State of California
AIR RESOURCES BOARD

Resolution 87-10

January 23, 1987

Agenda Item No.: 87-2-2

WHEREAS, Health and Safety Code Section 41805.5 requires the Air Resources Board ("Board"), in coordination with the air pollution control districts, to develop and publish test guidelines for landfill gas and ambient air testing at active solid waste disposal sites on or before February 1, 1987;

WHEREAS, the Board approved "Testing Guidelines for Active Solid Waste Disposal Sites" at a public meeting held December 18, 1986;

WHEREAS, Health and Safety Code Section 41805.5 defines a solid waste disposal site to include sites which accept or have accepted hazardous waste;

WHEREAS, the Air Resources Board staff, with the participation of representatives of local air pollution control districts, the Department of Health Services and the Water Resources Control Board, have prepared a proposed guidance document titled "Hazardous Waste Disposal Site Testing Guidelines" ("guidelines");

WHEREAS, Health and Safety Code Section 41805.5 requires owners of active solid waste disposal sites to submit a solid waste air quality assessment test report to the local air pollution control districts;

WHEREAS, Health and Safety Code Section 41805.5 requires the Air Resources Board to publish guidelines specifying air contaminants to be tested for and identifying acceptable testing, analytical and reporting methods;

WHEREAS, the California Environmental Quality Act and Board regulations require that no project having significant adverse environmental impacts be adopted as proposed is feasible alternatives or mitigation measures are available;

WHEREAS, the Board has held a noticed public meeting to consider approval of the proposed guidelines and has received and considered the comments presented by its staff, representatives of the districts, affected government agencies, affected businesses, and other interested persons and agencies on the proposed guidelines; and

WHEREAS, the Board finds that:

> The proposed "Hazardous Waste Disposal Site Testing Guidelines," with the "Testing Guidelines for Active Solid Waste Disposal Sites" adopted December 18, 1986, fulfill the requirements of Health and Safety Code Section 41805.5; and
>
> No significant adverse environmental impacts associated with the proposed guidelines have been identified, and no potentially adverse environmental effects are likely to result from the implementation of the proposed guidelines.

NOW, THEREFORE, BE IT RESOLVED that the Air Resources Board approves the "Hazardous Waste Disposal Site Testing Guidelines" dated January 23, 1987, as set forth in Attachment A.

BE IT FURTHER RESOLVED that the Executive Officer shall forward the guidelines to air pollution control districts for their use in evaluating solid waste disposal site air quality assessment test reports.

I hereby certify that the above
is a true and correct copy of
Resolution 87-10, as adopted by
the Air Resources Board.

Harold Holmes

Harold Holmes, Board Secretary

State of California

AIR RESOURCES BOARD

Hazardous Waste Disposal Site Testing Guidelines

January 1987

STATE OF CALIFORNIA GEORGE DEUKMEJIAN, *Governor*

AIR RESOURCES BOARD
1102 Q STREET
.O. BOX 2815
SACRAMENTO, CA 95812

February 2, 1987

Dear Sir or Madam:

Enclosed are testing guidelines which were prepared to meet the requirements of Health and Safety Code Section 41805.5 (AB 3374, Calderon, 1986). The *Testing Guidelines for Solid Waste Disposal Sites*, approved by Air Resources Board on December 18, 1986, were prepared for solid waste disposal sites which have accepted only non-hazardous waste. The *Hazardous Waste Disposal Site Testing Guidlelines*, approved by the Air Resources Board on January 23, 1987, were prepared for sites which have accepted hazardous waste or both hazardous and solid waste (co-disposal).

If you have any questions regarding the *Testing Guidelines for Solid Waste Disposal Sites*, please call Kerry Holliday at (916) 322-6005. For questions regarding the *Hazardous Waste Disposal Site Testing Guidelines*, please call Lynn Baker at (916) 323-8511.

Sincerely,

Bob Barham, Manager
Source Evaluation Section

State of California
AIR RESOURCES BOARD

Resolution 87-10

January 23, 1987

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Harold Holmes, Board Secretary

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Harold Holmes, Board Secretary

State of California
Air Resources Board

HAZARDOUS WASTE DISPOSAL SITE TESTING GUIDELINES

Prepared Pursuant to

California Health and Safety Code Section 41805.5

Prepared by

California Air Resources Board
Stationary Source Division
Toxic Pollutants Branch

and

California Air Pollution Control Officers Association
Landfill Gas Testing Guidelines Working Committee

January 23, 1987

ACKNOWLEDGEMENTS

This document was written with the help of the CAPCOA Guidelines Committee whose time, energy, and patience has been greatly appreciated. We would particularly like to thank:

District Representatives

Tom Brennan	Bay Area AQMD
Larry Borrelli	Monterey Bay Unified APCD
Eric Skelton	Sacramento County APCD
Carl Norstedt	San Bernardino County APCD
Paul Sidhu	San Diego County APCD
Stella Willcox	San Diego County APCD
Fred Lettice	South Coast AQMD

ARB Representatives

Robert Barham
Lynn Baker
Kerry Holliday

California Waste Management Board Representative

Bill Orr

State Water Resources Control Board Representative

Jeff Barnickol

Second Printing
February 1987

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HAZARDOUS WASTE DISPOSAL SITE TESTING GUIDELINES

Prepared Pursuant to
California Health and Safety Code Section 41805.5

I. INTRODUCTION

A. Background

AB 3374 (Calderon) (Health and Safety Code (HSC) Section 41805.5, included as Attachment 1) requires all active solid waste disposal sites which have accepted solid and/or hazardous waste to conduct measurements to determine the composition of landfill gases, the presence of specified air contaminants in the ambient air, and whether off-site subsurface migration of landfill gas is occurring. To implement this new statute, ARB, in consultation with the air pollution control districts (APCD), was directed to develop guidelines "specifying the air contaminants to be tested for, and identifying acceptable testing, analytical, and reporting methods to be employed in completing the report." These guidelines apply to sites which have accepted hazardous waste, or solid and hazardous wastes (co-disposal). Separate guidelines have been prepared for sites which have accepted only solid waste.

The testing suggested in these guidelines is designed to provide an initial screening of disposal sites to determine which sites in the state may pose a potential public health risk. The APCD will review the test reports, and if the APCD determines the sites may pose a health risk, the sites may have to conduct additional monitoring or take remedial action.

All disposal site owners must submit testing proposals to the APCD for approval before any testing can begin. Climate and land differences in different parts of the state may require variations in the test procedures. Accordingly, testing and procedure variations are allowed in the guidelines.

All active disposal sites are required to conduct testing by July 1, 1987. An active disposal site is one which is currently receiving or has received solid waste since January 1, 1984. HSC 41805.5 defines an inactive site as one which has not received solid waste since January 1, 1984. Inactive sites should have completed and filed a screening questionnaire with the local APCD before November 1, 1986. Inactive sites should contact their APCD for information on the questionnaire. If the test report is not complete by July 1, 1987, the APCD may place the disposal site on a compliance schedule which includes a date by which the report must be filed. This date may not be later than January 1, 1989.

B. Report To The Air Pollution Control Officer

HSC 41805.5 requires all disposal site owners or operators to submit a test report to the local air pollution control officer (APCO). The test report for active landfills is due on July 1, 1987. To comply with HSC 41805.5, the test report must contain:

"1. Chemical characterization test results to determine the composition of gas streams immediately above the solid waste disposal site, or immediately above the solid waste disposal site and within the solid waste disposal site, as appropriate, as determined by the district.

2. Analyses for specified air contaminants in the ambient air adjacent to the solid waste disposal site to determine the effect of the site on air quality.

3. Test results to determine if there is any underground landfill gas migration beyond the solid waste disposal site's perimeter."

Testing is conducted for all compounds listed in Attachment 2. The APCO may also require review of additional compounds upon identificaton of testing and health effects information. Section II contains the gas stream characterization procedures. For the gas stream characterization test at disposal sites with landfills containing hazardous or solid and hazardous wastes, the integrated surface sample or the landfill gas test and the integrated surface sample will be used to determine what is in the landfill gas. At surface impoundments containing liquid hazardous wastes, landspreading operations, waste piles (uncovered landfills), or drum burial sites, an integrated surface sample will be collected around the perimeter of the impoundment. Section III contains the ambient air testing procedures. For the ambient air test, the site operator will conduct 10 days of ambient air samples at the site perimeter. Section IV contains the gas migration testing procedures. For the gas migration test at co-disposal sites, one migration test well will be installed for each 1000 feet of site perimeter for sampling to determine if there is off-site gas migration. The perimeter probes will be installed between the site and areas where off-site migration would cause the greatest threat to public health and safety. At disposal sites which have received only hazardous waste, a maximum of four wells will be installed around the perimeter of the site.

HSC 41805.5 requires all solid waste assessment test reports to be filed by July 1, 1987. If, however, the report is not complete by that date, the APCO can place the disposal site on a compliance schedule which includes a date by which the report must be filed.

To ensure that an adequate hazardous waste test report is prepared, each disposal site owner must submit a proposal to the APCO. The proposal should include a description of the gas characterization system to be used, location of all monitoring wells both on and off the site, an ambient air monitoring plan including a meteorological data summary, and all the results of past air or landfill gas testing performed at the site, including the results of any testing done to prepare the proposal. Testing cannot begin until the APCO approves the monitoring plan.

C. Report To The Air Resources Board

Government Code Section 66796.54(b) requires the ARB to prepare a report to the legislature on "the extent of hazardous waste in solid waste disposal sites and the potential effects these hazardous wastes may have upon the ambient air quality of the state." In order to prepare this report the ARB will review the data gathered under the guidelines. The form for the report to the ARB is Attachment 3. This form should be completed by the site operator and forwarded to the APCO with the report. Once the APCO determines the hazardous waste assessment test report is adequate, the form should be forwarded to the ARB.

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II. GAS STREAM CHARACTERIZATION

HSC 41805.5 requires hazardous waste assessment test reports to include test results to determine the composition of gas streams immediately above the site, or immediately above the site and within the site, as appropriate, as determined by the APCO. Based on information provided on the individual disposal site, the APCO must determine which method is appropriate to characterize the site. The gas stream characterization may consist of one of the following methods:

1. Testing the air immediately above the surface or around the perimeter of the disposal site using the integrated surface sample, or

2. Testing the air immediately above the landfill surface and testing the gas within the landfill using both the integrated surface sample and the landfill gas sample.

The following gas characterization methods are recommended for different disposal operations:

TABLE 1: GAS CHARACTERIZATION METHODS

Disposal operation	Gas characterization method
Landfill	Integrated surface sample, or landfill gas test and integrated surface sample
Surface impoundment	Integrated surface sample
Landspreading	Integrated surface sample
Drum burial	Integrated surface sample
Waste pile (uncovered landfill)	Integrated surface sample

If the APCO approves characterization of the landfill gas by sampling the air immediately above the disposal site, then an integrated surface sample is taken. For landfilled and drum burial areas, the integrated surface sample involves sampling the air three inches above the landfill surface while a technician walks a prescribed course with the sampling equipment over one 50,000 square-foot grid of the landfill surface. The process is repeated for five 50,000 square-foot grid of the site and the samples are analyzed for the Attachment 2 compounds. For surface impoundments, waste piles, and landspreading operations, the integrated surface sample involves sampling the air around the perimeter of each impoundment while a technician walks around the impoundment. If the site accepted solid and hazardous waste, methane analysis is also required to gather information on overall site emissions.

Landfill gas testing involves taking samples of the landfill gas out of the interior of the landfill and testing them for the Attachment 2 compounds. The samples are also analyzed for oxygen and nitrogen for information on sample integrity. Carbon dioxide and methane concentrations will give information on gas production.

If the APCO approves characterization of the landfill gas by sampling the air immediately above the landfill surface and within the landfill, the operator should conduct the landfill gas testing as set out in these guidelines, and the integrated surface sampling for one 50,000 square-foot grid of the landfill.

Landfill gas testing requires the compounds listed in Attachment 2 to be determined to the "disposal site" detection limits. Integrated surface sampling requires the compounds listed in Attachment 2 to be determined to the "air" detection limits.

A. Landfill Gas Testing

If the disposal site has an operating interior gas collection system, samples should be taken from the system; additional wells need not be installed. Each installed well should be to a depth of at least 6 feet below the bottom of the intermediate or final cover. The well should not penetrate any leachate liner. During installation the contractor should take appropriate steps to mitigate the public nuisance of gas escape. All wells should be capped when not being sampled.

To locate the wells, draw a box around the landfilled area on a scale map with the box sides 100 feet outside the filled area edge. The sides should run north-south, east-west. Connect the opposite corners with diagonals. Locate 5 points: Point A at the diagonal intersection, point B at the center of the largest sector formed by the diagonals and the filled area, point C at the center of the next larger sector, point D at the center of the next larger sector, and point E at the center of the smallest sector. Figure 1 is an example. Five samples should be taken, one sample from each well and analyzed for the Attachment 2 compounds.

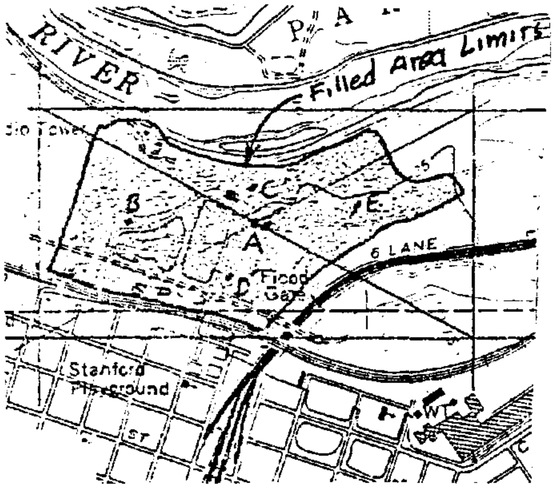

Figure 1: Well Location Example

To complete the HSC 41805.5 requirements for characterizing landfill gas, the owner should perform an investigation of methane emissions from one 50,000 square-foot grid of the disposal site along with the landfill gas test. This sample may be collected using an integrated surface sample as described in these guidelines or by taking methane measurements with a portable flame ionization detector, with a lower detection limit of 2 ppm. The grid and sampling method selected should be approved by the APCO.

1. Protocol

The technician should make certain the seal around the top of the well does not allow air infiltration. The well should not be sampled until 24 hours after the installation is complete. To sample the well, the technician attaches the pump and withdraws at least 2 well volumes from the well. The technician then attaches the bag and draws a ten liter sample at a one liter per minute rate. The bag should be in a light sealed container and should be analyzed within 72 hours.

If the APCO approves characterization of the landfill gas by sampling the air immediately above the landfill surface and within the landfill, the operator should conduct the landfill gas testing as set out in these guidelines, and the integrated surface sampling for one 50,000 square-foot grid of the landfill.

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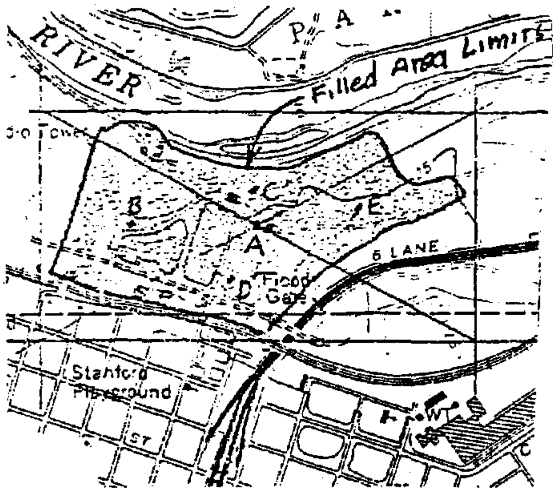
To locate the wells, draw a box around the landfilled area on a scale map with the box sides 100 feet outside the filled area edge. The sides should run north-south, east-west. Connect the opposite corners with diagonals. Locate 5 points: Point A at the diagonal intersection, point B at the center of the largest sector formed by the diagonals and the filled area, point C at the center of the next larger sector, point D at the center of the next larger sector, and point E at the center of the smallest sector. Figure 1 is an example. Five samples should be taken, one sample from each well and analyzed for the Attachment 2 compounds.



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If the owner chooses to leave the well intact for future sampling, the pipe should be capped or a valve installed to prevent gas leakage. If the owner removes the well, the hole should be filled and resealed to prevent gas escape.

2. Data

For each sample, the owner should record:

a. Date, time, and sample location.

b. Methane, CO_2, oxygen, and nitrogen concentrations.

c. Concentrations of compounds listed in Attachment 2. Analytical methods are included in Attachment 4.

d. The operating schedule, status, and gas quantity extracted for any landfill gas collection system for the previous 3 days for each day sampled.

B. Integrated Surface Sampling

The integrated surface sample is a method of characterizing disposal site emissions. Integrated surface sampling is designed to sample the emissions immediately after they have passed through the final landfill cover or after they have evaporated from a surface impoundment, waste pile, or landspreading operation. Because the sampling system will dilute the emitted landfill gas, use of more sensitive analytical methods are necessary to adequately characterize the sample.

For landfilled and drum burial areas, the owner will collect and analyze a minimum of five samples, one sample from each 50,000 square foot grid centered on points as determined in Figure 1 on page 4. Figure 2 is a typical walking pattern for each grid. For surface impoundments, waste piles, or landspreading operations, one sample will be collected from the air around the perimeter of each such disposal area on the site.

Sloped areas of the disposal site should be investigated along with the level areas. If investigation of the steep areas is a safety concern, the owner does not have to test these areas. The areas not to be tested must be approved prior to the testing by the APCO.

1. Number of Samples

One sample will be collected from each of the five grids, and one sample from near the edge of any surface impoundment, waste pile, or landspreading operation on the site.

2. Sampling Conditions

a. Average wind speed suitable for this sampling procedure is less than 5 miles per hour. Surface sampling should be terminated when the average wind speed exceeds 5 miles per hour or the instantaneous wind speed exceeds 10 miles per hour. Average wind speed is determined on a 10 minute average.

b. Surface monitoring is to be conducted when the disposal site is dry and no rain has fallen. The disposal site is considered dry when there has been no rain for the 72 hours prior to sampling.

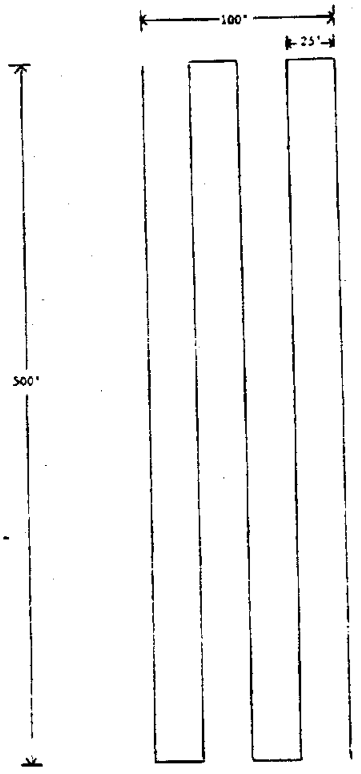

Figure 2: Walking Pattern
Source: South Coast AQMD

3. Equipment Description

An integrated surface sampler is a portable self-contained unit with its own internal power source. The integrated sampler consists of a stainless steel collection probe approximately 3.5 inches in diameter (funnel: 316 stainless steel), a flow meter, a pump, and a 10-liter Tedlar® bag enclosed in a light sealed cardboard box.

a. Power: Two 9 volt batteries.

b. Pump: One 12V DC pump. The diaphragm is made of nonlubricated Viton® rubber. The maximum pump unloaded flow rate is 4.5 liters per minute.

c. One 10-liter Tedlar® bag with a valve. The Tedlar® bag is contained in a light sealed cardboard box to prevent photochemical reactions from occurring during sampling and transportation. The valve is a push-pull type constructed of aluminum and stainless steel, with a Viton® o-ring seal.

d. Rotameter made of borosilicate glass with a flow range of 0 to 1 liter per minute. The scale is in milliliters with major graduations (labeled) every 5 ml and minor graduations every 1 ml.

e. Air Flow Control Orifice: Needle valve in the flow meter.

f. Funnel: 316 stainless steel.

g. Fittings, tubing and connectors: 316 stainless steel or Teflon®.

h. An anemometer with a continuous recorder: 3 cup assembly, range 0 - 50 miles per hour, with a threshold limit of 0.75 miles per hour or less.

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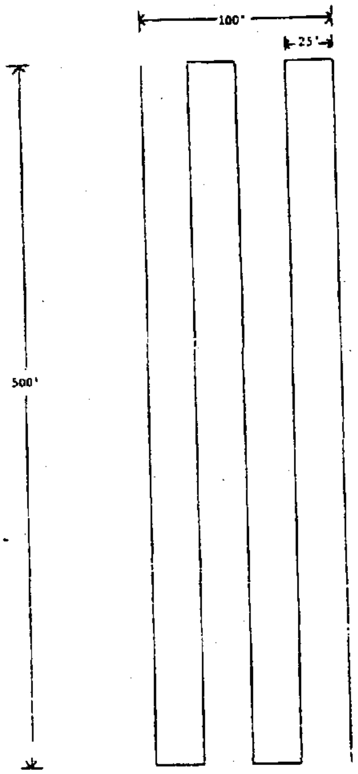

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e. Air Flow Control Orifice: Needle valve in the flow meter.

f. Funnel: 316 stainless steel.

g. Fittings, tubing and connectors: 316 stainless steel or Teflon®.

h. An anemometer with a continuous recorder: 3 cup assembly, range 0 - 50 miles per hour, with a threshold limit of 0.75 miles per hour or less.

4. Sampling Procedure

A portable bag sampler as described in the previous section will be used to collect an integrated surface sample from each grid, and around the perimeter of each surface impoundment, waste pile, or landspreading operation. During sampling at landfills or drum burial areas, the probe is to be placed approximately 2 to 3 inches above the disposal site surface. A separate gas sample of approximately 8 to 10 liters will be collected from each grid or disposal area. For 50,000 square foot grids, the sampler will be set at a flow rate of approximately 333 cubic centimeters per minute and the technician will walk through a course of approximately 2,600 linear feet as shown in Figure 2 over a continuous 25-minute period. For other grid sizes or disposal areas, collection rates and walk patterns should be fixed to collect 8 to 10 liters, if prior approval is obtained from the APCO.

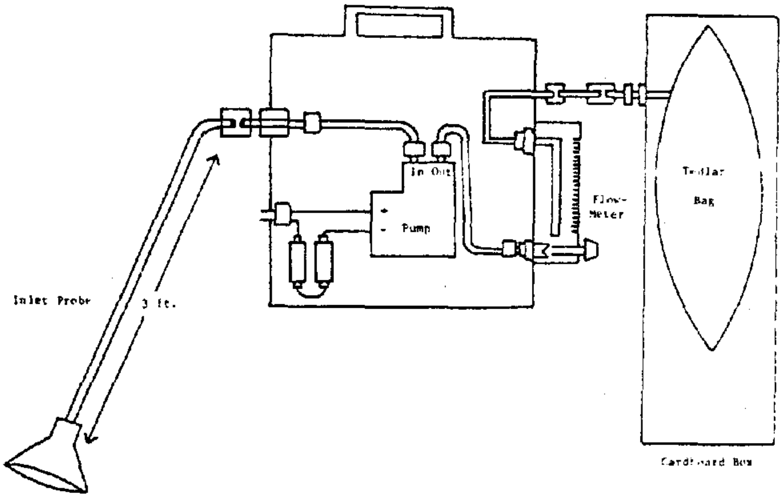

Figure 3: Integrated Surface Sampler
Source: South Coast AQMD

An anemometer and wind vane with continuous recorder will be installed at a site which is representative of the wind speeds and directions of the areas being sampled. The wind velocity should be recorded throughout the sampling period. The wind vane should be properly oriented.

5. Analytical Procedures

All bag samples collected should be analyzed within 72 hours of collection for total organic compounds and Attachment 2 compounds. The lower detection limits for these tests are listed in the "air" column of Attachment 2.

III. AMBIENT AIR MONITORING

HSC Section 41805.5 requires that air adjacent to disposal sites be tested and analyzed for specified air contaminants. To comply with HSC 41805.5, disposal site owners should conduct ambient air monitoring at the perimeter of the disposal site. The test should adequately characterize the contaminants in the air. The air column listed in Attachment

2 shows the lower detection limits to be achieved in parts per billion. Each disposal site should perform the ambient air sampling on ten separate, not necessarily consecutive, days. Ten days of ambient sampling provides an initial screening of hazardous waste disposal sites and allows for some daily variations in site operations, weather conditions, and emissions.

The disposal site operator is given the option of using one of three suggested procedures for testing the ambient air. These procedures were developed to cover differences in topography and climate which may occur at different sites. The option chosen will depend on the results of a meteorological survey conducted prior to ambient monitoring. Each option has two parts. One addresses sites with different day and night wind patterns and one addresses sites with the same day and night wind patterns.

A. OPTION 1

1. General Procedures

HSC Section 41805.5 requires that air adjacent to disposal sites be tested and analyzed for specified air contaminants. If the disposal site has a gas collection system which does not operate continuously, at least one of the sampling days should be a day before the gas collection system is turned on after a typical inoperative period. This option requires twenty-four hour samples to be taken on 10 separate, not necessarily consecutive, days.

2. Meteorological Survey

A meteorological survey should be conducted prior to ambient air sampling in order to determine the local wind flow patterns which will subsequently be used to help identify the number and location of samplers required for an effective ambient air monitoring program. The operator should submit the survey to the APCO prior to ambient sampling, as part of the monitoring plan. The survey should summarize how wind flow patterns at the site will be characterized based on: previously collected on-site meteorological data, data collected nearby (e.g., local airport data), proximity to water or terrain which may influence diurnal variations (e.g., daytime upslope winds, nighttime downslope, or sea breeze conditions), or a plan for on-site meteorological data collection prior to ambient monitoring. In completing an on-site meteorological survey prior to monitoring, wind sensors should be oriented with respect to north, located nine to twelve feet above the ground and a minimum of sixty feet from obstacles such as trees, shrubbery, and buildings.

3. Ambient Air Sampling

a. General Sampling Criteria

At the completion of the meteorological survey, and on approval of the APCO, ambient air sampling equipment will be installed at the appropriate locations which will be determined by:

1. Site topography,

2. Meteorological survey, and

3. Local land use patterns.

2 shows the lower detection limits to be achieved in parts per billion. Each disposal site should perform the ambient air sampling on ten separate, not necessarily consecutive, days. Ten days of ambient sampling provides an initial screening of hazardous waste disposal sites and allows for some daily variations in site operations, weather conditions, and emissions.

The disposal site operator is given the option of using one of three suggested procedures for testing the ambient air. These procedures were developed to cover differences in topography and climate which may occur at different sites. The option chosen will depend on the results of a meteorological survey conducted prior to ambient monitoring. Each option has two parts. One addresses sites with different day and night wind patterns and one addresses sites with the same day and night wind patterns.

A. OPTION 1

1. General Procedures

HSC Section 41805.5 requires that air adjacent to disposal sites be tested and analyzed for specified air contaminants. If the disposal site has a gas collection system which does not operate continuously, at least one of the sampling days should be a day before the gas collection system is turned on after a typical inoperative period. This option requires twenty-four hour samples to be taken on 10 separate, not necessarily consecutive, days.

2. Meteorological Survey

A meteorological survey should be conducted prior to ambient air sampling in order to determine the local wind flow patterns which will subsequently be used to help identify the number and location of samplers required for an effective ambient air monitoring program. The operator should submit the survey to the APCO prior to ambient sampling, as part of the monitoring plan. The survey should summarize how wind flow patterns at the site will be characterized based on: previously collected on-site meteorological data, data collected nearby (e.g., local airport data), proximity to water or terrain which may influence diurnal variations (e.g., daytime upslope winds, nighttime downslope, or sea breeze conditions), or a plan for on-site meteorological data collection prior to ambient monitoring. In completing an on-site meteorological survey prior to monitoring, wind sensors should be oriented with respect to north, located nine to twelve feet above the ground and a minimum of sixty feet from obstacles such as trees, shrubbery, and buildings.

3. Ambient Air Sampling

a. General Sampling Criteria

At the completion of the meteorological survey, and on approval of the APCO, ambient air sampling equipment will be installed at the appropriate locations which will be determined by:

1. Site topography,

2. Meteorological survey, and

3. Local land use patterns.

The sampling equipment should be located at or near the perimeter of the waste disposal site, in the clear and away from surrounding obstructions. The inlet probes for the ambient samplers should be located between six and nine feet off the ground (reaching height) and a minimum of sixty feet from obstacles such as trees, shrubbery and buildings. Air flow around the inlet probe should be unrestricted in an arc of at least 270 degrees with the predominant wind direction for greatest expected pollutant concentration potential included in the 270 degree arc. The sampler locations should be carefully selected to ensure the predicted prevailing wind patterns for the sampling date will come across the main body of the disposal site to the downwind station. Wind speed and direction measurements will continue to be collected throughout the ambient air sampling period to verify that the meteorological criteria are met.

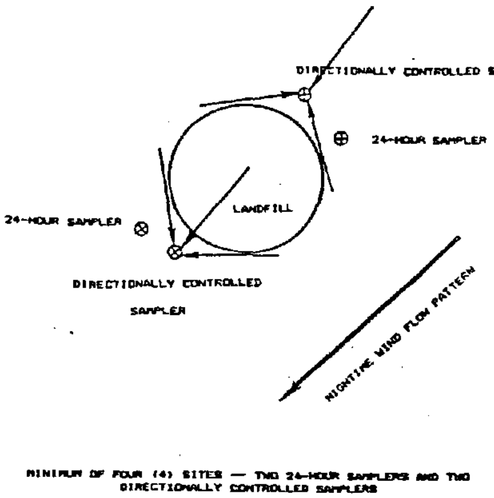

Figure 4: Option 1
Source: South Coast AQMD

Ambient air samples will be collected over a 24-hour period beginning and ending at 10:00 A.M. using the self-contained portable sampling units described in Equipment Description. In general, 24-hour and directionally controlled sampling will be required to ensure that maximum contaminant concentrations are identified for each sampling period. However, directionally controlled sampling may not be required at sites which have a constant wind direction for 24 hours. All samples will be removed from the samplers immediately after the 24-hour sampling period and analyzed for the required compounds. It is recommended that the sample be analyzed within 72 hours of collection.

b. Specific Sampling Criteria

i. At sites that experience different day and night wind flow patterns, a minimum of two 24-hour samplers and two directionally controlled samplers will be required. Twenty-four hour samplers will be placed at the upwind and downwind site perimeters based on the prevailing wind direction. The directionally controlled sampler(s) located downwind of the disposal site should be placed at sites which will sample under the stable (drainage) wind conditions identified in the meteorological survey. The directionally controlled sampler located upwind of the disposal site should be placed near the upwind 24-hour sampler. The 24-hour samplers will operate continuously for the specified 24 hours and the directionally controlled samplers will only operate when the wind direction is within a wind sector allowing air to pass across the disposal site to the downwind sampler. This will allow the downwind directionally controlled sampler(s) to only collect air that has *passed* over the disposal site and the upwind directionally controlled sampler to only collect air that has *not passed* over the disposal site.

ii. At sites that experience a constant wind direction for 24 hours, a minimum of two 24-hour samplers will be required. A 24-hour sampler will be place both upwind and downwind of the site based on the prevailing wind direction so that the upwind sampler only collects air that has *not passed* over the disposal site and the downwind sampler only collects air that has *passed* over the disposal site. Additional 24-hour samplers should be placed at locations which will sample under the stable (drainage) wind conditions identified in the meteorological survey. Since the wind direction does not change, these 24-hour samplers will act as directionally controlled samplers as well as 24-hour samplers. Comparison of the results from these samplers will provide information on ambient air quality standards and the effects the disposal site has on the ambient air quality.

4. Sampling Conditions

Ambient air sampling should be conducted on days when stable and unstable meteorological conditions are characterized by the following meteorological conditions:

a. Stable nights with average wind speeds of five miles per hour or less.

b. Daytime conditions with average wind speeds of ten miles per hour or less.

No sampling will be conducted under the following adverse meteorological conditions:

a. Precipitation

b. Twenty-four hour average wind speeds greater than ten miles per hour.

5. Equipment Description

a. Bag Sampler

1. Pump with a diaphragm made of non-lubricated Viton® rubber. The maximum pump unloaded flow rate is 4.5 liters per minute.

2. One 10-liter Tedlar® bag with a push-pull valve constructed of aluminum and stainless steel with a Viton® o-ring seal.

3. Rotameter made of borosilicate glass with a flow range of three to fifty cubic centimeters per minute. The scale is in millimeters with major graduations (labeled) every 5 mm and minor graduations every 1 mm.

4. Air flow control orifice made with 316 stainless steel capillary tubing.

5. Bypass valve.

6. Fittings, tubing and connectors made with 316 stainless steel or teflon.

7. Clock timer with an accuracy that should be better than 1%.

ii. At sites that experience a constant wind direction for 24 hours, a minimum of two 24-hour samplers will be required. A 24-hour sampler will be place both upwind and downwind of the site based on the prevailing wind direction so that the upwind sampler only collects air that has *not passed* over the disposal site and the downwind sampler only collects air that has *passed* over the disposal site. Additional 24-hour samplers should be placed at locations which will sample under the stable (drainage) wind conditions identified in the meteorological survey. Since the wind direction does not change, these 24-hour samplers will act as directionally controlled samplers as well as 24-hour samplers. Comparison of the results from these samplers will provide information on ambient air quality standards and the effects the disposal site has on the ambient air quality.

4. Sampling Conditions

Ambient air sampling should be conducted on days when stable and unstable meteorological conditions are characterized by the following meteorological conditions:

a. Stable nights with average wind speeds of five miles per hour or less.

b. Daytime conditions with average wind speeds of ten miles per hour or less.

No sampling will be conducted under the following adverse meteorological conditions:

a. Precipitation

b. Twenty-four hour average wind speeds greater than ten miles per hour.

5. Equipment Description

a. Bag Sampler

1. Pump with a diaphragm made of non-lubricated Viton® rubber. The maximum pump unloaded flow rate is 4.5 liters per minute.

2. One 10-liter Tedlar® bag with a push-pull valve constructed of aluminum and stainless steel with a Viton® o-ring seal.

3. Rotameter made of borosilicate glass with a flow range of three to fifty cubic centimeters per minute. The scale is in millimeters with major graduations (labeled) every 5 mm and minor graduations every 1 mm.

4. Air flow control orifice made with 316 stainless steel capillary tubing.

5. Bypass valve.

6. Fittings, tubing and connectors made with 316 stainless steel or teflon.

7. Clock timer with an accuracy that should be better than 1%.

b. Wind directionally controlled system

1. Wind direction sensor with a vane which has a range of 0 - 540 degrees and a threshold of 1.00 mile per hour or less.

2. Controller and indicator console with an indicator range of 0 - 360 degrees and an accuracy of ± 2% of full scale.

c. Wind speed and direction monitoring with continuous recorder.

1. Anemometer three cup assembly with a range of 0-50 miles per hour and a threshold of 0.75 miles per hour or less.

2. Wind vane with a range of 0 - 540 degrees and a threshold of 1.00 miles per hour or less.

6. Wind Data Reporting

Wind data (speed and direction) will be reported as an hourly average. For example, the data collected between 1:00 P.M. and 2:00 P.M. will be averaged and reported as the 1:00 P.M. hourly average. Wind speeds will be reported in miles per hour. Wind directions will be reported using the sixteen point scale (sixteen directional points corresponding to the mariner's compass rose on which each direction is equivalent to a 22 1/2 degree sector of a 360 degree circle). For example, wind directions would be N, NNE, NE, E ESE, SE, SSE, S, SSW, SW, WSW, W, WNW, NW, and NNW.

B. OPTION 2

1. General Procedures

HSC Section 41805.5 requires that air adjacent to disposal sites be tested and analyzed for specified air contaminants. These guidelines require that 24-hour and less than 24-hour ambient air sampling be conducted on 10 different, not necessarily consecutive, days.

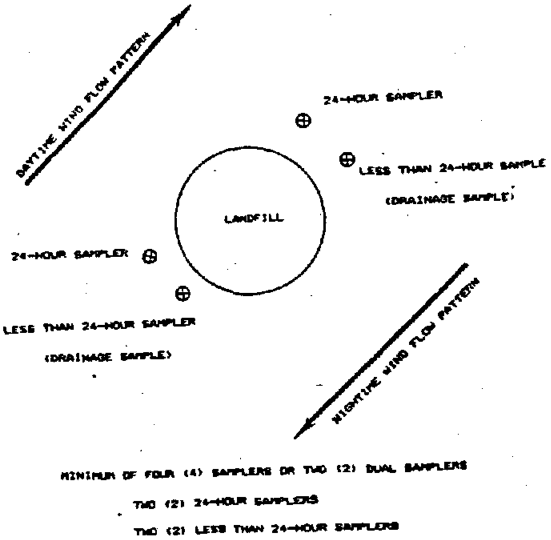

Figure 5: Option 2
Source: South Coast AQMD

2. Meteorological Survey

See Option 1.

3. Ambient Air Sampling

See Option 1, Subsection 3a, General Sampling Criteria.

a. At sites that experience different but predictable day and night wind flow patterns, a minimum of two 24-hour samplers and two less than 24-hour samplers will be required. One 24-hour sampler will be placed both upwind and downwind of the site based on the prevailing wind direction. The less than 24-hour sampler(s) located downwind of the disposal site should be placed at sites to sample under the stable (drainage) wind conditions identified in the meteorological survey. The less than 24-hour sampler located upwind of the disposal site should be placed near the upwind 24-hour sampler. The start and stop times for the less than 24-hour samplers will correspond to the stable (drainage) conditions identified by analyzing the hourly wind roses. The 24-hour samplers will operate continuously for the specified 24 hours and the less than 24-hour samplers will only operate when the wind direction is coming across the disposal site to the downwind sampler. This will allow the downwind less than 24-hour sampler(s) to only collect air that has *passed* over the disposal site and the upwind less than 24-hour sampler to only collect air that has *not passed* over the disposal site.

b. At sites that experience a constant wind direction for 24 hours, a minimum of two 24-hour samplers will be required. A 24-hour sampler will be place both upwind and downwind of the site based on the prevailing wind direction so that the upwind sampler only collects air that has *not passed* over the disposal site and the downwind sampler only collects air that has *passed* over the disposal site. Additional 24 hour samplers should be placed at locations which will sample under the stable (drainage) wind conditions identified in the meteorological survey. Since the wind direction does not change, these 24-hour samplers will act as directionally controlled samplers as well as 24-hour samplers. Comparison of the results from these samplers will provide information on ambient air quality standards and the effects the disposal site has on the ambient air quality.

4. Sampling Conditions

See Option 1.

5. Equipment Description

See Option 1.

6. Wind Data Reporting

See Option 1.

C. OPTION 3

1. General Procedures

HSC Section 41805.5 requires that air adjacent to disposal sites be tested and analyzed

2. Meteorological Survey

See Option 1.

3. Ambient Air Sampling

See Option 1, Subsection 3a, General Sampling Criteria.

a. At sites that experience different but predictable day and night wind flow patterns, a minimum of two 24-hour samplers and two less than 24-hour samplers will be required. One 24-hour sampler will be placed both upwind and downwind of the site based on the prevailing wind direction. The less than 24-hour sampler(s) located downwind of the disposal site should be placed at sites to sample under the stable (drainage) wind conditions identified in the meteorological survey. The less than 24-hour sampler located upwind of the disposal site should be placed near the upwind 24-hour sampler. The start and stop times for the less than 24-hour samplers will correspond to the stable (drainage) conditions identified by analyzing the hourly wind roses. The 24-hour samplers will operate continuously for the specified 24 hours and the less than 24-hour samplers will only operate when the wind direction is coming across the disposal site to the downwind sampler. This will allow the downwind less than 24-hour sampler(s) to only collect air that has *passed* over the disposal site and the upwind less than 24-hour sampler to only collect air that has *not passed* over the disposal site.

b. At sites that experience a constant wind direction for 24 hours, a minimum of two 24-hour samplers will be required. A 24-hour sampler will be place both upwind and downwind of the site based on the prevailing wind direction so that the upwind sampler only collects air that has *not passed* over the disposal site and the downwind sampler only collects air that has *passed* over the disposal site. Additional 24 hour samplers should be placed at locations which will sample under the stable (drainage) wind conditions identified in the meteorological survey. Since the wind direction does not change, these 24-hour samplers will act as directionally controlled samplers as well as 24-hour samplers. Comparison of the results from these samplers will provide information on ambient air quality standards and the effects the disposal site has on the ambient air quality.

4. Sampling Conditions

See Option 1.

5. Equipment Description

See Option 1.

6. Wind Data Reporting

See Option 1.

C. OPTION 3

1. General Procedures

HSC Section 41805.5 requires that air adjacent to disposal sites be tested and analyzed for specified air contaminants. These guidelines require that 24-hour ambient air sampling be conducted on 10 different, not necessarily consecutive, days.

2. Meteorological Survey

See Option 1.

3. Ambient Air Sampling

See Option 1, Subsection 3a, General Sampling Criteria.

a. At sites that experience different day and night wind flow patterns, a minimum of three 24-hour samplers will be required. One 24-hour sampler will be placed on both upwind and downwind of the site based on the prevailing wind direction. Additional 24-hour samplers will be located downwind of the disposal site at sites which will sample under the stable (drainage) wind conditions identified in the meteorological survey. In addition, one 24-hour sampler will be placed in the vicinity of the disposal site, approximately one mile away, so it will not be affected by the disposal site emissions. This 24-hour sampler should also be approximately one mile away from other possible major emission sources so that the sample it collects will represent the background concentrations for the area. This background sampler should be located in the clear and away from surrounding obstructions. Its inlet probe must be located between six and nine feet off the ground (breathing height) and a minimum of 60 feet from obstacles such as trees, shrubbery, and buildings. Air flow around the inlet probe must be unrestricted. All of the 24-hour samplers will operate continuously for the specified 24 hours. Comparison of the results from the samplers will provide information on the ambient air quality standards.

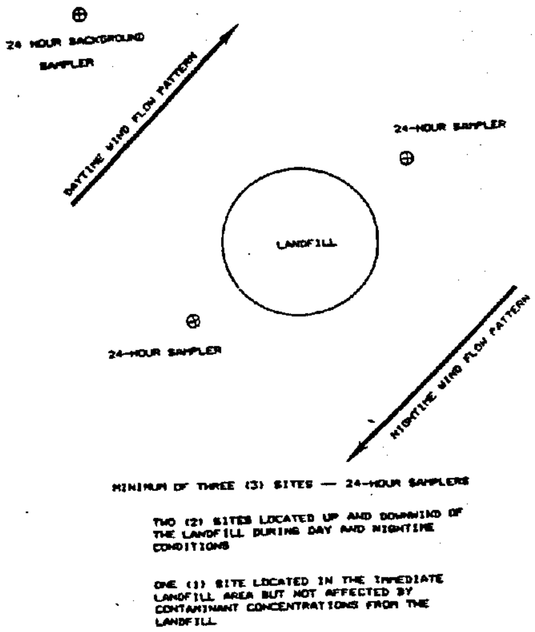

Figure 6: Option 3
Source: South Coast AQMD

b. At sites that experience a constant wind direction for 24 hours, a minimum of two 24-hour samplers will be required. A 24-hour sampler will be placed both upwind and downwind of the site based on the prevailing wind direction so that the upwind sampler only collects air that has *not passed* over the disposal site and the downwind sampler only collects air that has *passed* over the disposal site. Additional 24-hour samplers should be placed at locations which will sample under the stable (drainage) wind conditions identified in the meteorological survey. Since the wind direction does not change, these 24-hour samplers will act as less than 24-hour samplers as well as 24-hour samplers. In addition, one 24-hour sampler will be placed in the vicinity of the disposal site, approximately one mile away, so it will not be effected by the disposal site emissions. This 24-hour sampler should also be approximately one mile away from possible major emission sources so that the sample it collects will represent the background concentrations for the area. This background sampler should be located in the clear and away from surrounding obstructions. Its inlet probe should be located between six and nine feet off the ground (breathing height) and a minimum of sixty feet from obstacles such as trees, shrubbery and buildings. Air flow around the inlet probe should be unrestricted. All of the 24-hour samplers will operate continuously for the specified 24 hours.

4. Sampling Conditions

See Option 1.

5. Equipment Description

See Option 1.

6. Wind Data Reporting

See Option 1.

D. GENERIC ANALYTICAL METHODS

HSC Section 41805.5 directs the ARB to publish testing guidelines "specifying air contaminants to be tested for and identifying acceptable testing, analytical and reporting methods. The following generic analytical methods contain a brief description of the standard operating procedures (SOP) used by the ARB to sample and analyze specific compounds. Specific SOPs are contained in Attachment 4.

1. Method for Vinyl Chloride

Ambient samples are collected over a 24-hour period in a 30-liter Tedlar® bag using a low-volume sampler.

Samples are analyzed using chromatography with flame ionization or photo ionization detection and preconcentration techniques. The resultant concentration peak is identified by retention time and quantified by reference to calibration standards.

2. Method for Carbon Tetrachloride, Chloroform, Ethylene Dibromide, Ethylene Dichloride, Methyl Chloroform, Methylene Chloride, Perchloroethylene, and Trichloroethylene

Ambient samples are collected over a 24-hour period in a 30-liter Tedlar® bag using a low-volume sampler.

Samples are analyzed using gas chromatography with electron capture detection and preconcentration techniques. Resultant concentration peaks are identified by retention times and quantified by references to calibration standards.

addition, one 24-hour sampler will be placed in the vicinity of the disposal site, approximately one mile away, so it will not be effected by the disposal site emissions. This 24-hour sampler should also be approximately one mile away from possible major emission sources so that the sample it collects will represent the background concentrations for the area. This background sampler should be located in the clear and away from surrounding obstructions. Its inlet probe should be located between six and nine feet off the ground (breathing height) and a minimum of sixty feet from obstacles such as trees, shrubbery and buildings. Air flow around the inlet probe should be unrestricted. All of the 24-hour samplers will operate continuously for the specified 24 hours.

4. Sampling Conditions

See Option 1.

5. Equipment Description

See Option 1.

6. Wind Data Reporting

See Option 1.

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2. Method for Carbon Tetrachloride, Chloroform, Ethylene Dibromide, Ethylene Dichloride, Methyl Chloroform, Methylene Chloride, Perchloroethylene, and Trichloroethylene

Ambient samples are collected over a 24-hour period in a 30-liter Tedlar® bag using a low-volume sampler.

Samples are analyzed using gas chromatography with electron capture detection and preconcentration techniques. Resultant concentration peaks are identified by retention times and quantified by references to calibration standards.

3. Method for Benzene

Ambient samples are collected over a 24-hour period in a 30-liter Tedlar® bag using a low volume sampler.

Samples are analyzed using gas chromatography with photo ionization detection and preconcentration techniques. The resultant concentration peak is identified by retention time and quantified by reference to calibration standards.

IV. GAS MIGRATION

A. General

HSC Section 41805.5 requires disposal site owners to test for off-site underground gas migration. The testing should be done at the disposal site edge in wells with spacing determined by local geology and land use near the disposal site. Wells should be tested for the Attachment 2 compounds to the "disposal site" detection limits. At co-disposal sites, wells should also be tested for methane. Any existing perimeter monitoring system can be used if it can be shown to provide the necessary data.

For co-disposal sites, one perimeter sampling probe should be installed at the waste disposal site perimeter for each 1000 feet of site perimeter. The site perimeter is the outer edge of the area which is permitted to receive waste. All the wells should be placed at the site perimeter between the filled area and the areas off-site where gas migration would be a potential threat to public health or safety. For sites which accepted only hazardous waste, a maximum of four wells should be located around the perimeter of the site.

Samples should be taken from six feet below the surface. When the sampling wells are no longer in use, the wells should be closed using Department of Water Resources published criteria.

B. Protocol

1. Equipment Description

a. Pump with diaphragm made from non-lubricated Viton® rubber.

b. Battery to operate pump

c. Tedlar® bags

d. Various fittings

e. Flame ionization detector, or similar detector, with a lower detection limit of 2 ppm methane.

2. Sampling Procedure

If the disposal site has a gas collection system and the system does not operate continuously, then the probes should be sampled with the system operating and immediately before the system is restarted after an off period.

a. Attach the pump to the well.

b. Attach the Tedlar® bag and take a 10 liter sample.

c. Check the sample for the Attachment 2 compounds to the "disposal site" detection limits, and methane at co-disposal sites.

3. Data Reporting

For each sample, the owner should record:

a. Date, time, and sample location

b. The concentrations of the Attachment 2 compounds, and methane for co-disposal sites.

c. Whether any landfill gas collection system was operating.

V. QUALITY ASSURANCE FOR SAMPLING

A quality assurance plan for disposal site testing should be prepared and submitted to the APCO as part of the monitoring plan. The following quality assurance tasks are listed as an example of the information which should be included in the plan.

A. Quality Assurance Objectives

Quality assurance procedures for disposal site testing are designed to perform two primary functions. The first is to establish the necessary quality control activities relating to sample collection, sample analysis, siting of ambient monitors, and data validation. Secondly, the plan provides for assessment of data quality in terms of precision, accuracy, and completeness.

B. Sampling Methods

Specific sampling methods will be prepared in a monitoring plan for review by the APCO. The methods should include equipment specifications, acceptance testing, sample handling and chain of custody procedures such as length of time before analysis, temperature control on samples, and shipping procedures to prevent sample loss. The monitoring plan will outline measures to protect the sampling apparatus and media from interference or damage due to rain. Use of chain of custody forms is recommended. A sample chain of custody record is included as Attachment 5. Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, analysis and data reduction, sample number, initial and final time and flow, malfunctions, leak checks, and weather conditions (e.g., rain) which could influence sample results. The initial and final flow will be averaged for the 24-hour sampling period if a flow controller is not used. Tedlar bags should be recertified before each use. This involves purging the bags until no contamination is detected and checking for leaks.

A site description form should be included for each monitoring site listing sampling height, distances to obstructions, and showing the monitoring location with respect to the waste site on a map with scale.

a. Attach the pump to the well.

b. Attach the Tedlar® bag and take a 10 liter sample.

c. Check the sample for the Attachment 2 compounds to the "disposal site" detection limits, and methane at co-disposal sites.

3. Data Reporting

For each sample, the owner should record:

a. Date, time, and sample location

b. The concentrations of the Attachment 2 compounds, and methane for co-disposal sites.

c. Whether any landfill gas collection system was operating.

V. QUALITY ASSURANCE FOR SAMPLING

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A site description form should be included for each monitoring site listing sampling height, distances to obstructions, and showing the monitoring location with respect to the waste site on a map with scale.

Ambient sampling precision will be calculated from at least 2 samplers collocated at a site of expected maximum concentrations. The samplers should be located between 6 and 12 feet apart. Collocated samples will be collected daily for the 10 days of ambient sampling. One sampler will be designated as the primary sampler and the others will be designated as duplicate.

C. Analysis Methods

When possible, ARB approved methods for sample preparation and analysis should be used. If modifications are necessary, the changes should be fully documented in the monitoring plan and validation testing conducted. Validation testing should provide an assessment of accuracy, precision, interferences, applicable concentration ranges, recoveries, and limits of detection of the alternative method.

Each method developed for sample analysis should be documented in a Standard Operating Procedure and be available for review by the APCO before monitoring begins. The method documentation should include the quality control activities necessary to routinely monitor data quality such as the use of control samples, field blanks, and duplicate samples. The method should also include the frequency of analysis for quality control samples. Analysis of control samples is recommended before each day of lab analysis and after every tenth sample. Control samples should be analyzed to be within control limits previously established by the laboratory performing the analysis. If results are outside the control limits, the method should be reviewed, recalibrated, and the control sample reanalyzed. Field blanks should be included with each batch of samples. The identity of blank and spiked samples should be unknown to the analyst.

D. Calibration Procedures

The monitoring plan will specify calibration procedures including calibration intervals for recalibration, calibration standards, environmental conditions for calibrations, and a calibration record keeping system. When possible, National Bureau of Standards traceable gas standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

If elapsed time meters are used, rather than noting beginning and ending times, the meters should be checked and calibrated to within ± 5 minutes for a 24-hour period. Samplers operated with an automatic on/off timer should be calibrated so that the sampling period is 24 hours ± 15 minutes.

Flow meters or flow controllers with critical orifices should be calibrated against a referenced flow meter at the initiation of a monitoring period.

Sampling flows should be checked in the field and noted before and after each sampling period. Before flows are checked, the sampling system should be leak checked. The initial flow should be within ± 10% if a calibrated pressure transducer is used to check flows or within ± 15% if a calibrated rotameter is used. Flow meters should be recalibrated if flows are found to be outside of these control limits.

E. Preventative Maintenance

To prevent loss of data, spare pumps and sampling materials should be kept available in the field by the operator. A schedule should be prepared for checking sampling pumps, meteorological instruments, extension cords, crimps in sampling tubing, and leaks.

F. Data Validation - Precision, Accuracy, and Completeness

Average precision and accuracy, and respective standard deviations should be calculated for the entire data set. The following equation should be used to calculate data precision.

$$P = \frac{Y - X}{X} \times 100$$

where: P = calculated data precision

Y = concentration from duplicate sampler of collocated pair;

X = concentration from primary sampler of collocated pair.

Accuracy should be determined from the performance audit of flows or spiked samples and should be calculated using the following equation:

$$A = \frac{Y - X}{X} \times 100$$

where: A = calculated data accuracy

Y = measured concentration of spiked sample or measured flow;

X = known concentration of spiked sample or known flow.

Data completeness should be calculated as a percentage of valid data compared to the total possible amount of data if no invalidations had occurred. Data will be invalidated if the power is out at a site and the length of a sample cannot be verified, or if the sampling medium breaks during sampling or shipment for analysis. Data will be corrected to reflect discrepancies in the sampling flow based on the results of a flow audit.

G. Performance Audits

For sampling with sorbent tubes, a referenced flow measuring device with a standard limiting orifice should be used to verify the indicated flows on the samplers. Flow

E. Preventative Maintenance

To prevent loss of data, spare pumps and sampling materials should be kept available in the field by the operator. A schedule should be prepared for checking sampling pumps, meteorological instruments, extension cords, crimps in sampling tubing, and leaks.

F. Data Validation - Precision, Accuracy, and Completeness

Average precision and accuracy, and respective standard deviations should be calculated for the entire data set. The following equation should be used to calculate data precision.

$$P = \frac{Y - X}{X} \times 100$$

where:

P = calculated data precision

Y = concentration from duplicate sampler of collocated pair;

X = concentration from primary sampler of collocated pair.

Accuracy should be determined from the performance audit of flows or spiked samples and should be calculated using the following equation:

$$A = \frac{Y - X}{X} \times 100$$

where:

A = calculated data accuracy

Y = measured concentration of spiked sample or measured flow;

X = known concentration of spiked sample or known flow.

Data completeness should be calculated as a percentage of valid data compared to the total possible amount of data if no invalidations had occurred. Data will be invalidated if the power is out at a site and the length of a sample cannot be verified, or if the sampling medium breaks during sampling or shipment for analysis. Data will be corrected to reflect discrepancies in the sampling flow based on the results of a flow audit.

G. Performance Audits

For sampling with sorbent tubes, a referenced flow measuring device with a standard limiting orifice should be used to verify the indicated flows on the samplers. Flow audits should be conducted at least once during a monitoring period. Analytical audits should be conducted by spiking samples with referenced standards or by having another lab analyze split samples for comparison of results.

H. Quality Assurance Reports

Quality assurance activities and data will be summarized by the staff conducting the sampling and included as an attachment to the final data summary.

VII. TEST REPORT EVALUATION

HSC Section 41805.5(g) requires APCOs to evaluate the test reports. The test report data required by July 1, 1987 provides preliminary information on ambient air concentrations and landfill gas composition. If, after consulting with the Department of Health Services and the California Waste Management Board, an APCO determines that levels of tested air contaminants pose a health risk, the statute requires the district to take remedial action. Remedial action may include further ambient air monitoring, landfill gas testing, or installation of a landfill gas collection system.

If a district determines that a site poses a health risk, extended ambient air monitoring is recommended as part of the mitigation process. Additional air monitoring is also recommended at sites where the potential for public exposure or need for remedial action is uncertain. HSC Section 41805.5 (f) provides that districts may re-evaluate the status of a site and require additional testing as necessary.

CHAPTER _____

An act to repeal and add Section 66796.54 of the Government Code, and to repeal and add Section 41805.5 of the Health and Safety Code, relating to solid waste, and declaring the urgency thereof, to take effect immediately.

LEGISLATIVE COUNSEL'S DIGEST

AB 3374, Calderon. Solid waste: disposal sites: air monitoring: water pollution reports.

(1) Existing law requires the State Water Resources Control Board to submit annual reports on or before July 1, 1988, July 1, 1989, and July 1, 1990, on the extent and effect on water quality of hazardous wastes in solid waste disposal sites, with recommendations on needed actions to protect water quality.

This bill would change the dates that the reports are due from the board to January 1, 1989, January 1, 1990, and January 1, 1991, respectively.

(2) Existing law requires solid waste disposal sites to submit a solid waste assessment report to the board of the air pollution control district or the air quality management district by January 1, 1987. The district board is required to examine the report and notify the State Department of Health Services and the California Waste Management Board if the district board determines that hazardous waste is migrating into the air. The State Air Resources Board is required to submit a report to the Legislature on or before July 1 of 1988, 1989, and 1990, concerning hazardous waste in solid waste sites.

This bill would repeal those provisions and would instead require the owner of a solid waste disposal site, as defined, to submit a solid waste air quality assessment test report, as specified, to the district on or before July 1, 1987. The bill would also require the owner of an inactive solid waste disposal site, except as specified, to submit a screening questionnaire to the district on or before November 1, 1986, and to submit specified information required by the district based upon an evaluation of the questionnaire by the district. The bill would require the state board to develop guidelines for the test report and evaluation of the screening questionnaire by February 1, 1987, and to develop the screening questionnaire by October 1, 1986.

The bill would authorize a district to exempt a site from these provisions and to reevaluate the status of a solid waste disposal site and require the submission or revision of a test report.

A district would be required to evaluate all test reports for compliance with the state board's guidelines. The bill would require the district to take appropriate remedial action if the district determines, after evaluating the test report and consultation with the department and the California Waste Management Board, that the levels of specified air contaminants, as defined, pose a health risk or a threat to the environment.

The bill would delete the requirement that the state board submit a report to the Legislature by July 1, 1990.

(3) The bill would incorporate additional changes to Section 66796.54 of the Government Code proposed by AB 3088, if this bill and AB 3088 are both enacted and this bill is enacted last.

(4) The California Constitution requires the state to reimburse local agencies and school districts for certain costs mandated by the state. Statutory provisions establish procedures for making that reimbursement, including the creation of a State Mandates Claims Fund to pay the costs of mandates which do not exceed $50,000 statewide and other procedures for claims whose statewide costs exceed $500,000.

This bill would impose a state-mandated local program by requiring cities, counties, and districts which own a solid waste disposal site or an inactive site to submit a specified test report and by requiring air quality management districts and air pollution control districts to evaluate these reports and take specified actions.

The bill would provide that reimbursement shall be made pursuant to those statutory procedures and, if the statewide cost does not exceed $500,000, shall be payable from the State Mandates Claims Fund, except that, for certain costs, the bill would provide that no reimbursement is required for a specified reason.

(5) The bill would declare that it is to take effect immediately as an urgency statute.

The people of the State of California do enact as follows:

SECTION 1. Section 66796.54 of the Government Code is repealed.

SEC. 2. Section 66796.54 is added to the Government Code, to read:

66796.54. (a) On or before January 1, 1989, January 1, 1990, and January 1, 1991, the State Water Resources Control Board shall submit a report to the Legislature summarizing the extent of hazardous waste in solid waste disposal sites and the potential effects these hazardous wastes may have upon the quality of waters of the state, and recommending actions needed to protect the quality of water. Each report shall summarize the data from those solid waste water quality assessment test reports which have been submitted on or before January 1 of the preceding year to California regional water quality control boards pursuant to Section 13273 of the Water Code, and shall evaluate the accuracy of the solid waste water quality assessment tests conducted.

(b) On or before July 1, 1988, and July 1, 1989, the State Air Resources Board shall submit a report to the Legislature summarizing the extent of hazardous waste in solid waste disposal sites and the potential effects these hazardous wastes may have upon the ambient air quality of the state, and recommending actions needed to protect the quality of air. The reports submitted on July 1, 1988, and July 1, 1989, shall summarize the data from the solid waste air quality assessment test reports submitted to air quality maintenance districts and air pollution control districts on or before July 1, 1987, and January 1, 1988, respectively, pursuant to Section 41805.5 of the Health and Safety Code, and shall evaluate the accuracy of the solid waste assessment tests conducted.

SEC. 3. Section 66796.54 is added to the Government Code, to read:

66796.54. (a) On or before January 1, 1989, January 1, 1990, and January 1, 1991, the State Water Resources Control Board shall submit a report to the Legislature summarizing the extent of hazardous waste in solid waste disposal sites and the potential effects these hazardous wastes may have upon the quality of waters of the state, and recommending actions needed to protect the quality of water. Each report shall summarize the data from those solid waste water quality assessment test reports which have been submitted during the preceding year to California regional water quality control boards pursuant to Section 13273 of the Water Code, and shall evaluate the accuracy of the solid waste water quality assessment tests conducted.

(b) On or before July 1, 1988, and July 1, 1989, the State Air Resources Board shall submit a report to the Legislature summarizing the extent of hazardous waste in solid waste disposal sites and the potential effects these hazardous wastes may have upon the ambient air quality of the state, and recommending actions needed to protect the quality of air. The reports submitted on July 1, 1988, and July 1, 1989, shall summarize the data from the solid waste air quality assessment test reports submitted to air quality maintenance districts and air pollution control districts on or before July 1, 1987, and January 1, 1988, respectively, pursuant to Section 41805.5 of the Health and Safety Code, and shall evaluate the accuracy of the solid waste assessment tests conducted.

SEC. 4. Section 41805.5 of the Health and Safety Code is repealed.

SEC. 5. Section 41805.5 is added to the Health and Safety Code, to read:

41805.5. (a) Except as provided in subdivisions (b) and (c), the owner of a solid waste disposal site shall submit to the district on or before July 1, 1987, a solid waste air quality assessment test report that contains all of the following:

(1) Test results to determine if there is any underground landfill gas migration beyond the solid waste disposal site's perimeter.

(2) Analyses for specified air contaminants in the

certain costs, the bill would provide that no reimbursement is required for a specified reason.

(5) The bill would declare that it is to take effect immediately as an urgency statute.

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(b) On or before July 1, 1988, and July 1, 1989, the State Air Resources Board shall submit a report to the Legislature summarizing the extent of hazardous waste in solid waste disposal sites and the potential effects these hazardous wastes may have upon the ambient air quality of the state, and recommending actions needed to protect the quality of air. The reports submitted on July 1, 1988, and July 1, 1989, shall summarize the data from the solid waste air quality assessment test reports submitted to air quality maintenance districts and air pollution control districts on or before July 1, 1987, and January 1, 1988, respectively, pursuant to Section 41805.5 of the Health and Safety Code, and shall evaluate the accuracy of the solid waste assessment tests conducted.

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(b) On or before July 1, 1988, and July 1, 1989, the State Air Resources Board shall submit a report to the Legislature summarizing the extent of hazardous waste in solid waste disposal sites and the potential effects these hazardous wastes may have upon the ambient air quality of the state, and recommending actions needed to protect the quality of air. The reports submitted on July 1, 1988, and July 1, 1989, shall summarize the data from the solid waste air quality assessment test reports submitted to air quality maintenance districts and air pollution control districts on or before July 1, 1987, and January 1, 1988, respectively, pursuant to Section 41805.5 of the Health and Safety Code, and shall evaluate the accuracy of the solid waste assessment tests conducted.

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41805.5. (a) Except as provided in subdivisions (b) and (c), the owner of a solid waste disposal site shall submit to the district on or before July 1, 1987, a solid waste air quality assessment test report that contains all of the following:

(1) Test results to determine if there is any underground landfill gas migration beyond the solid waste disposal site's perimeter.

(2) Analyses for specified air contaminants in the

ambient air adjacent to the solid waste disposal site to determine the effect of the site on air quality.

(3) Chemical characterization test results to determine the composition of gas streams immediately above the solid waste disposal site, or immediately above the solid waste disposal site and within the solid waste disposal site, as appropriate, as determined by the district.

(4) Any other information which the district board may require, by emergency regulation.

The solid waste air quality assessment test report shall be prepared in accordance with the guidelines developed by the state board pursuant to subdivision (d).

(b) The owner of an inactive solid waste disposal site shall complete and submit the screening questionnaire, developed pursuant to subdivision (e), to the district on or before November 1, 1986, unless the owner is required to submit a report containing the same information specified in subdivision (a) pursuant to a federal, state, or district order, or unless exempted pursuant to subdivision (c). The district shall evaluate the submitted screening questionnaires in accordance with the guidelines developed pursuant to subdivision (e) and shall determine whether the owner of the site be required to submit all, or a portion of, the information required to be reported in a solid waste air quality assessment test report. The district shall notify the owner in writing on or before January 1, 1987, of the information identified in subdivision (a) to be submitted for the site. After receiving this notification, the owner of the inactive solid waste disposal site shall submit a solid waste air quality assessment test report containing the required information on or before January 1, 1988, to the district.

(c) A district may exempt from subdivisions (a) and (b) a solid waste disposal site or inactive solid waste disposal site which has accepted or now contains only inert and nondecomposable solids. To receive an exemption, the owner of the site shall submit, on or before November 1, 1986, a copy of all permits, all waste discharge requirements pertinent to the site, and any other data necessary for the district to determine whether an exemption should be granted to the site.

(d) On or before February 1, 1987, the state board, in coordination with the districts, shall develop and publish test guidelines for the solid waste air quality assessment report specifying the air contaminants to be tested for and identifying acceptable testing, analytical, and reporting methods to be employed in completing the report.

(e) On or before October 1, 1986, the state board, in coordination with the districts, shall develop and publish a screening questionnaire for inactive solid waste disposal sites and guidelines for evaluating the questionnaire by the districts pursuant to subdivision (b). The screening questionnaire and guidelines shall require an inactive solid waste disposal site to be evaluated based on the nature and age of materials in the site, the quantity of materials in the site, the size of the site, and other appropriate factors. The guidelines for evaluating the screening questionnaire shall require a district to weigh heavily the proximity of the site to residences, schools, and other sensitive areas, and to pay particular attention to potential adverse impacts on facilities such as hospitals and schools, and on residential areas, within one mile of the site's perimeter.

(f) A district may reevaluate the status of a solid waste disposal site, including sites exempted pursuant to subdivision (c), and require the owner to submit or revise a solid waste air quality assessment test report after January 1, 1987. The district shall give written notification to the owner of the solid waste disposal site that a solid waste air quality assessment test report is to be submitted, or that the existing report is to be revised, and the date by which the report is to be submitted.

(g) A district shall evaluate any solid waste air quality assessment test reports submitted pursuant to subdivisions (a), (b), and (f), and determine if the report's testing, analytical and reporting methods comply with the guidelines developed pursuant to subdivision (d). If the district determines that the solid waste air quality assessment test report complies with the guidelines, it shall evaluate the data. If the district determines, after evaluation of the report and consultation with the state department and the California Waste Management Board, that levels of one or more specified air contaminants pose a health risk to human beings or a threat to the environment, the district shall take appropriate remedial action.

(h) If a district determines that a solid waste air quality assessment test report does not comply with the guidelines developed pursuant to subdivision (d), the district shall provide the owner of the site with a written notice specifying the inadequacies of the report and shall require the owner to correct the deficiencies and resubmit the report by a date determined by the district.

(i) For the purpose of this section, the following definitions apply:

(1) "Inactive solid waste disposal site" means a solid waste disposal site which has not received any solid waste for disposal after January 1, 1984.

(2) "Landfill gas" means any untreated, raw gas derived through a natural process from the decomposition of organic waste deposited in a solid waste disposal site or from the evolution of volatile species in the waste.

(3) "Perimeter" means the outer boundary of the entire solid waste disposal site property.

(4) "Solid waste disposal site" means a place, location, tract of land, area, or premises in use, or which has been used, for the landfill disposal of solid waste, as defined in Section 66719 of the Government Code, or hazardous waste, as defined in Section 66714.8 of the Government Code, or both.

(5) "Specified air contaminants" means substances determined to be air contaminants by the state board in coordination with the districts. The state board and the districts shall consider determining the following compounds to be air contaminants for purposes of this paragraph: benzene, chloroethene, 1,2-dibromoethane, 1,2-dichloroethane benzyl chloride, chlorobenzene, dichlorobenzene, 1,1-dichloroethene, dichloromethane, formaldehyde, hydrogen sulfide, tetrachloroethylene, tetrachloromethane, toluene, 1,1,1-trichloroethane, trichloroethylene, trichloromethane, xylene, and any other substance deemed appropriate by the state board or a district.

SEC. 6. Section 3 of this bill incorporates changes to Section 66796.54 of the Government Code proposed by both this bill and AB 3088. It shall only become operative if (1) both bills are enacted and become effective on or before January 1, 1987, but this bill becomes operative first, (2) this bill repeals and adds Section 66796.54 of the Government Code and AB 3088 amends Section 66796.54 of the Government Code, and (3) this bill is enacted after AB 3088, in which case Section 66796.54 of the Government Code, as added by Section 2 of this bill, shall remain operative only until the operative date of AB 3088, at which time Section 3 of this bill shall become operative.

SEC. 7. Reimbursement to local agencies and school districts for costs mandated by the state pursuant to this act shall be made pursuant to Part 7 (commencing with Section 17500) of Division 4 of Title 2 of the Government Code and, if the statewide cost of the claim for reimbursement does not exceed five hundred thousand dollars ($500,000), shall be made from the State Mandates Claims Fund, except that no reimbursement is required by this act pursuant to Section 6 of Article XIII B of the California Constitution for the cost of the program or level of service mandated by this act that the local agency or school district has the authority to levy service charges, fees, or assessments sufficient to pay that cost.

SEC. 8. This act is an urgency statute necessary for the immediate preservation of the public peace, health, or safety within the meaning of Article IV of the Constitution and shall go into immediate effect. The facts constituting the necessity are:

In order to fully and fairly implement the provisions of Chapter 1532 of the Statutes of 1984 relating to disposal of hazardous waste, and to implement the reporting requirements of this act, as quickly as possible, it is necessary that this act take effect immediately.

determines, after evaluation of the report and consultation with the state department and the California Waste Management Board, that levels of one or more specified air contaminants pose a health risk to human beings or a threat to the environment, the district shall take appropriate remedial action.

(h) If a district determines that a solid waste air quality assessment test report does not comply with the guidelines developed pursuant to subdivision (d), the district shall provide the owner of the site with a written notice specifying the inadequacies of the report and shall require the owner to correct the deficiencies and resubmit the report by a date determined by the district.

(i) For the purpose of this section, the following definitions apply:

(1) "Inactive solid waste disposal site" means a solid waste disposal site which has not received any solid waste for disposal after January 1, 1984.

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(3) "Perimeter" means the outer boundary of the entire solid waste disposal site property.

(4) "Solid waste disposal site" means a place, location, tract of land, area, or premises in use, or which has been used, for the landfill disposal of solid waste, as defined in Section 66719 of the Government Code, or hazardous waste, as defined in Section 66714.8 of the Government Code, or both.

(5) "Specified air contaminants" means substances determined to be air contaminants by the state board in coordination with the districts. The state board and the districts shall consider determining the following compounds to be air contaminants for purposes of this paragraph: benzene, chloroethene, 1,2-dibromoethane, 1,2-dichloroethane benzyl chloride, chlorobenzene, dichlorobenzene, 1,1-dichloroethene, dichloromethane, formaldehyde, hydrogen sulfide, tetrachloroethylene, tetrachloromethane, toluene, 1,1,1-trichloroethane,

trichloroethylene, trichloromethane, xylene, and any other substance deemed appropriate by the state board or a district.

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In order to fully and fairly implement the provisions of Chapter 1532 of the Statutes of 1984 relating to disposal of hazardous waste, and to implement the reporting requirements of this act, as quickly as possible, it is necessary that this act take effect immediately.

ATTACHMENT 2

SPECIFIED AIR CONTAMINANTS

COMPOUND		Detection Limits, ppb Air	Disposal site
Chloroethene (Vinyl Chloride)	$CH_2:CHCl$	2	500
Benzene	C_6H_6	2	500
1,2-Dibromoethane (Ethylene Dibromide)	$BrCH_2CH_2Br$	0.5	1
1,2-Dichloroethane (Ethylene Dichloride)	$ClCH_2CH_2Cl$	0.2	20
Dichloromethane (Methylene Chloride)	CH_2Cl_2	1	60
Tetrachloroethene (Perchloroethylene)	$Cl_2C:CCl_2$	0.2	10
Tetrachloromethane (Carbon Tetrachloride)	CCl_4	0.2	5
1,1,1-Trichloroethane (Methyl Chloroform)	CH_3CCl_3	0.5	10
Trichloroethylene	$HClC:CCl_2$	0.6	10
Trichloromethane (Chloroform)	$CHCl_3$	0.8	2

LANDFILL REPORT

Landfill Name:

Location (Latitude and Longitude or UTM coordinates):

POPULATION	Within 1 mile	1 to 2 miles	2 to 3 miles

AMBIENT AIR SAMPLING Date __________

Concentrations, ppb

		UPWIND		DOWNWIND		BACKGROUND
COMPOUND	Laboratory Detection Limits, ppb	Site 1	Site 2	Site 1	Site 2	Background
Vinyl Chloride						
Benzene						
Ethylene Dibromide						
Ethylene Dichloride						
Methylene Chloride						
Perchloroethylene						
Carbon Tetrachloride						
Methyl Chloroform						
Trichloroethylene						
Chloroform						
Methane						

ATTACHMENT 4

The choice of analytical method is left up to the individual laboratory performing the analysis. The methods provided in Attachment 4 are provided as examples of methods which can be used to sample and analyze for the specified air contaminants identified in Attachment 2. The methods are used by ARB laboratories to quantify the compounds listed *at or below the detection limits specified in Attachment 2.* Table 4-1 summarizes the method detection limits achievable by these methods and the detection limits to be reported for these guidelines:

TABLE 4-1: METHOD DETECTION LIMITS

COMPOUND	Guideline	Method Detection Limits, ppb Haagen-Smit Laboratory	Aerometric Data Division
Chloroethene (Vinyl Chloride)	2	-	1
Benzene	2	0.5	0.5
1,2-Dibromoethane (Ethylene Dibromide)	0.5	0.01	0.005
1,2-Dichloroethane (Ethylene Dichloride)	0.2	0.2	0.1
Dichloromethane (Methylene Chloride)	1	1	0.6
Tetrachloroethene (Perchloroethylene)	0.2	0.004	0.01
Tetrachloromethane (Carbon Tetrachloride)	0.2	0.02	-
1,1,1-Trichloroethane (Methyl Chloroform)	0.5	0.004	0.004
Trichloroethylene	0.6	0.005	0.02
Trichloromethane (Chloroform)	0.8	0.004	0.02

Procedure for the Sampling and Analysis of Atmospheric C_1 to C_2 Halogenated Hydrocarbons
Method 103

1 Introduction

1.1 This procedure describes a method of sampling and analyzing atmospheric concentrations of C_1 to C_2 halogenated hydrocarbons in the range of 0.004 to 1.0 parts per billion (ppb).

1.2 Lower concentrations may be analyzed by increasing the sample volume and using a cryogenic trap to concentrate the sample.

1.3 Higher concentrations may be analyzed by direct injection of a diluted sample into a sample loop of a gas chromatograph.

1.4 Compounds which can be analyzed by this method are:

1.4.1 Dichloromethane, CH_2Cl_2, (methylene chloride)

1.4.2 Trichloromethane, $CHCl_3$, (chloroform)

1.4.3 1,2-Dichloroethane, $ClCH_2CH_2Cl$, (ethylene dichloride, EDC)

1.4.4 1,1,1-Trichloroethane, Cl_3CCH_3, (methyl chloroform)

1.4.5 Tetrachloromethane, CCl_4, (carbon tetrachloride)

1.4.6 Trichloroethene, $Cl_2C{=}CHCl$, (trichloroethylene, TCE)

1.4.7 1,2-Dibromoethane, $BrCH_2CH_2Br$, (ethylene dibromide, EDB)

1.4.8 Tetrachloroethene, $Cl_2C{=}CCl_2$, (perchloroethylene, PERC)

2 Method

2.1 Air is sampled into a Tedlar bag at a calibrated and controlled flow during selected time intervals as described in Appendix A, "Procedure for Atmospheric Tedlar Bag Sampling".

2.2 A measured volume of the air sample is transferred by a syringe into the chromatograph.

2.3 The components are separated by a specified column and analyzed by an electron capture detector.

2.4 An electronic integrator quantitates the halogenated hydrocarbons by integrating the peak areas and calculating concentrations from a factor determined during calibration with a halogenated hydrocarbons

Procedure for the Sampling and Analysis of Atmospheric C_1 to C_2 Halogenated Hydrocarbons
Method 103

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1.4.2 Trichloromethane, $CHCl_3$, (chloroform)

1.4.3 1,2-Dichloroethane, $ClCH_2CH_2Cl$, (ethylene dichloride, EDC)

1.4.4 1,1,1-Trichloroethane, Cl_3CCH_3, (methyl chloroform)

1.4.5 Tetrachloromethane, CCl_4, (carbon tetrachloride)

1.4.6 Trichloroethene, $Cl_2C{=}CHCl$, (trichloroethylene, TCE)

1.4.7 1,2-Dibromoethane, $BrCH_2CH_2Br$, (ethylene dibromide, EDB)

1.4.8 Tetrachloroethene, $Cl_2C{=}CCl_2$, (perchloroethylene, PERC)

2 Method

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2.2 A measured volume of the air sample is transferred by a syringe into the chromatograph.

2.3 The components are separated by a specified column and analyzed by an electron capture detector.

2.4 An electronic integrator quantitates the halogenated hydrocarbons by integrating the peak areas and calculating concentrations from a factor determined during calibration with a halogenated hydrocarbons standard mixture.

3 Apparatus

3.1 A sampler with bags is required for each site. The sampler and bags are prepared and operated as described in the "Procedure for Atmospheric Tedlar Bag Sampling".

3.2 A gas chromatograph (GC) equipped with a gas injection valve and freeze-out trap inlet system is required. An electron capture detector is used.

3.3 One GC column is required: A glass column (6 ft x 1/4 in O.D.) packed with 0.2 percent Carbowax 1500 on Supelco 80/100 mesh Carbopac C.

3.4 Other GC supportive apparatus used are a strip chart recorder, a remote controller, and an electronic integrator.

3.5 Ground glass syringes (50, 100, and 250 mL capacity) or other suitable devices to accurately transfer air samples from Tedlar bags to the sample inlet of the GC are used.

3.6 A large air-tight chamber is used to prepare standard gas mixtures.

3.7 The cryogenic traps holding the liquid nitrogen are Dewar containers.

4 Reagents

4.1 All gases used in the GC analysis shall be of the highest commercial quality available.

4.2 Helium shall have a purity of 99.995%.

4.3 Halogenated hydrocarbons reference liquid standards, 99% purity as listed in 1.4 are used to prepare a 10 ppb working standard mixture which is used as a span gas.

4.4 A mixture of 10 percent methane in argon is used as make-up gas in the GC.

4.5 Commercial liquid nitrogen (b.p. = -196°C) is used to cool the freeze-out trap.

5 Procedure

5.1 Bags and samplers are fabricated, tested, and operated as described in Appendix B, "Procedure for the Fabrication and Testing of Sample Bags".

5.2 The air sample is analyzed for C_1 to C_2 halogenated hydrocarbons by using either the loop method or the freeze-out trap method. The freeze-out trap method is used for ppb to ppt (parts per trillion) concentrations.

5.2.1 The procedure for the loop method follows:

5.2.2 The air sample is transferred from the gas sample bag and injected into the sample loop of the GC using a clean 100 mL syringe fitted with a Luer-lok to quick-connect adapter.

5.2.3 The gas sampling valve (rotary type) is equipped with a 1 mL loop.

5.2.4 The gas sampling valve is rotated and the sample enters the GC analyzer and is separated into component compounds.

5.2.5 A Carbowax 1500/Carbopak C column is used to separate the halogenated hydrocarbons. Typical operating conditions for the gas chromatograph are:

25 mL/min helium carrier gas flow
40 mL/min 10% methane in argon make-up flow gas
80°C 10-port valve compartment temperature
150°C injection port temperature
350°C detector temperature
6° to 160°C at 8°C/min programming column temperature
Backflush: 23 min.

5.2.6 Each separated component passes through the electron capture detector and yields a response proportional to its response factor and concentration.

5.2.7 Concentrations of halogenated hydrocarbons may be calculated using an electronic integrator.

5.3.1 The procedure for the freeze-out method follows:

5.3.2 Immerse the sample trap in liquid nitrogen (LN_2) and allow the temperature to stabilize while maintaining a flow of helium through the system.

5.3.3 After discarding about 50 mL of the sample, withdraw exactly 100 mL from the sample bag with a 100 mL syringe and transfer the sample into the trap.

5.3.4 Backfill the syringe with another 40 mL of helium and flush the 40 mL through the trap; then flush the carrier helium through the trap for three minutes.

5.3.5 Isolate the cryogenic trap by using the isolation valve which allows the carrier gas to by-pass the trap.

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5.3.4 Backfill the syringe with another 40 mL of helium and flush the 40 mL through the trap; then flush the carrier helium through the trap for three minutes.

5.3.5 Isolate the cryogenic trap by using the isolation valve which allows the carrier gas to by-pass the trap.

5.3.6 Replace the LN_2 Dewar flask with a Dewar containing hot water at about 90 deg C.

5.3.7 Allow the trap to warm up.

5.3.8 Inject the sample into the carrier gas stream by turning the GC sampling valve. The gas sample enters the GC analyzer and is separated into component compounds.

5.3.9 The instrument operating conditions are the same as those described in Section 5.2.5 above.

5.3.10 Each separated component passes through the electron capture detector and yields a response proportional to its response factor and concentration.

6 Calculations

6.1 The concentrations of halogenated hydrocarbons, in ppb, are calculated by an electronic integrator using the external standard method.

6.1.1 Concentration = Area x Response Factor x Dilution Factor

6.2 The Response Factor (RF) is calculated during calibration by the equation:

$$RF = \frac{\text{Concentration}}{\text{Area}}$$

6.2.1 Dilution Factor = $\dfrac{\text{Total volume of diluted sample}}{\text{Initial sample volume before dilution}}$

6.2.2 Replicate calibrations are averaged and the arithmetic mean is stored as the RF for subsequent analyses.

6.3 Concentrations may be converted from ppb to mg/m^3 by means of the following formula:

$$mg/m^3 = \frac{P \times (M.W.) \times (ppb) \times (10^6)}{(82.05) \times (T)}$$

Where:

P = Pressure in atmospheres
M.W. = Molecular weight of corresponding halogenated hydrocarbon
82.05 = Gas constant in cm^3 x atm./ ^oK-mole
T = Absolute temperature (^oK).

6.4 The concentration unit mg/m^3 is equivalent to ng/cm^3

7 Quality Control

7.1 Quality control procedures are followed in two areas: sampling and analysis.

7.2 The quality control procedures used in sampling are:

7.2.1 The Tedlar bag samplers are checked every 6 months for leakage and contamination. The interval is shortened if any malfunction is suspected. A written record is maintained of the history of each sampler. (See Appendix A).

7.2.2 The Tedlar bags are checked for leakage and contamination before being used for sampling. A log book is maintained with a complete history of bag usage. (See Appendix B).

7.3 The quality control procedures used in analyzing the sample are:

7.3.1 The accuracy of the method has not been determined.

7.3.1.1 Every six to nine months a calibration standard is prepared in a glass-lined Pfaudler Chamber maintained by the Environmental Laboratory Section of the Haagen-Smit Laboratory.

7.3.1.2 The chamber is repeatedly evacuated and flushed with zero air until it is shown by gas chromatographic analysis to be free of any significant contamination.

7.3.1.3 To prepare the standard, the chamber is re-evacuated and filled with zero air to a pressure of 5 psia.

7.3.1.4 A measured volume of a volumetrically prepared solution of halogenated hydrocarbons in methanol is injected via a heated injector into a stream of zero air as it is flowing into the chamber. The volume of the solution injected into the chamber is chosen so as to give the desired gas phase concentration of halogenated hydrocarbons when the chamber is pressurized to 16 psia with zero air.

7.3.2 Calibration standards are prepared periodically. The accuracy of the standard is verified and the procedure validated by comparing the concentration of tetrachloroethene in the chamber to that of an NBS standard.

7.3.2.1 A newly prepared chamber working standard is rejected unless the tetrachloroethene concentration based on calculation agrees within +/- 5% of the value determined by analysis, using the NBS standard for calibration.

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7.3.2 Calibration standards are prepared periodically. The accuracy of the standard is verified and the procedure validated by comparing the concentration of tetrachloroethene in the chamber to that of an NBS standard.

7.3.2.1 A newly prepared chamber working standard is rejected unless the tetrachloroethene concentration based on calculation agrees within +/- 5% of the value determined by analysis, using the NBS standard for calibration.

7.3.2.2 A newly prepared chamber working standard is rejected unless the relative response factors for all eight halogenated hydrocarbons of interest fall within +/- 10% of the historically established mean values.

7.3.3 A working chamber standard is checked at least every three months for conformity to criteria 7.3.2.1 and 7.3.2.2.

7.3.3.1 A new standard is prepared as frequently as required as determined by the above mentioned criteria.

7.3.3.2 Any reports generated after the standard ceases to be demonstratively within the established tolerances shall contain a cautionary explanation.

7.4 The gas chromatograph is calibrated periodically.

7.4.1 Calibration factors are determined on the basis of the mean values of the previous calibration runs which meet the criteria of 7.4.3.

7.4.2 Each day a calibration check is performed using the Pfaudler chamber standard to span the instrument.

7.4.3 If the response for each compound of interest is within 10% of the established calibration value, the established calibration factors are retained.

7.4.4 The calibration check is repeated if the response of the instrument has changed by more than 10% from the established values.

7.4.5 If the response is still out of tolerance, a quality assurance report is submitted, remedial action is initiated, and new calibration factors calculated.

7.4.6 Blank samples shall be analyzed daily after the calibration is completed and, whenever necessary, between samples.

7.5 The linearity of the instrument is checked periodically.

7.5.1 A gas chromatographic multipoint linearity check is performed annually with standards of at least four different concentrations and four replicate runs for each concentration. The concentrations should include the anticipated range of sample concentrations above the limit of detection.

7.5.2 The mean-square error due to lack of fit about the regression line is compared to the total mean-square error of the independent replicates about their individual means. The calibration is accepted if the F-ratio is less than the 95% rejection limit.

7.5.3 A repeated multipoint calibration should not differ from the previous calibration by more than 10%.

7.5.4 Any region of concentration that deviates more than 5% from the least-square line is considered nonlinear.

7.5.5 Data is reported only for compounds whose concentrations lie in the linear range.

7.6 Limits of detection are established.

7.6.1 The limit of detection (LOD) is based on three standard deviations (SD) of runs near the LOD (within 10 SD of the LOD, Winefordner and Long, 1983).

7.6.2 The LOD should be determined at least on an annual basis.

7.6.3 If the instrument response changes by more than 15%, the instrument must be checked and the LOD redetermined.

7.6.4 The presence in a sample of a very large adjacent peak will often raise the LOD in the sample.

7.7 Analytical instruments have quality control procedures.

7.7.1 Column conditions are checked periodically and as needed.

7.7.1.1 All GC accessible parameters is logged when a column is first installed. These parameters are checked daily and recorded on integrator reports.

7.7.1.2 The efficiency and resolution of the column are checked every month. If the tests show more than a 10% change, the column is replaced.

7.7.1.3 If the headpressure required to maintain a specified flow through the column increases by more than 100%, the column is replaced.

7.7.1.4 If the drift of retention times of peaks results in peak misidentification, all instrument parameters are checked.

7.7.2 Replicate analyses are a quality control procedure.

7.7.2.1 A duplicate analysis is performed on at least one sample per day.

7.7.2.2 If the duplicate analysis (replicate) differs by more than 20%, and if the concentration of the sample is higher than 3X LOD, then an additional analysis is performed.

7.5.3 A repeated multipoint calibration should not differ from the previous calibration by more than 10%.

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7.7.2.2 If the duplicate analysis (replicate) differs by more than 20%, and if the concentration of the sample is higher than 3X LOD, then an additional analysis is performed.

7.7.2.3 If the range of the replicate analyses is greater than the mean and if the concentration of the sample is greater than 3X LOD, the analyses are not acceptable.

7.7.2.4 If the range is within 20%, the mean and the standard deviation are reported.

7.7.2.5 If there is any reason to suspect the presence of an interferent (peak broadening, shift of retention time, shoulder formation, etc.), peak identification is verified using another analyzer (GC/MS), detector,or column.

7.7.2.6 When spiked samples are analyzed, the peak height and peak area ratios of the spiked and unspiked samples must be consistent.

7.7.3 Compound confirmation is a quality control procedure.

7.7.3.1 Ten percent of the analyses are confirmed by a different analytical system (different column or different detector, e.g. GC/MS).

7.7.3.2 If the confirmatory and the routine analyses differ by more than 20%, none of the analyses are acceptable.

7.8 Analytical reports undergo quality control procedures.

7.8.1 Data storage: raw data transmitted from the integrator are stored unmodified in electronic storage. Data are archived according to date, site, analyses, and project for easy retrieval. These data are kept for 3 years in the laboratory electronic storage.

7.8.2 All data above the minimum detection limits are reported to the requesting agency in hard copy or electronic format.

7.8.3 All reports are reviewed by at least two qualified staff before they are released.

8 Critique and Comments

8.1 Lower limits of detection have been established using the prescribed instrument conditions and using a 100 mL sample with the freeze-out trap technique.

8.1.1 Table 8.1.1 lists the lower limits of detection for the the compounds analyzed by this method.

8.2 Interferences are not usually a serious problem for light halogenated hydrocarbon analysis when the electron capture detector is used.

8.2.1 The electron capture detector is selective for the measurement of halogenated hydrocarbons. It is virtually insensitive to other hydrocarbons thus eliminating interferences from non-halogenated hydrocarbons.

8.2.2 Any halogenated hydrocarbons present in the sample having retention times very similar to the compounds of interest under the operating conditions described in this method will interfere. Therefore, proof of chemical identity requires confirmation.

8.2.3 Water vapor at normal ambient humidity in the sample does not interfere with the separation and quantification of halogenated hydrocarbons.

8.2.4 High concentrations of nitrogen oxides (500 ppm) and sulfur oxides (50 ppm) interfere in the determination of methylene chloride in the samples of stack emission sources.

8.3 The procedure described herein has both advantages and disadvantages:

8.3.1 This method provides a simple way of air sampling. The concentrations of halogenated hydrocarbons in the range of interest are stable for more than 24 hours in the bag, providing sufficient time for the analysis.

8.3.2 The sample is easily and repeatedly introduced into the instrument by means of a gas sampling valve.

8.3.3 A representative composite sample is readily obtained for any selected time interval because the air sampling flow rate is constant.

8.3.4 Both the upper and the lower limits of detection can be extended by concentrating a larger volume of the sample with a freeze-out trap or by diluting the sample in a Tedlar bag with nitrogen or by loop injection.

8.3.5 Interferences can be eliminated by selecting chromatographic conditions.

9 References

9.1 U.S. Environmental Protection Agency (19760, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I-Principles", EPA-600/9-76-005 Environmental Monitoring and Support Laboratory, Research Triangle Park, North Carolina 27711.

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9.2 Grimsrud, E. P., and Knighton, W. B., Anal. Chem. 54, 565 (1982)

9.3 Bennett, C. A., and Franklin, M. L., "Statistical Analysis in Chemistry and the Chemical Industry", John Wiley and Sons, Inc., New York, (1954), pp. 222-232.

9.4 Ullman, N. R., (1973), "Elementary Statistics", John Wiley and Sons, Inc., New York, pp. 282-298.

9.5 Winefordner, J. D. and Long, G. L., Anal. Chem. 55, 712 A (1983).

CAUTION Laboratory Operations Involving Carcinogens

Most halogenated hydrocarbons are identified as human carcinogens; therefore, appropriate precautions should be observed when handling these compounds. Do not release halogenated hydrocarbon vapors to the laboratory atmosphere at any time. When venting or purging, the vapor must be routed to outside air. The OSHA regulations pertaining to the use and handling of halogenated hydrocarbons are published in Title 29 of the Code of Federal Regulations available in the Federal Register, Volume 40, May 28, 1975, pp. 23073.

TABLE 8.1.1
LIMITS OF DETECTION

Compound	Limit of Detection ppb	Concentration ppb	Mean Area	Area St.Dev.	n	% Rel St.Dev.
Methylene Chloride	1	1.37	8,230	800	6	9.7
Chloroform	0.004	0.006	8,290	197	5	2.4
Methyl Chloroform	0.004	0.004	34,000	3600	5	10.6
Carbon Tetrachloride	0.02	0.028	13,900	676	5	4.9
		0.01	2,400	320	6	13.3
Trichloroethylene	0.005	0.0064	15,600	515	5	3.3
Ethylene Dibromide	0.01	0.009	3,150	430	5	13.7
Perchloroethylene	0.004	0.0047	102,700	6080	5	5.9
Ethylene Dichloride	0.2	0.3	61,778	4811	6	7.8
		0.09	26,677	2143	5	8

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Procedure for the Sampling and Analysis of Atmospheric Benzene
Method 102

1 Introduction

1.1 This procedure describes a method of sampling and analyzing atmospheric concentrations of benzene in the range of 0.5 to 1000 parts per billion (ppb).

1.2 Lower concentrations may be analyzed by increasing the sample volume and using a cryogenic trap to concentrate the sample.

1.3 Higher concentrations may be analyzed by direct injection of a sample into a sample loop of a gas chromatograph.

2 Method

2.1 Air is sampled into a Tedlar (polyvinyl fluoride) bag at a constant rate (30 to 40 mL/min) during selected time intervals by means of an automatic sampler.

2.2 After sampling, the ambient air bag sample is returned to the laboratory for analysis.

2.3 The sample is introduced into the gas chromatograph (GC) sample stream by means of gas injection valves and analyzed by a photoionization detector.

2.4 The GC data system quantitates benzene by integrating the peak area and calculating the concentration from factors determined during calibration with standards.

3 Apparatus

3.1 The sampler system consists of a diaphragm pump with a by-pass flow constrictor, a solenoid valve, a flow meter with a flow control valve, pressure regulator, fittings, and tubing to convey air samples to the Teflon bag. The entire assembly, including a 7-day timer and associated electrical circuitry to control the filling of the sample bags, is compactly mounted on a metal chassis and operates on a 110 VAC power supply.

3.2 Tedlar bags, 2 mil thickness, 50 liter capacity, equipped with stainless steel quick disconnect fittings are used to contain the sample. The bags are prepared in conformity with the ARB document, "Procedure for Fabrication and Testing of Sample Bags", (see Appendix B). For sampling, the bags are placed in rigid opaque containers to protect their contents from the sunlight.

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3.3 A gas chromatograph equipped with a gas sampling valve and either a sample loop or freeze-out inlet system and a photoionization detector is required. The detector operates at 10.2 eV.

3.4 A freeze-out system consisting of a U-shaped stainless steel trap filled with stainless steel clippings is used to concentrate the sample.

3.5 A stainless steel column (6 ft x 1/8 in) packed with 10% N,N-bis(2-cyanoethyl)formamide on 100/120 mesh Chromosorb PAW is used.

3.6 For a confirmation of the benzene analysis, an alternate column should be used such as a stainless steel GC column packed with 10% tricyanoethoxy propane (TCEP).

3.7 An analog recorder and an electronic integrator to quantify peak areas are required.

3.8 Ground glass syringes (100 mL capacity) or other suitable devices are needed to transfer air samples from the Tedlar bag to the GC sample inlet.

4 Reagents

4.1 The primary standard used in this analysis should be the National Bureau of Standards (NBS) benzene standard reference material.

4.2 Helium with a minimum purity of 99.995% should be used.

4.3 Commercial liquid nitrogen (b.p.=-196°) is used to cool freeze-out trap.

5 Procedure

5.1 All bags and samplers are prepared for sampling as outlined in Appendix A, "Procedures for Atmospheric Bag Sampling".

5.2 The air sample is analyzed for benzene by using either the loop method or the freeze-out method. The freeze-out method is used for lower benzene concentrations of less than 25 ppb.

5.2.1 The procedure for the loop method follows:

5.2.1.1 Transfer the air sample from the air sample bag and inject it into the sample loop of the gas chromatograph using a 100 mL syringe fitted with a Luer-lok to quick-connect adapter.

5.2.1.2 The gas sampling valve has a fixed volume sample loop of about 1 mL.

5.2.1.3 Rotate the gas sampling valve. This causes the sample to enter the gas chromatographic analyzer.

5.2.2 The procedure for the freeze-out method follows:

5.2.2.1 Immerse the sample trap in liquid nitrogen (LN_2) and allow the temperature to stabilize (approximately 5 min).

5.2.2.2 After flushing the syringe with about 40 mL of the sample withdraw exactly 40 mL from the sample bag with the syringe.

5.2.2.3 Transfer the sample into the trap.

5.2.2.4 Backfill the syringe with 40 mL of helium and flush the 40 mL through the trap; then flush helium through the trap for 2 minutes at 100 mL/min.

5.2.2.5 Stop the helium flushing process.

5.2.2.6 Isolate the cryogenic trap by using the isolation valve, which prevent the escape of the sample.

5.2.2.7 Remove the LN_2 Dewar from the trap and replace it with a Dewar containing hot water at about 80 degC.

5.2.2.8 Allow the trap to warm up.

5.2.2.9 Actuate the sampling valve, thereby causing the carrier gas stream to flush the sample into the gas chromatograph.

5.3 With the suggested stainless steel column (see item 3.5), typical operating conditions for both loop and freeze-out methods are:

Helium flow:	20 mL/min
Heating bath temperature for cryogenic trap:	80 degC
Column temperature:	ambient
Detector temperature:	150 degC

5.4 Concentrations of benzene may be calculated by using a chromatographic data system or any other suitable electronic integrating device.

6 Calculation

6.1 The benzene concentration in ppb is calculated by the data system using the external standard method:

Concentration = Area x Calibration Factor

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6 Calculation

6.1 The benzene concentration in ppb is calculated by the data system using the external standard method:

Concentration = Area x Calibration Factor

6.2 The calibration factor (CF) is calculated during calibration by the equation,

$$CF = \frac{conc}{Area}$$

The replicate calibrations are averaged and the arithmetic mean is stored as the CF to be used in subsequent analyses.

6.3 Concentrations may be converted from ppb to ug/m^3 by using the following formula:

$$ug/m^3 = \frac{(P) \times (MW) \times (ppb) \times (10^3)}{(82.05) \times (T)}$$

where:

P = pressure in atmospheres

MW = molecular weight of benzene, 78.11 g/mole

82.05 = gas constant, $\frac{cm^3 \times atm}{mol \times T}$

T = absolute temperature, degK

7 Quality Control

7.1 Quality control procedures are managed in two areas: sampling and analysis.

7.2 The sampling procedures use the following protocol:

7.2.1 The Tedlar bag samplers are checked every six months for leakage and contamination. The interval is shortened if any malfunction is suspected. A written record is maintained of the history of each sampler. (See Appendix A).

7.2.2 The Tedlar bags are checked for leakage and contamination before being used for sampling. A log book is maintained with a complete history of bag usage. (See Appendix B).

7.3 The analytical procedures use the following protocol:

7.3.1 Calibrations are performed periodically. Accuracy of the method cannot be determined without an accepted standard reference material (SRM) and independent accuracy evaluation.

7.3.1.1 An NBS traceable reference material of 0.25 ppm (parts per million) benzene in nitrogen is used to monitor the concentration of a secondary working standard.

7.3.1.2 Any secondary standards prepared from the reference standard must show the same response factor as the original reference standard. Intercomparisons are made on a monthly basis.

7.3.1.3 A working standard, prepared by diluting an NBS reference material of about 10 ppm to about 10 ppb, is generally used for daily calibrations.

7.3.1.4 The stability of working standards must be such that there is less than a 10% change in thirty days.

7.3.1.5 There shall be at least one working standard whose concentration lies within the interval of 5 to 20 ppb.

7.3.1.6 A second working standard of a higher concentration shall be prepared for use in two point calibrations.

7.3.1.7 A quality assurance audit of the standards is prepared annually.

7.3.2 Calibrations are performed on a daily schedule.

7.3.2.1 The daily calibration consists of at least two calibration points bracketing the anticipated sample concentrations.

7.3.2.2 The calibration is repeated if either the slope or the response at the limit of detection (LOD) of the fitted line changes by more than 5%. If the calibration fails on both runs, an NBS 0.25 ppm reference standard is used to validate the calibration.

7.3.2.3 If the lamp voltage is adjusted, allow time for the lamp to stabilize and repeat the calibration.

7.3.2.4 A record is kept of the lamp voltage settings and all preventative maintenance procedures i.e. lamp replacements, cleaning of lamp windows.

7.3.2.5 Blank samples are run daily between calibrations and sample analyses as necessary.

7.3.2.6 A single point span calibration may be substituted for the two point calibration procedure for a maximum of four consecutive days provided the response factor does not change by more than 10% during the time interval.

7.3.3 Linearity is a factor that is checked periodically.

7.3.3.1 A gas chromatographic linearity check is performed annually with standards of at least 4 different conthe concentration of a secondary working standard.

7.3.1.2 Any secondary standards prepared from the reference standard must show the same response factor as the original reference standard. Intercomparisons are made on a monthly basis.

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7.3.3 Linearity is a factor that is checked periodically.

7.3.3.1 A gas chromatographic linearity check is performed annually with standards of at least 4 different concentrations and 4 replicate runs for each concentration. The concentrations must bracket the anticipated range of sample concentrations.

7.3.3.2 The mean-square error due to lack of fit about the regression line is compared to the total mean-square error of the independent replicates about their individual means. The calibration is accepted if the F-ratio is less than the 95% rejection limit.

7.3.3.3 Any region of concentration that deviates more than 5% from the least square line is considered nonlinear.

7.3.3.4 Samples must be analyzed only in the linear range.

7.3.4 Limits of detection must be established.

7.3.4.1 The limit of detection (LOD) is based on three standard deviations (SD) of runs near the LOD (within 10 SD of the LOD, Winefordner and Long, 1983).

7.3.4.2 The LOD should be determined at least on an annual basis.

7.3.4.3 If the benzene calibration factor changes by more than 10%, The instrument must be checked and the LOD redetermined.

7.3.4.4 The presence in a sample of a compound producing in the chart display very large adjacent peaks will often raise the LOD in that sample.

7.3.5 GC column condition parameters should be checked and documented.

7.3.5.1 All GC accessible parameters should be logged when a column is first installed. These parameters should be checked daily and recorded on integrator reports.

7.3.5.2 The efficiency and resolution of the column should be checked every thirty days. If the tests show more than a 10% change the column needs replacement.

7.3.5.3 If the headpressure required to maintain a specified flow through the column increases by more than 100%, the column needs replacement.

7.3.5.4 If the drift of retention times of the peaks results in peak misidentification, all instrument parameters need to be checked.

7.3.6 Replicate analyses are performed regularly.

7.3.6.1 A duplicate analysis is performed on at least one sample each day.

7.3.6.2 If the duplicate analysis differs by more than 20%, and if the concentration of the sample is higher than 3X LOD, then an additional analysis is needed.

7.3.6.3 If the relative standard deviation (RSD) of the replicate analyses is greater than 15% and if the concentration of the sample is greater than 3 x LOD, none of the analyses for that day are acceptable.

7.3.6.4 If the range is within 20%, the mean and the standard deviation are reported.

7.3.7 Compound confirmation is a quality control procedure.

7.3.7.1 Ten percent of the analyses are to be confirmed by a different analytical system (different column or alternate detector, e.g. GC/MS).

7.3.7.2 If the confirmatory and the routine analyses differ by more than 20%, none of the analyses for that day are acceptable.

7.3.8 Analytical reports are filed.

7.3.8.1 Data storage: peak area and compound concentration data are stored unmodified in the electronic storage. Data are archived according to date, site, analysis, and project for easy retrieval. These data are kept for three years in the laboratory electronic storage.

7.3.8.2 All data above the minimum detection limits are reported to the requesting agency in hard copy or electronic format.

7.3.8.3 All reports are reviewed by at least two qualified staff before they are released.

8 Critique and Comments

8.1 The minimum measurable concentration of benzene has been determined to be 0.5 ppb using prescribed instrument conditions i.e. 40 mL sample, cryogenic trap.

8.1.1 Table 8.1.1 lists the lower limits of detection for the method and its associated statistics

8.2 The range of benzene measurement is 1.0 to 1000 ppb. The upper limit may be expanded by extending the calibration range, by diluting the sample, or by reducing the sample volume.

8.3 Any organic compound present in the sample having a retention time similar to that of benzene under the

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8.2 The range of benzene measurement is 1.0 to 1000 ppb. The upper limit may be expanded by extending the calibration range, by diluting the sample, or by reducing the sample volume.

8.3 Any organic compound present in the sample having a retention time similar to that of benzene under the operating conditions described in this method may interfere with the quantification. Proof of chemical identity for benzene requires confirmation by other means.

8.3.1 Benzene is positively identified by means of a gas chromatograph/mass spectrometer.

8.4 Advantages and disadvantages of Method 102 are listed below:

8.4.1 The air sampling equipment is easily set up and involves no liquids. The ambient concentrations of benzene are are stable for at least 24 hours in the Tedlar sampling bags if the sampling bags are kept away from direct sunlight and are not exposed to temperatures greater than 90°F.

8.4.2 A representative integrated sample is readily attainable because the equipment samples at a constant rate.

8.4.3 The sample is easily and repeatedly introduced into the GC by using a volumetric gas sampling valve or cryogenic trap.

8.4.4 The lower concentration limit of the analysis may be extended by concentrating the sample by freezing out a larger volume of the sample.

8.4.5 The polyvinyl fluoride (Tedlar) film sample bag is susceptible to leaks and permeation through the bag.

8.4.6 The sample is susceptible to contamination when it passes through the sampling system.

9 References

9.1 Bennett, C. A. and Franklin, N. L., "Statistical Analysis in Chemistry and the Chemical Industry", pp. 222-232, John Wiley & Sons, Inc., New York (1954).

9.2 Draper, N. R. and Smith, H., "Applied Regression Analysis", p.30, John Wiley & Sons, Inc., New York (1966).

9.3 Purnell, H., "Gas Chromatography", pp. 301-302, John Wiley & Sons, Inc., New York (1962).

9.4 U. S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I - Principles", Research Triangle Park, North Carolina 27711 (1976).

METHOD NO. ADDL002

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF VOLATILE ORGANICS IN AMBIENT AIR USING TENAX TRAP PRECONCENTRATION GAS CHROMATOGRAPHY AND TANDEM PHOTOIONIZATION/ELECTRON CAPTURE DETECTORS

1.0 SCOPE

This document describes a procedure for the determination of volatile halogenated hydrocarbons and aromatics having a boiling point of less than 120°C. This procedure is based on documents received from the ARB Haagen-Smit Laboratory, El Monte, as well as EPA Method T01.

2.0 SUMMARY OF PROCEDURE

Ambient air is continuously sampled and collected in a Tedlar bag over a 24 hour period and immediately sent to the laboratory for analysis. A sample from the bag is drawn through a sampling valve attached to a Tekmar LSC-2 Tenax Sample Concentrator (see Figure I) with a vacuum pump at 50 cc/min for four minutes (total sample volume: 200 cc). The organic constituents are trapped on Tenax and when the collection is complete, the Tenax is purged with 40 cc of helium to remove any trapped moisture. The sample is then thermally desorbed onto the head of the GC column. The GC column is temperature programmed and component peaks eluting from the column are sequentially detected and quantified, first by a photoionization detector (PID) and then by an electron capture detector (ECD). The components are identified based on retention times. Positive identification or confirmation requires the use of an appropriately configured GC/MS.

3.0 INTERFERENCES/LIMITATIONS

a. Components having similar GC retention times will interfere, causing misidentification and/or faulty quantitation.

b. Because of the very low sample concentrations, extreme care must be taken to insure that the sample is not degraded or contaminated by the Tedlar sampling bag, sampling apparatus, or delayed delivery to the laboratory. Exposure of the Tedlar sampling bag to temperatures greater than 25°C should be minimized.

c. Only components of the sample which can be detected by PID/ECD detectors will be quantified.

4.0 APPARATUS

a. Varian Model 6000 Gas Chromatograph/PID/ECD system equipped with a Varian Vista 402 dual channel data system.

b. Tekmar LSC-2 Sample Concentrator equipped with Tenax trap and sampling valves as shown in Figure 1.

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a. Varian Model 6000 Gas Chromatograph/PID/ECD system equipped with a Varian Vista 402 dual channel data system.

b. Tekmar LSC-2 Sample Concentrator equipped with Tenax trap and sampling valves as shown in Figure 1.

c. Matheson Model 8240 Mass Flow Controller accurately calibrated in the 5-100 cc/min range.

d. Laboratory timer, accurate to within 0.1 minutes.

e. Gas tight microliter syringe, 50 ul.

f. GC column - 10' x 2 mm i.d. glass column packed with 1 percent SP-1000 on Carbopack B, 60/80 mesh.

5.0 REAGENTS

a. Primary Gas Standard (Scott Specialty Gases - Research Triangle Institute Certified Series 1)

Compound	Concentration (ppb)
Chloroform	107
Carbon tetrachloride	105
Perchloroethene	106
Vinyl chloride	104
Benzene	107

b. Primary Gas Standard (Scott Specialty Gases - Research Triangle Institute Certified Series 2)

Compound	Concentration (ppb)
1,2-Dichloroethane	101
1,1,1-Trichloroethane	98
Trichloroethene	100
1,2-Dibromoethane	102

c. Stock Gas Standard - Scott-Marrin Blend (assayed against primary cylinders)

Compound	Concentration (ppb)
Dichloromethane	4272
Chloroform	528
1,2-Dichloroethane	3104
1,1,1-Trichloroethane	424
Carbon tetrachloride	46
Trichloroethene	336
1,2-Dibromoethane	5
Perchloroethene	43
Vinyl chloride	4736
Benzene	1888

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6.0 PROCEDURES

a. Sample Trapping

1. The preconcentration system is shown in Figure 1.

2. The high concentration inlet is used for high concentration calibration standards and for other samples with concentrations higher than ambient levels. The sample is introduced through the high concentration inlet and 6 port valve into an appropriate size loop of known volume. The sample then passes through a 10 port valve, mass flow meter, and vacuum pump. Before an analysis, the system is leak checked by blocking the sample inlet port and observing that the mass flow meter reading drops to zero. The high concentration inlet then is connected to a Tedlar sample bag valve and the gas bag valve is opened. The loop is then flushed with sample gas for three minutes. After three minutes of flushing, the 6 port valve is reset so that the sample contained in the loop is carried into the trap by the helium purge gas. This continues for three minutes to ensure that all of the contents of the loop are trapped.

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3. Ambient samples are introduced from Tedlar bags as described above, except that the sample loop is bypassed and the sample goes directly to the 10 port valve. After flushing the system with sample for three minutes, the 10 port valve is reset so that 200 cc's of sample is trapped (50 cc/min. for four minutes). After sample trapping is complete, the Tenax trap is flushed with 40 cc of helium to remove water vapor and any nonadsorbed reactive gases.

4. In both ambient and high concentration cases, after the sample has been trapped, the Tekmar LSC-2 heats the Tenax trap to 180°C while the trap is swept with the G.C.'s internal carrier gas for four minutes. The contents of the trap are thus desorbed and collected on the head of the G.C. column. The trap is baked out after the end of the desorption cycle. In the bakeout cycle, the trap is flushed with helium purge gas for eight minutes while being held at 225°C in order to prepare the trap for the next cycle. After bakeout the trap is isolated from the system and ready for the next sample.

b. Analysis

1. The concentrated sample is separated under the chromatographic condition detailed below. The resulting chromatogram (see Figure II) is then integrated and quantified by reference to calibration standard gases.

2. Instrument Conditions:

GC: Column: 10' x 2 mm i.d. glass column, packed with 1 percent SP-1000 on Carbopack B 60/80 mesh

Temperatures:
Injection: 200°C
Detector: 350°C
Oven: 45°C, hold for four minutes, 5°C/min ramp, to 210°C, hold for eight minutes

Flow Rates:
Carrier: He, 20 cc/min
ECD make up: N_2, 40 cc/min

Detectors:
ECD: Range X 10, Attenuation X 32
PID: Range X 1, Attenuation X 32, 10.2 ev lamp

Conc: Tekmar LSC-2:
Purge: 4 minutes
Desorb: 4 minutes at 180°C
Bake: 8 minutes at 225°C

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Purge: 4 minutes
Desorb: 4 minutes at 180°C
Bake: 8 minutes at 225°C

3. All blanks, standards, control samples, and ambient samples are spiked with surrogate compounds by injecting 50 microliters of the surrogate gas standard (5.e.) during sample trapping. The surrogate compounds, chosen such that they simulate the characteristics of the analytes of interest and are unlikely to occur in the environment, are added to insure that systematic errors or equipment failures will be noted and corrected promptly.

4. The first step in a calibration is to analyze a system blank. This is done by trapping and analyzing a 200 cc sample of auxiliary carrier gas. The system blank must be free of interfering peaks. A system blank must also be run after a high concentration sample is analyzed in order to detect any carry-over within the system.

5. A calibration is performed using a 1.25 cc loop of stock standard gas (5.c.). Two hundred cubic centimeters of helium gas is passed through the loop to carry the standard onto the trap. The calibration analysis is made as a normal analysis. The calculated concentration value for each component should be inspected to insure consistency with previous analyses. The stored chromatographic information may then be used to recalculate the response factors for the subsequent analyses. The G.C. data system will not accept updated response factors which are in excess of plus or minus 15 percent of historic data.

6. Following calibration, 200 cc of the control sample (5.d.) is concentrated on the trap and analyzed. The control sample data are plotted on control charts of the normal Shewhart type. Upper and lower warning limits are plus or minus two times the standard deviation. Any analysis which falls outside the upper and lower warning limits is repeated and the laboratory quality control officer is advised. Upper and lower control limits are plus or minus three times the standard deviation. If any analysis falls outside the upper or lower control limit, the method is discontinued until the out of control situation is remedied. The laboratory quality control officer is advised and provided with written documentation of the out of control condition and how it was remedied. All data generated prior to the out of control situation must be reviewed for possible decertification by laboratory management.

7. Multipoint calibrations are conducted monthly. Each multipoint calibration includes a trap blank and three standard concentration levels to bracket the concentration ranges expected in ambient air. If subsequent data indicate that the resulting least squares analyses are consistently acceptable, less frequent multipoint calibrations may be made.

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7.0 PERFORMANCE

a. All ambient field samples are analyzed in duplicate. The relative error between analyses must be less than 20 percent. Duplicate analyses having greater than 20 percent relative error must be decertified.

b. The percent recovery of the surrogate is recorded in the instrument laboratory workbook for each analysis. If this value is outside the 80% to 120% range, the sample analysis must be repeated.

8.0 METHOD SENSITIVITY, PRECISION AND ACCURACY

The method sensitivity, precision and accuracy are outlined in Table I. These data were produced with gaseous calibration standards, and using carrier gas as the sample matrix. The relative accuracy of the method, with the exception of dichloromethane, is based on reference to the Research Triangle Institute Certified Gas Standards (NBS traceable). Authoritative reference calibration standards for dichloromethane are under development at NBS but are not yet available. The concentration value of the present standard was assigned by the commercial manufacturer and found to be in good agreement with diluted pure dichloromethane prepared in our laboratory. The absolute accuracy of the method has not been determined by interlaboratory testing.

Figure I

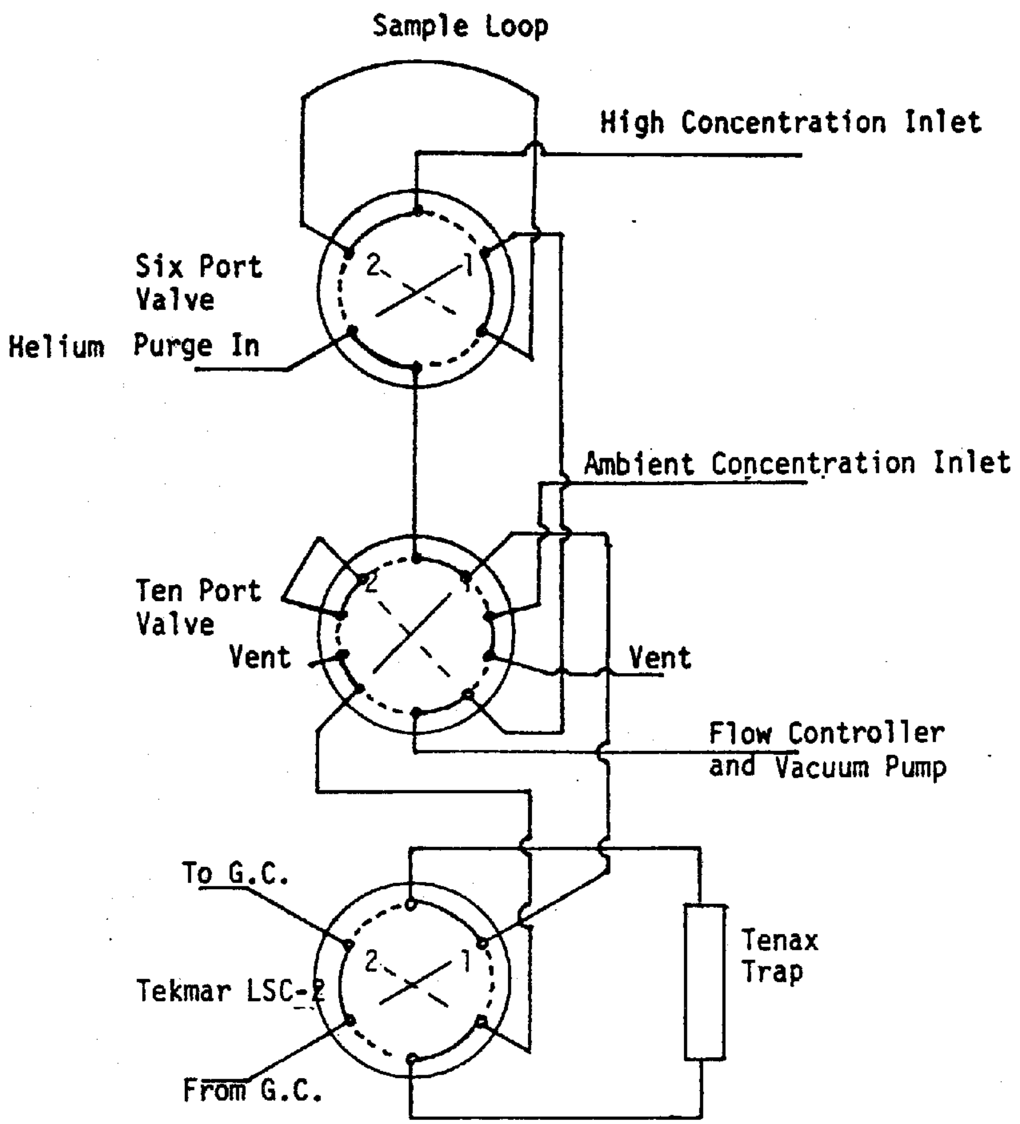
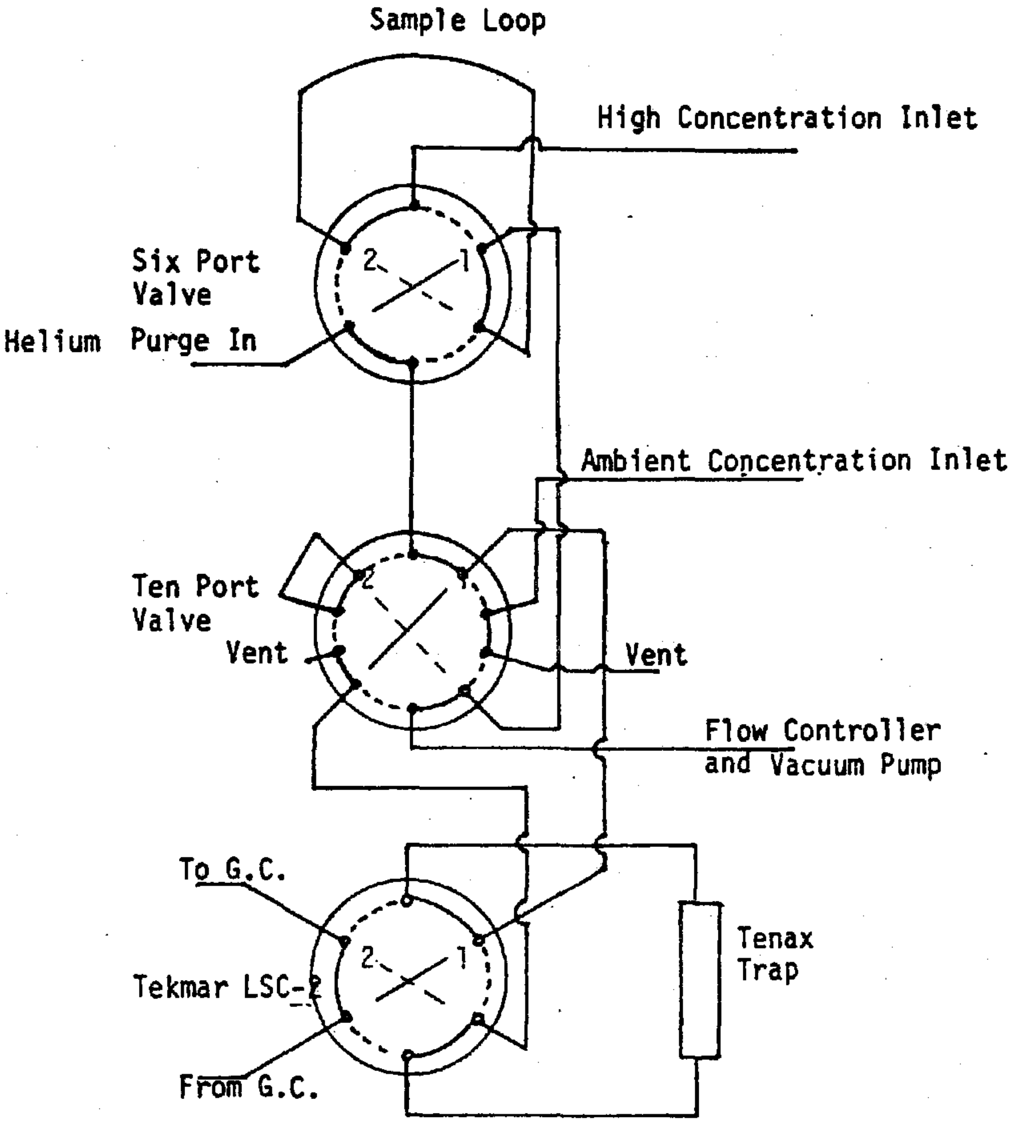


Figure 1. Schematic of concentrator system. Sampling Conditions are: 200 cc volume, purge at 40cc/min, 1 min., desorb at 180 C for 4 min., bake for 8 min. at 225 C.

SYSTEM GUIDE

Operational Step	Valve Position 6-Port	 10-Port	 LSC-2	Purge Gas
Loop Fill	1	1	1	Off
Loop Trap	2	1	1	On
Ambient Trap	1	2	1	Off
Trap Desorb	1	1	2	Off
Trap Bake Out	1	1	1	On



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PRELIMINARY DRAFT

Method ADDL004
August 27, 1985
Revision: Prelim. Draft 4
Approved:
Page 1 of 5 Pages

DATE__________ SIGNATURE__________

STATE OF CALIFORNIA
AIR RESOURCES BOARD
AEROMETRIC DATA DIVISION LABORATORY

Method For Determination Of Benzene, Xylenes, Toluene And Ethyl Benzene In Ambient Air Using Tenax Preconcentration And Gas Chromtography/Photoionization Detection

Introduction

This document describes a packed column GC/PID method to separate and quantitate the o-, m-, and p-xylene isomers plus benzene, toluene and ethyl benzene in ambient air samples. This method consists of preconcentrating ambient air samples using a Tenax trap and then thermally desorbing the components onto a packed glass column for analysis by PID. Air-actuated valves and data processing using a data system make this a highly automated system.

Apparatus

1. Varian Model 6000 Gas Chromatograph/HNu photoionization detector (GC/PID) system equipped with a Vista 402 Data System.
2. A sampling and analysis valve system consisting of a 6-port and 4-port valve, 1/8" x 6" Ni trap filled with 60/80 mesh Tenax and an injection system for standards as shown in Figure 1.
3. Matheson Model 8240 Mass Flow Controller accurately calibrated in the 5-100 cc/minute range and a Metal Bellows Pump for sampling.
4. Gas-tight microliter syringes with on/off valves for injection of standard gas mixtures.

Reagents and Standards

1. SRM-1806 benzene 10 ppm in nitrogen standard.
2. Chemical standards of highest purity available.
3. Methanol ACS grade.
4. Stock solutions for standards.

Table I

Method Sensitivity and Precision

Compound	Correlation Coefficient	Slope	R.S.D* (Percent)	Detector	LOD ppbv
Vinyl Chloride	0.997	0.946	16	PID	0.8
Dichloromethane	0.999	0.975	5	ECD	0.6
1,1-Dichloroethylene	0.991	0.966	6	ECD	0.05
Chloroform	0.999	0.901	3	ECD	0.02
1,2-Dichloroethane	0.999	1.054	7	ECD	0.1
1,1,1-Trichloroethane	0.999	0.989	9	ECD	0.01
Carbon Tetrachloride	0.999	0.980	6	ECD	0.005
Trichloroethylene	0.999	0.992	6	ECD	0.02
Benzene	0.998	0.950	10	PID	0.5
1,2-Dibromoethane	0.974	1.067	9	ECD	0.005
Tetrachloroethylene	0.994	1.080	10	ECD	0.01

---

* R.S.D. - Relative Standard Deviation at 5 x LOD, n = 5

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1,1-Dichloroethylene	0.991	0.966	6	ECD	0.05
Chloroform	0.999	0.901	3	ECD	0.02
1,2-Dichloroethane	0.999	1.054	7	ECD	0.1
1,1,1-Trichloroethane	0.999	0.989	9	ECD	0.01
Carbon Tetrachloride	0.999	0.980	6	ECD	0.005
Trichloroethylene	0.999	0.992	6	ECD	0.02
Benzene	0.998	0.950	10	PID	0.5
1,2-Dibromoethane	0.974	1.067	9	ECD	0.005
Tetrachloroethylene	0.994	1.080	10	ECD	0.01

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* R.S.D. - Relative Standard Deviation at 5 x LOD, n = 5

Stock solutions are prepared by dilution of pure chemicals into methanol. The following volumes are diluted to 50 ml using a volumetric flask.

Compound	Stock Standard ul/50 ml	Gas Standard-ppmv (10 ul/250 cc)	Trap Standard-ppbv (50 ul/200 cc)
Benzene	182	40	10
Toluene	217	40	10
Ethyl benzene	250	40	10
o-xylene	246	40	10
m-xylene	251	40	10
p-xylene	252	40	10

A 10 ul aliquot of the stock solution is injected into a 250 ml glass dilution bulb filled with zero air. The bulb is heated in an oven at 40°C for 1 hour. After equilibration, a gas-tight syringe is used to inject 1.8 ppb to 7.2 ppb samples in order to construct a calibration curve. The following data in Table I was obtained:

Table I

Compound	Slope	Correlation Coefficient	R.S.D. at 5.4 ppb (Percent)	M.D.L. (ppb)
Benzene	255	0.9998	1.3	0.5
Toluene	229	0.9996	5.6	1
Ethyl benzene	182	0.9995	2.7	0.5
p-xylene	169	0.9987	1.3	1
m-xylene	185	0.9982	3.5	1
o-xylene	161	0.9563	1.4	1

M.D.L. = Minimum Detectable Limit = Intercept + (3 x R.S.D. x Intercept)

Instrument Conditions

Column :	10 ft x 2 mm i.d. glass 5% SP1200/1.75% bentone on 100/120 Supelcoport
Injector Temperature :	200°C
Detector Temperature :	160°C
Detector Range :	X1
Detector Attenuation :	X32
PID Lamp :	10.2 eV
Valve Temperature :	180°C
Flow Rate :	30 ml/minute helium
Oven Temperature Program:	10°C for 1 minute 10°C to 45°C at 8°/minute 45°C to 100°C at 3°/minute

Procedure

Apparatus shown in Figure 1.

1. With the 6-port valve in the "Fill Position" and the 4-port valve closed, the Teflon sampling line is attached to the Tedlar sample bag. The sample line is then flushed for 5 minutes at a flow rate of 20 cc/minute. The isolated Tenax trap is cooled to 30°C during this initial flushing. (Relays 2, 3, 7, 8 off.)

2. When flushing is completed, the 4-port valve is switched to the "Fill Position" and sample is pumped through the trap for 10 minutes at 20 cc/minute. At the beginning of the trapping the internal standard and calibration gas standard are injected through the in-line injector into the gas stream. (Relay 3 on.)

3. At the end of 10 minutes the Tenax trap is isolated (4-port valve closed) and the trap heated to 210°C. The sample inlet is disconnected from the Tedlar sample bag and connected to the auxiliary carrier gas supply to sweep out any residual sample in the lines. (Relay 3 off, then Relay 8 on.)

4. The 6-port valve is switched to the "Sweep Position" allowing the carrier gas to be directed through the 4-port trap valve which is still in the isolated position. (Relay 2 on.)

5. With the GC oven and data system ready the 4-port valve is switched to the "Fill Position" and the data system and the column temperature program are started. (Relays 3, 7 on.)

6. The resulting chromatogram is analyzed and the results quantitated and tabulated. (See Figure 2.)

Automation of this system has been accomplished by use of relay switches/automatically actuated valves and a data system. The following chart details the automation:

Time (Minutes)	Relay On	Relay Off
0.00		2, 3, 7, 8
0.01	3	
10.01		3
10.10	8	
12.00	2	
13.00	3, 7	
23.00		2, 3
24.00		8

Relay 2 = 6-port valve
Relay 3 = 4-port valve
Relay 7 = data system
Relay 8 = Tenax trap heater

Procedure

Apparatus shown in Figure 1.

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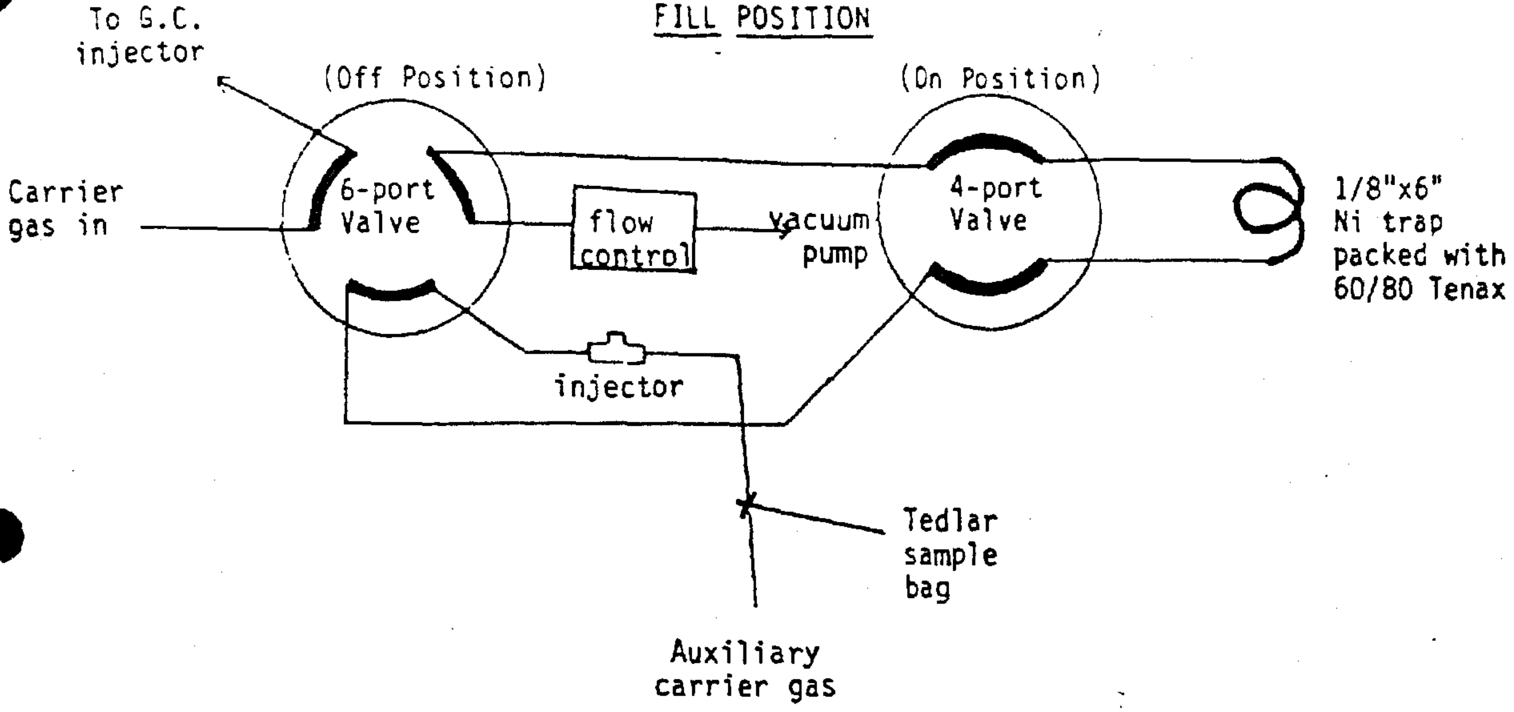
TRAP SYSTEM

FILL POSITION



SWEEP POSITION

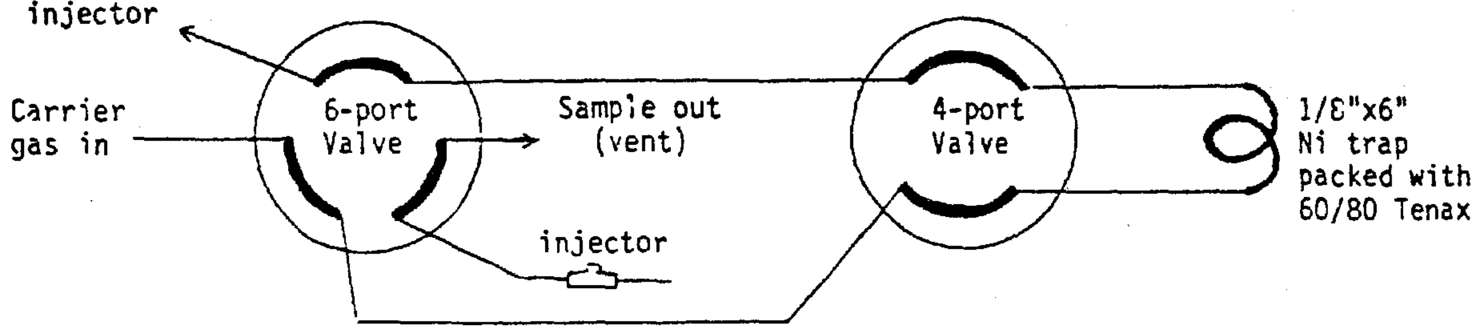
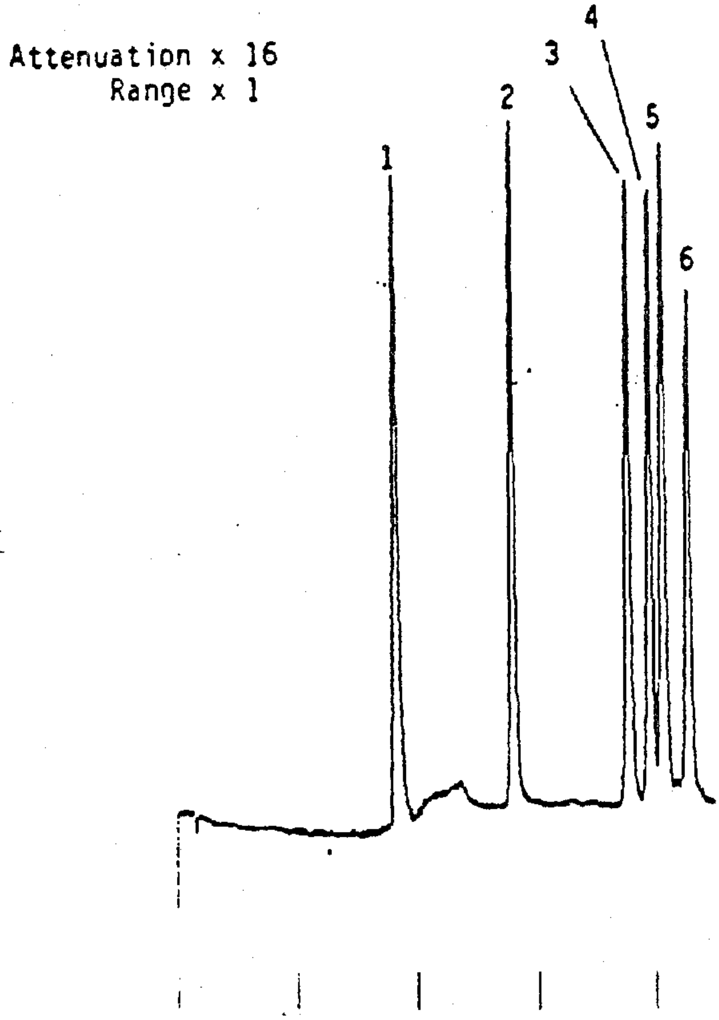


Figure 2

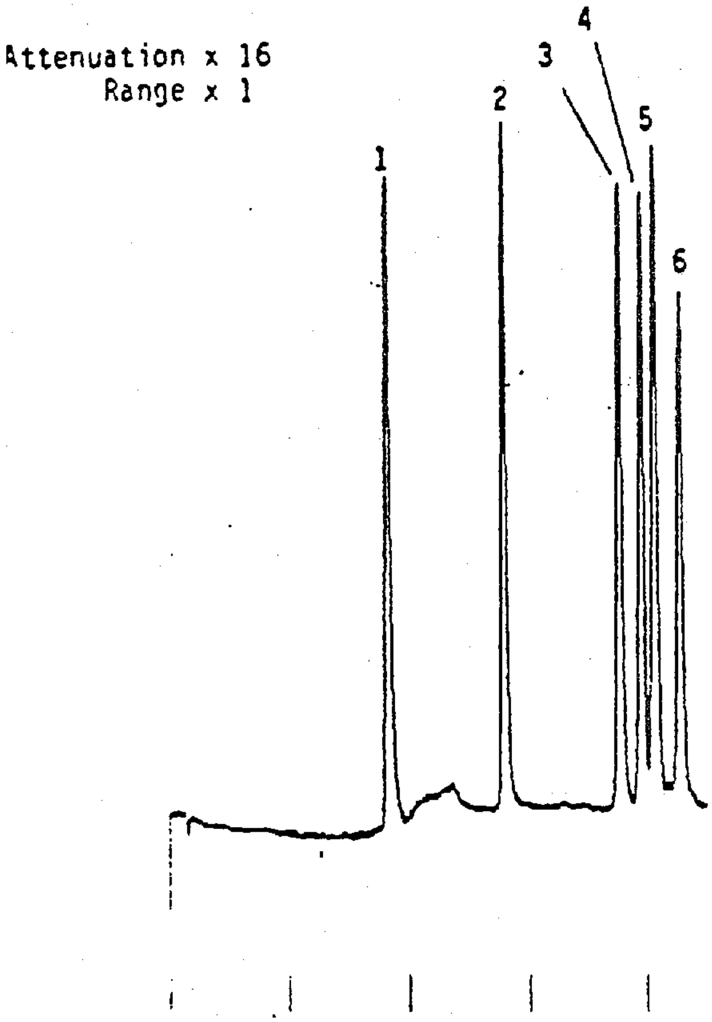
Standard Aromatic Mixture
10ppb/component



Compound 10 ppb each	Retention Time minutes
1. Benzene	9.114
2. Toluene	13.367
3. Ethyl benzene	18.834
4. p-xylene	19.766
5. m-xylene	20.350
6. o-xylene	21.404

Figure 2

Standard Aromatic Mixture
10ppb/component



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CHAIN OF CUSTODY RECORD

REPORTING AGENCY: ______________________

STATION ADDRESS: ______________________

STATION NAME: ______________________

STATION OPERATOR:*

Relinquished By:*	Received By:*	Date/Time
Relinquished By:*	Received By:*	Date/Time
Received for Laboratory By:*		Date/Time

Method of Shipment:

TO BE COMPLETED BY LABORATORY

SAMPLE NO.	LABORATORY NO.

DISPOSITION:

IMMEDIATE ANALYSIS ☐ STORAGE ☐ REFRIGERATOR ☐ ID ______ SECURED YES ☐

FREEZER ☐ ID ______ NO ☐

* Print name after signature.

[illegible]

FIRST CLASS