This acid digestion procedure is used to prepare EP and mobility-procedure extract samples and other wastewater samples for measurement of total metals by graphite furnace when SW-846 protocol is requested.

Basic Principles:

A mixture of nitric acid and the sample is refluxed in a covered beaker at low volume to dissolve metals. It is cooled and brought up to volume with deionized water. If the sample should go to dryness, it must be discarded and the sample reprepared.

Apparatus and Reagents:

For reagent preparation, shelf life, and storage conditions, see SOP-IO-007, "Preparation of Standards and Solutions."

1. 250-mL beakers or other appropriate beakers

2. Watch glasses

3. Nitric acid, HNO_3, 70.0% to 71.0%, Baker Instra-Analyzed reagent, 1.428 g/mL, or equivalent

4. 50-mL graduated cylinders or other appropriate graduated cylinders

5. 50-mL volumetric flasks or other appropriate Class A volumetric flasks

6. 60-mL Nalgene bottles or other appropriate Nalgene bottles

7. Hot plates

Safety Precautions:

Refer to SOP-IO-011, "Inorganic Analysis Safety Procedures."

Procedure:

For sample preservation, storage conditions, and holding times, see SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses."

Shake sample well. Use a 50-mL graduated cylinder to transfer 50 mL of well-mixed sample into a 250-mL beaker. Add 1.5 mL of HNO_3. Place the beaker on a hot plate and cautiously evaporate to low volume (10 to 20 mL), making certain

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that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 1.5-mL portion of HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

Continue heating (refluxing) for approximately 15 minutes. Uncover the beaker and evaporate to low volume (10 to 20 mL), not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 5 mL of deionized water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

Allow to cool. Transfer the solution to a 50-mL volumetric flask. Adjust volume to the mark with deionized water and mix. Transfer to a Nalgene bottle. The sample is now ready for analysis.

NOTE: For soluble metals analysis, filter unpreserved sample through 0.45 micron filter paper. Adjust the filtered sample to pH 2 or less with nitric acid preserving solution. Measure an appropriate volume of sample and digest as normal.

NOTE: If insufficient sample is submitted to allow using the method-stated volume or the sample contains high solids, one may use a smaller aliquot of the sample. Samples may be concentrated to meet lower than normal limits if approval is obtained from the client. Make appropriate acid, reagent, and spike volume adjustments based on sample final volume.

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Quality Assurance:

Perform a method blank, sample duplicate, sample matrix spike, sample matrix spike duplicate, and laboratory control sample with every digestion batch (20 samples or less).

5704.W60
021296

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Prepared by: Eugene K. Abel Date: 2-16-96

Approved by: Pamela Nayman Date: 2/19/96

Approved by: 972 Date: 2/22/96

Analysis #5710
Initiated Date: 01/04/94
Effective Date: FEB 01 1994

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Sample Preparation of Soil, Sediment, and Sludges for Graphite Furnace Analysis of Metals

Reference:

USEPA SW-846 Test Methods for Evaluating Solid Waste, Office of Solid Waste and Emergency Response, Washington, DC 20460, July 1992, Third Edition, Revision 1, Part I, Chapter 3, Method 3050A.

Scope:

This acid digestion procedure is used to prepare soil, sediment, and sludge samples for measurement of metals by graphite furnace spectroscopy following SW-846 protocol.

Basic Principles:

A representative 1 g as-received sample is digested with nitric acid and hydrogen peroxide. The digestate is then refluxed with nitric acid to complete the dissolution of metals for AA or ICP analysis.

Apparatus and Reagents:

For reagent preparation, shelf life, and storage conditions, see SOP-IO-007, Preparation of Standards and Solutions.

1. 250 ml beakers or other appropriate beakers

2. Watch glasses

3. Nitric Acid, HNO_3, 70.0%-71.0%, Baker Instra-Analyzed reagent, 1.428 g/ml, or equivalent

4. Nitric Acid (1:1) - Add 500 ml of HNO_3 to 500 ml of deionized water

5. Hydrogen Peroxide, 30% H_2O_2, Fisher, certified ACS or equivalent

6. Whatman No. 41 filter paper or equivalent

7. Funnels

8. 100 ml volumetric flasks or other appropriate volumetric flasks

9. 250 ml Nalgene bottles or other appropriate Nalgene bottles

10. Hot plates

11. Balance, capable of reading 0.01 g

NOTE: As long as the correct ratios are maintained, solutions may be prepared using multiples of indicated weights and volumes.

Safety Precautions:

Refer to SOP-IO-011, Inorganic Analysis Safety Procedures.

Procedure:

For sample preservation, storage conditions, and holding times, see SOP-IO-001, Preservation and Holding Times for Inorganic Analyses.

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Weigh 1 g (0.95-1.05 g to the nearest 0.01 g) of a thoroughly homogenized as-received sample into a 250 ml beaker. Add 10 ml of (1:1) HNO_3, swirl to mix, and cover with a watch glass. Heat the sample to approximately 95°C and reflux for about 10 to 15 minutes without boiling. Allow the sample to cool somewhat, add 5 ml of concentrated HNO_3, with the watch glass on reflux for about 30 minutes. Repeat this last step to ensure complete oxidation. Allow the solution to evaporate to about 5 to 10 ml without boiling, while maintaining a covering of solution over the bottom of the beaker (add deionized water if required).

After the second reflux step has been completed and the sample has cooled, add about 2 ml of deionized water and about 3 ml of 30% H_2O_2. With the cover on, heat cautiously until effervescence subsides.

Continue to add 30% H_2O_2 in 1 ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Add a total of 10 ml of 30% H_2O_2.

With the cover on, heat (reflux) for approximately 15 more minutes without boiling until the volume has been reduced to approximately 5 to 10 ml. Allow to cool somewhat.

Filter through a Whatman No. 41 filter paper into a 100 ml volumetric flask. Wash the beaker, residue, and paper thoroughly with deionized water. Adjust volume to the mark with deionized water and mix. Transfer the solution to a 250 ml Nalgene bottle. The sample is now ready for analysis.

NOTE: When special limits of quantitation are required by the client, use more sample weight.

NOTE: Use approximately 5 g for samples of liquid consistency.

NOTE: Dry solvents on a steam bath before digesting.

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Quality Assurance:

Perform a method blank, sample duplicate, sample matrix spike, sample matrix spike duplicate, and laboratory control sample with every digestion batch (20 samples or less).

5710.W60
010794

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Prepared by: Eugene K. Abel Date: 1-23-94

Approved by: [signature] Date: 1-24-94

Approved by: [signature] Date: 1/31/94

Analysis #5715
Initiated Date: 01/04/94
Effective Date: FEB 2 2 1996

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Sample Preparation of Potable Water and NPDES Wastewater for Graphite Furnace Analysis of Total Metals

Reference:

Methods for Chemical Analysis of Water and Wastes, USEPA 600/4-79-020, Section 200.0, Part 4.1.3, Office of R&D, USEPA-EMSL, Cincinnati, Ohio, Revised March 1983.

Scope:

This acid digestion procedure is used to prepare potable water and NPDES wastewater samples for measurement of total metals by graphite furnace.

Basic Principles:

A mixture of nitric acid and the sample is refluxed in a covered beaker at low volume to dissolve metals. It is cooled and brought up to volume with deionized water.

Apparatus and Reagents:

For reagent preparation, shelf life, and storage conditions, see SOP-IO-007, "Preparation of Standards and Solutions."

1. 250-mL beakers or other appropriate beakers

2. Watch glasses

3. Nitric Acid, HNO_3, 70.0%-71.0%, Baker Instra-Analyzed reagent, 1.428 g/mL, or equivalent

4. 50-mL graduated cylinders or other appropriate graduated cylinders

5. 50-mL volumetric flasks or other appropriate Class A volumetric flasks

6. 60-mL Nalgene bottles or other appropriate Nalgene bottles

7. Hot plates

Safety Precautions:

Refer to SOP-IO-011, "Inorganic Analysis Safety Procedures."

Procedure:

For sample preservation, storage conditions, and holding times, see SOP-IO-001, "Preservation and Holding Times for Inorganic Analyses."

Shake sample well. Use a 50-mL graduated cylinder to transfer 50 mL of well-mixed sample into a 250-mL beaker. Add 1.5 mL of HNO_3. Place the beaker on a hot plate and cautiously evaporate to low volume (10 to 20 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 1.5-mL portion of HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

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Continue heating (refluxing) for approximately 15 minutes. Uncover the beaker and evaporate to low volume (10 to 20 mL), not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 5 mL of deionized water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

Allow to cool. Transfer the solution to a 50-mL volumetric flask. Adjust volume to the mark with deionized water and mix. Transfer to a Nalgene bottle. The sample is now ready for analysis.

NOTE: For soluble metals analysis, filter unpreserved sample through 0.45-micron filter paper. Adjust the filtered sample to pH 2 or less with nitric acid preserving solution. Measure an appropriate volume of sample and digest as normal.

NOTE: If insufficient sample is submitted to allow using the method-stated volume or the sample contains high solids, one may use a smaller aliquot of the sample. Samples may be concentrated to meet lower than normal limits if approval is obtained from the client. Make appropriate acid, reagent, and spike volume adjustments based on sample final volume.

Quality Assurance:

Perform a method blank, sample duplicate, sample matrix spike, and laboratory control sample with every digestion batch (10 samples or less).

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Prepared by: Eugene K. Ahel Date: 2-16-96

Approved by: Pamona Nayman Date: 2/19/96

Approved by: 972 Date: 2/22/96

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Where quality is a science

Analysis #2213, 2540, 6868, 6869, 6976, 1837
Initiated Date: 04/03/91
Effective Date: MAY 1 4 1996

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Purgeable Aromatics in Soil Samples

Reference:

Methods 5030A, 8000A, and 8020A, *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition.

Scope:

This method is suitable for analyzing solid samples for the purgeable aromatic compounds listed in Table I. The limit of quantitation for all (BTEX) compounds is 5 µg/kg (ppb) for soils. This method is a modification of 5030A/8020A in that a modified midlevel methanol extraction is used.

Basic Principles:

This method is based on the purge-and-trap gas chromatography method where an inert gas (helium) is bubbled through 25 mL of methanol sample extract/deionized water solution. The volatile aromatics are purged from the solution and trapped on a sorbent trap. The trap is then heated and backflushed with gas to desorb the trapped aromatics onto a suitable gas chromatographic column. The gas chromatograph is then temperature programmed to separate the aromatics which are then detected and quantified by a photoionization detector (PID).

Interferences:

Samples with petroleum fractions that are less volatile than gasoline (i.e., kerosene, #2 fuel oil) may cause baseline ramping and may affect surrogate recoveries. In addition, samples with high organic contents may cause foaming of the methanolic (sample) extract in the sparge vessel. These interferences can be minimized by increasing the methanolic dilution (from 25x). Limits of quantitation must be raised to reflect the final dilution.

handling precautions for any compound can be found with the material safety data sheets (MSDS) available from the safety officer. Safety glasses and lab coats are required as personal protective equipment. Gloves are optional.

Standard Preparation:

NOTE: All neat compounds and standards (stocks and working) should be stored in an explosion-proof freezer between -10° and -20°C (14° to -4°F). These standards are stored in 12-mL vials with screw-cap lids and Teflon-lined silicone septa (may vary based on availability) for up to 180 days for stocks and up to 30 days for working standards.

Calibration solutions and all QC standards (i.e., check standard and spikes) are prepared from separate stock solutions.

All concentrations listed are approximate and assumed to be in solution unless stated otherwise.

1. Calibration stock solution (5000 ppb)

    a. Calibrate analytical balance capable of weighing 0.0001 g according to SOP-LA-017, "Maintenance and Calibration of Laboratory Balances" (see corporate operations manual).

    b. Fill a 10-mL volumetric flask approximately 2/3 full with reagent grade methanol. Stopper and tare.

    c. Beginning with the heaviest compound (*o*-xylene), weigh between 0.045 and 0.055 g of each compound using a capillary pipette. Record each weight. Stopper and tare the flask after each compound.

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All calibration/calculation data must be adjusted for these exact weights using the following calculation:

Component	Final Individual Component Conc. (µg/mL)	Weight (grams) of Neat Stock to 10 mL MeOH
MTBE	5000	0.0500
Benzene	5000	0.0500
Toluene	5000	0.0500
Ethylbenzene	5000	0.0500
p-Xylene	5000	0.0500
m-Xylene	5000	0.0500
o-Xylene	5000	0.0500

NOTE: Indicated weights are targets; actual weights should be within ±10% of target weight.

$$\frac{\textit{Compound weight (g)}}{\textit{Final volume (mL)}} \times \frac{1000\ mL}{1\ L} \times \frac{1000\ mg}{1\ g} = \textit{Concentration (mg / L)}$$

d. Bring flask to volume using a Pasteur pipette.

e. Working calibration solution "B" (50 ppm) - 0.1 mL Calibration stock to 10 mL methanol

f. Working calibration solution "A" (5.0 ppm) - 1.0 mL working calibration solution "B" to 10 mL methanol

g. Working calibration scheme

Methanol blank - 1 mL methanol to 24 mL deionized water

(1) Level 1 - 10 µL (working calibration solution "A") to methanol blank (2 ppb)

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(2) Level 2 - 20 µL (working calibration solution "A") to methanol blank (4 ppb)

(3) Level 3 - 50 µL (working calibration solution "A") to methanol blank (10 ppb)

(4) Level 4 - 10 µL (working calibration solution "B") to methanol blank (20 ppb)

(5) Level 5 - 20 µL (working calibration solution "B") to methanol blank (40 ppb)

2. Spike stock solution (5000 ppm)

   a. Follow steps 1.a. through 1.d. of calibration stock preparation.

   b. Working spike solution (10 ppm) - 20 µL spike stock to 10 mL methanol

   c. Add 20 µl of working spike solution to the sample syringe prior to injection for matrix spike and matrix spike duplicates. This is approximately 8 ppb in solution or 200 ppb in a soil sample.

3. Check standard stock solution (5000 ppm)

   a. Follow steps 1.a. through 1.d. of calibration stock preparation

   b. Intermediate check standard solution (250 ppm) - 0.50 mL check standard stock to 10 mL methanol

   c. Working check standard solution (25 ppm) - 1 mL intermediate solution to 10 mL methanol

   d. LOQ/MDL solution

      0.1 mL working check standard to 10 mL MeOH

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e. Add 10 µL of working solution (3.c.) to the sample syringe prior to injection yielding an approximate concentration of 10 ppb.

4. Alternate source check standard

This will be left to the analyst's discretion. The stock solution (and respective intermediate and working solutions) should either be prepared from neats with a different lot number from the same vendor, or may be purchased as a prepared working standard of known concentration(s).

5. Surrogate stock solutions (5000 ppm)

a. Trifluorotoluene (surr #1) - Weigh between 0.045 and 0.055 grams into a 10-mL volumetric flask and bring to final volume with methanol as described above.

b. *n*-Propylbenzene (surr #2) - Follow above procedure.

c. Fluorobenzene (surr #3) - Follow above procedure.

d. Working surrogate solution (100 ppm) - 0.5 mL of each surrogate stock solution to 25 mL methanol. Add 5 µL of working surrogate to each injection yielding an approximate concentration of 20 ppb in solution.

e. Alternate surrogate solutions, may be used to minimize interference. The solution preparation is as described above.

Sample Collection/Preparation:

A methanolic extract is diluted in deionized water before analysis. The methanol concentration is constant for all standards, blanks, and samples. See Analysis #2379, 5899, "Preparation and Extraction of Soil and Solid Samples for Determination of Purgeable Aromatics, Purgeable Halocarbons, and Gasoline Range Organics."

Soil samples are to be collected using the recommended sampling protocol in SW-846. Samples collected according to this protocol should be cooled at 2° to 6°C (36° to 43°F) at the time of collection until analysis. All samples must be analyzed within 14 days of collection.

Calibration:

Calibration is performed using internal standardization. A point-to-point calibration curve is used. The calibration factor (CF) as defined in Dept. 34 SOP-PA-032, "Manual Calculation of the Analyte Response/Calibration Factors, the Relative Standard Deviation for Analyte Response/Calibration Factors, and the Correlation Coefficient," is calculated for each analyte in each calibration level. If the relative standard deviation (RSD) of the CFs for any analyte is <20%, the average CFs may be used for the quantitation. If the RSD exceeds 20%, a calibration curve must be utilized. Alternately, a linear least squares fit to the calibration data may be used.

Once the system has been calibrated, the calibration curve is verified by analyzing a quality control check standard. If the recovery of any analyte is <85% or >115%, a new calibration must be performed.

The calibration is continually checked by analyzing a check standard after at least every ten samples.

Procedure (soils/solid wastes):

NOTE: The syringe and syringe plunger should be rinsed at least 3x with deionized water between samples. All standards, spikes, samples, and method blanks should contain 5 µL of working surrogate solution.

1. Set the purge-and-trap and GC conditions as described in Table II and Table III, respectively.

2. Always begin a run with a deionized water blank (deionized cleanup). This allows the system to run through a complete cycle, ensuring a clean system before running samples.

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3. Run a check standard to verify the calibration. See Standard Preparation section.

4. After the concentrator program reaches the Desorb cycle, the liquid can be drawn out of the sparge with the 30-mL syringe.

5. After the run time has expired, the program will advance to Standby. Inspect the chromatogram for acceptable surrogate/component recoveries.

6. One method blank of methanol must be run per shift. The dilution for the methanol extractions is 25x. Inject 1 mL of methanol used for the extractions into a 30-mL syringe containing 24 mL deionized water. Add 5 µL of surrogate solution. Inject into sparge. If a new bottle of methanol is opened for extractions during a batch, it must be run as a blank before use.

7. If starting a new batch, an LOQ standard must be run before any samples (see Standard Preparation). There is no acceptability limit for this standard; however, each compound being analyzed must be detected.

8. Prepare methanol extractions for the samples as per Analysis #2379, 5899.

9. Once the samples have been extracted, prepare and analyze as a methanol blank (step 7). If the odor of the extract indicates high organic content, a further dilution (greater than 25x) should be made, keeping the methanol concentration constant.

10. If the amount of analyte in the sparge is higher than the fifth calibration level, the sample must be repeated at a higher dilution. Before continuing with the analysis of samples, a deionized water blank (deionized cleanup) should be run immediately following any samples determined to be over calibration range, to ensure that the high levels present will not carryover into the next sample injection.

11. Continue analysis of samples in this manner until ten samples have been analyzed, at which time a new check standard must be analyzed.

12. If analyzing for BTEX, a BTEX matrix spike and matrix spike duplicate must also be performed for every 20 samples analyzed. The matrix spikes are prepared by injecting 20 µL 10-ppm BTEX spiking standard into the 25-mL syringe which already contains 1 mL of methanol extract, 24 mL of deionized water, and 5 µL of surrogate standard.

Calculations:

The concentration of BTEX components in the sample is calculated as follows:

$$\frac{\textit{comp. peak ht.}}{\textit{cal. comp. peak ht.}} \times \frac{\textit{cal.}}{\textit{conc.}} \times \frac{\textit{avg. cal. TFT ht.}}{\textit{sample TFT ht.}} \times \textit{DF} = \frac{\textit{concentration}}{\textit{ppb}}$$

Where:

comp. peak ht. = the height of the component in the sample

cal. comp. peak ht. = the closest height of the same component in the calibration

cal. conc. = the concentration of the component in the calibration used for the cal. comp. peak ht.

avg. cal. TFT ht. = the average internal standard (TFT) height from the calibration

sample TFT ht. = the internal standard (TFT) height of the sample

DF = dilution factor; soil samples have a default value of 25 prior to any dilutions due to sample matrix.

Identification of Analytes:

Comparison of sample peak retention times to standard peak retention times is used to tentatively identify compounds. A window of ±3 standard deviations from the average retention time based on five to six previously analyzed QC check standards can also be used as the basis for identification. Further considerations should also include normal vs. abnormal peak shape and the shift in retention times of the surrogates and internal standards. Ultimately, the experience and discretion of the analyst should weigh heavily in the interpretation of the chromatogram.

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Dilution of Samples:

Sample which contain levels of analytes above the dynamic range of the method (the highest-level calibration standard) must be reanalyzed. A dilution(s) is performed so that all target analytes can be quantitated and fall within the dynamic range of the method. If the instrument has been running on sequence, the analyst must determine if there is carryover present. It may be necessary to analyze a reagent water blank (cleanup blank) to ascertain all analytes are below the LOQ. If they are not, the cleanup blank is repeated until analyte levels are below the quantitation limit.

Quality Control:

1. Surrogates

   In order to monitor both the performance of the analytical system and the effectiveness of the method, each standard, matrix spike, sample, and method blank are spiked with 5 µL of surrogate solution. Surrogate recoveries (NPB and FB) must be between 75% and 125%. The internal standard, TFT, must have a recovery between 70% and 120%. If two or more surrogates are out of specifications, the sample is repeated. If the surrogate(s) is still out of specification, a QC check standard is analyzed. If the QC check is within specifications, matrix interference is suspected and the analyst can continue. If the QC check standard is out of specifications, recalibrate and re-analyze the sample.

2. Method blank (methanol dilution)

   The values for any analyte detected in the method blank should be <2.5 µg/kg. The values are in spec if between 2.5 and 5 µg/kg, but if clean samples are to be analyzed, and potentially reported to the MDL, this could lead to a false reportable values in the samples; therefore, a methanol cleanup should be run followed by a repeat injection of the method blank.

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3. Check standard

As stated previously, the calibration curve is verified at least every ten samples by analyzing a quality control check standard which contains every analyte of interest. If the recovery for any analyte falls outside the 85% to 115% range, repeat the analysis with a new standard. If the check standard is still out of specification, a new calibration must be performed.

4. Matrix spike (MS) and matrix spike duplicate (MSD)

These are performed on one sample in every batch of 20 samples. The recovery for each analyte of interest should be between 75% and 125%. The maximum relative percent deviation (RPD) is 20%. RPD is calculated as follows:

$$RPD = \left[2 \times \frac{R1 - R2}{R1 + R2}\right] \times 100$$

If the MS and/or MSD is out of specifications a laboratory control sample (LCS) must be analyzed. If the LCS is within specifications, analysis can continue. If the LCS is out of specifications, the QC and LCS must be re-extracted and reanalyzed. No sample analysis is valid until the LCS is within specifications. If the LCS is out of specifications on the re-extraction, a check standard is analyzed. If the check standard is within specifications, the LCS solution is suspect and should be reprepared and QC re-extracted. If the check standard is out of specifications, recalibrate the instrument. All samples analyzed before the failed QC must be repeated.

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Prepared by: Matthew E Barton Date: 5/9/96

Approved by: Jerry S. Collins Date: 5/9/96

Approved by: [signature] 972 Date: 5/13/96

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Table I

Compounds Analyzed as Part of the Purgeable Aromatic Scan or as Individuals

Compound	Analysis #
Methyl tertiary-butyl ether (MTBE)*	1837, 2464
Benzene	2540
Cumene*	6868
Toluene	--
Styrene*	6869
Ethylbenzene	--
p-Xylene	--
m-Xylene	--
o-Xylene	--

*These compounds are not normally reported but can be reported upon client request.

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Table II

Purge-and-Trap Conditions

Trap Type	T*	CPB/CSS*
Purge Flow (mL/min)	40	40
Purge Time (min)	8	8
Dry Purge (min)	8	8
Desorb Preheat (°C)	170	245
Desorb Temp (°C)	180	250
Desorb Time (min)	4	4
Bake Temp (°C)	220	260
Bake Time (min)	9	9
Heated Value and Line Temps (°C)	100 to 130	100 to 130

*T = Tenax CBP = Carbopack B CSS = Carbosieve S-III

NOTE: Higher bake temperatures and times may be used to remove analytes which may carryover after the analysis of samples containing high levels of volatiles.

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Table III

GC Conditions

	Column 1
Detector Temp (°C)	250
Injector Temp (°C)	200
Carrier Flow (mL/min)	35
Detector Makeup Flow (mL/min)	–
Temperature Program	
Initial Temp (°C)	45
Initial Hold (min)	3
Ramp (°C/min)	4
Final Temp (°C)	145
Final Hold (min)	1

The PID detector sensitivity should be set so that 1. µg/L of benzene gives a S/N ratio of at least 10:1. If the sensitivity of the PID is not sufficient to reach this level, the lamp should be replaced or cleaned. Alternatively, the purge and trap concentrator should be checked for leaks and/or poor trap performance.

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Analysis #2379, 5899
Initiated Date: 11/19/91
Effective Date: FEB 28 1996

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Preparation and Extraction of Soil and Solid Samples for the Determination of Purgeable Aromatics, Purgeable Halocarbons, and Gasoline Range Organics

Reference:

1. "Method for the Determination of Gasoline Range Organics," *EPA Underground Storage Tank Work Group Draft*, American Petroleum Institute, Revision 6, 8/18/93.

2. Methods 8020A, 5030A, and 8000A, *Test Methods for evaluating Solid Waste*, EPA SW-846, Third Edition.

Related Reference:

1. "Total Petroleum Hydrocarbons Analysis - Gasoline Method," California Department of Health Services, LUFT Task Force.

2. Method 8015B (modified), *Test Methods for Evaluating Solid Waste*, EPA SW-846, Third Edition.

Scope:

This method is used to extract solid samples for the determination of purgeable aromatics, purgeable halocarbons, and/or gasoline range organics. It may also be used for the determination of single analytes from these scans. As per EPA documentation, a solid sample has a holding time of 14 days after collection to be extracted. However, no EPA mandate has been established to document a hold-time for these extractions.

This method is based on the midlevel method from EPA method 5030A of SW-846. A solid is shaken with methanol, the methanol decanted, diluted into water, and the water analyzed by purge and trap gas chromatography. See specific analyses methods for further explanation of purge and trap chromatography.

Apparatus:

1. 40 mL screw-capped vials

2. Top-loading balance capable of weighing to 0.01 g with 100-g capacity.

3. Spatula

Safety Precautions:

Due to the potentially toxic nature of samples submitted by clients, safety precautions must be observed when handling samples. Protective eyewear and lab coats are required while subsampling. Gloves are optional, but recommended. Samples may also be subsampled in a fume hood if a strong odor is detected.

Procedure:

1. Each sample to be analyzed shall be received, unhomogenized, in a "zero-headspace" container to preserve any aromatics, and to ensure accuracy of the method. When one or both of the previous criteria cannot be achieved, an analysis comment shall be utilized to outline any inadequacies.

2. Weigh 20 g ± 0.1 g into a tared, 40-mL screw-capped vial. Record the sample number and the weight in the appropriate extraction notebook. Be sure the sample number is also written on the vial before setting the sample aside. Other information to be written into the extraction note includes: MeOH number, MeOH lot number, and batch number where MeOH was checked (see below). When it is not possible to use 20 g of sample due to the nature of the sample's matrix or limited sample volume, then smaller sample weights may be used. However, a minimum of 5 g must be utilized.

3. Add 20 mL of reagent methanol, which has been previously analyzed and found to be free of any volatile organics, to the vial containing the weighed

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sample. Seal the screw cap on the vial to prevent leakage. If the sample is not dense enough to be covered by 20 mL of methanol, or if the sample absorbs the full 20 mL, a smaller sample weight may be used (see above).

NOTE: If less than 20 g of sample is available, maintain a 1:1 sample to MeOH ratio if possible.

4. Once the methanol has been added, shake the sample vigorously for 2 minutes. After the sample has settled for at least 1 hour, or until a sufficient MeOH layer has formed, decant the methanol into a 12-mL screw-capped vial. Be sure to record the sample number on the side of this vial also.

   NOTE: The MeOH may be left on the sample for a maximum of 24 hours before decanting is required. Centrifuging may be required to remove suspended particles from the MeOH layer.

5. Samples shall be stored in an explosion-proof refrigerator until analyzed. After analysis, decant the separated MeOH back into the original 40-mL vial and discard as hazardous waste. A sample shall not be discarded until after 30 days from submittal, or as per client requirements.

6. See specific analytical method for dilution information.

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Prepared by: Matthew E Dat[illegible] Date: 2/26/96

Approved by: [illegible] Date: 2/26/96

Approved by: [illegible] 972 Date: 2/26/96

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Analysis #4833
Initiated Date: 01/15/93
Effective Date: MAR 0 1 1994

Extraction Procedure for the Determination of GC Fingerprint on Petroleum Products in Soil or Solid Waste Matrices

References:

1. EPA SW-846, Method 3550, Sonication Extraction.

2. Sonicator Ultrasonic Processor and Cell Disruptor Operations Manual, Sound Heat Systems, Inc., 1985.

Scope:

This procedure is applicable for petroleum products extraction from soils or solid wastes for TPH by GC/FID (Analysis #4703, 5256, and 5300), Petroleum Fuels by GC/FID (Analysis #4835), Qualitative GC Fingerprint (Analysis #2012), or TPH by GC/FID - DRO (Analysis #5321 or 5547).

The analysis method should be consulted for more specific application information. Many "nonpetroleum" organics are also extracted by this procedure and may interfere with petroleum product characterization and/or quantitation.

Basic Principles:

A measured weight of soil or solid waste sample is blended with anhydrous sodium sulfate. This mixture is then serially extracted with methylene chloride using a sonic probe disrupter. The serial extracts are combined, dried, and concentrated to

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approximately 1 ml, which is brought to a final volume of 5 ml. The extracts are analyzed by Gas Chromatography using FID detection (by one of the methods listed in the Scope section).

Apparatus:

1. Sonic probe apparatus, Heat Systems-Ultrasonics, Inc. Model W-385, or equivalent

2. Kuderna-Danish - 500 ml, with three-ball Snyder column and 10 ml graduated ampule

3. Chromatographic column: Pyrex 20 mm ID, approximately 400 mm long with a plain stem

4. Water or steam bath

5. 11 cm diameter Buchner funnels

6. 11 cm Whatman 3 filter paper

7. 500 ml Filters flasks

Reagents:

1. Methylene Chloride - Pesticide quality or equivalent (Optima Grade)

2. Acetone - Pesticide quality or equivalent

3. Carbon Disulfide - Glass distilled, HPLC/spectral grade

4. Sodium Sulfate - Reagent grade prepared by baking at 400°C for 4 hours prior to use, to remove organic contaminants

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5. Surrogate Standards - Chlorobenzene, Standards Grade - Chem. Service, o-Terphenyl, 99% - Aldrich Chem. Co. or equivalent

6. Spiking concentration of surrogate standards:

   For stock solution, accurately weigh (to 0.1 mg) 0.8 g o-Terphenyl and 0.5 g chlorobenzene into a 200 ml volumetric containing several ml of acetone. Bring the flask to volume with acetone. This stock solution is stored in a freezer and is stable for six months.

   For a working solution of the surrogate standards, make a DF 10 of the above stock in acetone. This solution is stored in a freezer and is stable for six months.

7. Spiking Solution: See Reagents section of Methods 4835 and 4703 for the preparation of the spiking solution. Unless otherwise instructed, use 1.0 ml of this spiking solution in each sample.

Preparation of Glassware:

All glassware is soaked in dilute "Chem-solv" for at least four hours, rinsed several times with tap water, rinsed several times with deionized water. Kuderna-Danish glassware is oven dried at 115°C.

Sample Collection:

Samples should be collected in 8 oz glass containers with minimal headspace and kept cool (4°C) until extraction is performed. Holding time until extraction is 14 days. The analysis should be performed within 40 days from extraction.

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Safety Precautions:

All concentration steps should be carried out in a hood. Direct exposure of skin and respiratory tract to methylene chloride, carbon disulfide, or acetone should be avoided. Many sample materials to be analyzed by this method are "unknowns" and may contain toxic materials. Use good laboratory practice for handling of unknowns.

Extraction Procedures:

1. Soils and solid wastes are not homogenized before being subsampled for extraction.

2. Weigh 60 g of the solid into a 250 ml beaker. An attempt should be made to get a representative sampling of the contents of the sample container.

   NOTE: While weighing the sample please record visual and olfactory observations relating to its petroleum/organic content (such as strong gasoline smell, weak oil smell, dark oil material present, solvent-like odor, etc.).

3. Add 60.0 g of sodium sulfate to the beaker and stir thoroughly using a clean glass stirring rod. Record the LLI number, the initial weight, and any comments about the sample in the extraction log. Spiking solution as specified by the analytical method is added to the sample at this time (See Reagent #7). Add 1.0 ml of the surrogate working solution.

4. Add 100 ml of methylene chloride to the beaker.

5. Set up the sonic probe as described in the manual.

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6. Immerse the tip of the sonic probe approximately 1 to 2 cm below the surface of the liquid in the beaker containing the sample.

7. Disrupt the sample:

   a. If using the medium tip, turn to full output (10) for 3 minutes.

   b. If using the large tip, turn to (6) for 3 minutes.

8. Remove the probe from the sample.

9. Decant the liquid from the beaker into a filter funnel setup consisting of a Buchner funnel containing Whatman 3 filter paper. The funnel is connected to a 500 ml filter flask with a 4 to 6 psi vacuum.

   NOTE: Be sure to turn the vacuum off immediately after solvent is no longer observed dripping from the funnel.

10. Repeat Steps 4 through 9 using the same beaker, filter paper and Buchner funnel for each sample. Perform a third extraction in the same manner.

11. Before placing the probe into a new sample, rinse with both deionized water and acetone and wipe with a papertowel to remove any soil present from the previous sample.

12. Rinse the filter paper with 10 ml of methylene chloride.

13. Pour collected extracts into a Kuderna-Danish, add a glass boiling bead to the K-D, attach a 3-ball Snyder column and wet the column with methylene chloride.

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14. Place each K-D apparatus on a steam bath and concentrate the solvent to about 1 ml volume. Allow the apparatus to cool for at least ten minutes. Approximately 1 or 2 ml will condense into the ampule during this time. Remove the Snyder column and flask, rinsing the joints with a small amount of methylene chloride.

15. Quantitatively transfer the entire contents of the ampule to a 5.0 ml volumetric flask marked with the appropriate sample identification. Mix well and transfer a portion of the solution to a GC vial marked with the appropriate sample number. Transfer the rest of the solution to a 12 ml glass vial also marked with the appropriate sample number. The vial cap used should have a teflon liner. Store the 12 ml vial in the freezer--dated with the prep date, and put the GC vials in a vial file and store them in the GC Instrument Room.

    NOTE: If high levels of petroleum are expected based on preliminary observations, dilutions should also be prepared, bottled, and documented.

16. Prepare a DF 5 of the surrogate working solution with $MeCl_2$. Bottle a portion in a labeled GC vial so that it can be run with the batch of samples. Store the remainder of the solution in a 12 ml vial that has been appropriately labeled with the rest of the vials in the freezer.

Calculations:

See analysis method.

Statistical Information:

See analysis method.

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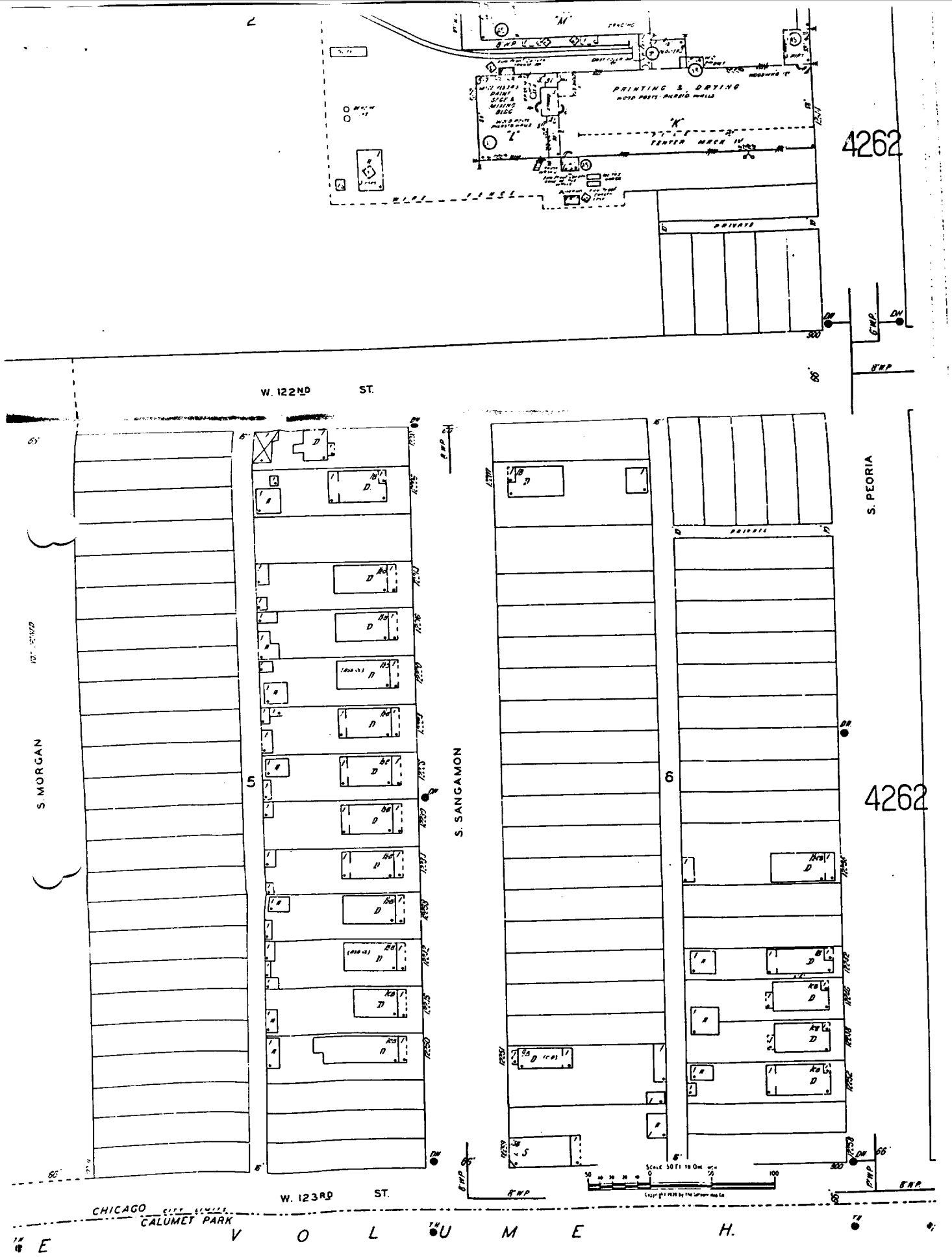
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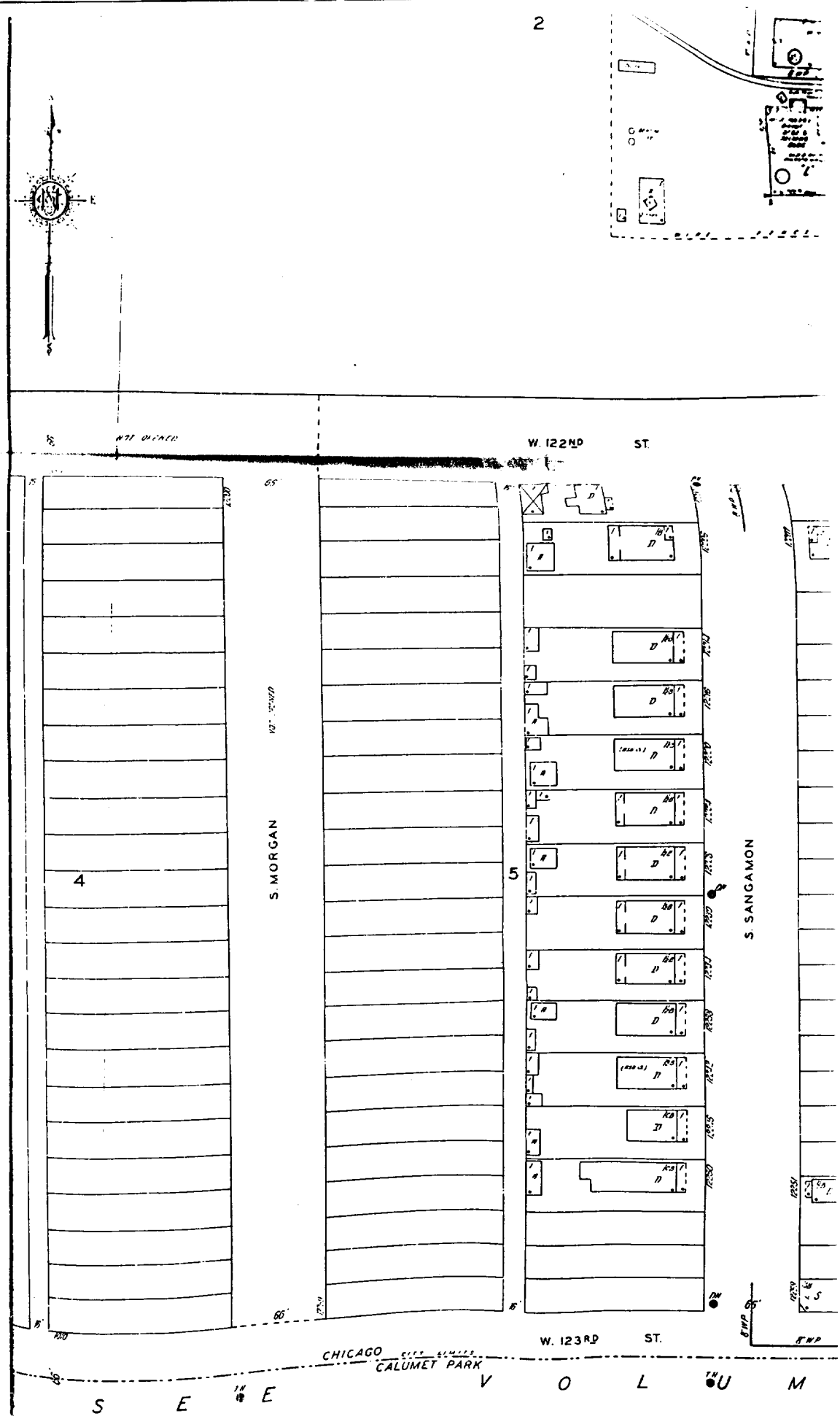
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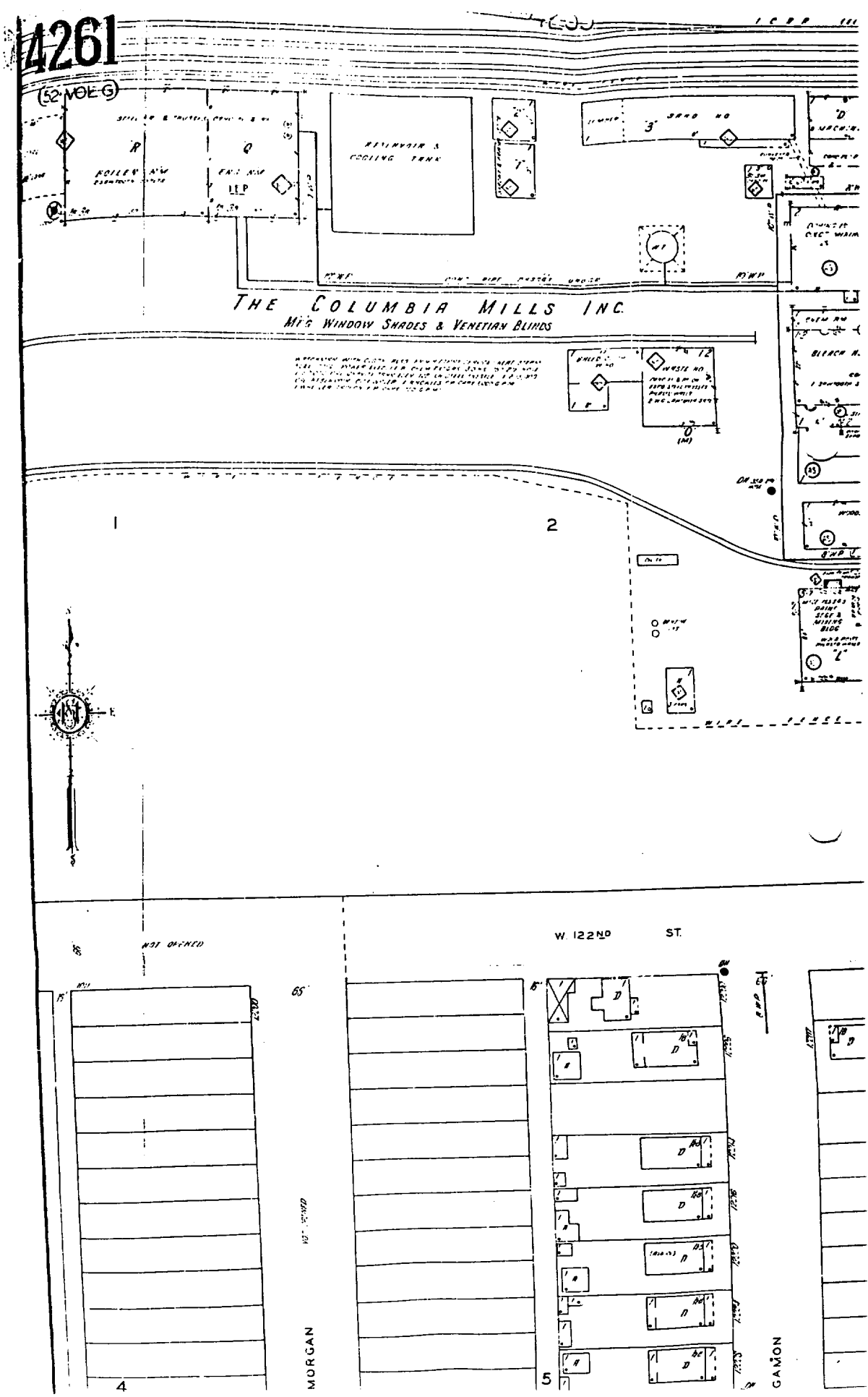
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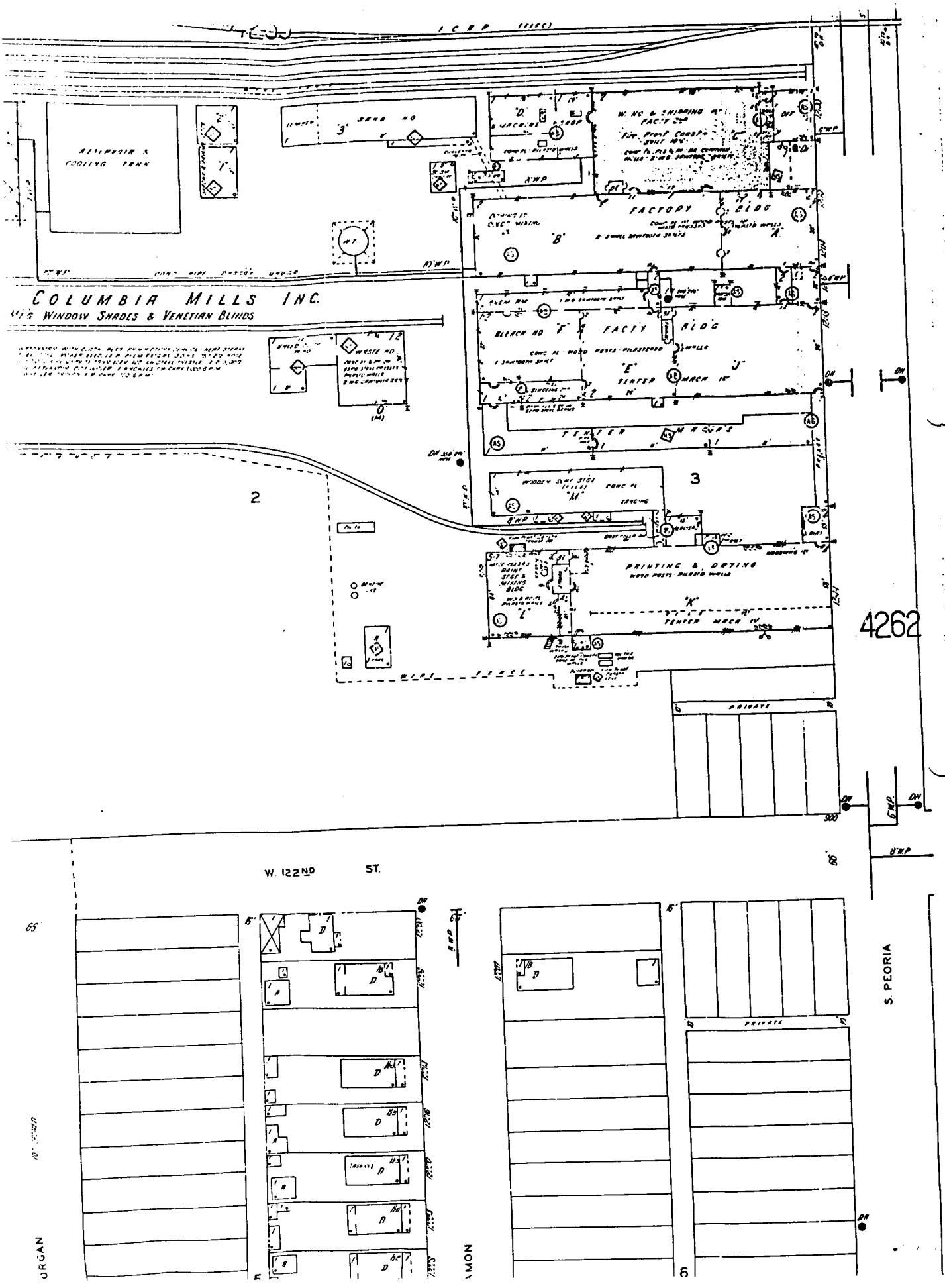

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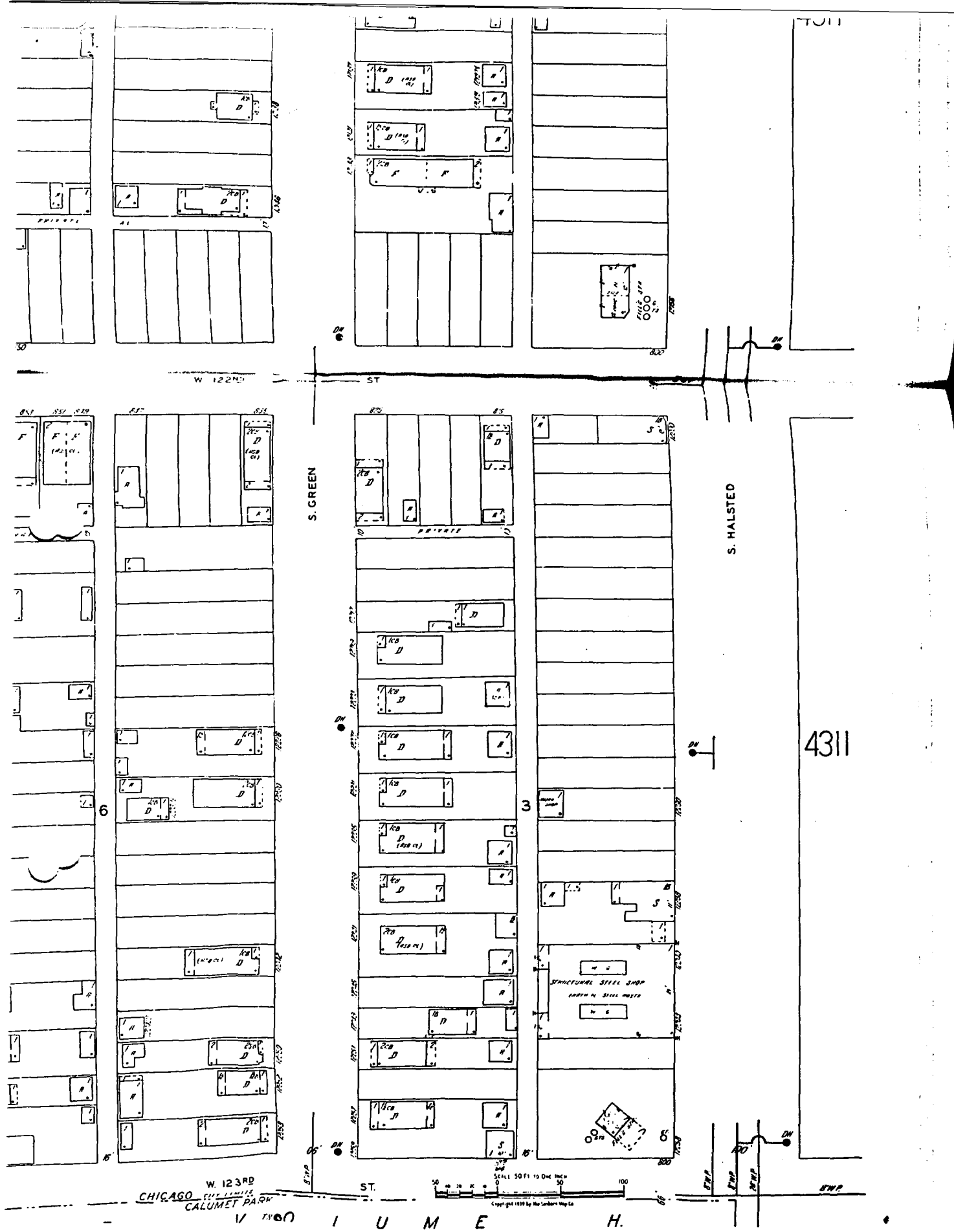
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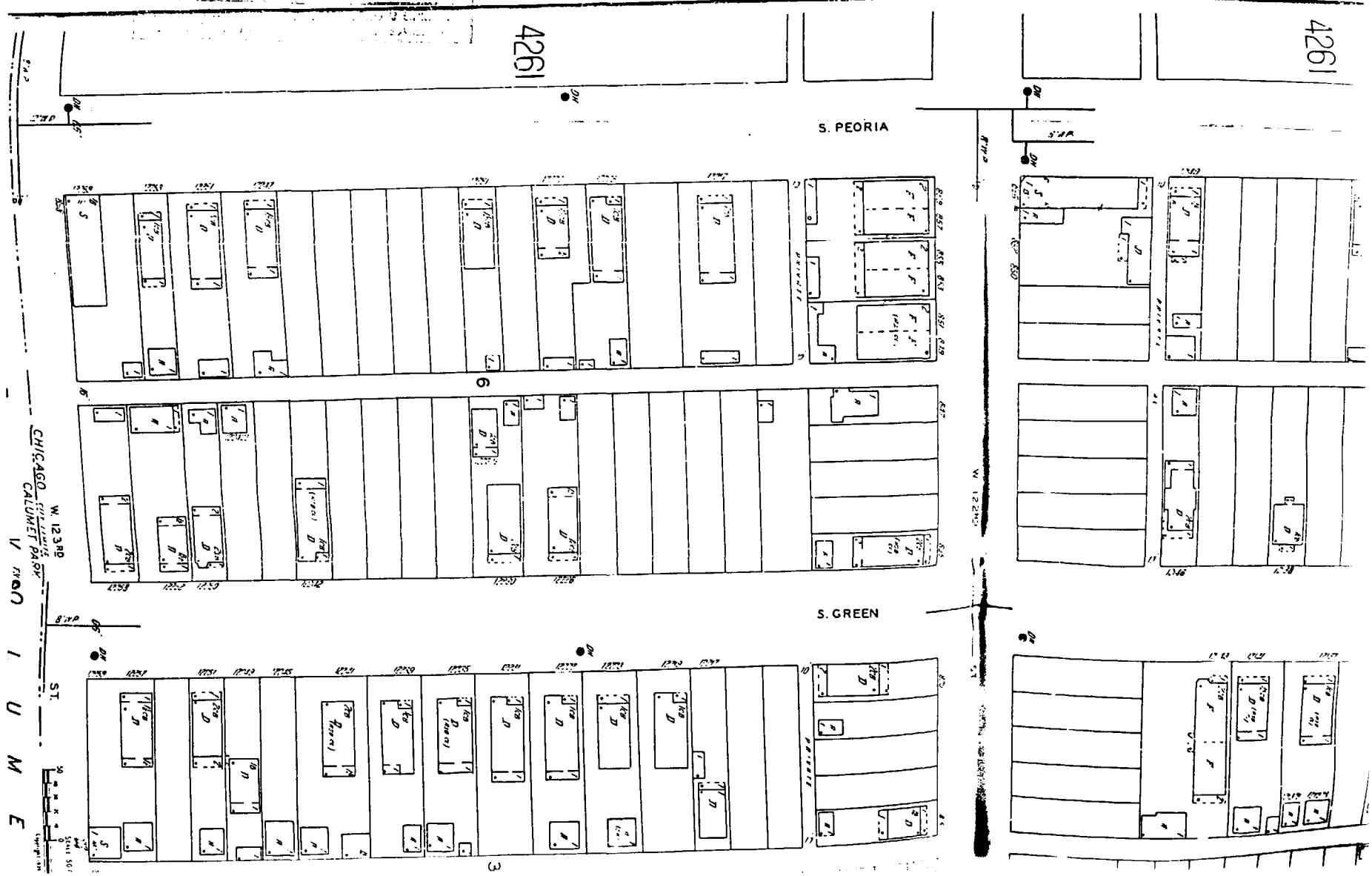
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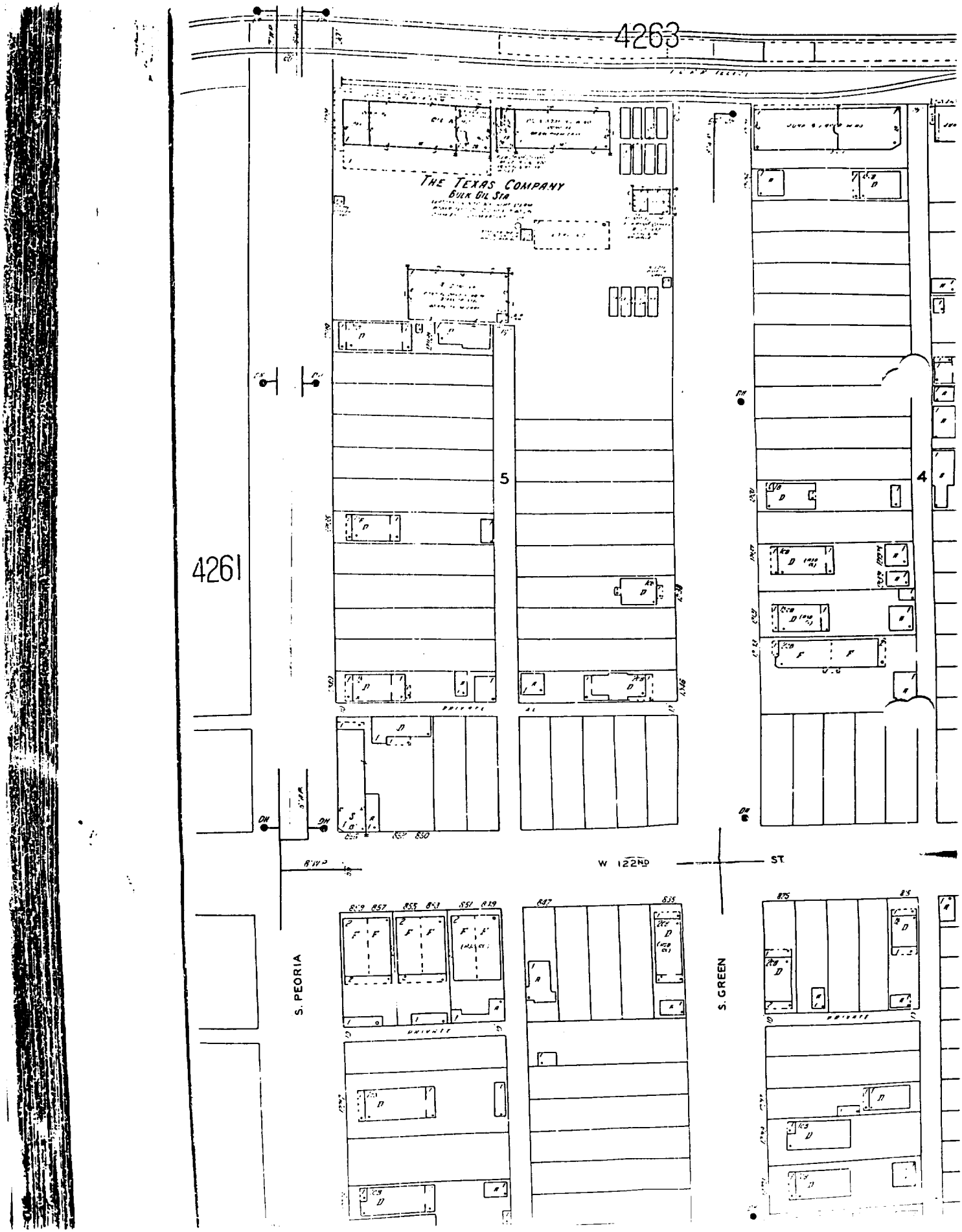
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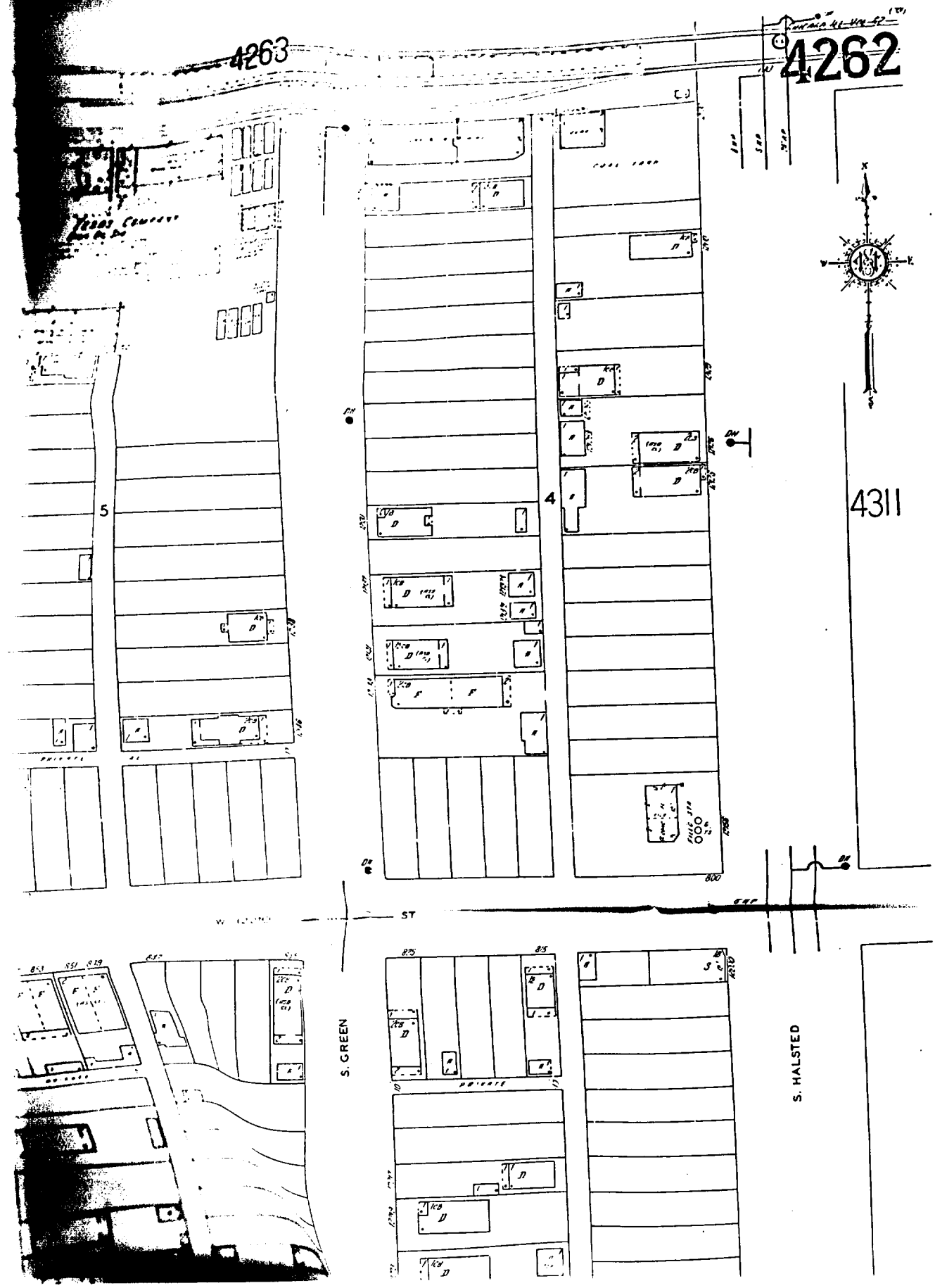
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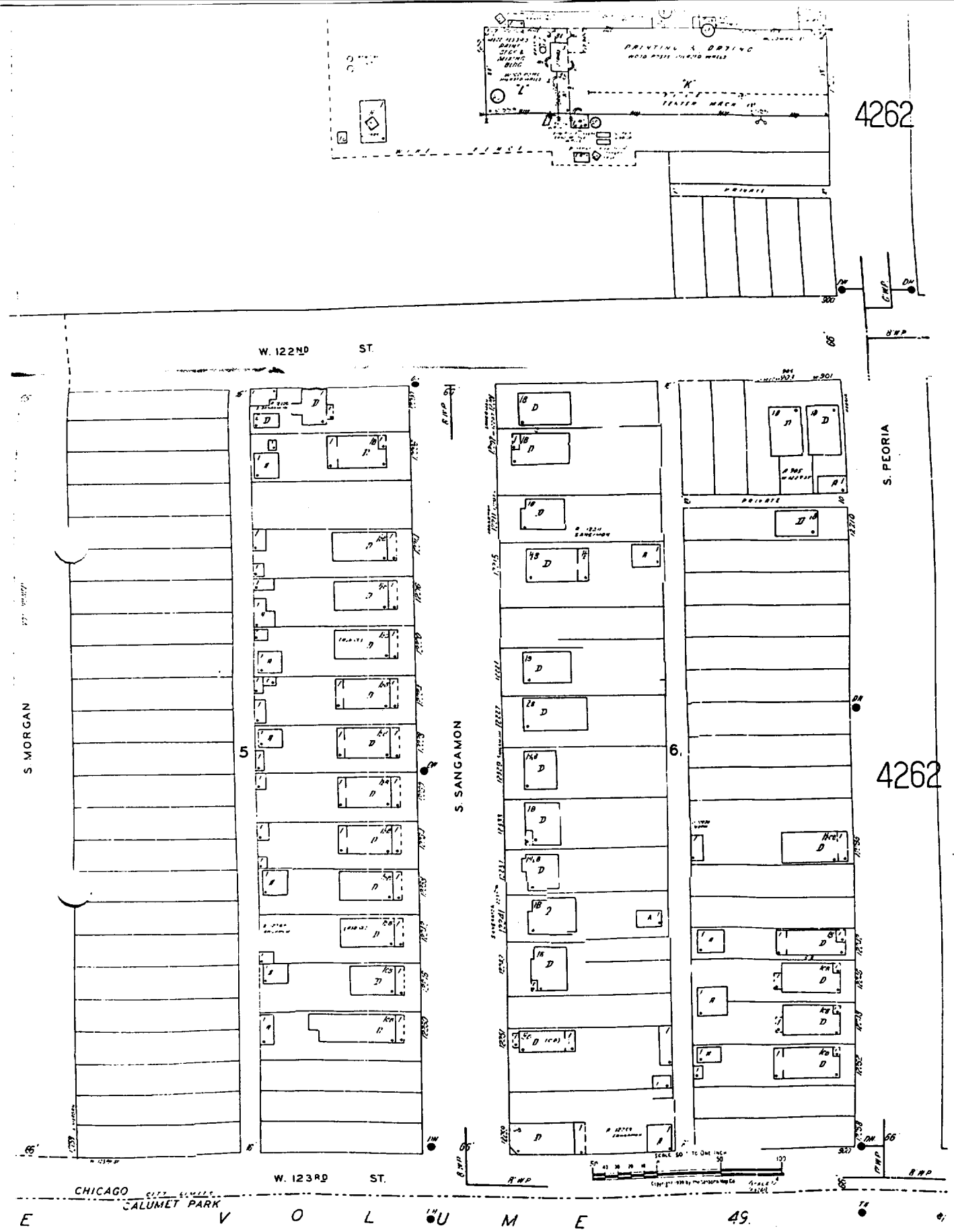
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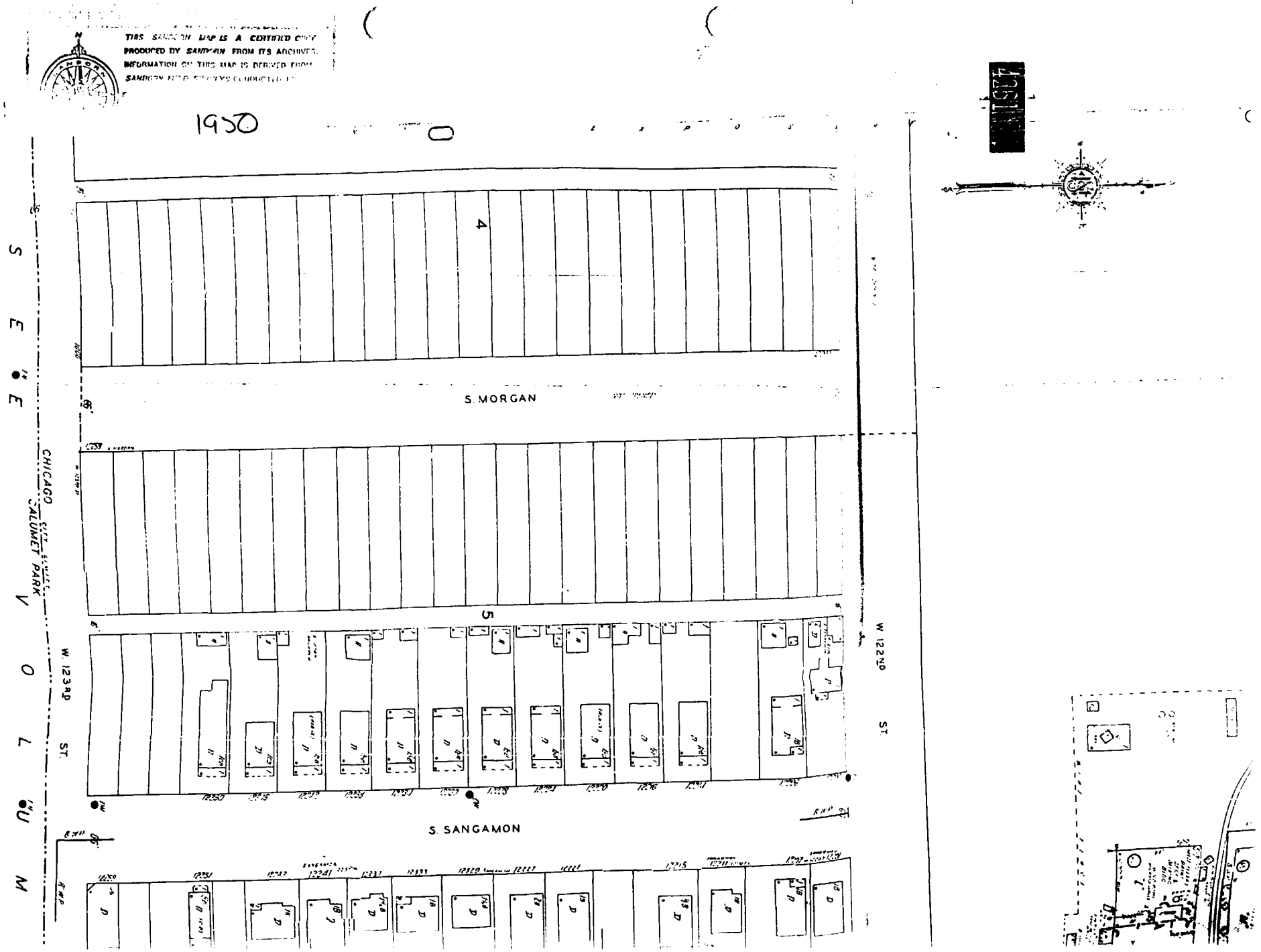
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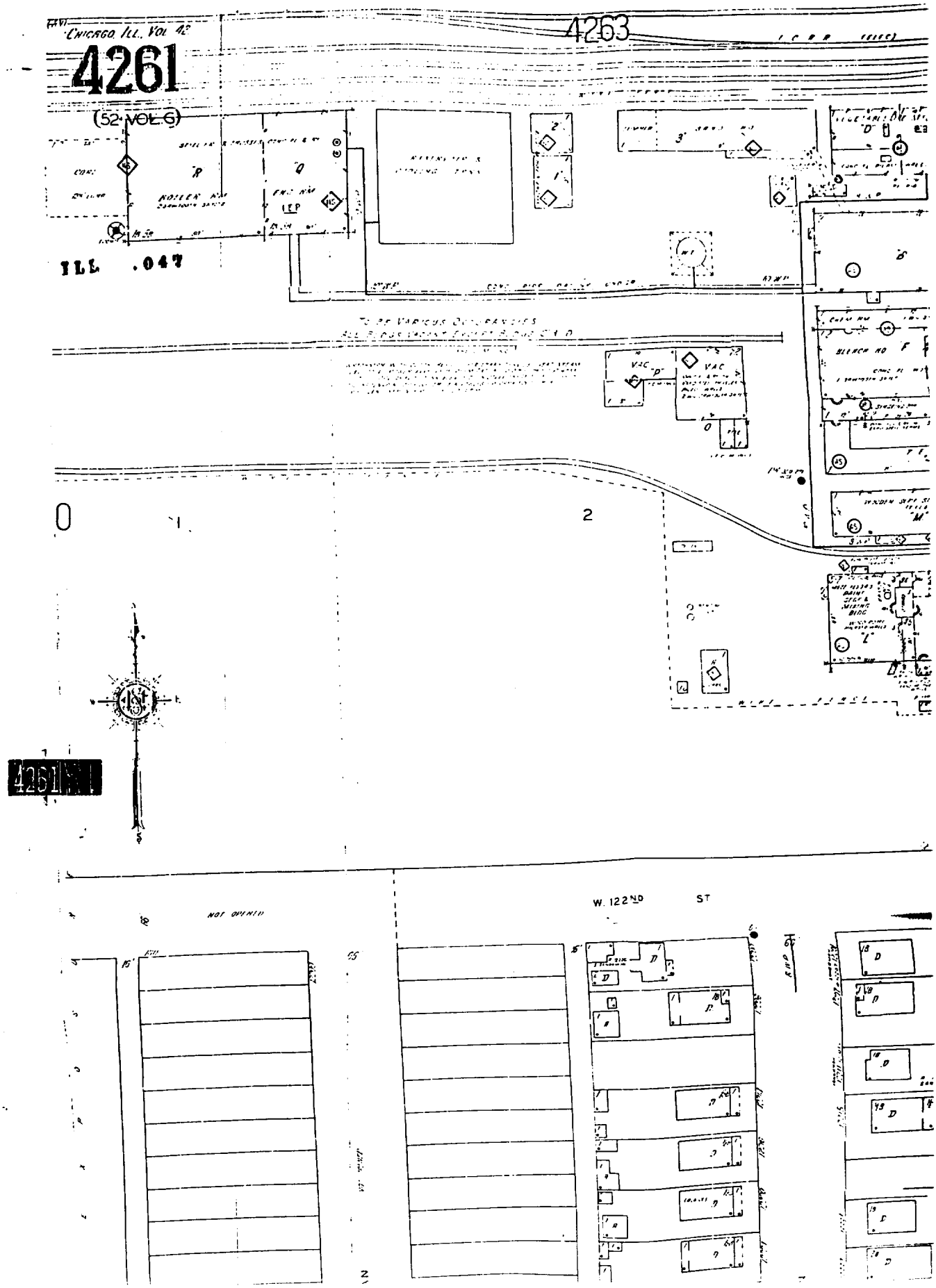
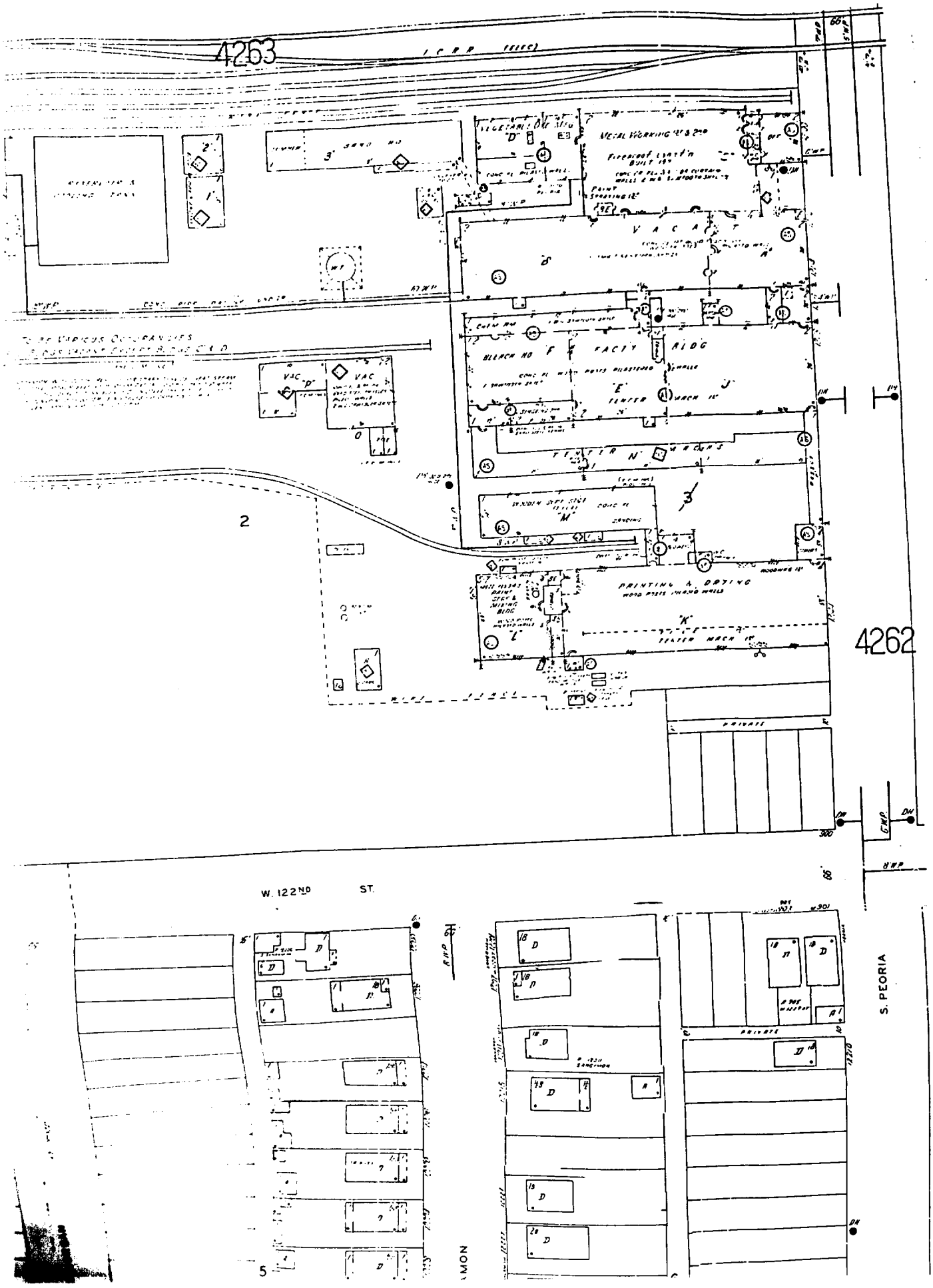
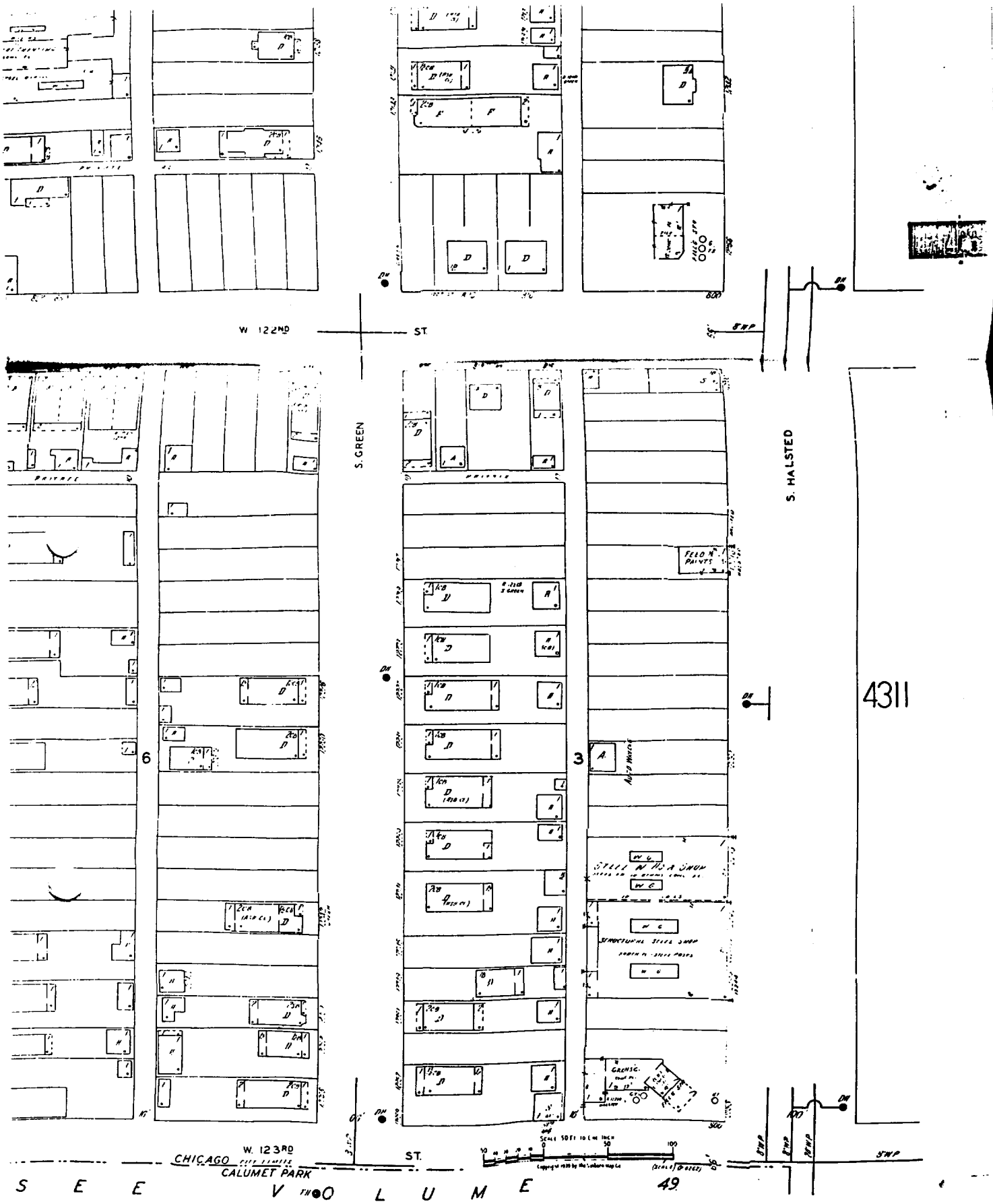
CALUMET PARK
S E E V O L U M

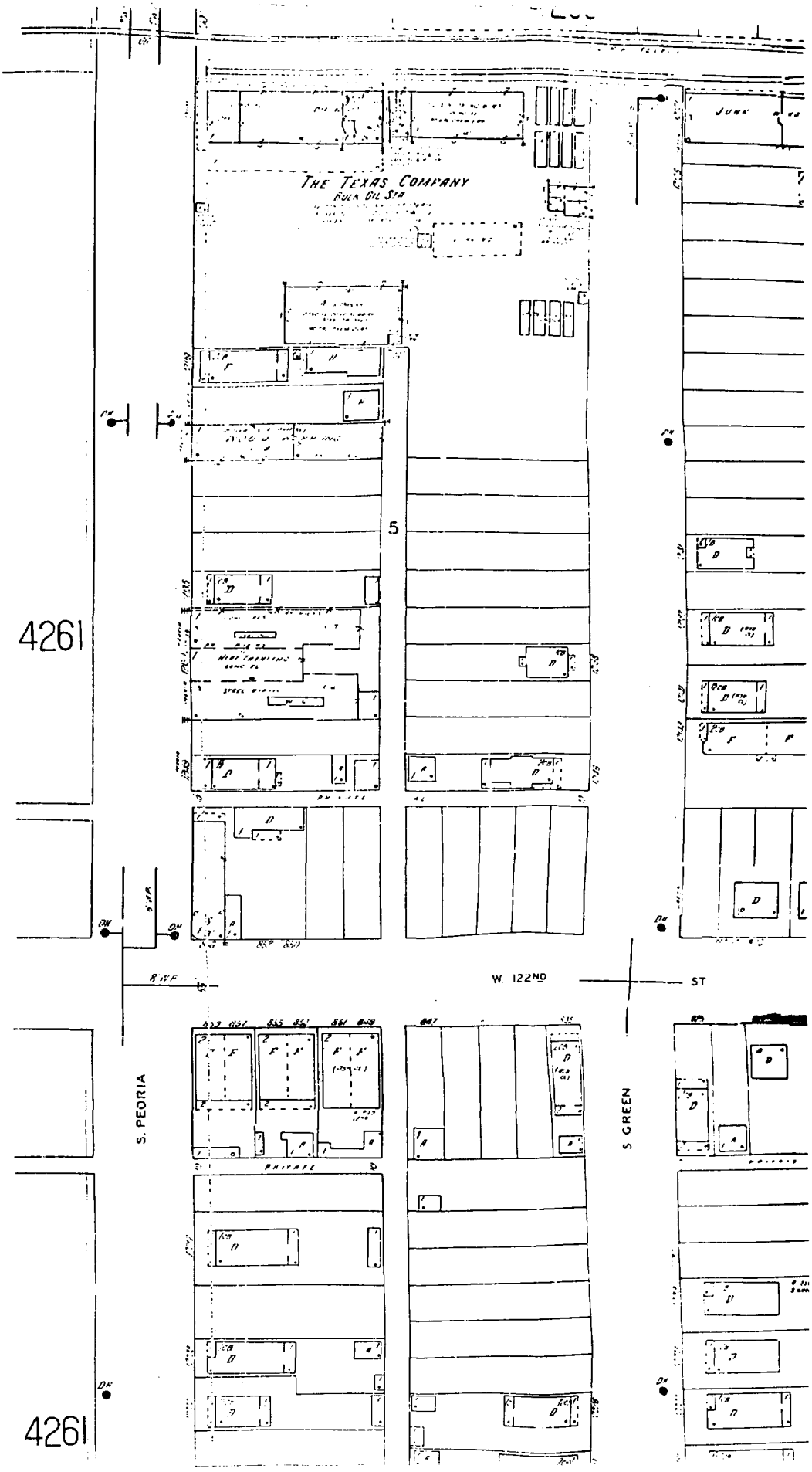


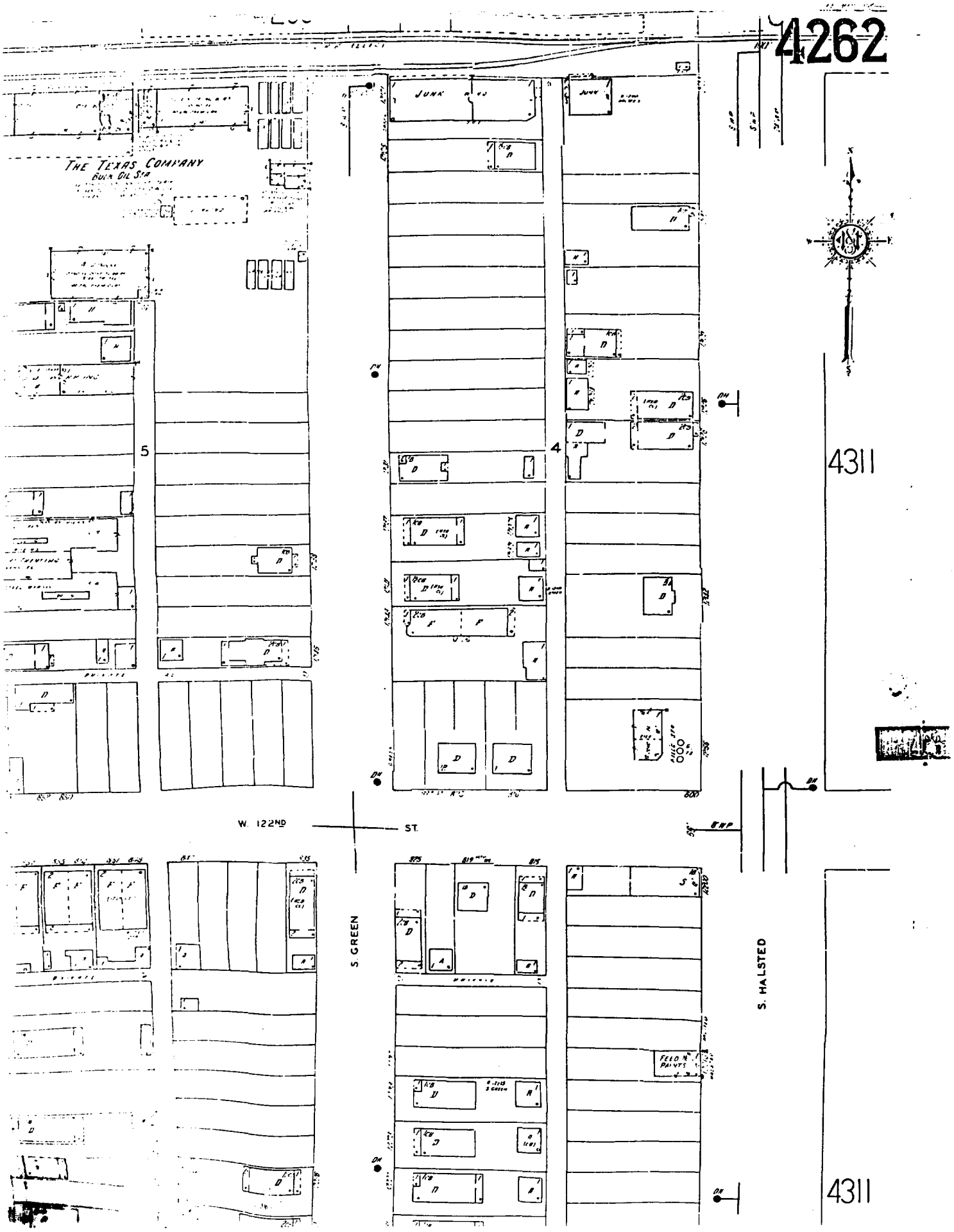
CHICAGO, ILL., VOL 42
4261
(52 VOL 6)
4263
ILL .047
TO BE VARIOUS OCCUPANCIES
VAC
BLEACH HO
NOT OPENED
W. 122ND ST

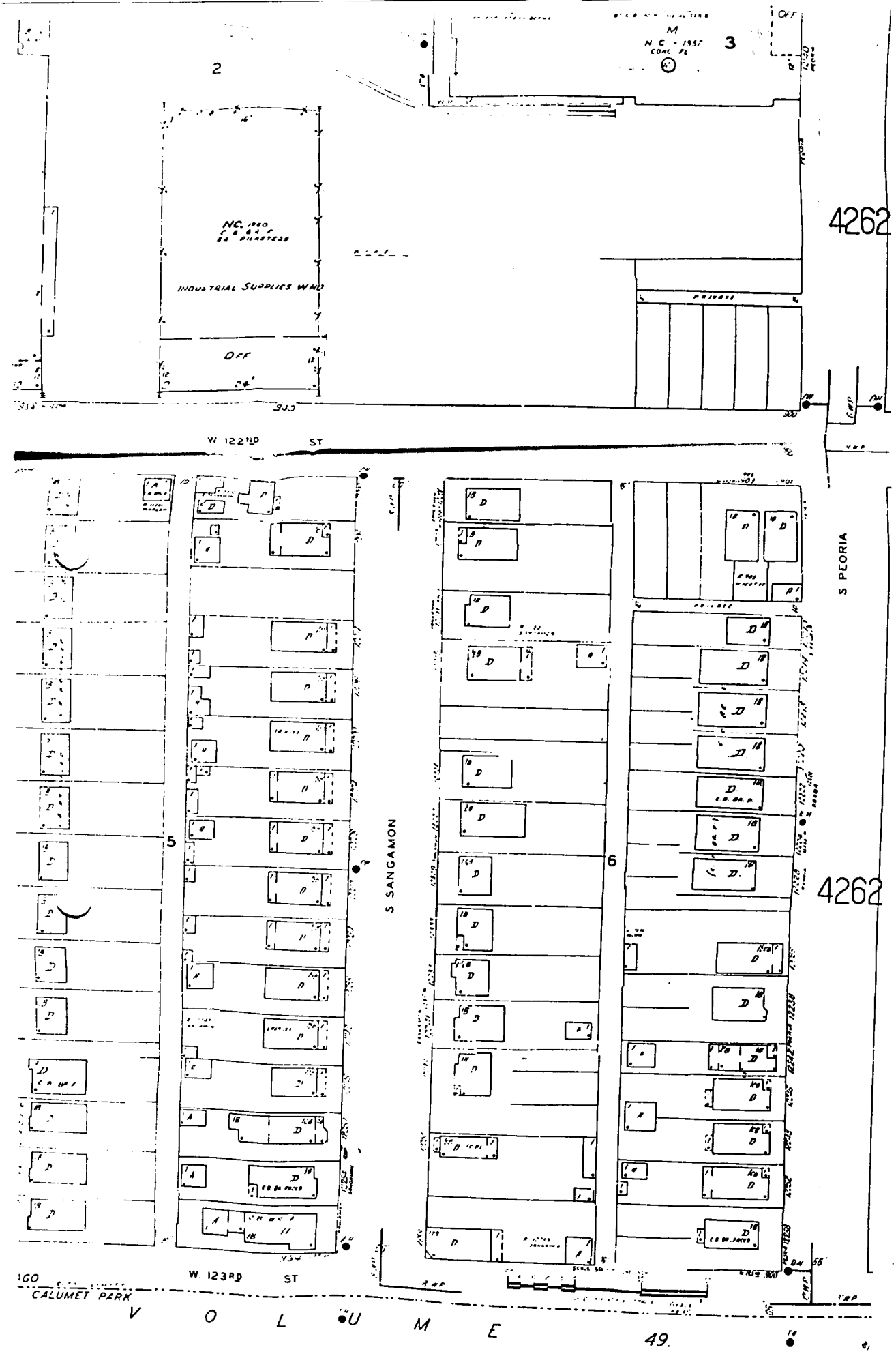

4263
4262
METAL WORKING
VACANT
FACTY BLDG
PRINTING & DRYING
W. 122ND ST.
S. PEORIA
PRIVATE
2
5


W. 122ND ST.
S. GREEN
S. HALSTED
4311
6
3
W. 123RD ST.
CHICAGO
CALUMET PARK
SEE VOLUME 49

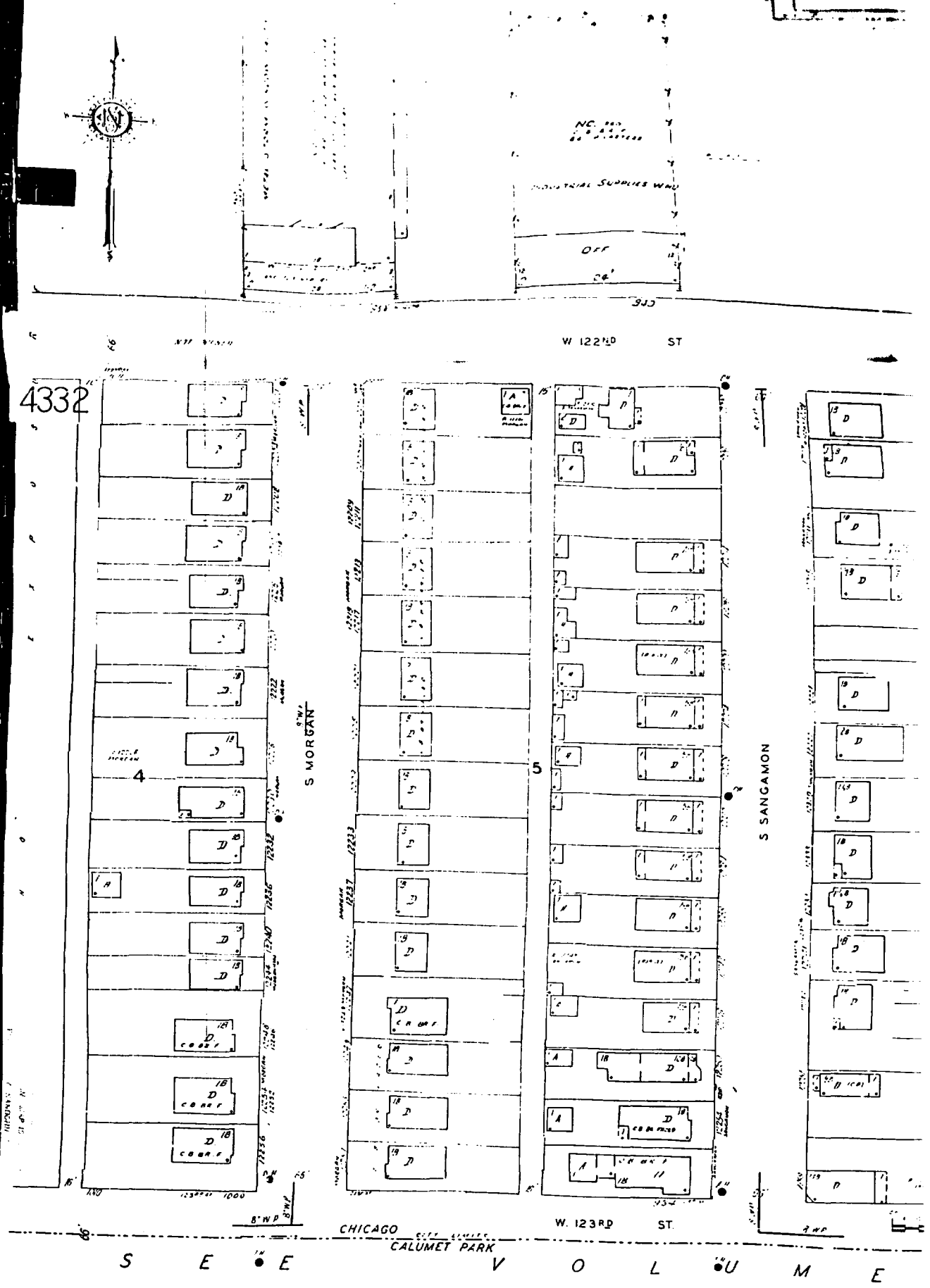
THIS [illegible] MAP IS A CERTIFIED COPY
PRODUCED BY SANBORN FROM ITS ARCHIVES.
INFORMATION ON THIS MAP IS DERIVED FROM
SANBORN FIELD SURVEYS CONDUCTED IN:
1950

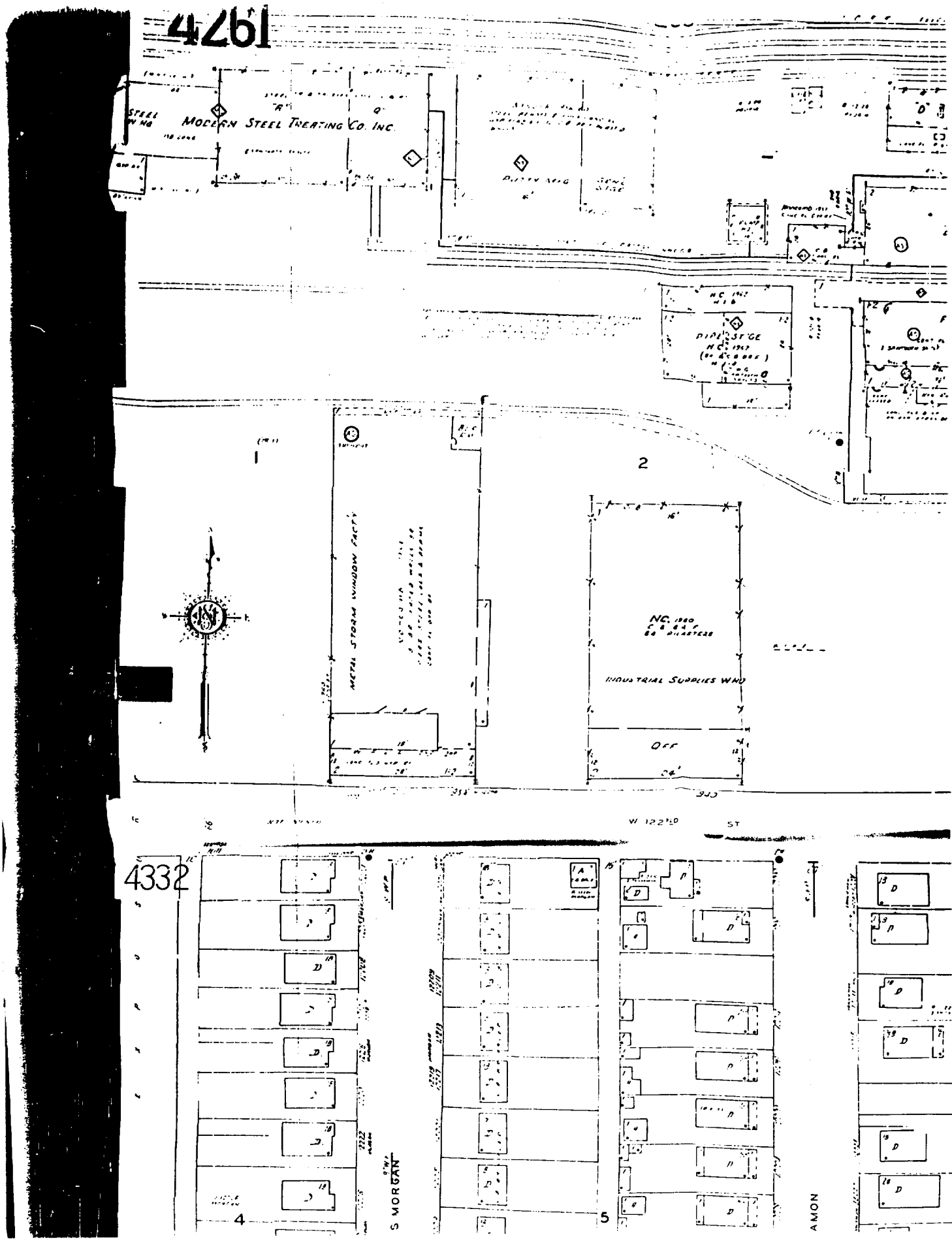

THE TEXAS COMPANY
JUNK
5
4261
W 122ND
ST
S. PEORIA
S GREEN
PRIVATE
4261

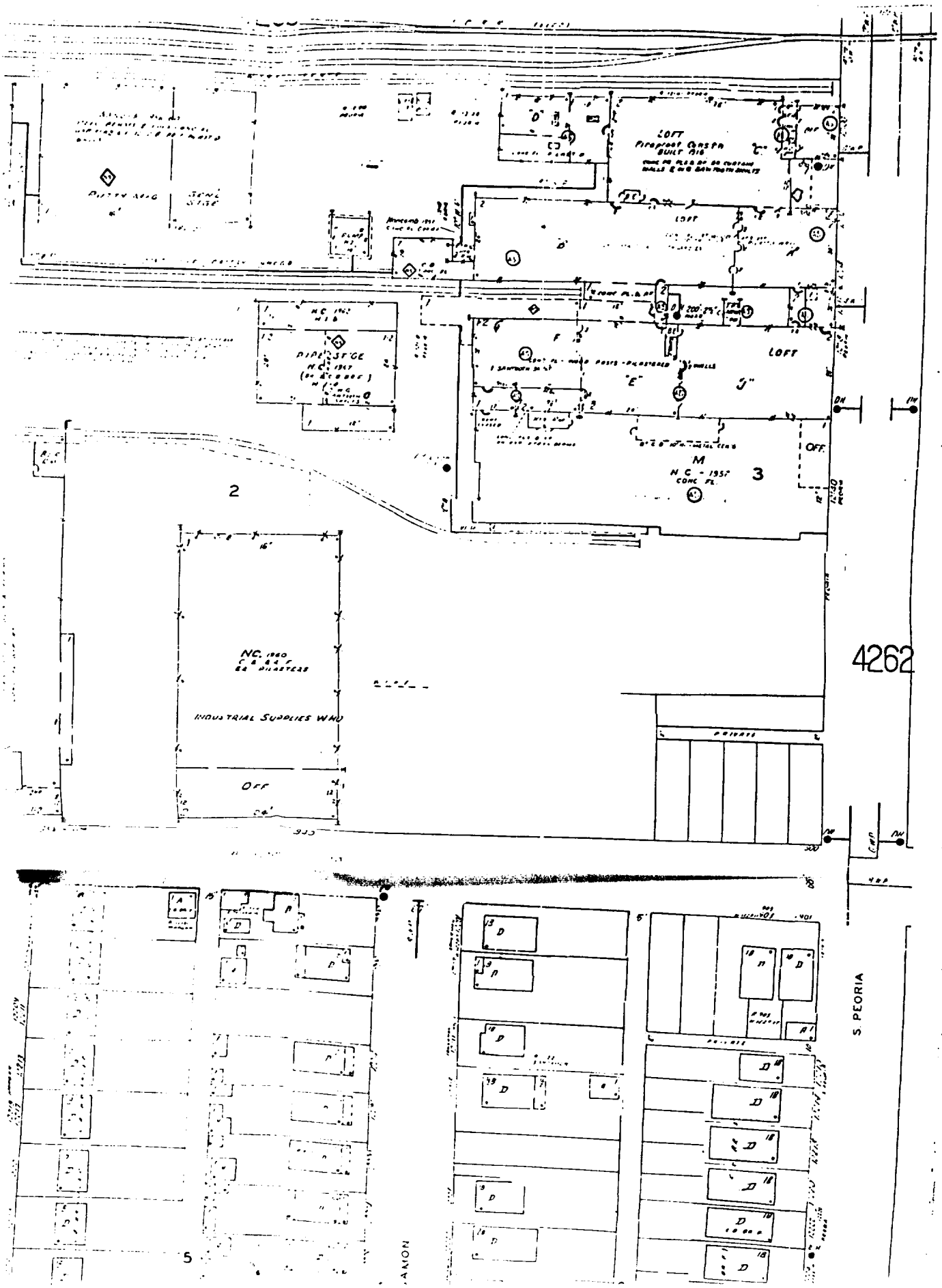

4262
THE TEXAS COMPANY
BULK OIL STA
JUNK
5
4
4311
W. 122ND ST.
S. GREEN
S. HALSTED
FIELD'S PAINTS
4311

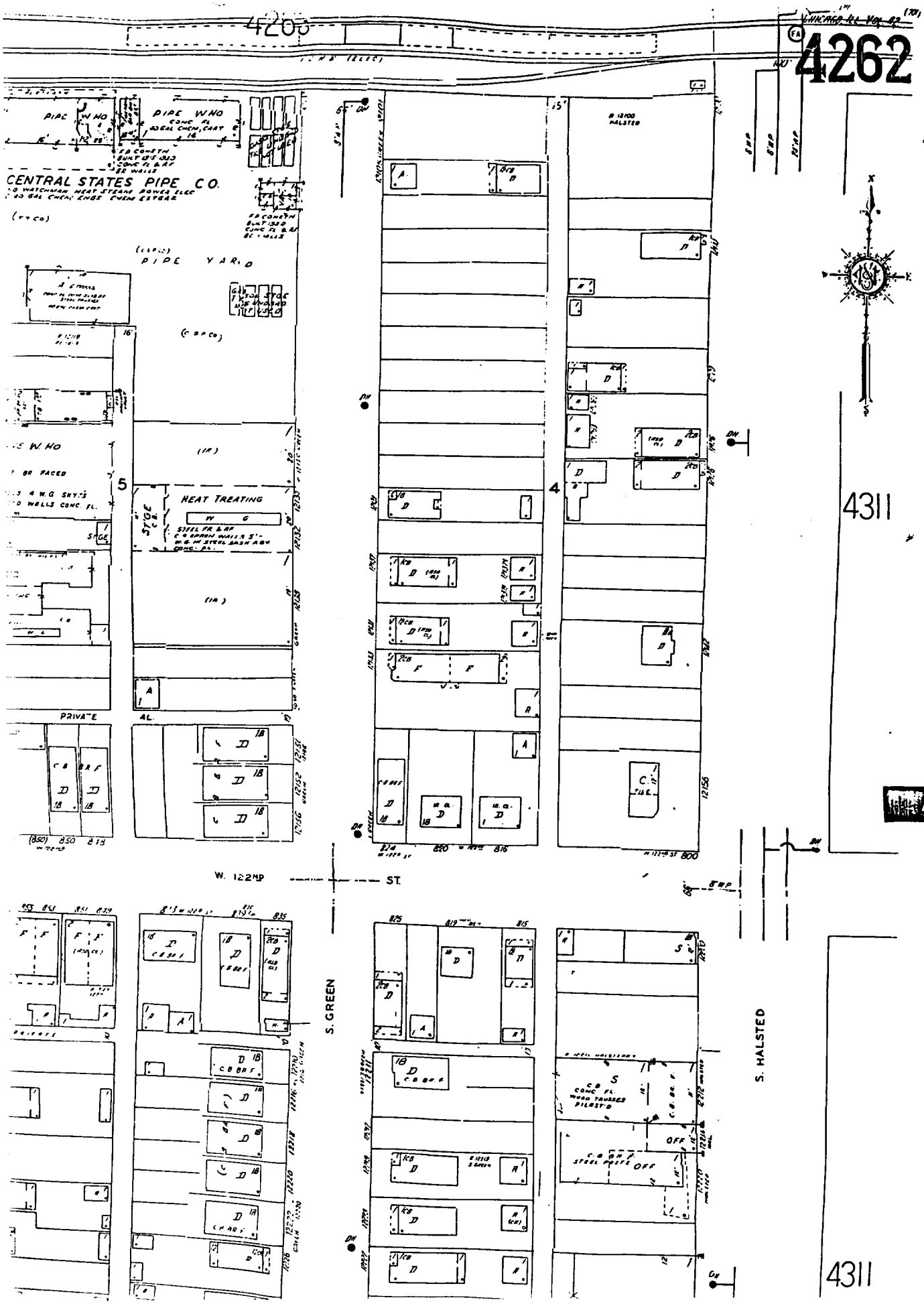


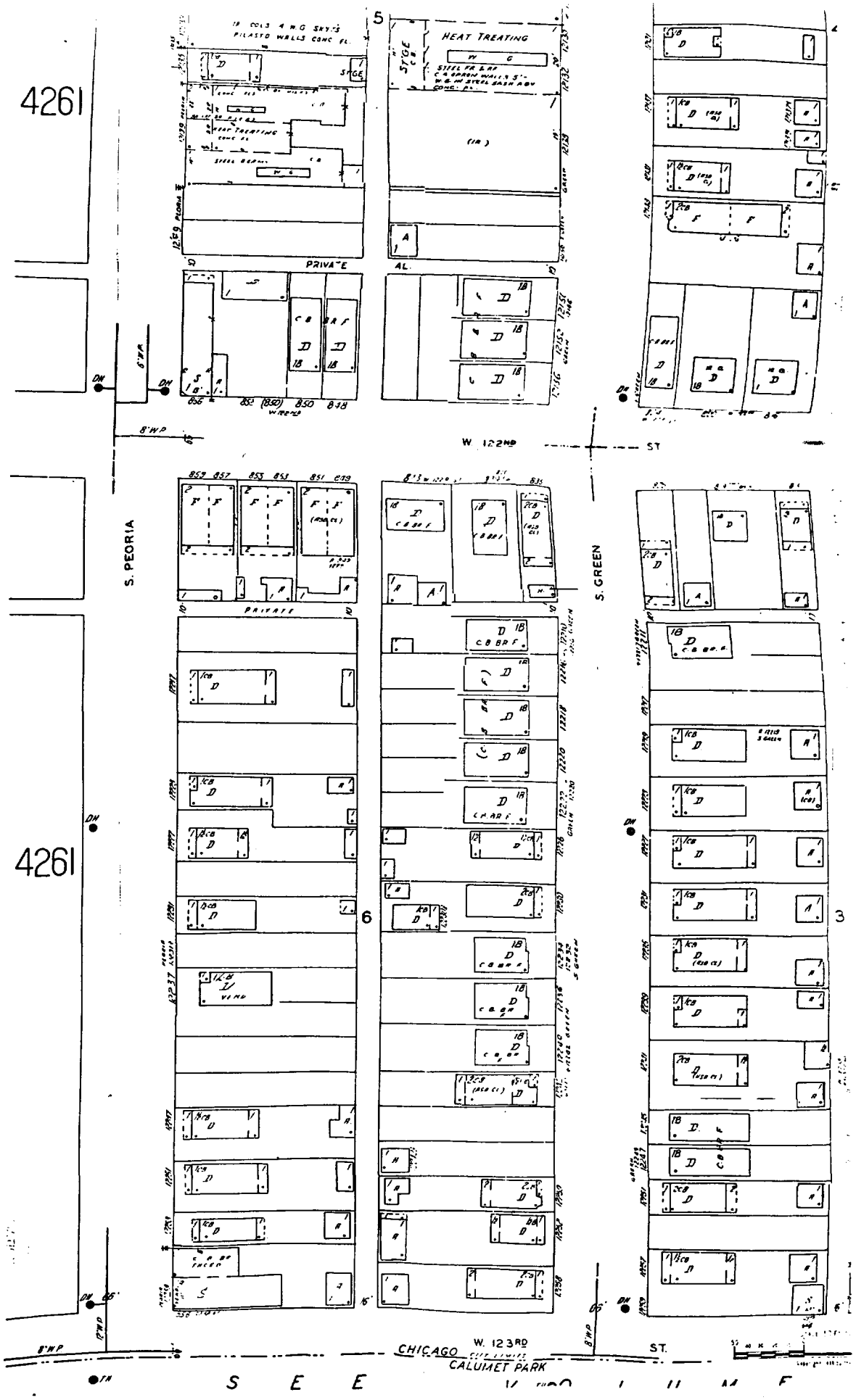
2
3
M
N C - 1957
CONC FL
OFF
NC. 1960
INDUSTRIAL SUPPLIES WHD
OFF
24'
PRIVATE
4262
W 122ND ST
S PEORIA
S SANGAMON
5
6
4262
W. 123RD ST
CALUMET PARK
V O L U M E 49.


4332
W 122ND ST
S MORGAN
S SANGAMON
4
5
W. 123RD ST.
CHICAGO
CALUMET PARK
S E E V O L U M E

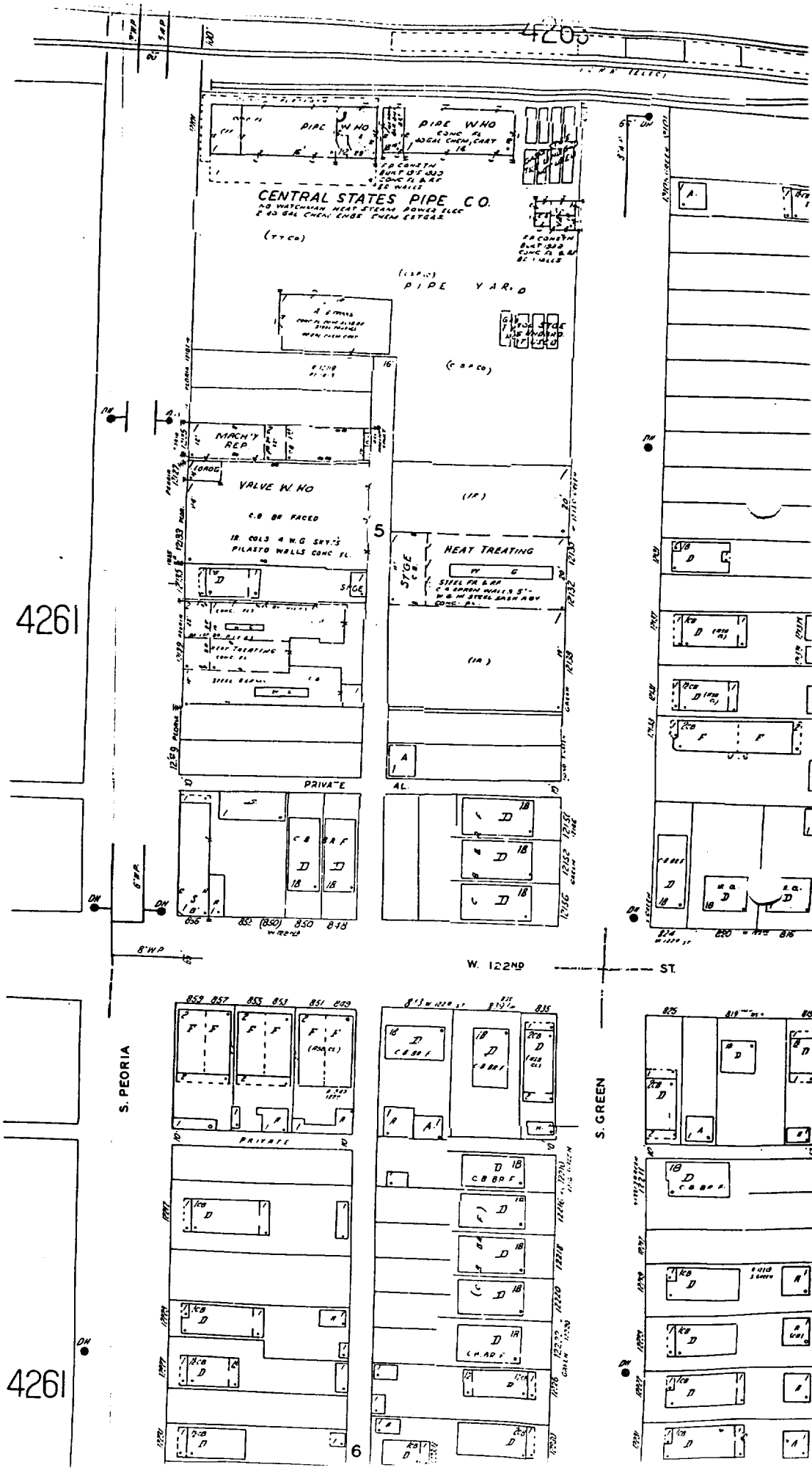

4261
MODERN STEEL TREATING CO. INC.
PIPE STGE
1
2
METAL STORM WINDOW FACT'Y
NC. 1960
INDUSTRIAL SUPPLIES WHO
OFF
W 122ND ST
4332
S MORGAN
4
5
AMON

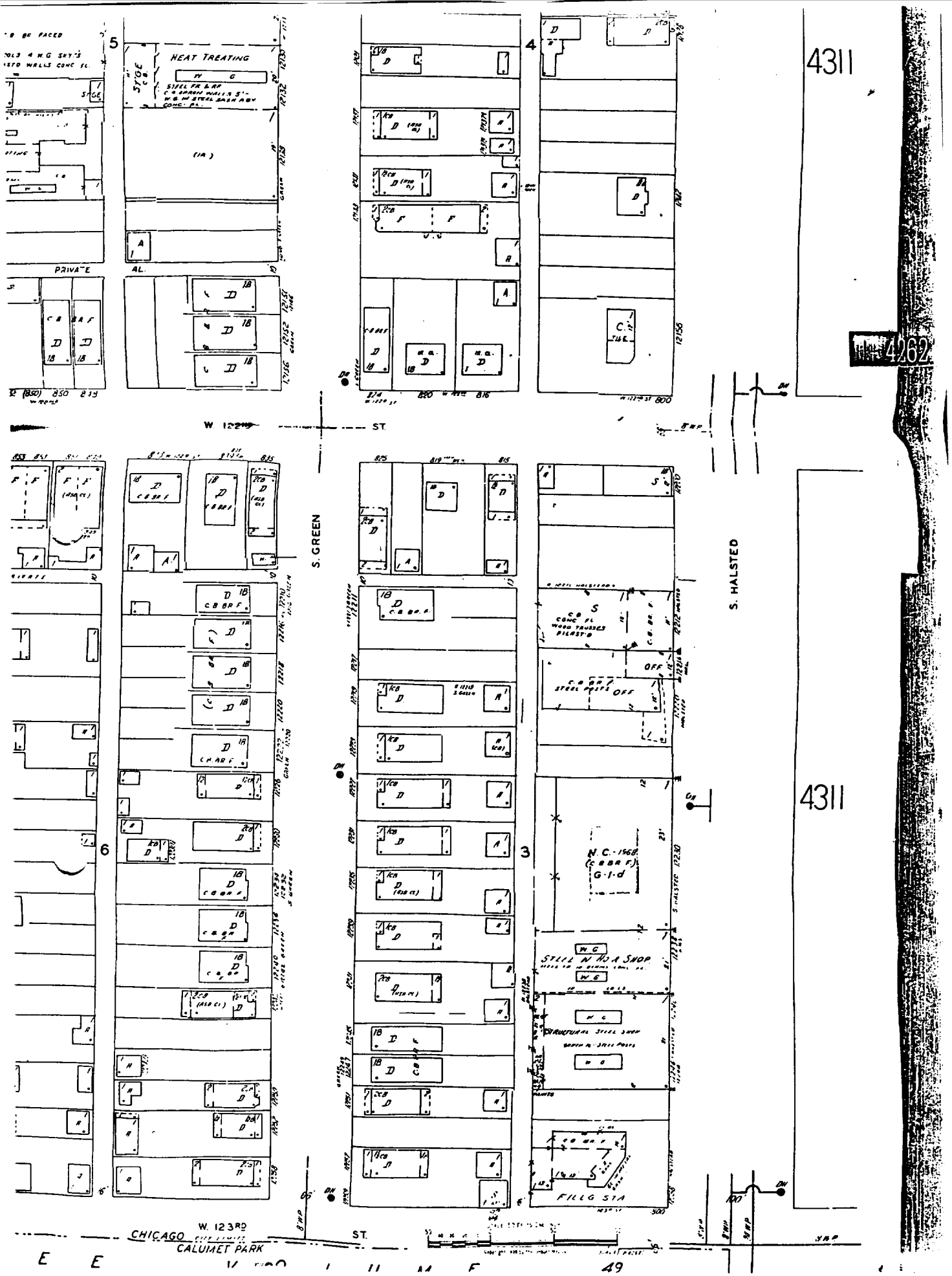

LOFT
Fireproof Constn
BUILT 1916
LOFT
LOFT
PIPE STGE
N.C. 1962
N.C. 1957
LOFT
OFF.
M
N.C. - 1957
CONC. FL.
3
2
N.C. 1960
INDUSTRIAL SUPPLIES WHO
OFF
4262
S. PEORIA
5


4262
4200
CENTRAL STATES PIPE CO.
PIPE YARD
HEAT TREATING
PRIVATE
W. 122ND ST.
S. GREEN
S. HALSTED
4311
4262
4311


4261
HEAT TREATING
PRIVATE
W. 122ND ST
S. PEORIA
S. GREEN
4261
PRIVATE
W. 123RD ST.
CHICAGO
CALUMET PARK

1975


4200
PIPE W.HO
PIPE W.HO
CENTRAL STATES PIPE CO.
PIPE YARD
MACH'Y REP
VALVE W.HO
HEAT TREATING
STGE
5
4261
PRIVATE
AL.
W. 122ND ST.
S. PEORIA
S. GREEN
PRIVATE
6
4261



HEAT TREATING
PRIVATE
AL.
W. 122ND ST.
S. GREEN
S. HALSTED
4311
4262
4311
N. C. - 1968
G-1-d
STEEL W HO A SHOP
STRUCTURAL STEEL SHOP
FILLG STA
W. 123RD ST.
CHICAGO
CALUMET PARK
49