PROCESS EMISSIONS OF PLASTIC OPERATIONS

Protocols for Source Sampling of Organic Gases
Generated during Plastic Processes

FINAL REPORT

TO:

The Society of the Plastics Industry, Inc.

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EXECUTIVE SUMMARY

The objective of these experiments was to identify the best collection and analytical techniques available to conduct **source sampling** during plastics processing, and use them to prepare sampling protocols. Source samples of emissions from polymers in various processes were obtained in order to choose a set of **target substances** that would be representative of emissions in industrial settings. The study of previously published reports and the detection of emissions from seven plastic processes and five polymers permitted a reasonable basis to choose the **target substances.**

The **target substances** recommended to be routinely sampled from five commercial grade plastic materials studied were : for polystyrene (PS): styrene, ethylbenzene, toluene and benzene; for polyethylene (PE): formaldehyde, formic acid and benzene; for acrylonitrile-butadiene-styrene (ABS): styrene, xylene, toluene and acrylonitrile; for polyvinyl chloride (PVC): *vinyl chloride, *hydrochloric acid, benzene and toluene; and for unsaturated polyester bulk molding compound (BMC): styrene. Solid condensation aerosols were also measured in most experiments, therefore total aerosols were also recommended for routine sampling of process emissions. Criteria for selection of **target substances** were: positive identification, being present above ten times the detection limit of the analytical method and having regulatory interest. (Note: compounds marked with an asterisk were sampled but not detected in these experiments but are nonetheless recommended for routine sampling).

These initial procedures represent the necessary preliminary steps to be the basis for a complete protocol to quantify emissions to be used by the plastics industrial processor. The methods of collection were standard industrial hygiene sampling methods. Analysis was conducted by a commercial analytical laboratory accredited by the American Industrial Hygiene Association (AIHA) and the Commonwealth of Massachusetts.

Samples were taken for seven basic plastic processes and one compounding operation as follows: Extrusion processes: strand ; sheet; blown film and extrusion coating, Injection molding, Thermoforming and Compression Molding, (including a compounding operation).

The focus of the process emissions evaluated in this project is the emissions generated by the melting of the polymer per se. Emissions originated from additives (e.g., stabilizers, chain transfer additives, plasticizers and colorants) may appear in the results but are not the focus of this study. The methods described here are only suitable to evaluate emissions of thermoplastic processes where the polymers are melted in a normal steady state operation or the compounding and cure of the thermoset polyester. Non-steady state operations, such as purging may generate additional decomposition products of industrial hygiene interest. Their generation during plastic production should be evaluated but their collection and analysis were beyond the scope of this study.

I. INTRODUCTION

A. Objectives and Scope

This report presents the results of the first phase of the development of a protocol to characterize emissions generated during plastic processes. The initial task in this project was to identify and perform quantitative analysis on selected organic vapors and measure gravimetrically aerosols generated from some plastic processes. The emissions were collected at the peak off-gassing stage of the plastic production cycle. The sampling strategy consisted of the collection of **source sampling** using industrial hygiene sampling collection equipment on industrial size plastics production machinery at the University of Massachusetts Lowell. The collection and analytical methods described here could be generalized and applied to the identification and relative quantification of organic vapors and aerosols originated from a plastic melt. Once a broad spectrum of organic chemicals was identified and their relative concentrations determined, a decision was made to choose **target substances** suitable for quantification of emissions. These choices were based on two criteria; i.e., the relative amounts produced and the regulatory interest of the substances identified. This initial work is the necessary preliminary steps to be the basis for a complete protocol to quantify emissions to be used by the plastics processor. The methods of collection were standard industrial hygiene sampling methods. Analyses were conducted by a commercial analytical laboratory accredited by the American Industrial Hygiene Association (AIHA) and the Commonwealth of Massachusetts. The objective of this arrangement was to make these procedures available to any plastics processor on a routine basis.

Samples were taken for seven basic plastic processes and one compounding operation as follows: Extrusion processes: strand ; sheet; blown film and extrusion coating, Injection molding, Thermoforming and Compression Molding (including a compounding operation). Five commercially available plastic materials were used for different processes. They were: polystyrene (PS), polyethylene (PE) (high density polyethylene (HDPE) and linear low density polyethylene (LLDPE)), acrylonitrile-butadiene-styrene (ABS), polyvinyl chloride (PVC) and unsaturated polyester BMC (UP).

A total of 30 sample sets were collected to identify organic chemicals through gas chromatography/mass spectrometry (GC/MS) methods. These identified a grand total of 76 quantifiable analytes (relative to a MS calibrating chemical). Two additional sample sets were collected to identify oxygenated compounds from PE extrusion. The analytical technique for these two last sets was High Pressure Liquid Chromatography /Ultra Violet (HPLC/UV). Eight quantifiable aldehydes and organic acids were identified. Aerosols generated from some processes were measured gravimetrically as total aerosols (15 samples) and benzene soluble aerosols (17 samples) for a total of 32 aerosol samples.

The focus of this project was the emissions generated by the melting of the polymer per se. Emissions originated from additives (e.g., stabilizers, chain transfer additives, plasticizers and colorants) may appear in the results but are not the focus of this study. Their generation is not discussed in this report, since their chemical nature and purpose was not identified to the researchers in any of the commercial grade polymers used in the experiments. The methods described here are suitable to evaluate emissions of thermoplastic processes where the polymers are melted in a normal steady state operation

or the compounding and cure of the thermoset polyester. Operations like purging (before and after steady state production) generate additional decomposition products (1). Emissions from thermal decomposition of additives, mold releases and decomposition products generated during purging and non-steady state conditions may be of particular industrial hygienic interest. Their generation during plastic production operations should be evaluated but their collection and analysis were beyond the scope of this report.

B. Review of the Literature

In the production of most plastics, polymers are melted and then shaped in processes such as extrusion, injection molding and thermoforming to obtain the desired final form. During processing, the hot polymer undergoes thermal degradation with the generation of various chemical species. The mechanisms of polymer degradation by heat have been identified as: random chain scission, elimination and de-polymerization (1).

In the presence of air, some hot polymers emit oxygenated degradation products. Laboratory studies of mechanisms of thermal oxidation of some polymers have shown the production of low molecular weight (from one to three carbons) oxygenated forms, such as aldehydes, ketones and organic acids (2).

De-polymerization has as its principal degradation product the monomer or monomers forming the polymer chain. A second mechanism of monomer generation is the release of un-reacted monomer trapped in the plastic material (1).

The variables controlling the generation of emissions have been reported to be: a) the operating temperature; b) the rate of melted mass produced; c) the surface area of the

melted product; and d) the polymer residence time in the processing machine (3), (3). Very few systematic evaluations of thermoplastic process emissions are found in the literature where industrial size machinery has been evaluated. Studies in the U.S. are mostly laboratory evaluations (5) or studies of products of pyrolytic decomposition (6). Three U.S. field studies of thermoplastic emissions from styrene containing polymers were found in the literature (7), (8), (9).

More extensive laboratory and field industrial hygiene evaluations of thermoplastic processes emissions were conducted in Scandinavian countries by the Swedish Work Environment Fund (4), (10), (11). The organic vapors were collected in charcoal tubes and analyzed mostly by GC (no MS) and High Pressure Liquid Chromatography (HPLC). There is no detailed description of the plastic processing machinery (4). No information is provided on what specific process (e.g., injection molding, extrusion, etc.) generated what level of contaminant. The polymers used were commercial plastics of European origin (3).

II. MATERIALS AND METHODS

A. Description of Machinery and Operating Conditions

Sampling collection took place at the University of Massachusetts Lowell, Plastics and Composite Development Center (UML-PCDC) located in the College of Engineering. UML-PCDC has complete processing machinery and testing materials for a vast selection of plastics. The processing equipment used was industrial size. Industrial quantities of technical grade materials and industrial production routines were employed. The UML-PCDC facilities are equivalent to a medium size industrial plastics production facility.

The characteristics of the plastics process machinery used in this project are summarized in Table I. The materials used in each machine are also identified in the same Table. A description of each plastic used appears in Table II.

Operating conditions, such as temperatures, flow rates and sample times are presented in the results section corresponding to each process and raw material (Tables V to XIII). As indicated in Table I, all the UML-PCDC laboratories are equipped with General Exhaust Ventilation (GEV). In addition, three pieces of equipment (the injection molding machine, the thermoforming press and the compounding mixer) have Local Exhaust Ventilation (LEV). The ventilation status of the machinery was not relevant to the sampling conducted in this project. The objective was to bypass any LEV or GEV system by placing sample probes within six inches of the molten polymer.

B. Description of Plastic Raw Material Used

Commercially available plastics were used in the 30 sampling campaigns. Each plastic was used in the specific process for which it was recommended in the supplier's specifications. No quantitative information on additives was provided by the manufacturers. The plastics used by process appear in Table II.

C. Description of Sample Collection and Analytical Methods

A typical experimental run took place on days when no other processes or machines were in operation at the UML-PCDC. Prior to the initial warmup period of a processing machine, a background sample was collected to identify any lingering laboratory air contamination around the processing area. The organic chemicals found in the background sample were subtracted from the final results of the process sample taken during steady state operations. Once the background laboratory air sample was collected, the process machine warmup was initiated. When the recommended operational temperatures, pressures and flow rates were stabilized, steady state was reached and the process sample was collected. It took from one to two hours, depending on the process and the polymer, before steady state was reached. Between 30 and 60 minutes after steady state was achieved, the sampling procedure was started (Precise sampling times and other aspects of sample collection are described in detail when specific methods are described below). This methodology was followed for all sampling campaigns where the analytical method was GC/MS, as well as when the analytes were aldehydes or organic acids. A detailed description of the procedures follows.

1. Sampling for Organic Vapors via GC/MS Analysis

a) Sample Collection

Different thermal desorption tubes were used depending on the analyte. Either a **Carbotrap* 300** tube(for aromatics) or a **Carbotrap 200** tube (for aliphatics), was used as the collection device to capture emissions generated in the processes studied. Figures 1 to 5 in Appendix A illustrate the sample probe locations for an injection molding experiment (Figure 1); for an extrusion paper coating experiment (Figure 2); for an extrusion blown film experiment (Figure 3); for a thermoforming experiment (Figure 4) and for a low pressure compression molding experiment (Figure 5). Details of the Carbotrap tube are shown in Figure 6 (12). The sampling methodology is standard industrial hygiene practice used routinely by the Occupational Safety and Health Administration (OSHA), the Environmental Protection Agency (EPA) and the National Institute for Occupational Safety and Health (NIOSH) and is described in detail in readily available references (13).

(Note: **Carbotrap** is a trade name of Supelco a subsidiary of the Rohm and Haas Co.).

1) Sample Train The sample train consists of: 1) a Gillian Air Sampling Pump calibrated to draw air at 100 cm^3/min. (calibration procedures appear in Appendix D); 2) **Tygon** tubing connecting the pump to the adsorption tube ; and 3) the Carbotrap tube (**Carbotrap 300 or 200**). The configuration is similar to Figure 7.

Once the sample was taken (usually between 5 and 6 liters of air) the tube was capped and sent to the laboratory for analysis.

2) Sampling Procedure The sample collector (**Carbotrap** tube) is placed approximately 6 inches from where the molten plastic exits the process machine. The sample collectors were placed as close to the hot plastic as practicable, to assure capture of the plume of vapors emitted from the molten material. For details of each collection point see Figures 1 to 5. Three samples were collected for each experiment as follows: first, the sample of laboratory air collected one hour before the initiation of the melting process to assess the extent of contamination of the experimental area; second, the sample of the emission plume at least 30 minutes after the process was equilibrated at steady state for temperature, pressure and flow rates; third, a blank sample (unused sample tube) was shipped to the analytical laboratory with every sample set. The analytical laboratory was not provided with information about which tubes were samples or blanks in order for them to be able to perform blind analysis. Other sampling details by process appear in the description of each experiment.

At the end of each sampling campaign, the emissions, background and blank samples were shipped to the laboratory where they were analyzed within 48 hours of collection as recommended by NIOSH (See NIOSH Method S 1501). Samples were kept under refrigeration (38°F) while awaiting analysis.

b) Analytical Procedure

The Carbotrap tube is desorbed "ballistically" (from 35 °C to 335 °C in 16 seconds) in a Thermal Desorption Unit (Supelco TDU). The effluent is rapidly transferred to the GC column for separation. The GC column was a SUPELCOWAX 10 capillary. This column separates the organic chemicals in the sample (11). The MS procedure follows

immediately after the GC separation. The effluent is passed through a MS detector for identification and quantification of the organics in the sample. The MS quantification of the substances in the sample is made by comparison with a calibrating substance (e.g., benzene). Results are reported as mass equivalent of the calibrating chemical (14).

Carbotrap 300 was used when aromatic organics emission were expected. This was the case for emissions from PS, ABS and polyester BMC. A Carbotrap 200 column was used in situations where aliphatic or polar organics were expected (PE and PVC)(15). After sample collection the sampler was thermo-desorbed and analyzed by GC/MS as explained above. The analysis was performed in accordance with **EPA Method 624** for Volatile Organics. Sensitivity and other data of the analytical method appear with the information supplied from the analytical laboratory in Appendix B. Complete copies of all the analytical methods appear in Appendix D. This analytical methodology was chosen because it permits complete desorption by heat and is sensitive to very low quantities of organic chemicals (13).

2. Sampling for Aldehydes

Vapors from emissions are collected in the locations illustrated in Figures 1, 2 and 3. The collection device consisted of two impingers (bubblers) in series containing a solution of iso-octane and di-nitrophenyl hydrazone. Air was sampled through the bubblers for one hour at a rate of 1 L/min. The solution was then quantitatively evaluated by High Pressure Liquid Chromatography/Ultraviolet (HPLC/UV). The procedure used was **EPA Method TO-5** (Impinger Collection, HPLC/UV). This method was selected because it is specific for aldehydes and unlike GC/MS, the results are not reported as mass equivalents

of a surrogate compound. A complete copy of the method is included in Appendix D.

3. Sampling for Organic Acids

Vapors from emissions were collected in the locations illustrated in Figures 1, 2, 3 and 4 using a silica gel adsorption tube. The sampling train was identical with the one used with Carbotrap tubes (see above). For analysis, the vapors were desorbed with de-ionized water and analyzed using HPLC. The column used was an Aminex HPX-87H ion exclusion column. The solvent was 0.01 H_2SO_4 at 1 ml/min. This method was recommended by the H&ES Analytical Chemistry Laboratory of the Dow Chemical Company, Midland MI (16). This method is a variation of **OSHA Method 28** for organic acids (see copy in Appendix D).

4. Sampling for Aerosols

a) Total Aerosols

The Total Aerosol designation in industrial hygiene practice include solid particles regardless of size, i.e., include respirable and not respirable sizes. They are collected in a filter with no size selective device preceding the sample train. Total aerosols were collected in the locations described in Figures 1, 2 and 3. The sampling train is described in Appendix A, Figure 8. The polystyrene cassette holds 37 mm diameter filters. The cassette was open for sampling to the laboratory air. The filter was a PVC 5 um pore membrane tared filter. Air was sampled for one hour at 2 L/min. After 24 hours of filter drying in a desiccator, the sample was weighed to 0.01 mg. The method used was **NIOSH Method 0500**. A copy of the procedure is included in Appendix D.

b) Benzene Soluble Aerosols

This method was used for the purpose of differentiating organic from inorganic (dust) aerosols. Benzene soluble aerosols represent the organic vapors condensed in the particles collected. It is measured as the weight of the benzene soluble fraction of the Total Aerosols collected. Benzene Soluble Aerosols represent then, the sum of organic aerosols collected in a filter plus the condensed organics from the gaseous emissions that are soluble on benzene. Therefore, the weight of emissions collected by this method could, in some cases, be greater than the solid products of condensation collected by the method of Total Aerosols above. The procedure used for collecting Benzene Soluble Aerosols is identical to Total Aerosols, except that a Teflon (PTFE) 2 um size tared filter was used in a sealed cassette. For analysis, the filter was washed with pure benzene and the benzene soluble materials were determined gravimetrically. The method used was **NIOSH Method 5023.** A complete copy is included in Appendix D.

This sample technique permits analysis for the presence of semi-volatile organic air compounds that could be present in the vapor or particle phases of thermal emissions.

c) Lead Aerosols

The same procedure was used for lead as outlined above for Total aerosols. The analytical method for lead analysis is Atomic Absorption Spectrophotometry (AA). This procedure to detect lead aerosols was used in processes where the raw material was PVC. The method used was **NIOSH Method 7082.** A copy is included in Appendix D.

5. Sampling for Hydrochloric Acid

Samples were collected on silica gel adsorbent tubes following the procedure outlined for organic acids. Sampling was for one hour at 100 cm^3/min. The tubes are desorbed and analyzed by Ion Chromatography. The method used was **NIOSH Method 7903.** A copy is provided in Appendix D.

III. RESULTS

A. Organic Emissions Identified by Process

Seven sampling campaigns measured emissions from four different extrusion processes. They were: a) strand; b) sheet; c) blown film and d) extrusion paper coating. The polymers studied were PS, PE, ABS and PVC. A list of the organic chemicals identified in these processes appears in Table III. Sampling procedures and methodology were described above. Diagrams of sampler locations appear in Appendix A.

Two selection criteria for GC/MS analysis results were fulfilled by the chemicals identified in the table: first, the chemical had to be positively identified by the analytical method, and second, it had to be present in an amount ten times the detection limit. This criteria was considered to be adequate since the background concentrations measured in the laboratory air were less than 1/10 the detection limit of the method (>0.001 ugm) and generally this amount identified the target substances of interest.

Aldehydes and organic acids in the PE experiments were identified by a different collection and analytical method, i.e., HPLC/UV (see Tables VII and VIII). The procedures in these experiments were quantitative and specific for aldehydes and organic acids.

Table IV shows the emissions identified in three processes: a) injection molding; b) thermoforming and c) compression molding. Five polymers were studied: PS, PE, ABS, polyester BMC and PVC.

Identical selection criteria apply for this table as applied to Table III.

B. Organic Emissions by Polymer

Tables V to XI show the relative mass percentage of organic chemical emissions during the steady state processes studied and analyzed by GC/MS and HPLC/UV. The values in the tables were calculated by dividing the amount of each component by the total of all these identified components plus all other measured but un-identified components. Thus comparisons can be made within each experiment to examine the relative amounts of the various emissions. It was not possible to calculate any absolute amounts of emissions, per unit of polymer processed. This was because although the sample collected was representative of the emission stream, it did not contain the total emissions generated, or even a known proportion of the emissions. Therefore, it was not possible to compare the amount of emissions from one process, e.g., extrusion with another such as thermoforming.

The relative emission percentages are calculated as the proportions by weight of the emission amounts of a compound in micrograms per kilogram of melted polymer going through the plastics process machine. Emission amounts were measured during the sampling time at steady state. The same sampling and analytical instruments and techniques (GC/MS) and (HPLC/UV) were used for each series of experiments with each polymer in the various plastic processes studied.

The tables of results also present the highest temperature recorded during the process. The profile of operating temperatures typically varies between 5 and 20 °F below the value reported in the Tables. However, it was considered that the critical parameter for the generation of emissions is the highest recorded temperature in the process.

It also should be observed that the mass of vapors collected during the sampling process is not a stoichiometric amount of the total mass of vapors emitted during a given process. The amounts collected during each sampling period were a fraction of the total emissions generated by the melted polymer during the process. The total emission plume was not collected, and the sample points chosen were but one of the sources of emissions (probably the highest) so that the total amount of emissions should be, by logic, higher that the amounts reported here. It is also important to point out that the percentage emissions are steady state values that ignored purging at the beginning and end of the processes and did not involve any upset conditions. It is known that in those circumstances, emissions increase and additional decomposition products from the plastic melt are expected (6).

1. Experiments with Polystyrene

Table V summarizes the percentage organic emission of PS in four plastic processes. The analysis were conducted with GC/MS procedures. The organic vapors were collected with a Carbotrap 300 tube which is specifically recommended for identification of aromatic organic compounds. The procedures detailed in the methods sections were followed. Sample collection locations are described in Figures 1 to 5 in Appendix A. The highest emission detected in these experiments was styrene, followed by its dimers and trimers, as well as other aromatics. The only non-aromatic compounds detected were benzaldehyde and acetophenone. The footnotes of the table should be taken into consideration to interpret the results.

The results of these experiment for polystyrene (Tables V, XII, XIII) confirm earlier European and U.S. studies where styrene and aerosols were the highest relative emissions

from thermal degradation of PS (7)(10).

2. Experiments with Polyethylene

Three different sets of experiments were conducted to identify polyethylene (PE) emissions. In the first set, emissions were collected in **Carbotrap** tubes for desorption and analysis by GC/MS. The objective was to identify aliphatic compounds. The second set was planned to collect aldehydes and other oxygenated compounds. Emissions were collected in impingers containing di-nitro phenyl hydrazone and analyzed by HPLC/UV. This method is specific for aldehydes and ketones. The third set was planned to collect organic acids by collecting emissions in a silica gel tube, followed by HPLC/UV analysis.

a) Organic Vapors Analyzed by GC/MS

Table VI summarizes the percentage of relative organic emission of PE in thr e processes. The first column shows the emission percentages of an extrusion paper coating operation. Molten PE from an extruder was coated onto a moving paper roll. A preliminary experiment using a **Carbotrap 300** collection tube emitted complex organics that were detected as "unknown aromatics" in the GC/MS analysis. These results were interpreted as contaminants generated from the paper being coated. It was also observed that the detection tube (**Carbotrap 300**), which is designed to collect aromatic organics, might have failed to capture aliphatic polar organics. It is known from the literature that these later compounds are emitted from molten PE (12).

Based on these observations, the experiment was repeated extruding PE under coating conditions, but removing the paper roll and using a sample collector tube (**Carbotrap 200**) specifically designed to collect aliphatic organics. The objective of the

changes was twofold: to collect aliphatic organic emissions missed in the preliminary experiment in the **Carbotrap 200** tube, and to avoid any contaminant originated from the paper in the coating operation.

The results with the **Carbotrap 200** tube identified a high percentage of aldehydes and other polar compounds absent in the preliminary experiment. The results are shown in the first column of Table VI. These results prompted a second sampling campaign to quantitatively measure the aldehydes generated in PE extrusion for paper coating.

The emissions evaluated from the two other PE processes (LLDPE Blown Film and HDPE Injection molding) were also collected in **Carbotrap 200** tubes. The percentages of organics emitted appear in Table VI.

The results of this experiment confirm earlier European studies where oxygenated compounds were the highest emissions from thermal degradation of PE (10).

b) Aldehydes analyzed by HPLC/UV

Table VII summarizes the mass percentage of the emissions of aldehydes from the extrusion paper coating processes previously studied (LLDPE Paper Coating, Table VI, first column). Identical machines, materials, temperatures and sampling conditions as in the first experiment were used. The aldehydes in this table were individually determined with their specific calibration factor. HPLC/UV was used in this experiment to quantitatively measure each aldehyde generated from the PE melt. Results appear in Table VII. The high generation of formaldehyde confirms previous PE emission studies (4), (11).

c) Organic Acids analyzed by HPLC/UV

Table VIII summarizes the mass percentage of the emissions of organic acids

generated from the PE melt. HPLC was used as the analytical technique, since it is more suited for organic acid detection (16). The analytical details appear in Appendix D. The only organic acid above the detection limit of the method was formic acid. It has been suggested (3) that some of the organic acids reported in previous studies (11) might be direct products of oxidation of the high levels of aldehyde emissions generated.

3. Experiments with Acrylonitrile-butadiene-styrene (ABS)

Table IX summarizes the mass percentage of the relative emissions generated from three processes using ABS as the raw material. Since the emissions expected were aromatic organic chemicals, the collection tube was a **Carbotrap 300** and vapors were analyzed by GC/MS, as described in the methods section. The principal emissions were styrene, acrylonitrile and some benzene derivatives. The presence of acrylonitrile is confirmed from previous reports (16).

4. Experiments with Polyvinyl Chloride

Table X summarizes the mass percentage of the relative emissions generated from three processes where PVC was used as raw material. **Carbotrap 200** collection tubes were used since polar aliphatic compounds were expected. The organic vapors were analyzed by GC/MS in the usual manner described in the materials and methods section. Very small amounts of emissions were detected in these sets of experiments. Only the extrusion process generated significant emissions. However, is not clear if the emissions are from the polymer itself or the additives in the plastic. Vinyl chloride was not detected under the conditions of these experiments. The detection limit for GC/MS was 0.001ugm.

Samples were collected and analyzed for hydrochloric acid during the three

experiments. The collection media used was silica gel tubes and the analysis was performed by Ion Chromatography (**NIOSH Method 7903**). All the samples reported levels below the detection limits.

Lead aerosol samples were also collected during the three experiments and analyzed by Atomic Absorption Spectrophotometry (AA) (**NIOSH Method 7082**). The samples were below detection limits of the method (>O.OO1 ugm).

5. Experiments with Compression Molding of (BMC)

Table XI summarizes the mass percentage of the relative emissions generated during mixing of materials and compression molding of a thermoset polyester formulation. The recipe included: a thermoset resin, styrene, calcium stearate and carbonate, glass fibers and catalyst. **Carbotrap 300** tubes were used since aromatic organic emissions were expected. The collected organic vapors were analyzed by GC/MS. The process of MS analysis was changed slightly by the introduction of 3 additional calibrating substances for the MS quantification procedure (toluene, chlorobenzene, dicholoro ethylene, as well as the original calibrating substance: benzene). The only significant emission was styrene for both mixing and molding.

C. Aerosol Emissions by Polymer

1. Total Aerosol Emissions

Generation of polymer aerosol emissions (i.e., solid condensates of organic products) was observed in various processes with different polymers. The results are summarized in Table XII. The gravimetric sampling procedure (**NIOSH Method 0500**) used requires that the filters collected be desiccated for 24 hours previous to weighing. Therefore, any

volatiles captured in the filter evaporate before the weighing procedure. The generation of particulate emissions was confirmed from past experimental reports (3), (6), (9). PS, PE and ABS seem to generate measurable amounts of aerosols, as shown in the results.

2. Benzene Soluble Aerosols

Table XIII summarizes the results of emissions of aerosols reported as the weight of organics extracted from the filter with benzene. The methodology of sampling and analysis permits the inclusion of condensate vapors in the gravimetric analysis in addition to the solid aerosols. Since the sampling cassettes for this collection and analysis method are sealed and there was not a desiccation process before weighing, the results in the table include both solid aerosols and condensate organics. The method used was **NIOSH Method 5023.**

IV. CONCLUSIONS

The principal objective of these experiments was to identify the best collection and analytical techniques available to conduct **source sampling** during plastics processing, and use them to prepare sampling protocols. Source samples of emissions from polymers in various processes were obtained in order to choose a set of **target substances** that would be representative of emissions in industrial settings. Preliminary sampling protocols for source emission identification were developed for five commercial plastics in seven plastics processes. The study of previously published reports and the detection of emissions from seven plastic processes and five polymers permitted a reasonable basis to choose the **target substances**. The target substances chosen from these experiments are identified in Table XIV. The focus of the project was to identify emissions generated by the melting of the polymers per se during steady state operations. Emissions originated by additives or during non-steady state operations are beyond the scope of this study.

The continuation of this project will permit the development of specific sampling protocols that will allow for a more accurate measurement of the emissions of the target substances identified here.

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VI. TABLES

Table I

Characteristics of Plastics Process Machinery at University of Massachusetts-Lowell Plastics Engineering Department			
Process	Machinery	Model	Material
Extrusion[1] Strand Die	Welex	24:1 L/D 2 inch Dia.	PS, ABS, PVC
Extrusion[1] Sheet Die	Modern Plastic Mach.	150.20 Die Width 15"	PS, ABS
Extrusion[1] Paper-coating	Modern Plastic Mach.	20:1 L/D 1.5 inch Dia.	PE (LLDPE)
Extrusion[1] Blown-Film	Blown Film MPM	VEXCL 028	PE (LLDPE)
Injection Molding [2]	Battenfeld	BA 750	PS, ABS, PE(HDPE), PVC
Thermoforming[2]	Comet Lab. Thermoformer	1424 Sheet Fed	PS, PVC, UP(BMC)
Compounding [2]	Baker Perkins	Sigma Blade Mixer	UP(BMC)

Notes on Table I:

1 = All extruders are one stage.

2 = Machines equipped with local exhaust ventilation (LEV). The remaining machines under general exhaust ventilation (GEV).

PS = Polystyrene

PE = Polyethylene

LLDPE = Linear low density polyethylene

HDPE = High density polyethylene

ABS = Acrylonitrile-butadiene-styrene

PVC = Polyvinyl chloride

UP(BMC) = Unsaturated Polyester (Bulk Molding Compound)

Table II

Plastic Raw Materials used in Process Emissions Experiments				
Extrusion Processes				
	Strand	Sheet	Blown Film	Paper Coat
Polystyrene	General Purpose PS Extr. Grade	General Purpose PS Extr. Grade		
Polyethylene			LLDPE Extr. Grade	LLDPE Extr. Grade
ABS	ABS Extr. Grade	ABS Extr. Grade		
PVC	Flexible PVC Extr. Grade			
Injection Molding Thermoforming and Bulk Molding				
	Injection	Thermoforming	Molding	Mixing
Polystyrene	Gen. Purp. PS Injec. Grade	Gen. Purp. PS Sheet*		
Polyethylene	HDPE Injec. Grade			
ABS	ABS Injec. Grade			
UP(BMC)			High Temp.# UP-styrene	High Temp.# UP-styrene
PVC	Rigid PVC Injec. Grade	Gen. Purp. Crystal PVC		

Notes on Table II:

All the plastics are commercial chemical products containing a variety of processing aids, impact modifiers, fillers, plasticizers, lubricants and pigments. Some or all of these additives can volatilize during the melting process.

* = PS Sheet commercially available, not extruded at UMass Lowell.

= Microwave cookware resin formulation.

TABLE III

Selected* Process Emissions Identified by Air Sampling
(Analysis by GC/MS, HPLC/UV, Ion Chromatography)

EXTRUSION PROCESSES				
	Strand	Sheet	Blown Film	Extr. Coating
PS	Styrene Styrene Dimer Ethylbenzene Toluene Benzaldehyde Acetophenone Benzene	Styrene Styrene Dimer Styrene Trimer Ethylbenzene Toluene Benzaldehyde Acetophenone Benzene		
PE			Trimethyl-pentane Xylene Ethylhexane Trimethyl-hexane Octene Decane Benzene (Toluene)[1] (Ethylbenzene)[1]	Formaldehyde+ Acetaldehyde+ Propional+ Valeraldehyde+ Acrolein+ Formic Acid& Benzene Xylene (3) Trimethyl- C_4H_{10}, C_5H_{12}, C_6H_{14} (3) Alkanes C_8, C_9, C_{10}

	Strand	Sheet	Blown Film	Extr. Coating
ABS	Acrylonitrile Styrene Toluene Cumene Benzaldehyde Propylbenzene Ethylbenzene SAN Dimer Styrene Dimer Phenol Subst. Nitrogenated compounds	SAN Dimer Styrene Toluene Cumene Benzaldehyde Propylbenzene Xylene Acrylonitrile Styrene Dimer Phenol Subst. Nitrogenated compounds		
PVC	Octadecane Nonanol Oxirene Styrene Cyclopropane Dimethyl-pentanol Xylenes Benzene			

Notes on Table III

* = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit (>0.001 ug for GC/MS). **Some of the organic chemicals could have been originated from the additives in the plastics used as raw materials.** Unless otherwise noted, all compounds analyzed by GC/MS were collected in **Carbotrap 300** or **200** adsorption tubes (all collection tubes were **Carbotrap 300** except for Polyethylene/Paper Coating and PVC experiments where **Carbotrap 200** was used). Collection was followed by thermo-desorption and the samples were analyzed by Gas Chromatography (GC) for separation and Mass Spectrometry (MS) for identification and relative quantification. The analytical procedure used was **EPA Method 624**. Exceptions to this method are listed below.

\+ = Samples collected in two bubblers in series with a solution of DNPH and iso-octane. Analysis was performed by HPLC/UV. **EPA Method TO-5.**

Notes on Table III Continuation:

& = Samples collected on silica gel tubes and analyzed by HPLC/UV.

1 = Emissions of Toluene and Ethylbenzene in Blown film were unexplained, since they are not expected to be generated by the polymer. It is possible that could be generated by additives or laboratory contamination.

PS = Polystyrene

PE = Polyethylene

ABS = Acrylonitrile-butadiene-styrene

SAN = Styrene-acrylonitrile co-polymer.

TABLE IV

Selected* Process Emissions Identified by Air Sampling
Analysis Performed by GC/MS

INJECTION MOLDING AND THERMOFORMING				
	Injection	Thermoforming	Bulk Molding	Compounding
PS	Xylene Isomers Ethylbenzene Toluene	Styrene Toluene Benzaldehyde Xylene Isomers		
PE	Tetramethyl-butane Alkanes > C_9 (Toluene)[1] (Ethylbenzene)[1]			
ABS	Styrene Xylene Toluene Ethylbenzene Tri-methyl-decane Isomer Naphthalene-carbo-nitrile			
UP BMC			Styrene $(CH_3)_4$-butane $(CH_3)_4$-decane Benzaldehyde Propyl benzene	Styrene Dimethyl-nonane Trimethyl-decane
PVC	Toluene Styrene Benzene Octanol Octacosane Dimethyl-undecane Ethylbenzene Xylenes	Oxirene Toluene Ethyl-hexyl-acetic acid Benzaldehyde $(CH_3)_3$-decane Xylenes		

See notes on Table IV on next page:

Notes on Table IV

* = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit (>0.001 ug for GC/MS). **Some of the organic compounds could have originated from the additives present in each plastic.** Unless otherwise noted, all the emissions were collected using a Carbotrap 300 tube. Collection was followed by thermo-desorption and the samples were analyzed by Gas Chromatography and Mass Spectrometry (GC/MS). The analytic procedures used were **EPA Methods 624 and 8240. Carbotrap 300** tubes were used to collect organic vapors for PS and ABS. **Carbotrap 200** tubes were used for PE and PVC.

1 = Emissions of Toluene and Ethylbenzene in Injection Molding of PE were unexplained, since they are not expected to be generated by the polymer. It is possible that could be generated by additives or laboratory contamination.

PS = Polystyrene

PE = Polyethylene

ABS = Acrylonitrile-butadiene-styrene

PVC = Polyvinyl chloride

UP = Unsaturated polyester (Bulk Molding Compound)

Table V

Mass Percentages of Vapors Collected Based on Amounts of Selected[1] Emissions of Polystyrene				
	Extrusion Strand	Extrusion Sheet	Inj. Mold.	Thermfm.
Steady State Mat. Flow-Rate (kg/hr)	10.4	5.3	4.0	2.6
Highest Operating Temperature (°F)	445	466	440	220
Effluents Identified	%	%	%	%
Styrene	50	66	45.8	48
Styrene Dimer	38	5.3	12.5	ND
Styrene Trimer	ND	15	ND	ND
Ethylbenzene	1.5	3	ND	1
Propylbenzene	0.5	0.3	16.7	ND
Acetophenone	0.5	*	ND	ND
Toluene	0.4	0.6	4.2	4
Benzaldehyde	0.2	2	ND	5
Benzene	*	*	4.2	ND
Xylene Isomers	ND	*	16.7	2
Total % Selected[1] Organics Quantified	91	92	100	60
% Not Quantified Organics	9	8	0	40

Notes on Table V see next page:

Notes on Table V:
The absolute amounts of organic emissions collected varied widely depending on the process. They ranged from total organics collected of 0.02 to 85 ugm depending on the circumstances of the different processes. Therefore it is not possible to compare the percentages generated between processes, i.e., between columns.

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were subtracted from the concentrations found in the sample. The collection tube for all experiments was Carbotrap 300.

ND = Not Detected

* = Identified but not accurate quantification could be made because of the very small amount of the organic vapor collected from the process.

Table VI

Mass Percentages of Vapors Collected Based on Amounts of Selected[1] Emissions of Polyethylene			
	LLDPE[2] Extrusion	LLDPE Blown Film	HDPE Injec. Molding
Steady State Material Flow-Rate (kg/hr)	3.48	2.48	2.64
Highest Operating Temperature (°F)	620	500	450
Effluents Identified	%	%	%
Benzene	ND	0.4	ND
Tetra-Methylbutane	2.1	ND	14.3
Xylene Isomers	ND	9.4	ND
Trimethyl-Pentane	8.0	16.3	ND
Trimethyl-Hexane	5.7	6.5	ND
Ethyl-Hexane	ND	7.7	ND
Decane Isomers	14.8	4.5	ND
Nonane Isomers	7.4	ND	*
Octane Isomers	17.1	3.3	ND
Unknown Alkanes	7.2	1.2	42.8
Unknown Aldehydes	30.2	ND	ND
Total % Selected[1] Organics Quantified	92.6	85.8@	100@
% Organics not Quantified	7.4	14.2	0.0
% Toluene[3]	ND	19.1	28.6
% Ethylbenzene[3]	ND	17.5	14.3

For Notes on Table VI see next page.

Notes on Table VI

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were substracted from the concentrations found in the sample. The collection tube for all experiments was **Carbotrap 200**. The procedure used was EPA Method 624.

2 = Polyethylene was extruded in a paper-coating operation but the paper was eliminated to avoid vapors that could be generated by the heating of the paper. Vapors were collected on a **Carbotrap 200** tube. The tube was then thermo-desorbed and analyzed by **GC/MS**.

3 = Emissions of Toluene and Ethylbenzene in the Blown film and Injection Molding experiments were unexplained since they are not expected to be generated by the polymer. It is possible that these two compounds could have been generated by additives or laboratory contamination.

ND = Not Detected

@ = Toluene and Ethylbenzene included in the total % of quantified organic emissions

LLDP = Linear low density polyethylene

HDPE = High density polyethylene

* = Identified but not accurate quantification could be made because of the very small amount of the organic vapor collected from the process.

Table VII

Mass Percentages of Aldehydes[1] from Extruded Polyethylene		
	LLDPE[2] Extrusion Paper-Coating	LLDPE[3] Extrusion No-Paper
Steady State Material Flow-Rate (kg/hr)	3.48	3.48
Highest Operating Temperature (°F)	617	620
Aldehydes Identified	%	%
Formaldehyde	27.50	44.00
Acetaldehyde	30.00	34.66
Acrolein	6.00	5.34
Propionaldehyde	12.50	16.00
Valeraldehyde	24.00	ND
Total % Aldehydes+ Quantified	100.00	100.00

Notes on Table VII

1 = Aldehydes were collected and analyzed by EPA Method TO-5. Vapors are collected in a solution of iso-octane and di-nitrophenyl hydrazone (DNPH) contained in two bubblers in series. The solution was analyzed by HPLC/UV.

2 = Polyethylene was extruded in a paper-coating operation. Vapors for aldehyde analysis were collected in two bubblers in series, as described above. The sample probe was placed at the point were the hot PE sheet met the paper roll near the exit of the die.

Notes on Table VII (continuation):

3 = Polyethylene was extruded in a paper-coating operation in an identical set-up from the previous experiment but no paper was used. The sample probe was placed at the point were the hot PE sheet was exiting from the die.

+ = Other aldehydes and ketones were also present at concentrations below the detection limits of the analytical method (v.g.: acetone, crotonaldehyde, isobutyraldehyde, methyl-ethyl-ketone and benzaldehyde.

ND = Not Detected

Table VIII

Mass Percentages of Organic Acids[1] from Extruded Polyethylene	
	LLDPE[2] Extrusion
Steady State Material Flow-Rate (kg/hr)	3.48
Temperature (°F)	620
Sampling Time (minutes)	60
Organic Acids Analyzed by HPLC	%
Acetic Acid	ND
Formic Acid	100
Acrylic Acid	ND
Total % Organic Acid Quantified	100

Notes on Table VIII:

1 = Organic Acids were collected and analyzed by a modified OSHA-38 method for organic acids. Vapors were collected in a silica gel collection tube. The sample was then desorbed in a methanol solution and analyzed by HPLC/UV.

2 = Polyethylene was extruded in a paper-coating operation whithout paper.

\+ = Other organic acids were also present at concentrations below the detection limits of the analytical method (e.g.: acetic acid and acrylic acid).

ND = Below the detection limits of the collection and analytical method.

Table IX

Mass Percentages of Vapors Collected Based on Amounts of Selelected[1] ABS Organic Emissions			
	Extrusion Strand	Extrusion Sheet	Inj. Mold
Steady State Mat. Flow-Rate (kg/hr)	8.40	6.22	0.946
Highest Operating Temperature (F)	450	450	460
Effluents Identified	%	%	%
Acrylonitrile	0.3	ND	ND
Styrene	21.9	18.4	ND
Styrene dimer	1.5	0.7	ND
Unknown styrenic	3.5	1.9	ND
SAN dimer	0.5	0.1	ND
Alpha-methyl styrene	ND	1.3	ND
Xylene isomer	0.5	10.5	4.9
Styrene/Xylene isomer	ND	ND	35.2
C_4-Benzene isomer	ND	6.9	ND
C_5-Benzene isomer	2.8	1.1	ND
Ethyl Benzene	4.2	ND	3.4
Methyl(methyl-ethenyl) benzene isomer	5.1	ND	ND
$C_{10}H_{16}$ isomer	ND	15.8	ND
Substituted phenol	23.5	7.5	ND
Trimethyl bicyclo-heptanol	3.4	2.4	ND
Trimethyl decane isomer	ND	ND	9.3

Trimethyl bicyclo-heptane	5.0	3.0	ND
2,6-Bis (Dimethylethyl) methyl Phenol isomer	4.4	ND	ND
Toluene	2.7	2.5	16.7
Cumene	3.0	2.1	1.9
Benzaldehyde	1.8	ND	10.5
n-propyl benzene	1.6	1.0	ND
Unknown nitrogen compound	7.0	5.4	ND
Dichlorobenzene*	ND	ND	9.6
Unknown C_{16} Alcohol	ND	3.2	ND
Total % Selected[1] Oraganics Quantified	92.4	83.8	91.4
% Organics not Identified	7.6	16.2	8.60

Notes on Table IX:

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were substracted from the concentrations found in the sample. The collection tube for all experiments was Carbotrap 300. The procedure used was EPA Method 624.

ND = Not Detected

* = Possibly generated from additives

Table X

Mass Percentages of Vapors Collected Based on Amounts of Selected[1] PVC Organics			
	Extrusion Strand	Thermoforming	Injection Molding
Steady State Material Flow Rate (kg/hr)	15	3.48	0.5
Highest Operating Temperature (°F)	355	320	400
Effluents Identified	%	%	%
Benzaldehyde	nd	6.2	nd
Trimethyldecane	nd	2.5	nd
Acetic Acid-ethyl hexyl ester	nd	14.9	nd
Benzene	0.4	2.5	5.4
Ethylbenzene	0.1	1.3	*
Tetrachloroethylene	nd	0.2	nd
Toluene	nd	17.4	39.5
Xylenes (total)	0.1	3.7	1.5
1-Octanol	nd	nd	11.5
Decane,2,9-Dimethyl	nd	nd	3.7
Undecane,2,10-Dimethyl	nd	nd	4.8
Octacosane	nd	nd	4.0
Styrene	0.5	nd	26.5
Trichloroethylene	*	nd	1.0
Oxirane {(2-Ethyl Hexyl) oxy) Methyl)}	8.4	51.0	nd
1-Pentanol,2,3, Dimethyl	0.3	nd	nd

Cyclopropane, Pentanol	18.7	nd	nd
1-Nonanol	17.3	nd	nd
5-Octadecane	23.5	nd	nd
9-Octadecane	26.2	nd	nd
1-Hexadecane	4.4	nd	nd
Total % Selected[1] Organics Quantified	99.9	99.7	97.9
% Organics not Identified	0.1	0.3	2.1

Notes to Table X:

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were substracted from the concentrations found in the sample. The collection tube used for all experiments was **Carbotrap 300**.

nd = Not Detected

* = Compound identified but no accurate quantification could be made because of the very small amount of the organic vapor collected from the process.

Table XI

Mass Percentages of Vapors Collected Based on Amounts of Selected[1] Emissions of Polyesters (BMC)		
	Compression Molding	Material Mixing
Material Flow (kg/Cycle)	1.50	1.50
Highest Operating Temperature (°F)	270	270
Effluents Identified	%	%
Styrene	97.5	91.8
Dimethyl-nonane	nd	2.2
Tri-methyl-decane	0.3	1.6
Tetra-methyl-butane	1.8	nd
Isopropyl-benzene	*	nd
Benzaldehyde	0.3	nd
Total % of Selected[1] Organica Quantified	99.9	95.6
% Organics not Quantified	0.1	4.4

Notes on Table XI:

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were substracted from the concentrations found in the sample. The collection tube used for all experiments was **Carbotrap 300.**

nd = Not Detected

* = Compound identified but no accurate quantification could be made because of the very small amount of the organic vapor collected from the process.

Table XII

Aerosol Concentrations in mg/m^3 (Total Particulate) Measured during Process Emissions Experiments				
Extrusion Processes				
	Strand	Sheet	Blow Film	Paper Coating
Polystyrene	14.00	1.12	-	-
Polyethylene	-	-	0.48	5.19
ABS	7.66	1.79	-	-
PVC	ND	-	-	-
Injection Molding and Thermoforming				
	Injection	Thermoforming	BMC	Mixing (BMC)
Polystyrene	0.41	ND	-	-
Polyethylene	ND	-	-	-
ABS	ND	-	-	-
Polyester	-	-	ND	ND
PVC	ND	ND	-	-

Notes on Table XII:

Samples were collected in a tared 37-mm, 5um PVC filter for one hour at 2 L/minute. The filters were weighed in an exact balance with a 0.01 mg sensitivity. This method is **NIOSH Method 0500 .**

ND = Sampled but non detected.

\- = Not sampled, experiment not run.

Table XIII

Benzene Soluble Particulate Concentrations in mg/m^3 Measured during Process Emissions Experiments				
Extrusion Processes				
	Strand	Sheet	Blown Film	Paper Coating
Polystyrene	6.32	0.08	-	-
Polyethylene	-	-	5.58	7.56
ABS	31.91	20.30	-	-
PVC	ND	-	-	-
Injection Molding and Thermoforming				
	Injection	Thermoforming	BMC	Mixing (BMC)
Polystyrene	0.17	ND	-	-
Polyethylene	ND	-	-	-
ABS	ND	-	-	-
Polyester	-	ND	ND	ND
PVC	ND	ND	-	-

Notes on Table XIII:

Samples were collected in a tared 37-mm, 2um PTFE membrane filter for one hour at a sampling rate of 2 L/minute. The filters without desiccation were extracted with benzene and weighed in an exact balance with a 0.01 mg sensitivity. This is **NIOSH Method 5023.**

ND = Sampled but not detected.

\- = Not sampled, experiment not run.

Table XIV

Recommended Target Substances Generated During Steady State Plastic Processes Experiments	
Plastic	Target Substance
Polystyrene[1]	Styrene, Ethylbenzene, Toluene, Benzene[3]
Polyethylene[1]	Formaldehyde, Formic Acid Benzene[3]
ABS[1]	Styrene, Xylene Toluene, Acrylonitrile
PVC	Vinyl Chloride[2], Hydrochloric Acid[2] Benzene[3], Toluene
BMC	Styrene

Note on Table XIV:

1 = Polystyrene, Acrylonitrile-butadiene-styrene (ABS) and Polyethylene generate solid condensation particulate during process melting. Total Particulate sampling is also recommended for these plastics as an indicator of emissions.

2 = Not detected in these experiments but recommended as **target substance** because of regulatory interest.

3 = Present in very small amounts but recommended as a **target substance** because of regulatory interest.

VII. APPENDIXES

APPENDIX A

FIGURES 1-5

Sampling locations

FIGURES 6-8

Sampling Trains for Organic Vapors and Aerosols

APPENDIX B

ESA Laboratories

Methods Standards and Detection Limits

APPENDIX C

Analytical Methods for

1. Organic Vapors EPA - 624 (8240 A)

2. Aldehydes EPA - TO 5

3. Organic Acids OSHA - 38
   (as Acrylic Acid) Dow Chemical Modifications

4. Aerosol Sampling

   * Total Dust NIOSH - 0600

   * Benzene Soluble
     Particulate NIOSH - 5023

   * Lead NIOSH - 7082

5. Inorganic Acids
   Hydrochloric Acid NIOSH - 7903

Appendix D

Calibration Sampling Equipment

VII. APPENDIXES

APPENDIX A

FIGURES 1-5

Sampling locations

FIGURES 6-8

Sampling Trains for Organic Vapors and Aerosols

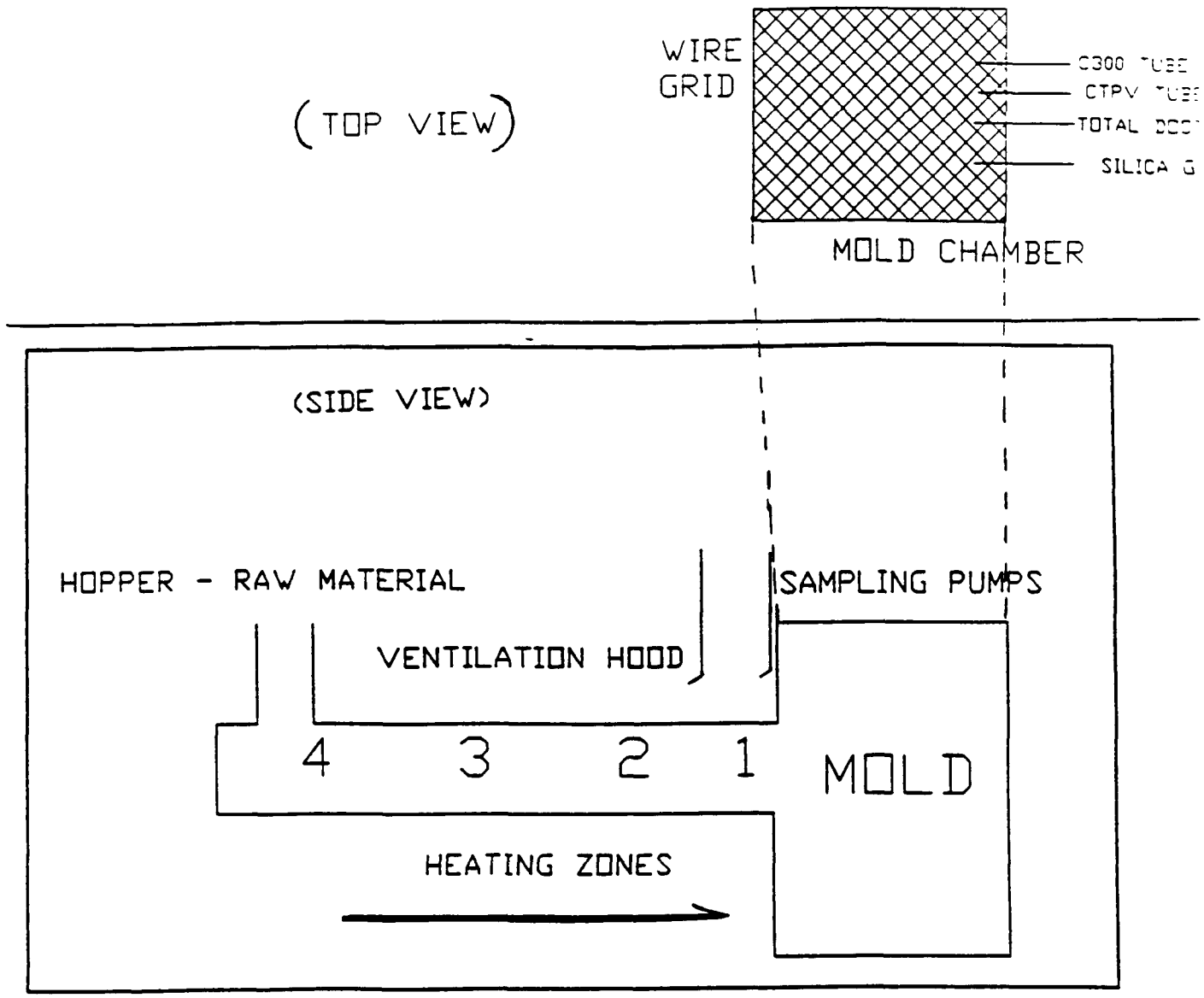
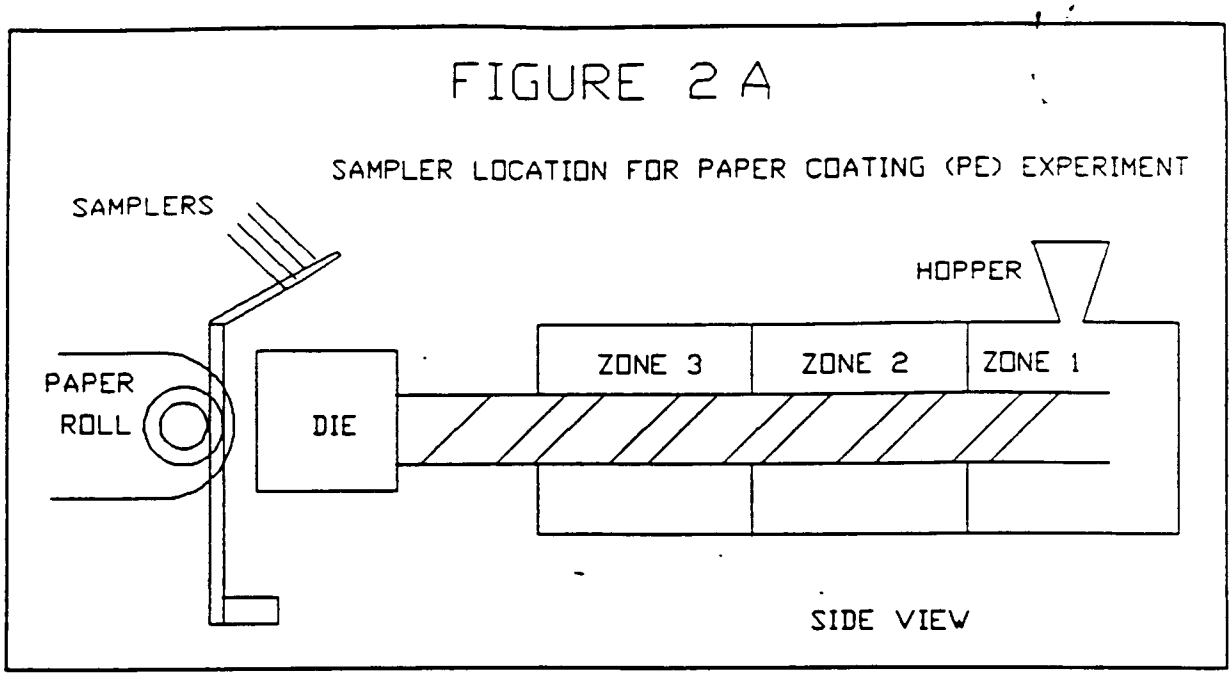
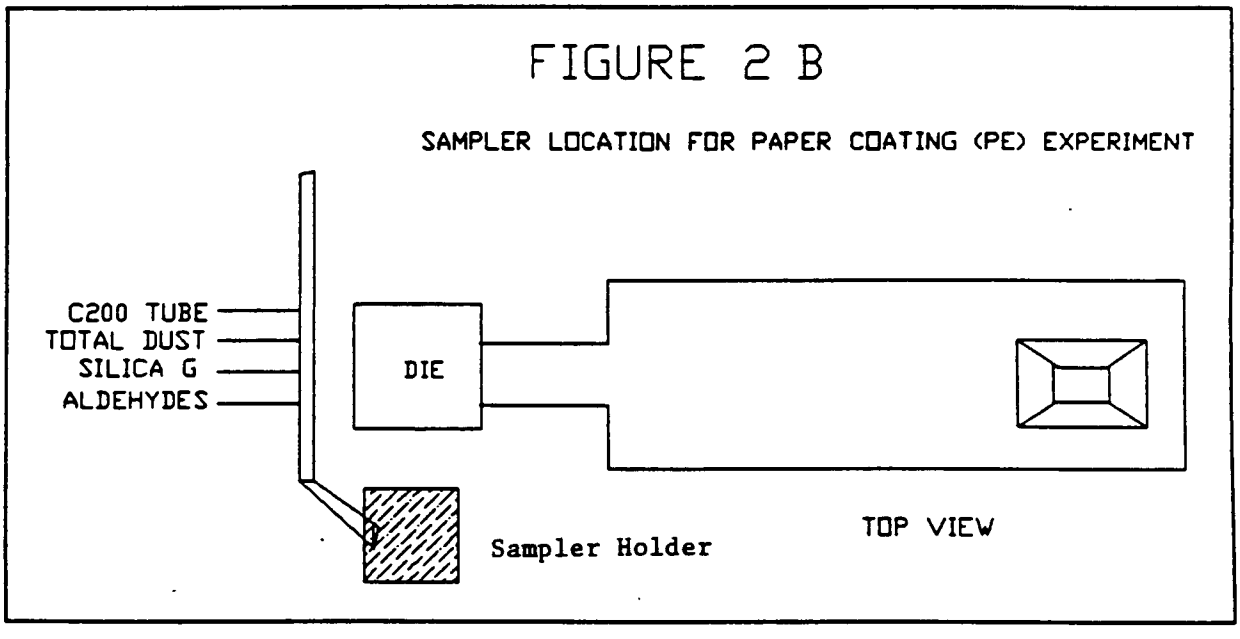


FIGURE 1

SAMPLER LOCATION FOR INJECTION MOLDING EXPERIMENT

CTL032230





Figures 2A and 2B . Sampler Locations for Extrusion Coating Experiment

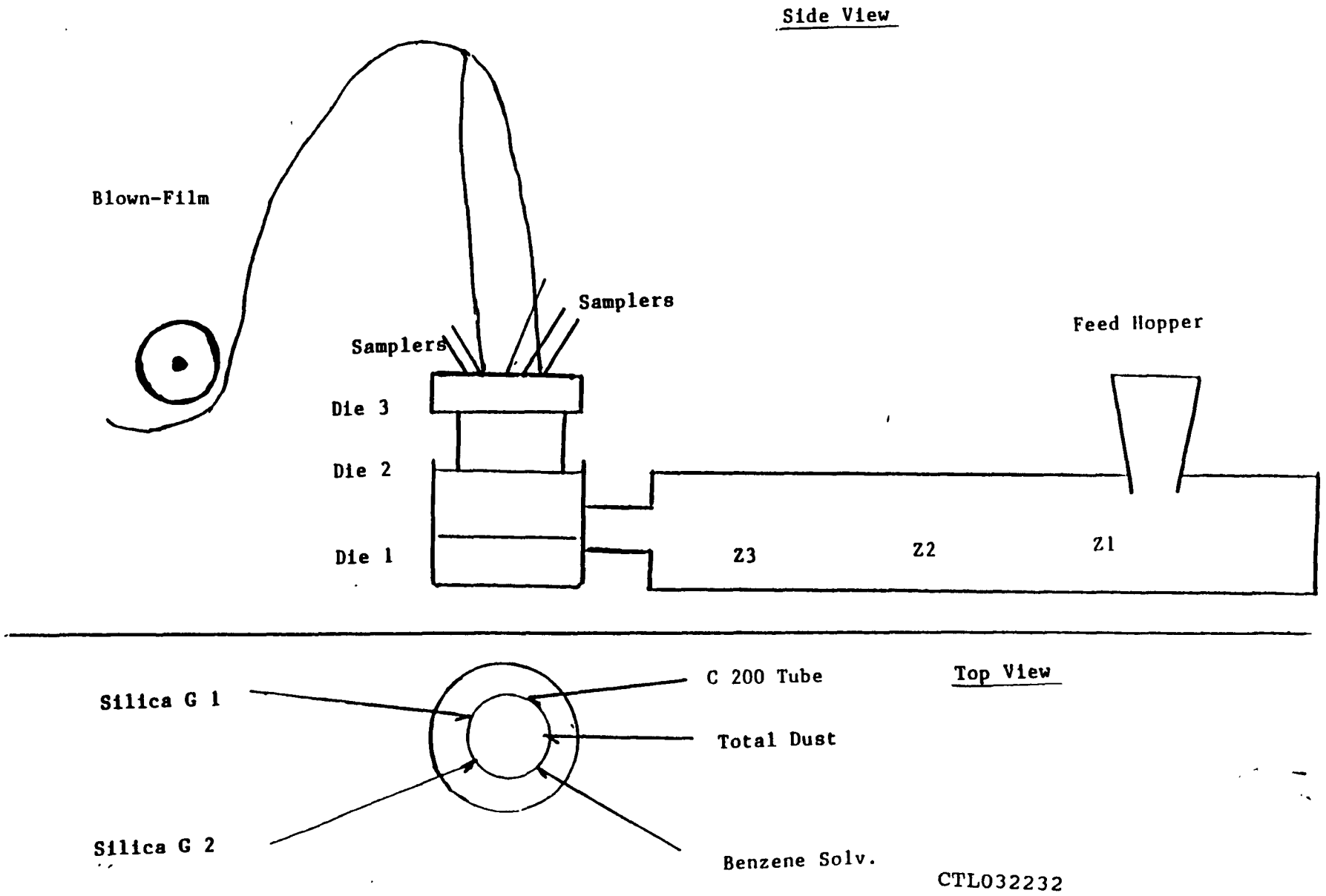


Figure 3

Sampler Location for Extrusion Blown-Film Experiment

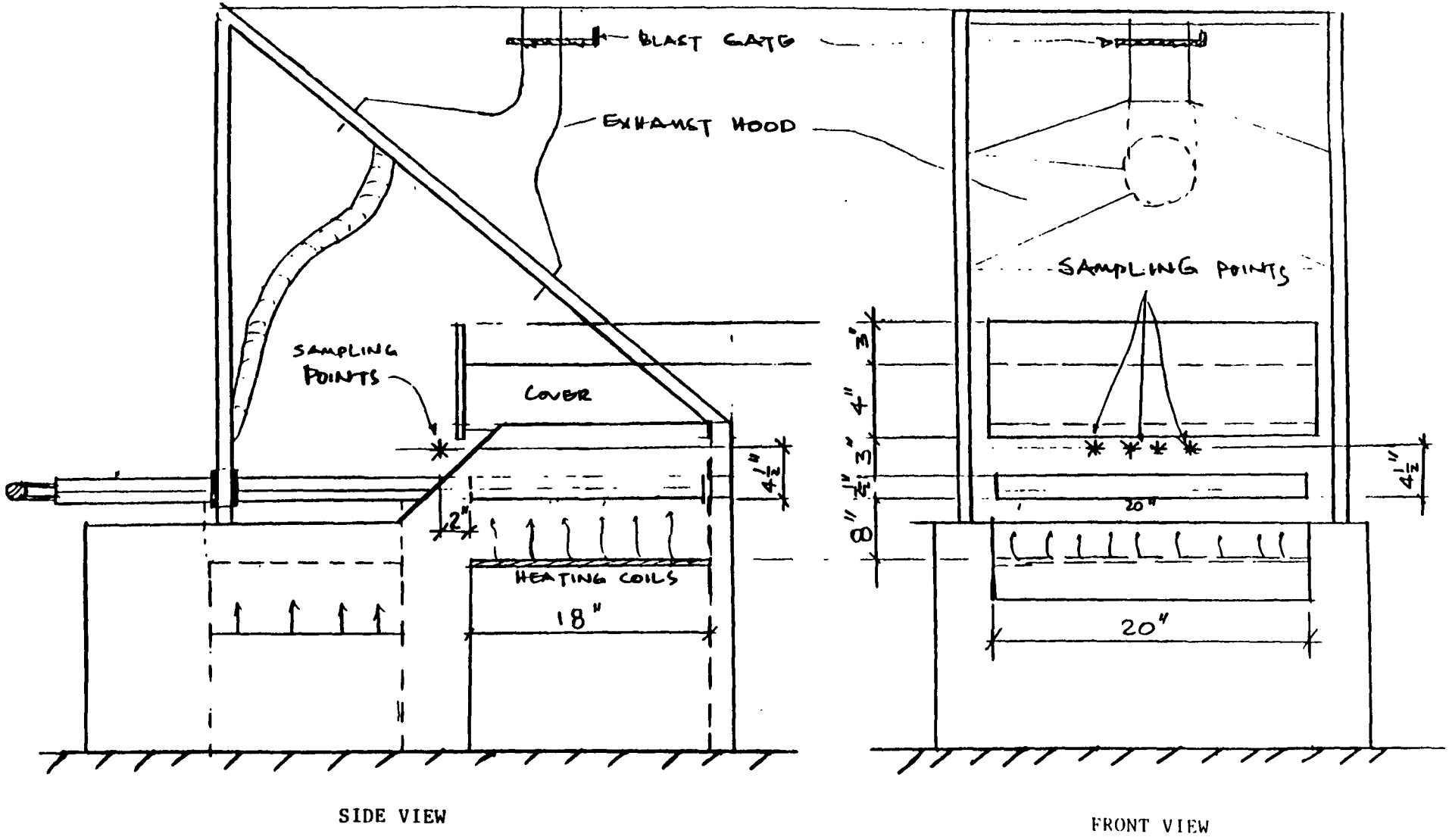


Figure 4. Sampler Locations for Thermoforming Experiment

CTL032233

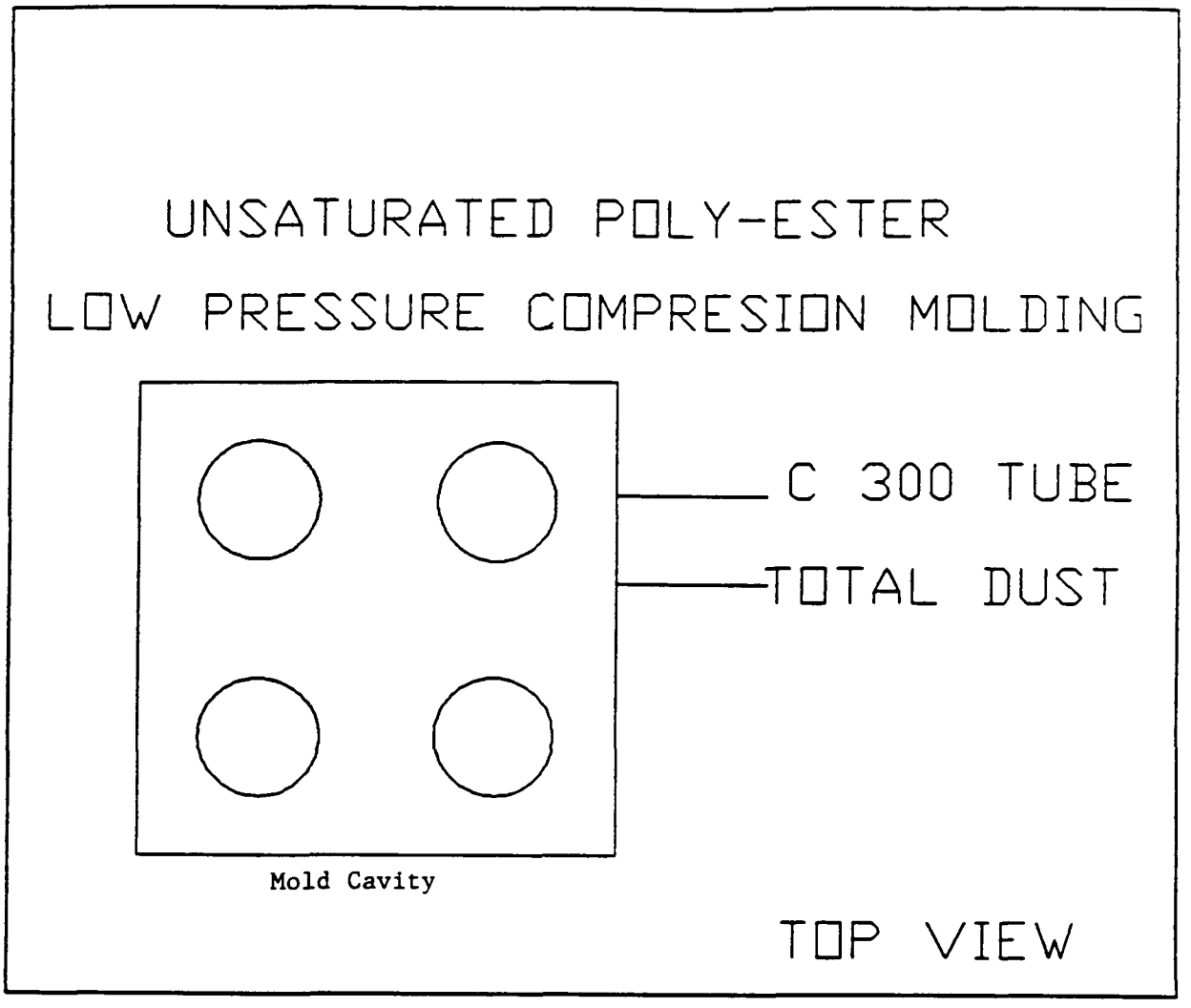
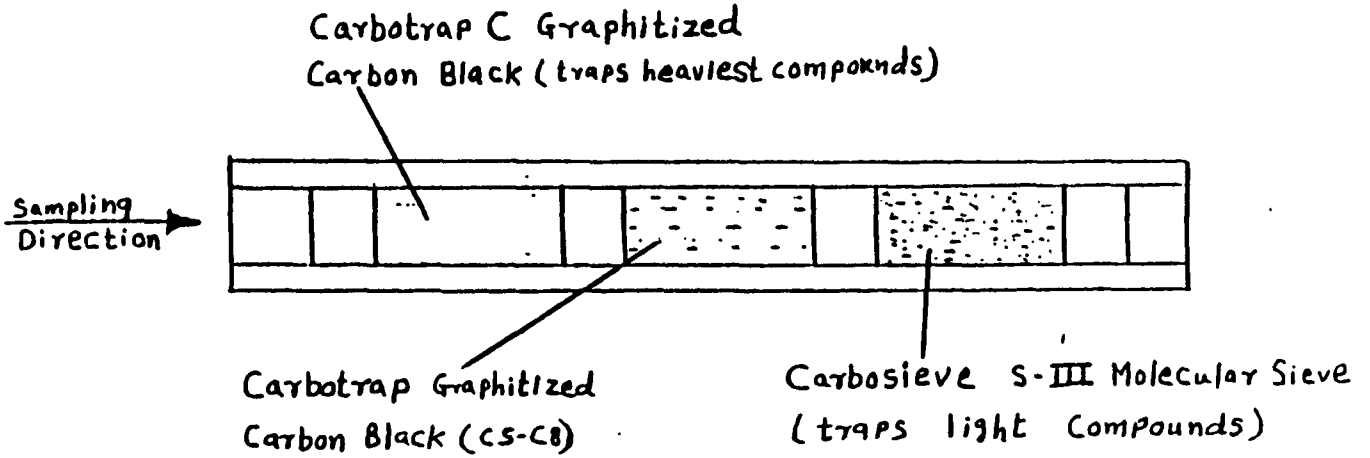
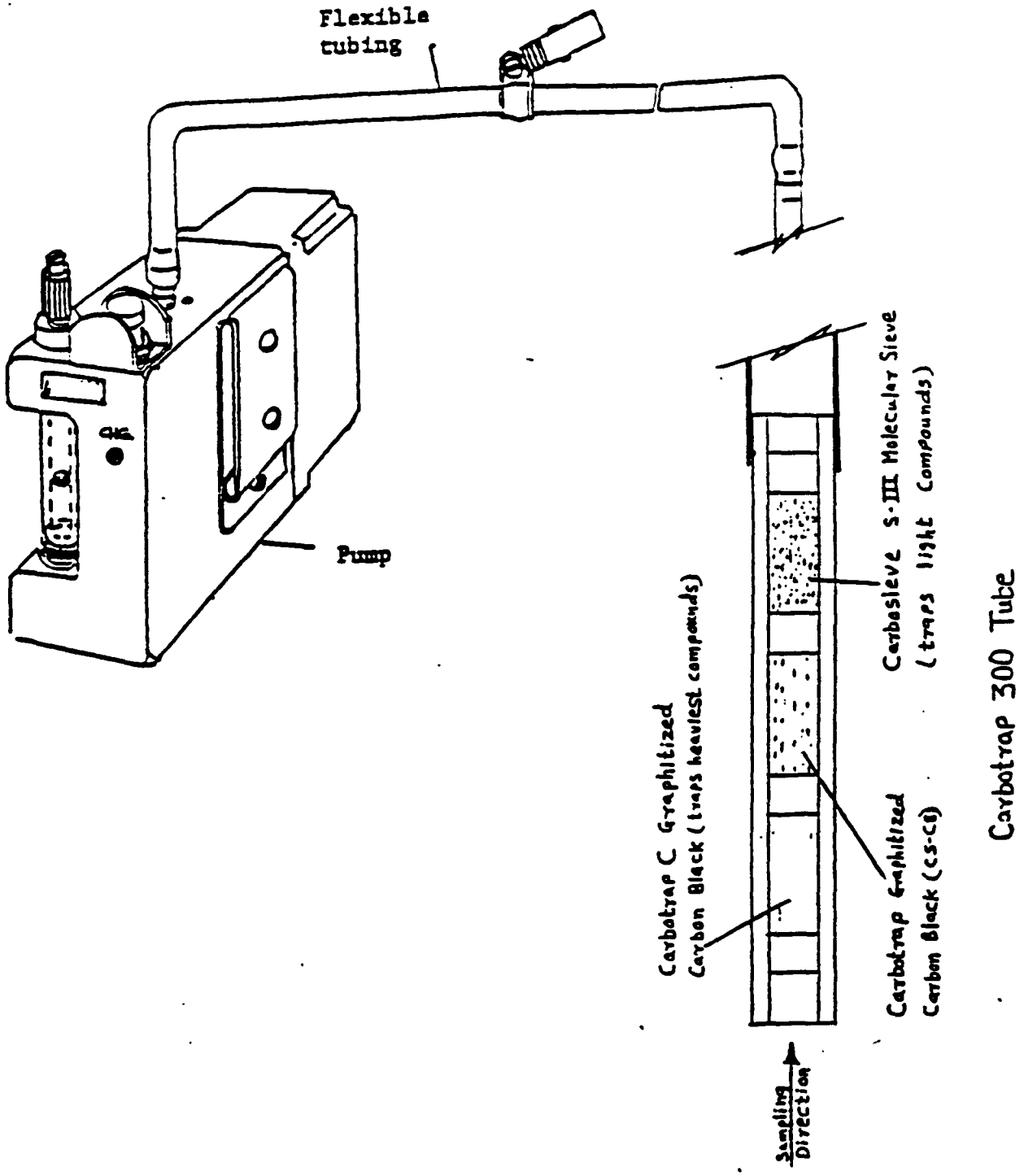


Figure 5. Sampler Location for Unsaturated Polyester Experiment



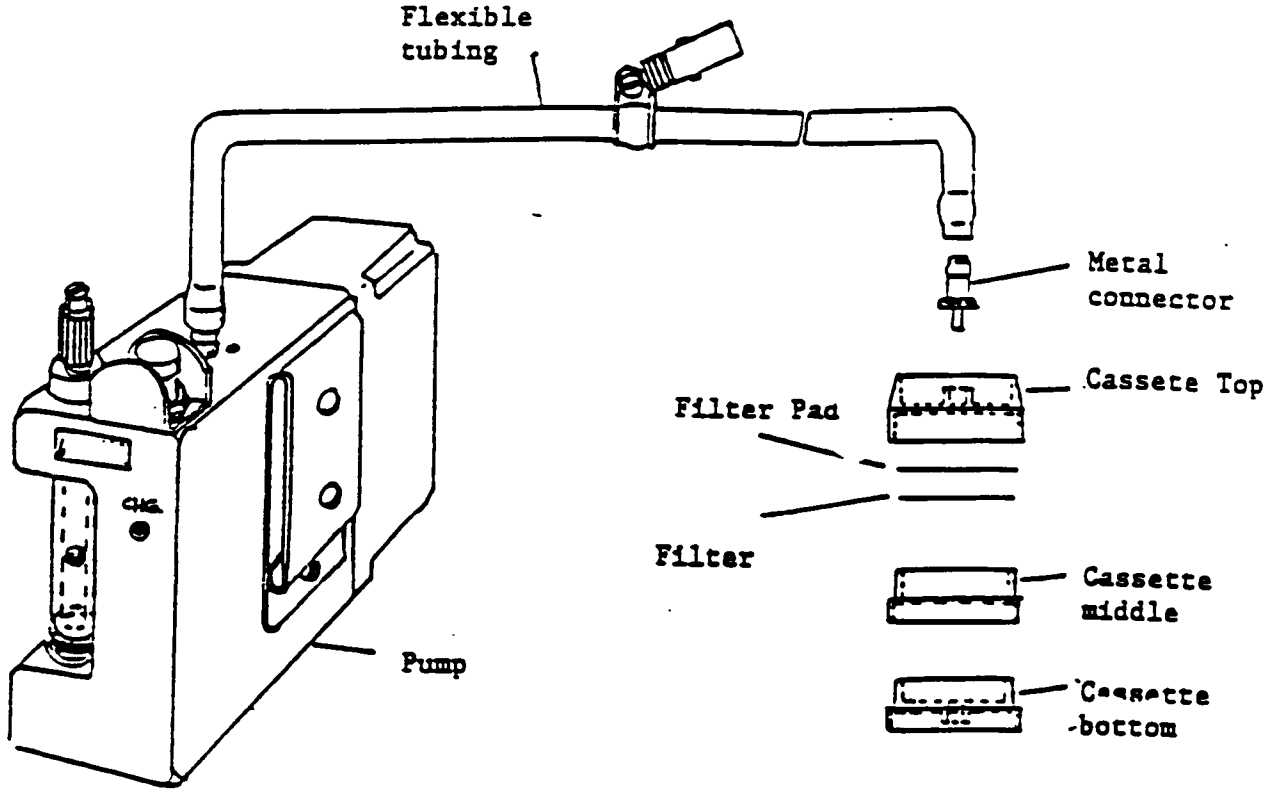
Carbotrap 300 Tube

Figure 6. Sampling Tube for GC/MS Analysis.



Sample Train for Organic Vapor Measurements

Figure 7



Sample train for Total Dust Measurements

Figure 8

APPENDIX B

ESA Laboratories

Methods Standards and Detection Limits

OVERVIEW OF ESA LABORATORIES

ESA Laboratories (ESAL) is an industrial hygiene, environmental and clinical laboratory specializing in analyses directed toward the protection of the occupational workforce as well as the general public. As such, ESAL concentrates it's efforts on the analysis of samples which are collected by field personnel as part of an overall program of health protection. ESAL specializes in the analysis of samples by anodic stripping voltammetry, atomic absorption, gas chromatography and gas chromatography/mass spectrometry.

ESAL was formed in 1972 to initially demonstrate the feasibility of instrumentation manufactured by it's parent company, ESA, Inc. Initial work concentrated on the determination of lead in blood by anodic stripping voltammetry. The laboratory operation developed into a complete industrial hygiene laboratory offering services in the determination of trace metals, organic solvents and asbestos. In 1986, ESAL acquired a GC/MS and began expansion into the environmental analysis market. Environmental services are limited to the analysis of trace metals, organic solvents, pesticides, PCB's, and volatile organics.

ESAL is licensed by the U.S. Department of Health and Human Services (CDC) and a variety of state departments of public health to perform the analysis of biological fluids and tissues for trace metals. ESAL is accredited by the American Industrial Hygiene Association (organic solvents, metals, asbestos) and is certified by the Massachusetts DEQE and similar agencies in the states of New York, New Hampshire, Rhode Island, Connecticut and Maine for the analysis of environmental samples for trace metals, pesticides, PCB's and volatile organics (EPA 624).

ESAL currently employs 15 people including laboratory technicians, chemists, and office staff.

Analytical instrumentation includes anodic stripping voltammetry, atomic absorption spectrophotometry, UV/vis spectrophotometry, gas chromatography, liquid chromatography, ion chromatography and gas chromatography/mass spectrometry (equipped with purge & trap for volatile organics in soil and water, and thermal desorption for organics collected from air).

ESAL has access to the facilities, capabilities and personnel of its parent company which is located in the same building.

CTL032239

THERMAL DESORPTION GC/MS

Compounds which can be trapped by Carbotrap 300 Tubes and detected by Thermal Desorption GC/MS:

Acetophenone
Acrylonitrile
Allyl Chloride
Benzene
Benzyl Chloride
Benzylamine
Bromoform
2-Butanone
n-Butanol
n-Butylamine
Carbon Tetrachloride
2-Chloropropene
Chlorobenzene
Chloroform
Cumene
Cyclohexanone
p-Cresol
1,4-Dichlorobenzene
1,2-Dichloroethane
1,1-Dichloroethylene
n-Decane
Ethylbenzene
2-Ethoxyethylacetate
n-Heptane
1-Hexane
4-Heptanone
Methylene Chloride
2-Methyl-2-propanol
Nitrobenzene
n-Octane
n-Pentanoic Acid
n-Pentane
Propionic Acid
Phenol
Tetrachloroethylene
Toluene
1,1,1 Trichloroethane
Trichloroethylene
Vinyl Chloride
o,m,p-Xylene

Compounds requiring higher desorption temperatures:

Isopropylbenzene
n-Propylbenzene
n-Decane
n-Butylbenzene
Biphenyl
n-Hexylbenzene
n-Dodecane
n-Octylbenzene
n-Tetradecane

POLYSTYRENE PROCESSING

Target Substance	TLV-TWA	Analytical Method
Benzene	10 (PEL 1)	Collection on Carbo-trap 300 Tubes. Determination by Thermal Desorption GC/MS, Detection limit (0.1μg) 0.01 ppm for a 10 L sample
Styrene	50	
Xylene	100	
Toluene	100	
Isopropyl benzene	-	
Ethyl benzene	100	
		Alternate Method:
		Charcoal Tube Collection, CS2 Desorption, GC/FID detection (3μg) 0.1 ppm for a 30 L sample.

Low and High Density Polyethylene Processing

Target Substance	TLV-TWA (PPM)	Analytical Method
Ethene Ethane 2-Ethyl-hexane	Simple Asphyxiants (see TLV Book Pg 8)	
Aldehydes & Ketones formaldehyde* acetaldehyde	1 (0.3) 100	EPA Method TO-5, Impinger method using 2,4-dinitrophenyl-hydrazine solution to derivatize the aldehydes and ketones, detection by HPLC/UV. Compounds detected include: Formaldehyde, Acetaldehyde, Acrolein, Acrolein, Propanal, Croton-aldehyde, Isobuty-raldehyde, Methyl-Ethyl Ketone, Benzaldehyde, Hexanal, Detection Limit: 0.01 PPM for a 50 L sample
Propionaldehyde (Propanal)	-	

*A number of methods for Formaldehyde passive are available.

ACIDS

Target Substance	TLV-TWA	Analytical Method
Acrylic Acid	10(2)	OSHA Method 28 2-XAD-8 absorbent tubes. Detection by HPLC/UV, Collection at 100 mL/Min Max of 24 L. Detection Limit: 0.02 PPM for a 24 L sample
Formic Acid	5	OSHA Method ID112, Impinger method using 0.01 N NaOH, detection by Ion Chromatography. Detection Limit: 0.01 PPM for a 100 L sample
CO	50	Indicator Tube

Acrylonitrile/Butadiene/Styrene (ABS)

Target Substance	TLV-TWA (PPM)	Analytical Method
Acrylonitrile	2	Collection on Carbo-trap 300 Tubes. Determination by GC/MS, Detection Limit: (0.01 μg) 0.01 PPM for a 10 L sample
Butadiene	10	
Styrene	100	
Benzene	10 (PEL 1)	
Ethyl Benzene	100	
Phenol	5	
Cresol	5	
		Alternate Method: Charcoal tube Collection, CS2 Desorption, GC/FID detection. Detection Limit: (3μg) 0.1 PPM for a 30 L sample.
Phenol	5	OSHA Method 32, XAD-2 Tube. Detection by HPLC/UV, Detection limit: 0.1 PPM for a 24 L sample.
Cresol	5	

Acrylonitrile/Butadiene/Styrene (ABS) [cont.]

Target Substance	TLV-TWA	Analytical Method
Hydrogen Cyanide	10	OSHA Method ID120, Filter cassette plus midget impinger with 0.1N NaOH Ion Specific Electrode or colorimetric detection. Detection Limit: 0.25 PPM for a 100L sample.
Ammonia	25	Detector Tube OSHA ID164: Impinger (0.1N H2S04) Ion Specific Electrode or colorimetric detection. Detection Limit: 0.25 PPM for a 100 L sample.
NO + NO2	2	Detector Tube

Polyvinyl Chloride (PVC)

Target Substance	TLV-TWA	Analytical Method
Vinyl Chloride Benzene	5 10 (PEL 1)	Collection on Carbo-trap 300 Tubes. Determination by Thermal Desorption GC/MS, Detection Limit: (0.1μg) 0.01 PPM for 10 L sample. Alternate Method: Charcoal Tube Collection, CS2 Desorption, GC/FID detection. Detection Limit: Vinyl Chloride 0.20 PPM for a 5 L sample.
Hydrogen Chloride	5	OSHA File - Impinger method using 0.1 N NaOH. Ion Specific Electrode Detection, Detection Limit: 0.5 PPM for a 15 L sample. Alternate Method: NIOSH 7903, Silica Gel Tube (washed). Ion Chromatography detection. Detection Limit: 0.1 PPM for a 100 L sample.

APPENDIX C

Analytical Methods for

1. Organic Vapors EPA - 624 (8240 A)

2. Aldehydes EPA - TO 5

3. Organic Acids OSHA - 38
   (as Acrylic Acid) Dow Chemical Modifications

4. Aerosol Sampling

   * Total Dust NIOSH - 0600

   * Benzene Soluble
     Particulate NIOSH - 5023

   * Lead NIOSH - 7082

5. Inorganic Acids
   Hydrochloric Acid NIOSH - 7903

1. Organic Vapors EPA - 624 (8240A)

CTL032248

The ESA Lab Note
ESA Laboratories, Inc.
43 Wiggins Avenue
Bedford, MA 01730
(617) 275-0100

Testing: "For A Healthier Environment"

Determination of Volatile Organic Compounds (VOC's) in Air
by Thermal Desorption/Gas Chromatography/Mass Spectrometry
TD/GC/MS

Introduction:

This ESA Lab Note describes the procedure at ESAL to determine VOC's in air collected on solid sorbent tubes by TD/GC/MS.

Sample Collection:

Samples are collected on Carbotrap (TM) 300 thermal desorption tubes manufactured by Supelco. These are three part solid sorbent tubes capable of trapping and transfering a wide variety of organic compounds. A complete description of the Carbotrap 300 tube is found in Supelco GC Bulletin 849A and 846B (available from ESAL). Samples are collected at a flow rate of 100-200 ml/min for a maximum volume of 10-20 liters.

Instrumentation:

Thermal Desorption of the Carbotrap 300 tubes is performed on a Supelco Thermal Desorption Unit. The desorbed VOC's are transferred via a heated transfer line onto a 75 meter DB624 Megabore Capillary Column at 5 degrees C. Separation and detection is accomplished with a Finnigan Model 5100 GC/MS/Data System. The system provides full scan electron impact spectra for identification and quantification of eluting compounds.

Mass Spec Tuning:

The Mass Spectrometer is tuned daily according to manufaturers instructions using perfluorotributylamine. This assures proper resolution and peak shape as well as correct ion abundances.

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The ESA Lab Note
ESA Laboratories, Inc.
43 Wiggins Avenue
Bedford, MA 01730
(617) 275-0100

Testing: "For A Healthier Environment"

BFB Criteria:

After tuning the Mass Spec system must pass the BFB (Bromofluorobenzene) performance criteria as specified in EPA Method 624 and 8240. This assures that the system is functioning properly for correct identification purposes. BFB Spectra, enhanced mass listing and ion abundance ratios are also submitted with each analytical batch to document proper instrument tuning each day.

Initial Calibration:

Once the GC/MS system is properly tuned according to BFB criteria, a five point calibration curve is run consisting of the solvents listed on the report form. Each calibration standard is thermally desorbed onto a Carbotrap 300 tube which is then run exactly like the samples. Thus standards and samples are run in a similar manner. Method Blanks are also run to ensure contamination free determination.

Internal Standards/Surrogates

To insure accurate results, each tube (samples, standards and blanks) are spiked with three internal standards and three surrogate standards. The GC/MS system uses the internal standards for both qualitative and quantitative analysis for those compounds listed on the report form. First, the instrument looks for each internal standard based on its Mass Spectra and retention time window. Once the internal standards are found, the instrument predicts the retention time of each compound. To be found the compound must meet retention time and mass spectral criteria. Once compounds have been identified their amount is based on the calibration curve. As a check on the overall procedure, three surrogate compounds are quantitated and the results reported on each report form. This checks the over-all operation of the method from thermal desorption thru GC separation and MS identification/quantitation. The procedure described above is basically what is done in EPA Methods 624 and 8240.

The ESA Lab Note
ESA Laboratories, Inc.
43 Wiggins Avenue
Bedford, MA 01730

Testing: "For A Healthier Environment"

Daily Calibration:

Every analytical sequence contains a continuing calibration check standard to insure instrument stability. Response factors from the daily check standard for each of the target compounds are calculated and compared to the mean response factors for each target from the initial five point calibration. Deviation from the initial calibration is calculated and tabulated for each target compound (as %RSD) and submitted with each analytical batch. Method blanks are run daily to assure contamination free analyses.

Individual Sample QA/QC:

Internal standard areas for each sample are compared to the Internal Standard areas of th check standard. Surrogate recoveries are calculated and reported for each sample. The Mass Spectrum of all positive target compound hits are hardcopied. Non-target compounds are identified by comparison of their mass spectra with the NBS Mass Spectral Library of 42,000 + compounds. Along with the name of the compound, the scan number and the library fit parameter are also reported. A fit of 1000 is perfect; values above 800 are considered sufficient for a match. All this information is hardcopied from the MS system. Non-targets are quantitated (estimated) versus the nearest internal standared. Some target compounds (particularly the gases at the beginning) must be estimated and searched for manually due to their poor response and difficult chromatography.

Quality control charts are kept to monitor surrogate recovery on a continuing basis.

Method Detection Limit:

Approximately 0.002 ug for each target compound.

ESA LABORATORIES, INC.
43 WIGGINS AVENUE
BEDFORD, MA 01730
(617) 275-0100 FAX: (617) 275-5529

_____ ESAL BATCH#: _____

_____ DATE RECEIVED: _____

_____ DATE ANALYZED _____

_____ DATE REPORTED: _____

_____

PO#/RELEASE: _____

SAMPLE ID: _____ ESAL SAMPLE#: _____

THERMAL DESORPTION GC/MS
QUANTITATIVE TARGET COMPOUND ANALYSIS - LEVEL I

ANALYTE	RESULT ug	ANALYTE	RESULT g
Benzene	ND	1,1-Dichloroethylene	ND
Chlorobenzene	ND	trans-1,2-Dichloroethylene	ND
Ethylbenzene	ND	1,2-Dichloropropane	ND
Styrene	ND	Methylene chloride	ND
Toluene	ND	1,1,2,2-Tetrachloroethane	ND
m/p-Xylene	ND	Tetrachloroethylene	ND
o-Xylene	ND	1,1,1-Trichloroethane	ND
		1,1,2-Trichloroethane	ND
Bromoethane	ND	Trichloroethylene	ND
Carbon tetrachloride	ND	Trichlorofluoromethane	ND
Chloroethane	ND	Vinyl Chloride	ND
Chloroform	ND		
Chloromethane	ND	Acetone	ND
Dibromochloromethane	ND	Carbon disulfide	ND
1,1-Dichloroethane	ND	2-Hexanone (MBK)	ND
1,2-Dichloroethane	ND	4-Methyl-2-pentanone (MIBK)	ND

ND = Not Detected, Limit of Detection = 0.002ug

SURROGATE STANDARDS	Expected NG	Determined NG	%Recovery %
1,2-Dichloroethane-D4	____	____	____
Toluene-D8	____	____	____
Bromofluorobenzene	____	____	____

[COST: $250.00]

INTERNAL STANDARDS	Expected NG	Determined NG	%Recovery %
1,4-Difluorobenzene	____	____	____
Chloro Benzene (D5)	____	____	____

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_____

ESAL BATCH#: _____

DATE RECEIVED: _____
DATE ANALYZED: _____
DATE REPORTED: _____

PO#/RELEASE: _____

SAMPLE ID: _____

ESAL SAMPLE#: _____

THERMAL DESORPTION GC/MS
QUANTITATIVE TARGET COMPOUND ANALYSIS - LEVEL II

ANALYTE	RESULT ug	ANALYTE	RESULT ug
Benzene	ND	Dibromochloromethane	ND
Bromobenzene	ND	c-1,2-Dibromo-3-chloropropane	ND
n-Butylbenzene	ND	t-1,2-Dibromo-3-chloropropane	ND
sec-Butylbenzene	ND	1,2-Dibromoethane	ND
tert-Butylbenzene	ND	Dibromomethane	ND
Chlorobenzene	ND	1,1-Dichloroethane	ND
2-Chlorotoluene	ND	1,2-Dichloroethane	ND
4-Chlorotoluene	ND	1,1-Dichloroethylene	ND
1,2-Dichlorobenzene	ND	cis-1,2-Dichloroethylene	ND
1,3-Dichlorobenzene	ND	trans-1,2-dichloroethylene	ND
1,4-Dichlorobenzene	ND	1,2-Dichloropropane	ND
Ethylbenzene	ND	1,3-Dichloropropane	ND
Isopropylbenzene	ND	2,2-Dichloropropane	ND
p-Isopropyltoluene	ND	1,1-Dichloroptopylene	ND
Naphthalene	ND	Hexachlorobutadiene	ND
n-Propylbenzene	ND	Methylene chloride	ND
Styrene	ND	1,1,1,2-Tetrachloroethane	ND
Toluene	ND	1,1,2,2-Tetrachloroethane	ND
1,2,3-Trichlorobenzene	ND	Tetrachloroethylene	ND
1,2,4-Trichlorobenzene	ND	1,1,1-Trichloroethane	ND
1,2,4-Trimethylbenzene	ND	1,1,2-Trichloroethane	ND
1,3,5-Trimethylbenzene	ND	Trichloroethylene	ND
m/p-Xylene	ND	Trichlorofluoromethane	ND
o-Xylene	ND	1,2,3-Trichloropropane	ND
Bromochloromethane	ND	Vinyl chloride	ND
Bromodichloromethane	ND	Acetone	ND
Bromoform	ND	2-Butanone MEK	ND
Bromomethane	ND	Carbon disulfide	ND
Carbon tetrachloride	ND	2-Hexanone (MBK)	ND
Chloroethane	ND	4-Methyl-2-pentanone (MIBK)	ND
Chloroform	ND	Vinyl acetate	ND
Chloromethane	ND		

[COST: $325.00]

Limit of Detection = 0.002ug

SURROGATE STANDARDS	Expected NG	Determined NG	%Recovery %
1,2-Dichloroethane-D4	_____	_____	_____
Toluene-D8	_____	_____	_____
Bromofluorobenzene	_____	_____	_____
INTERNAL STANDARDS	**NG**	**NG**	**%**
1,4-Difluorobenzene	_____	_____	_____
Chloro Benzene (D5)	_____	_____	_____

CTL032253

The ESA Lab Note
ESA Laboratories, Inc.
43 Wiggins Avenue
Bedford, MA 01730
(617) 275-0100

Testing: "For A Healthier Environment"

Thermal Desorption GC/MS

Quantitative Target Compound Analysis
Level III

Includes:

1. Quantitative Determination of Compounds listed in Level II
2. NBS 42,000 + library search on every peak.
3. Quantitation of non-target compounds by comparison to response factor of nearest Internal Standard.

Cost:

$400 per sample.

VOLATILE ORGANICS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS): PACKED COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
Acetone	67-64-1	pp	a
Acetonitrile	75-05-8	pp	a
Acrolein	107-02-8	pp	a
Acrylonitrile	107-13-1	pp	a
Allyl alcohol	107-18-6	pp	a
Allyl chloride	107-05-1	a	a
Benzene	71-43-2	a	a
Benzyl chloride	100-44-7	pp	a
Bromoacetone	598-31-2	pp	a
Bromochloromethane (I.S.)	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
4-Bromofluorobenzene (surr.)	460-00-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
2-Butanone	78-93-3	pp	a
Carbon disulfide	75-15-0	pp	a
Carbon tetrachloride	56-23-5	a	a
Chlorobenzene	108-90-7	a	a
Chlorobenzene-d_5 (I.S.)	108-90-7	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
2-Chloroethanol	107-07-3	pp	a
2-Chloroethyl vinyl ether	110-75-8	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
Chloroprene	126-99-8	a	pc
3-Chloropropionitrile	542-76-7	ND	pc
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a
Dibromomethane	74-95-3	a	a
1,4-Dichloro-2-butene	764-41-0	pp	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
1,2-Dichloroethane	107-06-2	a	a
1,2-Dichloroethane-d_4(surr.)	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloro-2-propanol	96-23-1	pp	a
cis-1,3-Dichloropropene	10061-01-5	a	a
trans-1,3-Dichloropropene	10061-02-6	a	a
1,2:3,4-Diepoxybutane	1464-53-5	a	a
1,4-Difluorobenzene (I.S.)	540-36-3	a	a
1,4-Dioxane	123-91-1	pp	a
Epichlorohydrin	106-89-8	i	a
Ethanol	64-17-5	i	a
Ethylbenzene	100-41-4	a	a
Ethylene oxide	75-21-8	pp	a
Ethyl methacrylate	97-63-2	a	a
2-Hexanone	591-78-6	pp	a
2-Hydroxypropionitrile	78-97-7	ND	pc
Iodomethane	74-88-4	a	a
Isobutyl alcohol	78-83-1	pp	a
Malononitrile	109-77-3	pp	a
Methacrylonitrile	126-98-7	pp	a
Methylene chloride	75-09-2	a	a
Methyl iodide	74-88-4	a	a
Methyl methacrylate	80-62-6	a	a
4-Methyl-2-pentanone	108-10-1	pp	a
Pentachloroethane	76-01-7	i	pc
2-Picoline	109-06-8	pp	a
Propargyl alcohol	107-19-7	pp	a
b-Propiolactone	57-57-8	pp	a
Propionitrile	107-12-0	pp	a
n-Propylamine	107-10-8	a	a
Pyridine	110-86-1	i	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
Toluene-d_8 (surr.)	108-88-3	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a
1,2,3-Trichloropropane	96-18-4	a	a
Vinyl acetate	108-05-4	a	a
Vinyl chloride	75-01-4	a	a
Xylene (Total)	1330-20-7	a	a

a Adequate response by this technique.
b Chemical Abstract Services Registry Number.
pp Poor purging efficiency resulting in high EQLs.
i Inappropriate technique for this analyte.
pc Poor chromatographic behavior.

1.2 Method 8240 can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Table 1 for a list of compounds, retention times, and their characteristic ions that have been evaluated on a purge-and-trap GC/MS system.

1.3 The estimated quantitation limit (EQL) of Method 8240 for an individual compound is approximately 5 µg/Kg (wet weight) for soil/sediment samples, 0.5 mg/Kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 2). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 To increase purging efficiencies of acrylonitrile and acrolein, refer to Methods 5030 and 8030 for proper purge-and-trap conditions.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with organic-free reagent water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 The purge-and-trap process - An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept

through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank, prepared from organic-free reagent water and carried through the sampling and handling protocol, can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of organic-free reagent water to check for cross contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-concentration sample.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.5 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running calibration and reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10 μL, 25 μL, 100 μL, 250 μL, 500 μL, and 1,000 μL. These syringes should be equipped with a 20 gauge (0.006 in. ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe - 5 mL, gas-tight with shutoff valve.

4.4 Balances - Analytical, 0.0001 g, and top-loading, 0.1 g.

4.5 Glass scintillation vials - 20 mL, with screw caps and Teflon liners or glass culture tubes with a screw cap and Teflon liner.

4.6 Volumetric flasks, Class A - 10 mL and 100 mL, with ground-glass stoppers.

4.7 Vials - 2 mL, for GC autosampler.

4.8 Spatula - Stainless steel.

4.9 Disposable pipets - Pasteur.

4.10 Heater or heated oil bath - Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.11 Purge-and-trap device - The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.11.1 The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized, provided equivalent performance is demonstrated.

4.11.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning. However, the column must be run through the temperature program prior to analysis of samples.

4.11.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake out mode. The desorber design illustrated in Figure 2 meets these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.11.5 Trap Packing Materials

4.11.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.11.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.11.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, lot #M-2649, by crushing through 26 mesh screen (or equivalent).

4.12 Gas chromatograph/mass spectrometer system

4.12.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.12.2 Column - 6 ft x 0.1 in. ID glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.12.3 Mass spectrometer - Capable of scanning from 35-260 amu every 3 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.

4.12.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 3) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.12.5 Data system - A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.3.1 Place about 9.8 mL of methanol in a 10 mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.2 Add the assayed reference material, as described below.

5.3.2.1 Liquids - Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.4 Transfer the stock standard solution into a Teflon sealed screw cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.3.5 Prepare fresh standards every two months for gases. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be

prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 25% difference.

5.4 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Section 5.3, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 µg/10 mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis.

5.6 Internal standards - The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.3 and 5.4. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L.

5.7 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared.

5.8 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 5.3 and 5.4). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the target analytes may be included). Calibration standards must be prepared daily.

5.9 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.10 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards in methanol be stored at -10°C to -20°C in screw cap amber bottles with Teflon liners.

5.11 Methanol, CH_3OH. Pesticide quality or equivalent. Store apart from other solvents.

5.12 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

5.12.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

CAUTION: Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and a vacuum is maintained at < 10 mm Hg for at least two hours using a two stage mechanical pump. The vacuum system is equipped with an all glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 0.1 mg/mL of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw cap bottle in an area that is not contaminated by solvent vapors.

5.12.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, an organic-free reagent water/tetraglyme blank must be analyzed.

5.13 Polyethylene glycol, $H(OCH_2CH_2)_nOH$. Free of interferences at the detection limit of the analytes.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC/MS system with a 10 μL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct

injection be used. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.2 Initial calibration for purge-and-trap procedure

7.2.1 Recommended GC/MS operating conditions

Electron energy:	70 volts (nominal).
Mass range:	35-260 amu.
Scan time:	To give 5 scans/peak, but not to exceed 7 sec/scan.
Initial column temperature:	45°C.
Initial column holding time:	3 minutes.
Column temperature program:	8°C/minute.
Final column temperature:	220°C.
Final column holding time:	15 minutes.
Injector temperature:	200-225°C.
Source temperature:	According to manufacturer's specifications.
Transfer line temperature:	250-300°C.
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.2.2 Each GC/MS system must be hardware tuned to meet the criteria in Table 3 for a 50 ng injection or purging of 4-bromofluorobenzene (2 µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.3 Assemble a purge-and-trap device that meets the specification in Section 4.11. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.4 Connect the purge-and-trap device to a gas chromatograph.

7.2.5 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device (use freshly prepared stock solutions when preparing the calibration standards for the initial calibration.) Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5 mL glass syringe fitted with a 15 cm, 20 gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14 gauge needle that forms the sample inlet will permit insertion of the 20 gauge needle. Next, using a 10 µL or 25 µL microsyringe equipped with a long needle (Section 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Section 5.6). Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10 µL of

the internal standard solution (Section 5.4). Close the 2 way syringe valve at the sample inlet.

7.2.6 Carry out the purge-and-trap analysis procedure as described in Section 7.4.1.

7.2.7 Tabulate the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Section 7.5.2). The RF is calculated as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

7.2.8 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.2.8.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.8.2 Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

7.2.8.3 Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.9 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs).

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

RSD = relative standard deviation.
$\bar{x}$ = mean of 5 initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

The %RSD for each individual CCC should be less than 30 percent. This criterion must be met in order for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.3 Daily GC/MS calibration

7.3.1 Prior to the analysis of samples, inject or purge 50 ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12 hour shift.

7.3.2 The initial calibration curve (Section 7.2) for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Section 7.3.3) and CCC (Section 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.3.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Section 7.2.9 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF_i} - RF_c}{\overline{RF_i}} \times 100$$

where:

$\overline{RF_i}$ = average response factor from initial calibration.
RF_c = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (> 25% difference), for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins.

7.3.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (- 50% to + 100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4 GC/MS analysis

7.4.1 Water samples

7.4.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are: the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (HECD); and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Section 7.2.1.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Section 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Section 7.2.8).

7.4.1.6 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas tight syringe.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10 to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Section 7.4.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5 mL syringe with the diluted sample as in Section 7.4.1.6.

7.4.1.8 Add 10.0 µL of surrogate spiking solution (Section 5.3) and 10 µL of internal standard spiking solution (Section 5.4) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking

solution to 5 mL of sample is equivalent to a concentration of 50 µg/L of each surrogate standard.

7.4.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.4.1.10 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

7.4.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial program temperature of 45°C.

7.4.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic-free reagent water (or methanol followed by organic-free reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.4.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.4.1.15 For matrix spike analysis, add 10 µL of the matrix spike solution (Section 5.7) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.4.1.16 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Sections 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 Water miscible liquids

7.4.2.1 Water miscible liquids are analyzed as water samples after first diluting them at least 50 fold with organic-free reagent water.

7.4.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100 mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5 mL gas tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5 mL syringe filled with organic-free reagent water by adding at least 20 μL, but not more than 100 μL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may be used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/Kg) or the high-concentration method (> 1 mg/Kg).

7.4.3.1 Low-concentration method - This is designed for samples containing individual purgeable compounds of < 1 mg/Kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples. See Figure 5 for an illustration of a low soils impinger.

7.4.3.1.1 Use a 5 g sample if the expected concentration is < 0.1 mg/Kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/Kg.

7.4.3.1.2 The GC/MS system should be set up as in Sections 7.4.1.2-7.4.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.4.3.1.3 Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of surrogate spiking solution (Section 5.3) and internal standard solution (Section 5.4) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10 µL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 µg/Kg of each surrogate standard.

7.4.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Section 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent dry weight of the soil/sediment sample. This includes waste samples that are amenable to percent dry weight determination. Other wastes should be reported on a wet-weight basis.

7.5.3.1.5.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before re-weighing. Concentrations of individual analytes are reported relative to the dry weight of sample.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.4.3.1.6 Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, the procedures in Sections 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.4.3.1.7 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minute.

7.4.3.1.8 Proceed with the analysis as outlined in Sections 7.4.1.11-7.4.1.16. Use 5 mL of the same organic-free reagent water as in the reagent blank. If saturated peaks

occurred or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.4.3.1.9 For low-concentration sediment/soils add 10 µL of the matrix spike solution (Section 5.7) to the 5 mL of organic-free reagent water (Section 7.4.3.1.3). The concentration for a 5 g sample would be equivalent to 50 µg/Kg of each matrix spike standard.

7.4.3.2 High-concentration method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with reagent tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing internal standards. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/Kg should be analyzed by this method.

7.4.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20 mL vial. Use a top loading balance. Note and record the actual weight to 0.1 gram and determine the percent dry weight of the sample using the procedure in Section 7.4.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of solvent into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

NOTE: Sections 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of appropriate solvent to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100 µL aliquot of each of these extracts in Section 7.4.3.2.6 will give a concentration equivalent to 6,200 µg/Kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Sections 7.4.1.2-7.4.1.4. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.4.3.2.5 Table 4 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.4.3.2.6 Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 µL of internal standard solution. Also add the volume of solvent extract determined in Section 7.4.3.2.5 and a volume of extraction or dissolution solvent to total 100 µL (excluding methanol in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the organic-free reagent water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Section 7.4.1.11-7.4.1.16. Analyze all reagent blanks on the same instrument as that use for the samples. The standards and blanks should also contain 100 µL of solvent to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the high-concentration sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Section 5.3), and 1.0 mL of matrix spike solution (Section 5.7) as in Section 7.4.3.2.2. This results in a 6,200 µg/Kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 µL aliquot of this extract to 5 mL of organic-free reagent water for purging (as per Section 7.4.3.2.6).

7.5 Data interpretation

7.5.1 Qualitative analysis

7.5.1.1 An analyte (e.g. those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass

spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.5.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.5.1.1.2 (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum). (2) The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting

peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5.2 Quantitative analysis

7.5.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g. see Table 5).

7.5.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste:

$$\text{concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
RF = Response factor for compound being measured (Section 7.3.6).
V_o = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil, Sludge, and Waste:

High-concentration:

$$\text{concentration } (\mu g/Kg) = \frac{(A_x)(I_s)\ (V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

Low-concentration:

$$\text{concentration } (\mu g/Kg) = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscible waste above.
V_t = Volume of total extract (μL) (use 10,000 μL or a factor of this when dilutions are made).
V_i = Volume of extract added (μL) for purging.
W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

7.5.2.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The percent dry weight of the sample (as calculated in Section 7.4.3.1.5) should be reported along with the data in either instance.

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Required instrument QC is found in the following sections:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Section 7.2.2.

8.2.2 There must be an initial calibration of the GC/MS system as specified in Section 7.2.

8.2.3 The GC/MS system must meet the SPCC criteria specified in Section 7.3.3 and the CCC criteria in Section 7.3.4, each 12 hours.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 mg/L in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.3.2 Prepare a QC reference sample to contain 20 μg/L of each analyte by adding 200 μL of QC reference sample concentrate to 100 mL of organic-free reagent water.

8.3.3 Four 5 mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Section 7.4.1.

8.3.4 Calculate the average recovery ($\bar{x}$) in μg/L, and the standard deviation of the recovery (s) in μg/L, for each analyte using the four results.

8.3.5 For each analyte compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{x}$ for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.3.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.3.6.1 or 8.3.6.2.

8.3.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.3.2.

8.3.6.2 Beginning with Section 8.3.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.3.2.

8.4 For aqueous and soil matrices, laboratory established surrogate control limits should be compared with the control limits listed in Table 8. The limits given in Table 8 are multilaboratory performance based limits for soil and aqueous samples, and therefore, the single laboratory limits must fall within those given in Table 8 for these matrices.

8.4.1 If recovery is not within limits, the following procedures are required.

8.4.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.4.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.4.1.3 If no problem is found, re-extract and re-analyze the sample.

8.4.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4.2 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using organic-free reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

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5. Budde, W.L. and J.W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April 1980.

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TABLE 1.
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Ethylene oxide	1.30	44	44, 43, 42
Chloromethane	2.30	50	52, 49
Dichlorodifluoromethane	2.47	85	85, 87, 101, 103
Bromomethane	3.10	94	96, 79
Vinyl chloride	3.80	62	64, 61
Acetonitrile	3.97	41	41, 40, 39
Chloroethane	4.60	64	66, 49
Methyl iodide	5.37	142	142, 127, 141
Methylene chloride	6.40	84	49, 51, 86
Carbon disulfide	7.47	76	76, 78, 44
Trichlorofluoromethane	8.30	101	103, 66
Propionitrile	8.53	54	54, 52, 55, 40
Allyl chloride	8.83	76	76, 41, 39, 78
1,1-Dichloroethene	9.00	96	61, 98
Bromochloromethane (I.S.)	9.30	128	49, 130, 51
Allyl alcohol	9.77	57	57, 58, 39
trans-1,2-Dichloroethene	10.00	96	61, 98
1,2-Dichloroethane	10.10	62	64, 98
Propargyl alcohol	10.77	55	55, 39, 38, 53
Chloroform	11.40	83	85, 47
1,2-Dichloroethane-d_4(surr)	12.10	65	102
2-Butanone	12.20	72	43, 72
Methacrylonitrile	12.37	41	41, 67, 39, 52, 66
Dibromomethane	12.53	93	93, 174, 95, 172, 176
2-Chloroethanol	12.93	49	49, 44, 43, 51, 80
b-Propiolactone	13.00	42	42, 43, 44
Epichlorohydrin	13.10	57	57, 49, 62, 51
1,1,1-Trichloroethane	13.40	97	99, 117
Carbon tetrachloride	13.70	117	119, 121
1,4-Dioxane	13.70	88	88, 58, 43, 57
Isobutyl alcohol	13.80	43	43, 41, 42, 74
Bromodichloromethane	14.30	83	85, 129
Chloroprene	14.77	53	53, 88, 90, 51
1,2:3,4-Diepoxybutane	14.87	55	55, 57, 56
1,2-Dichloropropane	15.70	63	62, 41
cis-1,3-Dichloropropene	15.90	75	77, 39
Bromoacetone	16.33	136	43, 136, 138, 93, 95
Trichloroethene	16.50	130	95, 97, 132
Benzene	17.00	78	52, 71
trans-1,3-Dichloropropene	17.20	75	77, 39
1,1,2-Trichloroethane	17.20	97	83, 85, 99
3-Chloropropionitrile	17.37	54	54, 49, 89, 91
1,2-Dibromoethane	18.40	107	107, 109, 93, 188
Pyridine	18.57	79	79, 52, 51, 50

TABLE 1.
(Continued)

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
2-Chloroethyl vinyl ether	18.60	63	65,106
2-Hydroxypropionitrile	18.97	44	44,43,42,53
1,4-Difluorobenzene (I.S.)	19.60	114	63.88
Malononitrile	19.60	66	66,39,65,38
Methyl methacrylate	19.77	69	69,41,100,39
Bromoform	19.80	173	171,175,252
1,1,1,2-Tetrachloroethane	20.33	131	131,133,117,119,95
1,3-Dichloro-2-propanol	21.83	79	79,43,81,49
1,1,2,2-Tetrachloroethane	22.10	83	85,131,133
Tetrachloroethene	22.20	164	129,131,166
1,2,3-Trichloropropane	22.20	75	75,77,110,112,97
1,4-Dichloro-2-butene	22.73	75	75,53,77,124,89
n-Propylamine	23.00	59	59,41,39
2-Picoline	23.20	93	93,66,92,78
Toluene	23.50	92	91,65
Ethyl methacrylate	23.53	69	69,41,99,86,114
Chlorobenzene	24.60	112	114,77
Pentachloroethane[a]	24.83	167	167,130,132,165,169
Ethylbenzene	26.40	106	91
1,2-Dibromo-3-chloropropane	27.23	157	157,75,155,77
4-Bromofluorobenzene (surr.)	28.30	95	174,176
Benzyl chloride	29.50	91	91,126,65,128
Styrene	30.83	104	104,103,78,51,77
Acetone	--	43	58
Acrolein	--	56	55,58
Acrylonitrile	--	53	52,51
Chlorobenzene-d_5 (I.S.)	--	117	82,119
Chlorodibromomethane	--	129	208,206
1,1-Dichloroethane	--	63	65,83
Ethanol	--	31	45,27,46
2-Hexanone	--	43	58,57, 100
Iodomethane	--	142	127,141
4-Methyl-2-pentanone	--	43	58,57,100
Toluene-d_8 (surr.)	--	98	70,100
Vinyl acetate	--	43	86
Xylene (Total)	--	106	91

a The base peak at m/e 117 was not used due to an interference at that mass with a nearly coeluting internal standard, chlorobenzene-d_5.

TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQL) FOR VOLATILE ORGANICS[a]

Volatiles	Estimated Quantitation Limits[b] Ground water µg/L	Low Soil/Sediment µg/Kg
Acetone	100	100
Acetonitrile	100	100
Allyl chloride	5	5
Benzene	5	5
Benzyl chloride	100	100
Bromodichloromethane	5	5
Bromoform	5	5
Bromomethane	10	10
2-Butanone	100	100
Carbon disulfide	100	100
Carbon tetrachloride	5	5
Chlorobenzene	5	5
Chlorodibromomethane	5	5
Chloroethane	10	10
2-Chloroethyl vinyl ether	10	10
Chloroform	5	5
Chloromethane	10	10
Chloroprene	5	5
1,2-Dibromo-3-chloropropane	100	100
1,2-Dibromoethane	5	5
Dibromomethane	5	5
1,4-Dichloro-2-butene	100	100
Dichlorodifluoromethane	5	5
1,1-Dichloroethane	5	5
1,2-Dichloroethane	5	5
1,1 Dichloroethene	5	5
trans-1,2-Dichloroethene	5	5
1,2-Dichloropropane	5	5
cis-1,3-Dichloropropene	5	5
trans-1,3-Dichloropropene	5	5
Ethylbenzene	5	5
Ethyl methacrylate	5	5
2-Hexanone	50	50
Isobutyl alcohol	100	100
Methacrylonitrile	100	100
Methylene chloride	5	5
Methyl iodide	5	5
Methyl methacrylate	5	50
4-Methyl-2-pentanone	50	50
Pentachloroethane	10	10

TABLE 2.
(Continued)

Volatiles	Estimated Quantitation Limits[b] Ground water µg/L	Low Soil/Sediment µg/Kg
Propionitrile	100	100
Styrene	5	5
1,1,1,2-Tetrachloroethane	5	5
1,1,2,2-Tetrachloroethane	5	5
Tetrachloroethene	5	5
Toluene	5	5
1,1,1-Trichloroethane	5	5
1,1,2-Trichloroethane	5	5
Trichloroethene	5	5
1,2,3-Trichloropropane	5	5
Vinyl acetate	50	50
Vinyl chloride	10	10
Xylene (Total)	5	5

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following information for further guidance on matrix dependent EQLs.

b EQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight of each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

[c]EQL = [EQL for low soil sediment (Table 2)] X [Factor]. For non-aqueous samples, the factor is on a wet weight basis.

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TABLE 3.
BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 4.
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS
OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500- 10,000 µg/Kg	100 µL
1,000- 20,000 µg/Kg	50 µL
5,000-100,000 µg/Kg	10 µL
25,000-500,000 µg/Kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

a The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

b Dilute and aliquot of the methanol extract and then take 100 µL for analysis.

TABLE 5.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromoform
Bromomethane	2-Butanone
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	2-Chloroethyl vinyl ether
Chloromethane	Dibromomethane
Dichlorodifluoromethane	1,4-Dichloro-2-butene
1,1-Dichloroethane	1,2-Dichloropropane
1,2-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	trans-1,3-Dichloropropene
1,1-Dichloroethene	1,1,1-Trichloroethane
trans-1,2-Dichloroethene	1,1,2-Trichloroethane
Iodomethane	Trichloroethene
Methylene chloride	Vinyl acetate
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Ethyl methacrylate
2-Hexanone
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylene

TABLE 6.
CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethyl benzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in µg/L.
$\underline{s}$ = Standard deviation of four recovery measurements, in µg/L.
$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.
p, p_s = Percent recovery measured.
D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 624 and were calculated assuming a QC check sample concentration of 20 µg/L. These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Benzene	0.93C+2.00	0.26$\bar{x}$-1.74	0.25$\bar{x}$-1.33
Bromodichloromethane	1.03C-1.58	0.15$\bar{x}$+0.59	0.20$\bar{x}$+1.13
Bromoform	1.18C-2.35	0.12$\bar{x}$+0.34	0.17$\bar{x}$+1.38
Bromomethane	1.00C	0.43$\bar{x}$	0.58$\bar{x}$
Carbon tetrachloride	1.10C-1.68	0.12$\bar{x}$+0.25	0.11$\bar{x}$+0.37
Chlorobenzene	0.98C+2.28	0.16$\bar{x}$-0.09	0.26$\bar{x}$-1.92
Chloroethane	1.18C+0.81	0.14$\bar{x}$+2.78	0.29$\bar{x}$+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62$\bar{x}$	0.84$\bar{x}$
Chloroform	0.93C+0.33	0.16$\bar{x}$+0.22	0.18$\bar{x}$+0.16
Chloromethane	1.03C-1.81	0.37$\bar{x}$+2.14	0.58$\bar{x}$+0.43
Dibromochloromethane	1.01C-0.03	0.17$\bar{x}$-0.18	0.17$\bar{x}$+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{x}$-1.45	0.30$\bar{x}$-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14$\bar{x}$-0.48	0.18$\bar{x}$-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{x}$-1.45	0.30$\bar{x}$-1.20
1,1-Dichloroethane	1.05C+0.36	0.13$\bar{x}$-0.05	0.16$\bar{x}$+0.47
1,2-Dichloroethane	1.02C+0.45	0.17$\bar{x}$-0.32	0.21$\bar{x}$-0.38
1,1-Dichloroethene	1.12C+0.61	0.17$\bar{x}$+1.06	0.43$\bar{x}$-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14$\bar{x}$+0.09	0.19$\bar{x}$+0.17
1,2-Dichloropropane[a]	1.00C	0.33$\bar{x}$	0.45$\bar{x}$
cis-1,3-Dichloropropene[a]	1.00C	0.38$\bar{x}$	0.52$\bar{x}$
trans-1,3-Dichloropropene[a]	1.00C	0.25$\bar{x}$	0.34$\bar{x}$
Ethyl benzene	0.98C+2.48	0.14$\bar{x}$+1.00	0.26$\bar{x}$-1.72
Methylene chloride	0.87C+1.88	0.15$\bar{x}$+1.07	0.32$\bar{x}$+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16$\bar{x}$+0.69	0.20$\bar{x}$+0.41
Tetrachloroethene	1.06C+0.60	0.13$\bar{x}$-0.18	0.16$\bar{x}$-0.45
Toluene	0.98C+2.03	0.15$\bar{x}$-0.71	0.22$\bar{x}$-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12$\bar{x}$-0.15	0.21$\bar{x}$-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14$\bar{x}$+0.02	0.18$\bar{x}$+0.00
Trichloroethene	1.04C+2.27	0.13$\bar{x}$+0.36	0.12$\bar{x}$+0.59
Trichlorofluoromethane	0.99C+0.39	0.33$\bar{x}$-1.48	0.34$\bar{x}$-0.39
Vinyl chloride	1.00C	0.48$\bar{x}$	0.65$\bar{x}$

x′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

a Estimates based upon the performance in a single laboratory.

b Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

FIGURE 1.
PURGING CHAMBER

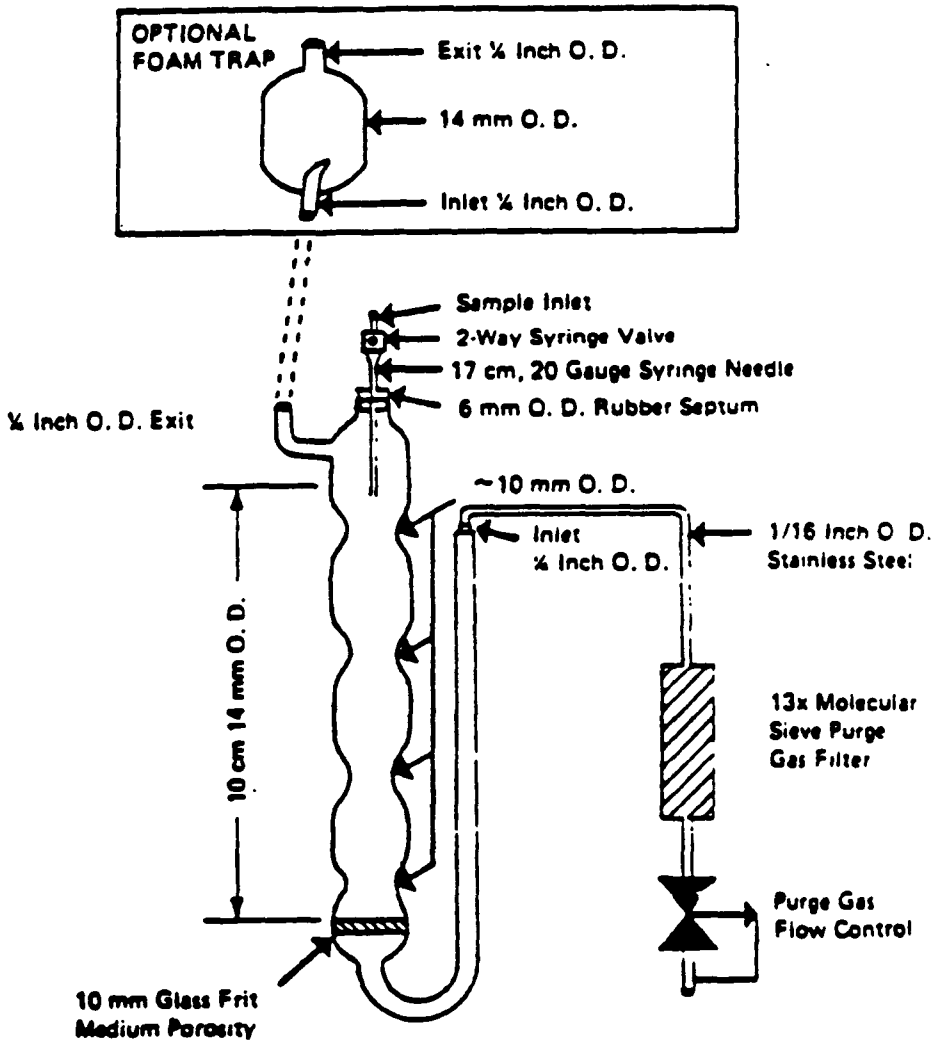

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FIGURE 2.
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE
DESORB CAPABILITY FOR METHOD 8240

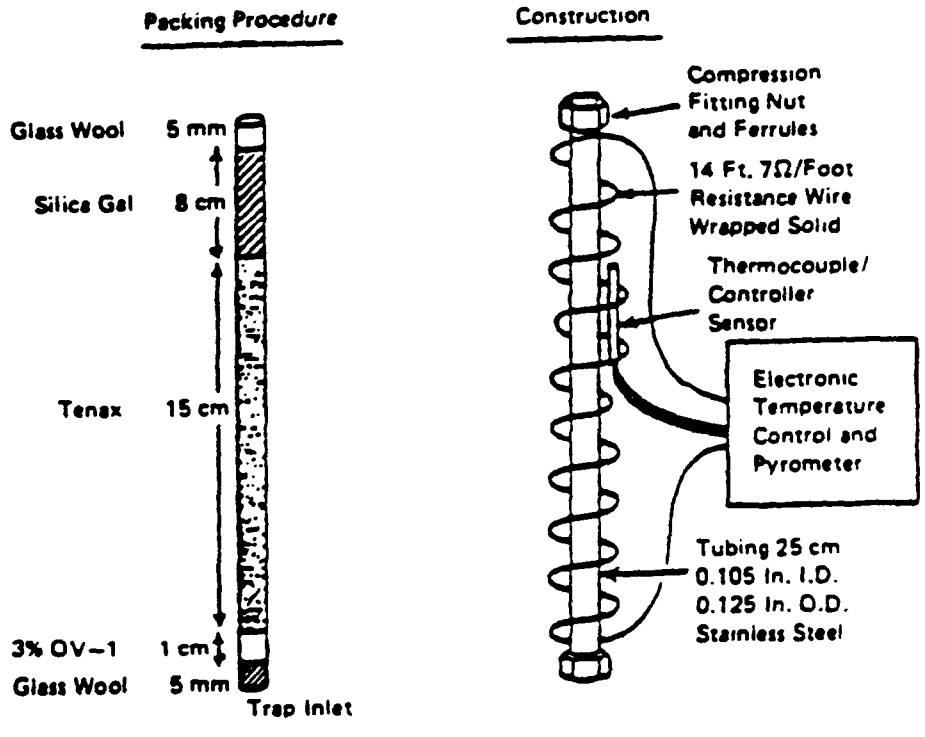

FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE FOR METHOD 8240

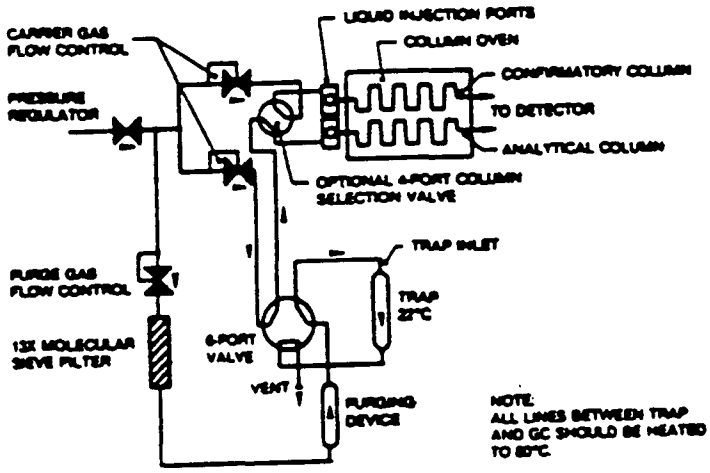

FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE FOR METHOD 8240

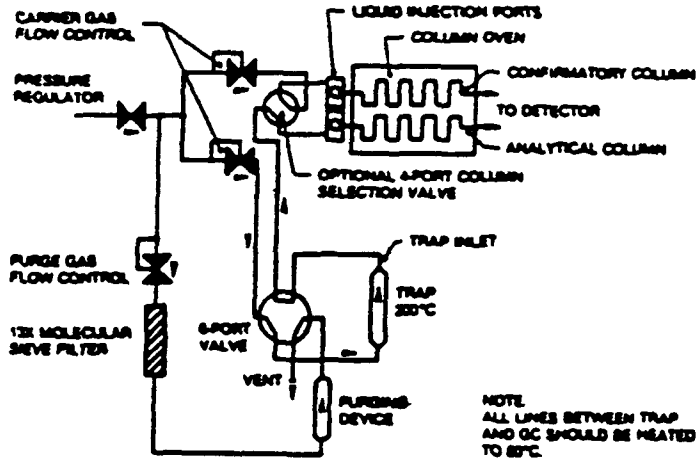

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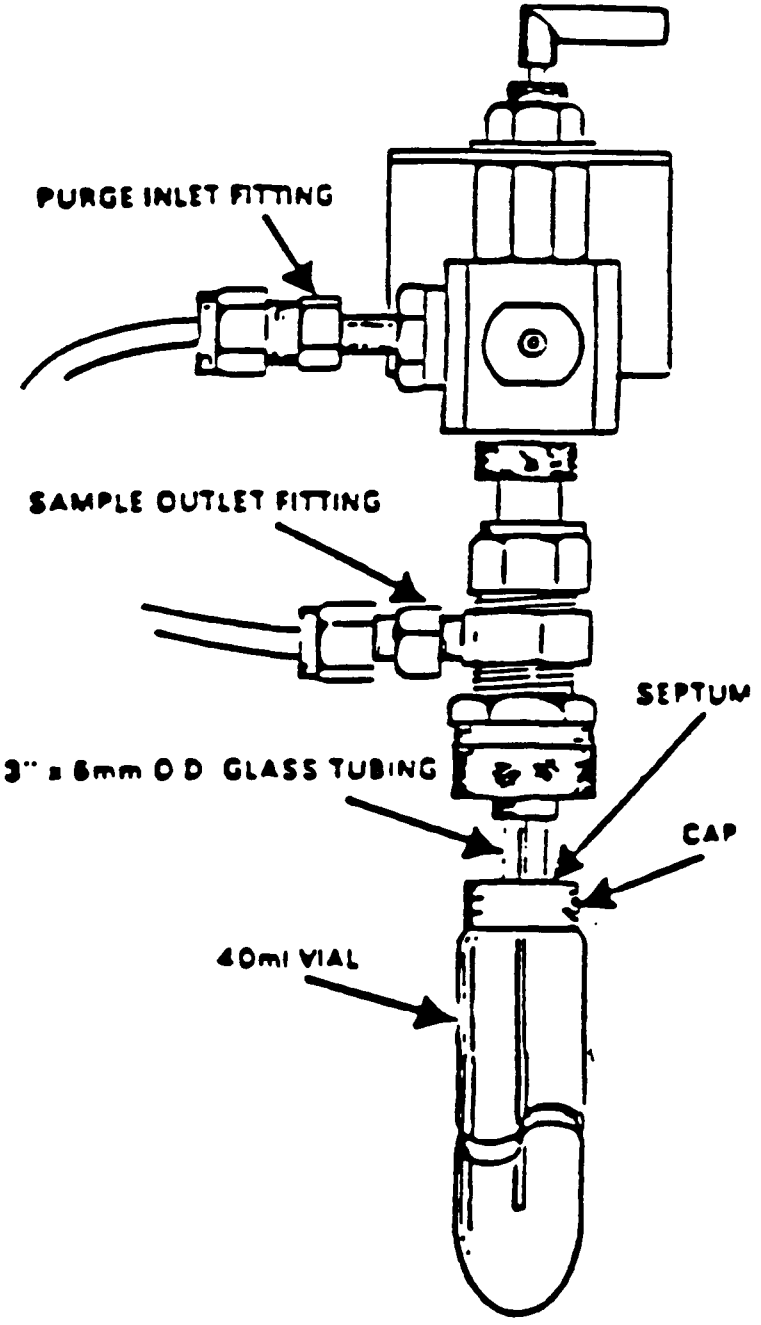
FIGURE 5.
LOW SOILS IMPINGER



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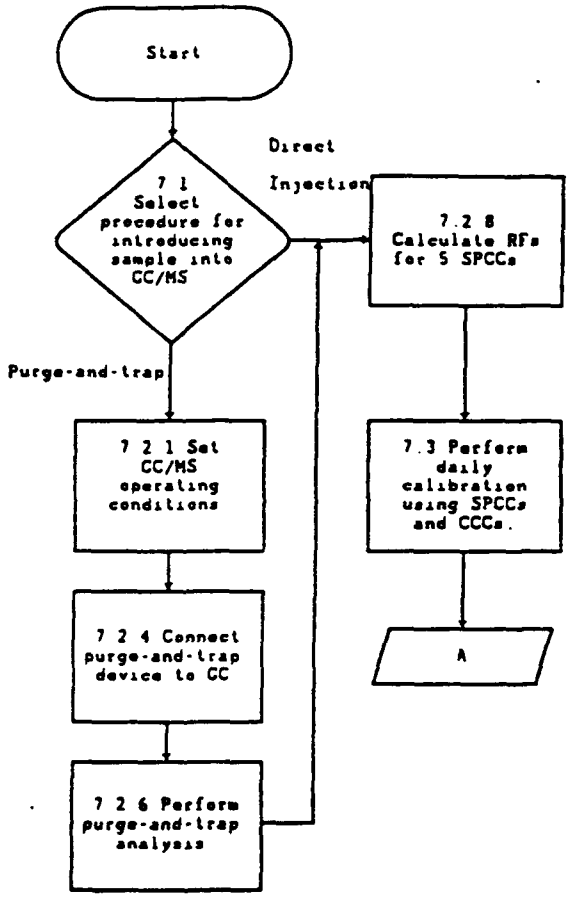
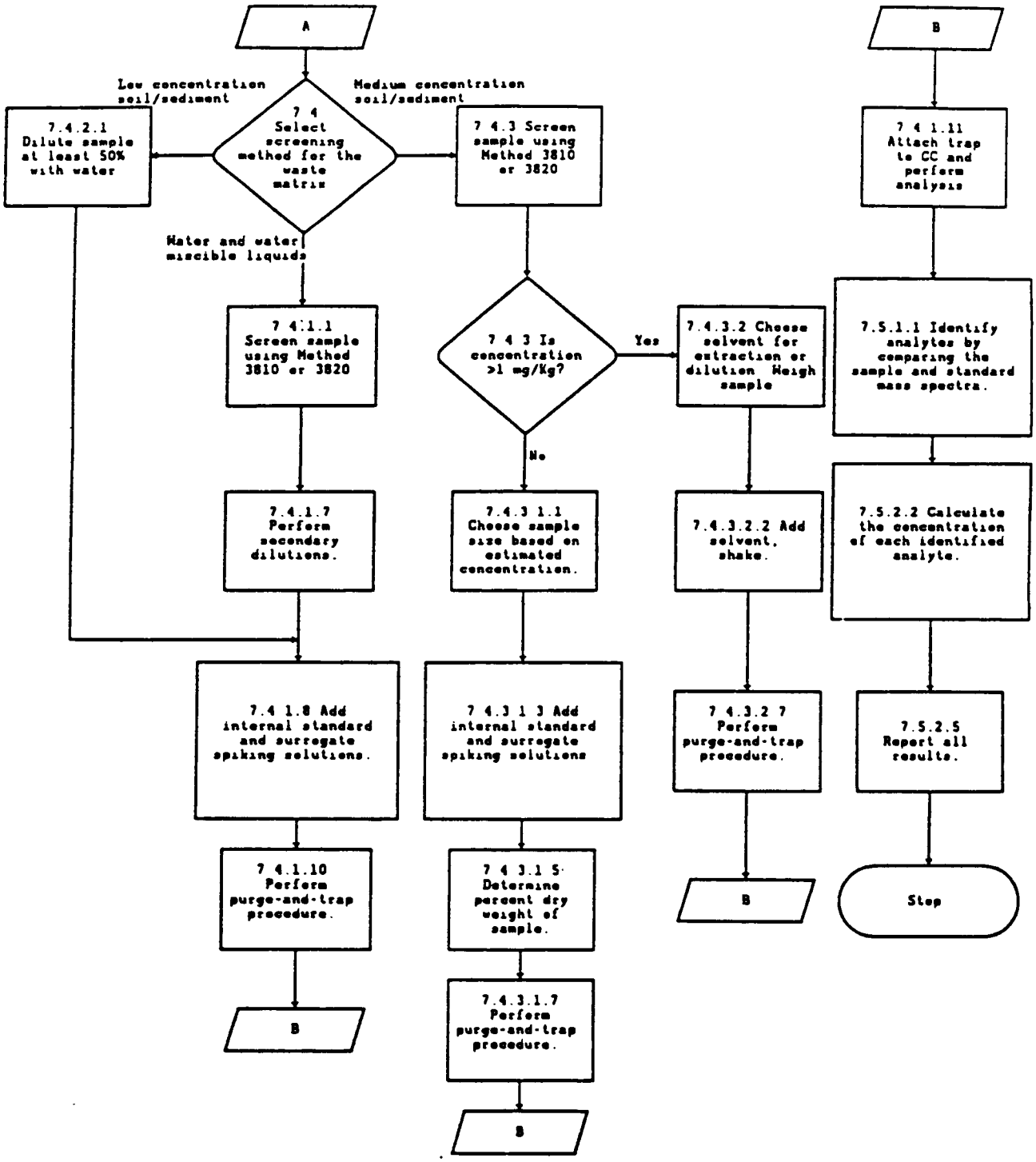

Start
7 1 Select procedure for introducing sample into GC/MS
Direct Injection
7.2 8 Calculate RFs for 5 SPCCs
Purge-and-trap
7 2 1 Set GC/MS operating conditions
7 2 4 Connect purge-and-trap device to GC
7 2 6 Perform purge-and-trap analysis
7.3 Perform daily calibration using SPCCs and CCCs.
A


A
Low concentration soil/sediment
Medium concentration soil/sediment
7.4 Select screening method for the waste matrix
7.4.2.1 Dilute sample at least 50% with water
7.4.3 Screen sample using Method 3810 or 3820
Water and water miscible liquids
7.4.1.1 Screen sample using Method 3810 or 3820
7.4.3 Is concentration >1 mg/Kg?
Yes
No
7.4.3.2 Choose solvent for extraction or dilution Weigh sample
7.4.1.7 Perform secondary dilutions.
7.4.3.1.1 Choose sample size based on estimated concentration.
7.4.3.2.2 Add solvent, shake.
7.4.1.8 Add internal standard and surrogate spiking solutions.
7.4.3.1.3 Add internal standard and surrogate spiking solutions
7.4.3.2.7 Perform purge-and-trap procedure.
7.4.1.10 Perform purge-and-trap procedure.
7.4.3.1.5 Determine percent dry weight of sample.
B
7.4.3.1.7 Perform purge-and-trap procedure.
B
B
7.4.1.11 Attach trap to GC and perform analysis
7.5.1.1 Identify analytes by comparing the sample and standard mass spectra.
7.5.2.2 Calculate the concentration of each identified analyte.
7.5.2.5 Report all results.
Stop

CTL032295

2. Aldehydes EPA - To5

METHOD TO5 Revision 1.0
April, 1984

METHOD FOR THE DETERMINATION OF ALDEHYDES AND KETONES IN AMBIENT AIR USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1. Scope

1.1 This document describes a method for determination of individual aldehydes and ketones in ambient air. With careful attention to reagent purity and other factors the method can detect most monofunctional aldehydes and ketones at the 1-2 ppbv level.

1.2 Specific compounds for which the method has been employed are listed in Table 1. Several studies have used the same basic method, with minor procedural differences, for analysis of ambient air (1-3).

2. Applicable Documents

2.1 ASTM Standards:
D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis (s)

2.2 Other Documents
Ambient air studies (1-3).
U.S. EPA Technical Assistance Document (4)

3. Summary of Method

3.1 Ambient air is drawn through a midget impinger containing 10 mL of 2N HCl/0.05% 2,4-dinitrophenylhydrazine (DNPH reagent) and 10 mL of isooctane. Aldehydes and ketones readily form stable 2,4-dinitrophenylhydrazones (DNPH derivatives).

3.2 The impinger solution is placed in a screw-capped vial having a teflon-lined cap and returned to the laboratory for analysis. The DNPH derivatives are recovered by removing the isooctane layer, extracting the aqueous layer with 10 mL of 70/30 hexane/methylene chloride, and combining the organic layers.

3.3 The combined organic layers are evaporated to dryness under a steam of nitrogen and the residue dissolved in methanol.

3.4 The DNPN derivatives are determined using reversed phase HPLC with an ultraviolet (UV) adsorption detector operated at 370 nm.

4. Significance

4.1 Aldehydes and ketones are emitted into the atmosphere from chemical operations and various combustion sources. In addition, several of these compounds (e.g. formaldehyde and acetaldehyde) are produced by photochemical degradation of other organic compounds. Many of these compounds are acutely toxic and/or carcinogenic, thus requiring their determination in ambient air in order to assess human health impacts.

4.2 Conventional methods for aldehydes and ketones have generally employed colorimetric techniques wherein only one or two compounds are detected, or the sum of numerous compounds is determined. The method described herein provides a means for specifically determining a wide variety of aldehydes and ketones at typical ambient concentrations.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(5). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

6.1 The only significant interferences in the method are certain isomeric aldehydes or ketones which may be unresolved by the HPLC system. Such interferences can often be overcome by altering the separation conditions (e.g. using alternate HPLC columns or mobile phase compositions).

6.2 Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The reagent must be prepared within 48 hours before use and must be stored in an uncontaminated environment before and after sampling to minimize blank problems. Acetone contamination is apparently unavoidable. Consequently, the method cannot be used to accurately measure acetone levels except in highly contaminated environments.

7. Apparatus

7.1 Isocratic HPLC system-consisting of high pressure pump, injection valve, Zorbax ODS column (25 cm x 4.6 mm ID), variable wavelength UV detector, and data system or stripchart recorded. See Figure 3.

7.2 Sampling system-capable of accurately and precisely sampling 100-1000 mL/minute of ambient air. See Figure 1.

7.3 Stopwatch

7.4 Friction top metal can e.g. one-gallon (paint can) - to hold DNPH reagent and samples

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional)

7.7 Analytical balance - 0.1 mg sensitivity

7.8 Reciprocating shaker

7.9 Midget impingers - jet inlet type - 25 mL volume.

7.10 Ice bath - for cooling impingers during sampling.

7.11 Nitrogen evaporator with heating block - for concentrating samples

7.12 Suction filtration apparatus - for filtering HPLC mobile phase.

7.13 Volumetric flasks - 100 mL and 500 mL.

7.14 Pipettes - various sizes, 1-10 mL.

7.15 Helium purge line (optional) - for degassing HPLC mobile phase.

7.16 Erlenmeyer flask, 1-liter - for preparing HPLC mobile phase.

7.17 Graduated cylinder, 1 liter - for preparing HPLC mobile phase.

7.18 Microliter syringe, 10-25 µL - for HPLC injector.

8. Reagents and Materials

8.1 Bottles, 10 oz. glass, with teflon-lined screw cap - for storing DNPH reagent.

8.2 Vials, 50 mL, with teflon-lined screw cap - for holding samples and extracts.

8.3 Disposable pipettes and bulbs.

8.4 Granular charcoal.

8.5 Methanol, hexane, methylene chloride, isooctane - distilled in glass or pesticide grade.

8.6 2,4-Dinitrophenylhydrazine - highest purity available (20% moisture).

8.7 Nitrogen, compressed gas cylinder - 99.99% purity for sample evaporation.

8.8 Polyester filters, 0.22 µm - Nuclepore or equiv.

8.9 DNPH derivatives of the components of interest - synthesized from DNPH and neat aldehydes according to reference (7). Recrystallized from ethanol before use.

9. Preparation of DNPH Reagent

9.1 Each batch of DNPH reagent should be prepared and purified within 48 hours of sampling, according to the procedure described in this section.

9.2 Two hundred and fifty milligrams of solid 2,4-dinitrophenylhydrazine and 90 mL of concentrated hydrochloric acid are placed into a 500 mL volumetric flask and the flask is filled to the mark with reagent water. The flask is then inverted several times or sonified until all of the solid material has dissolved.

9.3 Approximately 400 mL of the DNPH reagent is placed in a 16 ounce glass screw-capped bottle having a teflon-lined cap. Approximately 50 mL of a 70/30 (V/V) hexane/methylene chloride mixture is added to the bottle and the capped bottle is shaken for 15 minutes on a reciprocating shaker. The organic layer is then removed and discarded by decanting as much as possible and using a disposable pipette to remove the remaining organic layer.

9.4 The DNPH reagent is extracted two more times as described in 9.3. The bottle is then tightly capped, sealed with teflon tape, and placed in a friction top can (paint can) containing a 1-2 inch layer of granulated charcoal. The bottle is kept in the sealed can prior to use.

9.5 A portion of the DNPH reagent is analyzed using the procedure described in Section 11 prior to use in order to ensure that adequate background levels are maintained.

10. Sampling

10.1 The sampling apparatus is assembled and should be similar to that shown in Figure 1. EPA Method 6 uses essentially the same sampling system (8). All glassware (e.g. impingers, sampling bottles, etc.) must be thoroughly rinsed with methanol and oven dried before use.

10.2 Prior to sample collection the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. In general flow rates of 100-1000 mL/minute are useful. Flow rates greater than ~1000 mL/minute should not be used because impinger collection efficiency may decrease. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the entire system is sealed. ASTM Method D3686 describes an appropriate calibration scheme not requiring a sealed flow system downstream of the pump.

10.3 Ideally a dry gas meter is included in the system to record total flow. If a dry gas meter is not available the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours the flow rate should be measured at intermediate points during the sampling period. Ideally a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

10.4 To collect an air sample two clean midget impingers are loaded with 10 mL of purified DNPH reagent and 10 mL of isooctane. The impingers are connected in series to the sampling system and sample flow is started. The following parameters are recorded on the data sheet (see Figure 3 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotometer setting, DNPH reagent batch number, and dry gas meter and pump identification numbers.

10.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total flow should not exceed ~80 liters. The operator must ensure that at least 2-3 mL of isooctane remains in the first impinger at the end of the sampling interval (i.e. for high ambient temperatures lower sampling volumes may be required).

10.6 At the end of the sampling period the parameters listed in 10.4 are recorded and the sample flow is stopped. If a dry gas meter is not used the flow rate must be checked at the end of the sampling interval. If the flow rate at the beginning and end of the sampling period differ by more than 15% the sample should be marked as suspect.

10.7 Immediately after sampling the impingers are removed from the sampling system. The contents of the first impinger are emptied into a clean 50 mL glass vial having a teflon-lined screw cap. The first impinger is then rinsed with the contents of the second (backup) impinger and the rinse solution is added to the vial. The vial is then capped, sealed with teflon tape and placed in a friction top can containing 1-2 inches of granular charcoal. The samples are stored in the can, refrigerated until analysis.

10.8 If a dry gas meter or equivalent total flow indicator is not used the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 \ldots . Q_N}{N}$$

where

Q_A = Average flow rate in mL/minute.

$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at the beginning, end, and intermediate points during sampling.

N = Number of points averaged.

10.9 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1)Q_A}{1000}$$

V_m = Total volume sampled in liters at measured temperature and pressure

T_2 = Stop time

T_1 = Start time ($T_2 - T_1$ given in minutes)

11. Sample Analysis

11.1 Sample Preparation

11.1.1 The samples are returned to the laboratory in 50 mL screw-capped glass vials. To recover the DNPH derivatives the following procedure is employed.

11.1.2 The vials are shaken in a horizontal position on a reciprocating shaker for 10 minutes. The vials are then removed from the shaker and the isooctane layer is removed and placed in a second clean 50 mL screw-capped glass vial using a disposable pipette.

11.1.3 The remaining aqueous layer is extracted with 10 mL of 70/30 (V/V) hexane/methylene chloride in the same manner as described in 11.1.2. The organic layer is removed and combined with the isooctane extract.

11.1.4 The combined organic extracts are then concentrated to dryness at 40°C under a steam of pure nitrogen. When the sample just reaches dryness the vial is removed from the nitrogen stream and a measured volume (2-5 mL) of methanol is added to the vial. The vial is tightly capped and stored refrigerated until analysis.

11.2 HPLC Analysis

11.2.1 The instrument is assembled and calibrated as described in Section 12. Prior to each analysis the detector baseline is checked to ensure stable operation.

11.2.2 A 5-25 µL aliquot of the sample, dissolved in methanol, is drawn into a clean HPLC injection syringe. The sample injection loop is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection and the point of injection is marked on the stripchart recorder.

11.2.3 After approximately one minute, the injection valve is returned to "load" position and the syringe and valve are flushed with methanol in preparation for the next sample analysis.

11.2.4 After elution of the last component of interest the acquisition is terminated and the component concentrations are calculated as described in Section 13.

11.2.5 After a stable baseline is achieved the system can be used for further sample analyses as described above.

11.2.6 If the concentration of a component exceeds the linear range of the instrument the sample should be diluted with methanol, or a smaller volume can be injected onto the HPLC.

12. HPLC Assembly and Calibration

12.1 The HPLC system is assembled as shown in Figure 3. The typical chromatographic performance and operating parameters are shown in Figure 4.

12.2 Mobile phase is prepared by mixing 800 mL of methanol and 200 mL of reagent water. This mixture is filtered through a 0.22 µm polyester membrane filter in an all glass and teflon suction filtration apparatus. The filtered mobile phase is degassed by purging with helium gas for 10-15 minutes (~ 100 mL/minute) or by heating to ~60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (~ 50 psi) or short length (6-12 inches) of 0.01 inch I.D. teflon tubing should be placed after the detector to further eliminate mobile phase outgassing.

12.3 The mobile phase is placed in the HPLC solvent reservoir and the pump flow is set at 1 mL/minute and allowed to pump for 20-30 minutes prior to the first analysis. The detector is switched on at least 30 minutes prior to the first analysis and the detector output is displayed on a stripchart recorder or similar output device at a sensitivity of .008

absorbance units full scale (AUFS). Once a stable baseline is achieved the system is ready for calibration.

12.4 Calibration standards are prepared in methanol from the solid DNPH derivatives. Individual stock solutions of ~ 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of methanol. These individual solutions are used to prepare calibration standards containing all of the derivatives of interest at concentrations of 0.1 - 10 mg/L, which spans the concentration of interest for most ambient air work.

12.5 All calibration runs are performed as described for sample analyses in Section 11. Before initial use the operator should inject a series of calibration standards (at least three levels) spanning the concentration range of interest. Using the UV detector, a linear response range of approximately 0.1 to 10 mg/L should be achieved, for ~ 10 uL injection volumes. Linear response is indicated where a correlation coefficient of a least 0.999 for a linear least squares fit of the data (concentration versus area response) is obtained.

12.6 Once linear response has been documented an intermediate concentration standard near the anticipated levels for each component, but at least 10 times the detection limit, should be chosen for daily calibration. The response for the various DNPH components should be within 10% day to day. If greater variability is observed more frequent calibration may be required to ensure that valid results are obtained.

12.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_c = \frac{C_c \times V_I}{R_c}$$

where

RF_c = response factor for the component of interest in nanograms injected/response unit (usually area counts).

C_c = concentration of component in the daily calibration standard (mg/L).

V_I = volume of calibration standard injected (µL).

R_c = response for component of interest in calibration standard (area counts).

13. Calculations

13.1 The volume of air sampled is often reported uncorrected for atmospheric conditions (i.e. under ambient conditions). However, the value can be adjusted to standard conditions (25°C and 760 mm pressure) using the following equation:

$$V_S = V_m \times \frac{P_A}{760} \times \frac{298}{273 + T_A}$$

where

V_S = total sample volume at 25°C and 760 mm Hg pressure (liters).

V_m = total sample volume under ambient conditions (liters). Calculated in 10.9 or from dry gas meter reading.

P_A = ambient pressure (mmHg).

T_A = ambient temperature (°C).

13.2 The concentration of each aldehyde (as the DNPH derivative is calculated for each sample using the following equation:

$$W_d = RF_c \times R_d \times \frac{V_E}{V_I}$$

where

W_d = total quantity of derivative in the sample (μg).

RF_c = response factor calculated in 12.7

R_d = response for component in sample extract (area counts or other response units).

V_E = final volume of sample extract (mL).

V_I = volume of extract injected onto the HPLC system (μL).

13.3 The concentration of aldehyde in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \text{ (or } V_s)} \times \frac{MW_A}{MW_d} \times 1000$$

where

C_A = concentration of aldehyde in the original sample (ng/L).

V_m or V_s are as specified in Section 13.1.

MW_A and MW_d are the molecular weights (g/mole) of the aldehyde and its corresponding DNPH derivative, respectively.

13.4 The aldehyde concentrations can be converted to ppbv using the following equation:

$$C_A(\text{ppbv}) = C_A(\text{ng/L}) \times \frac{24.4}{MW_A}$$

where

C_A(ng/L) is calculated using V_s.

14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs).

14.1.1 Each user should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, 2) preparation, purification, storage and handling of DNPH reagent and samples, 3) assembly, calibration and operation of the HPLC system, and 4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

14.2 HPLC System Performance

14.2.1 The general appearance of the HPLC chromatograph should be similar to that shown in Figure 4.

14.2.2 The HPLC system efficiency and peak asymmetry factor should be determined in the following manner. A solution of the formaldehyde DNPH derivative corresponding to at least 20 times the detection limit should be injected with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. The peak asymmetry factor is determined as shown in Figure 5, and should be between 0.8 and 1.8.

14.2.3 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \left(\frac{t_r}{W_{1/2}} \right)$$

where

N = column efficiency, theoretical plates
t_r = retention time of components (seconds)
$W_{1/2}$ = width of component peak at half height (seconds)

A column efficiency of >5,000 should be obtained.

14.2.4 Precision of response for replicate HPLC injections should be ± 10% or less, day to day, for calibration standards. Precision of retention times should be ± 2%, on a given day.

14.3 Process Blanks

14.3.1 Prior to use a 10 mL aliquot of each batch of DNPH reagent should be analyzed as described in Section 11. In general, formaldehyde levels equivalent to >5 ng/L in a 60 liter sample should be achieved and other aldehyde levels should be <1 ng/L.

14.3.2 At least one field blank should be shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the reagent. The same performance criteria described in 14.3.1 should be met for process blanks.

14.4 Method Precision and Accuracy

14.4.1 Analysis of replicate samples indicates a precision of ± 15-20% relative standard deviation can be readily achieved. Each laboratory should collect parallel samples periodically (at least one for each batch of samples) to document their precision in conducting the method.

14.4.2 Precision for replicate HPLC injections should be ± 10% or better, day to day, for calibration standards.

14.4.3 Method accuracy is difficult to assess because of the difficulty in generating accurate gaseous standards. Literature results indicate (1-3) recoveries of 75% or greater are achieved for a broad range of aldehydes. Each laboratory should periodically collect field samples wherein the impinger solution is spiked with a known quantity of the compound of interest, prepared as a dilute methanol solution. Formaldehyde cannot be spiked in this manner and therefore a solution of the DNPH derivative should be used for spiking purposes.

14.4.4 Before initial use of the method each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Recoveries of >70 ± 20% and blank levels of <5 ng/L for formaldehyde and 1 ng/L for the other compounds (assuming a 60 liter air sample) should be achieved.

References

(1) Grosjean, D., Fung, K., and Atkinson, R., "Measurements of Aldehydes in the Air Environment", Proc. Air Poll. Cont. Assoc., Paper 80-50.4, 1980.

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(4) Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air", EPA-600/4-83-027. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

(5) Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis", American Society for Testing and Material, Philadelphia, Pennsylvania, 1983.

(6) Berry, D. A., Holdren, M. W., Lyon, T. F., Riggin, R. M., and Spicer, C. W., "Turbine Engine Exhaust Hydrocarbon Analysis-Interim Report on Task 1 and 2", Report on Contract No. F-08635-82-C-0131, Air Force Engineering and Services Center, Tyndall AFB, Florida, 1983.

(7) Shiner, R., Fuson, R., and Curtin, D., "The Systematic Identification of Organic Compounds", John Wiley and Sons, Inc., 5th ed., New York, 1964.

(8) "Method 6 Determination of SO_2 Emissions from Stationary Sources", Federal Register, Vol. 42., No. 160, August 1977.

TABLE 1. ALDEHYDES AND KETONES FOR WHICH THE METHOD HAS BEEN EVALUATED

Compound	Molecular Weight		Typical Relative Retention Time[a]
	Derivative	Compound	
Formaldehyde	210	30	1.0
Acetaldehyde	224	44	1.3
Acrolein	236	56	1.6
Propanal	238	58	1.7
Acetone	238	58	1.9[b]
Crotonaldehyde	250	70	2.3
Isobutyraldehyde	252	72	2.4
Methyl Ethyl Ketone	252	72	2.8
Benzaldehyde	286	106	3.2
Pentanal	266	86	3.7
o-Tolualdehyde	300	120	4.8
m-Tolualdehyde	300	120	5.1
p-Tolualdehyde	300	120	5.3
Hexanal	280	100	5.7

(a) Using HPLC conditions shown in Figure 4. Formaldehyde = 1.0

(b) Acetone background levels in the reagent prevent its determination in most cases.

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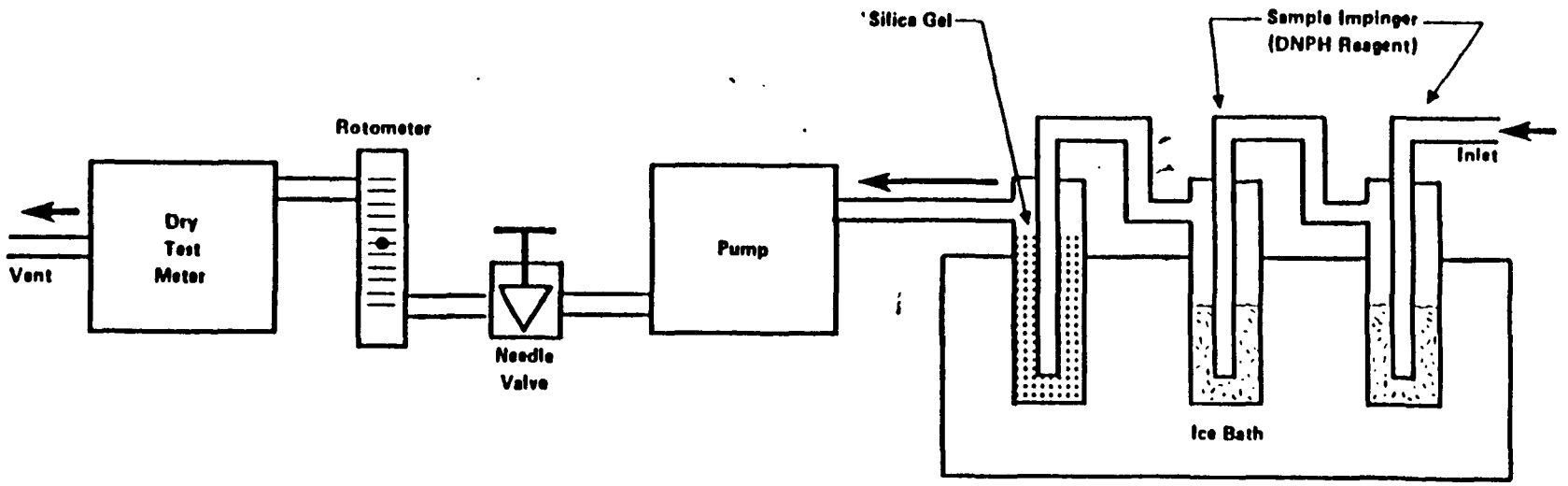

T05-18

FIGURE 1. TYPICAL SAMPLING SYSTEM

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SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT: _____ DATE(S) SAMPLED: _____

SITE: _____ TIME PERIOD SAMPLED: _____

LOCATION: _____ OPERATOR: _____

INSTRUMENT MODEL NO: _____ CALIBRATED BY: _____

PUMP SERIAL NO: _____

SAMPLING DATA

Sample Number: _____

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

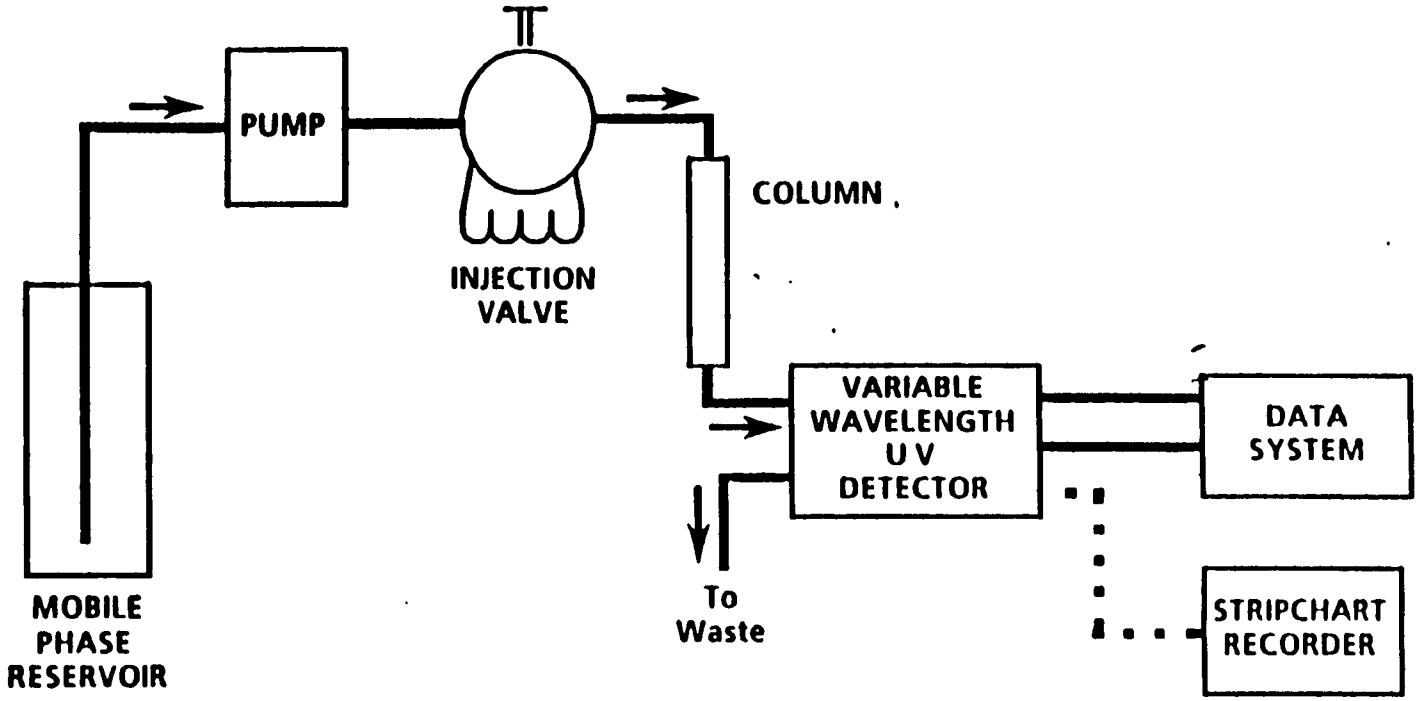
Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ Liters

$$= \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \text{_____ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).
** Use data from dry gas meter if available.

FIGURE 2. EXAMPLE SAMPLING DATA SHEET



T05-20

FIGURE 3. TYPICAL HPLC SYSTEM

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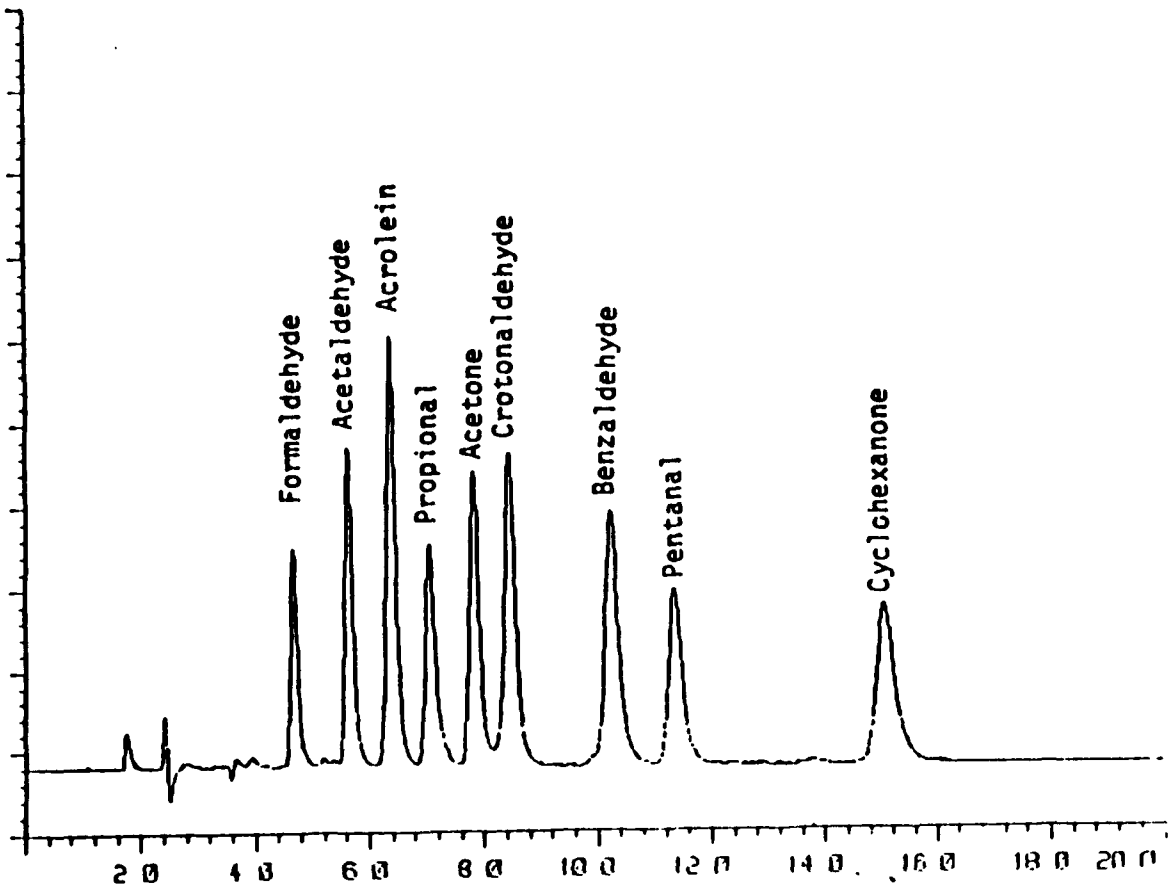

FIGURE 4. TYPICAL HPLC CHROMATOGRAM

Column - Zorbax ODS, 250 x 4.6 mm
Mobile Phase - 80/20 Methanol/H_2O
Flow Rate - 1 mL/Minute
Detector - UV at 370 nm

CTL032317

3. Organic Acids OSHA - 38
Dow Chemical Modifications
(for Formic, Acetic and Acrylic Acids)

ACRYLIC ACID

Method no.:	28
Matrix:	Air
Target concentration:	2 ppm (5.9 mg/m³) see Toxic Effects Section 1.1.2.
Procedure:	Samples are collected by drawing a known volume of air through two XAD-8 sampling tubes connected in series. Samples are desorbed with 1/1 methanol/water and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) detector.
Recommended air volume and sampling rate:	24 L at 0.1 L/min
Detection limit of the overall procedure: (Based on the recommended air volume)	0.014 ppm (0.042 mg/m³)
Reliable quantitation limit:	0.014 ppm (0.042 mg/m³)
Standard error of estimate at the target concentration: (See Table 4.8.1. and Figure 4.8.1.)	7.13%
Status of method:	A sampling and analytical method which has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: April, 1981 Chemist: Kevin Cummins

Organic Methods Evaluation Branch
OSHA Analytical Laboratory
Salt Lake City, Utah

1. General Discussion

1.1. Background

1.1.1. History of procedure

A number of analytical methods are reported in the literature for the analysis of acrylic acid. Although a polarographic method has been publisned, most of these methods involve either gas, liquid, or paper chromatographic techniques (Ref. 5.1.). A direct method of analysis using reverse phase high performance liquid chromatography was developed and used in this study. This method is sensitive, selective, and easy to apply, and it also permits the simultaneous analysis of a number of other acrylate monomers and acrylic acid precursors.

A previous attempt by Brown to use octadecasilane (ODS) based HPLC columns for the analysis of acrylic acid was unsuccessful (Ref. 5.2). It has been recognized in this laboratory for some time that polar molecules of low molecular weight can often be retained and chromatographed in the reverse phase mode using Zorbax ODS packed columns and a high percent of water in the mobile phase. This method, when coupled with an ion suppression technique, proved successful for the retention and separation of acrylic acid. A retention time of approximately six minutes is obtained with a Dupont Zorbax ODS eight-micron, silica packed column and a 96/4, water/acetonitrile mobile phase containing 0.1% by volume of phosphoric acid. The phosphoric acid serves to suppress the ionization of acrylic acid resulting in the retention of the undissociated form of the molecule. Under these conditions acrylic acid is separated from the potential interferences: methacrylic acid, acrylamide, acrolein, acrylonitrile, and acetic acid. Propanoic acid, a saturated precursor of acrylic acid, can be resolved from acrylic acid in a 13 minute analysis at 1 mL/min flow rate using a 0.1% aqueous phosphoric acid mobile base. Acrylic acid, because of its unsaturated nature, is approximately 100 times more sensitive at 210 nm on a weight basis than propanoic acid. This method permits the detection of acrylic acid in the presence of very high levels of propanoic acid.

No published data was found regarding a collection method for acrylic acid from air. In a personal communication, it was reported that silica gel tubes coated with either hydroquinone or p-methoxyhydroquinone were being evaluated as a means of sampling acrylic acid in air (Ref. 5.4.). Both of these compounds are commonly used in the acrylic-

acrylate industry to prevent polymerization of a variety of monomeric substances. No decomposition of acrylic acid was observed in evaluations performed at this laboratory using either hydroquinone treated or untreated silica gel tubes. It should be noted, however, that the standard used in this evaluation contained low, unspecified levels of p-methoxyhydroquinone inhibitor.

Further evaluations indicated that some problems with the retention of acrylic acid on SKC silica gel tubes could arise if air sampling is being performed for an extended time in humid atmospheres. No loss of acrylic acid from the front section of a silica gel tube occurred if 80% relative humidity air was sampled for one hour at a 0.1 L/min flow rate. With longer sampling times, a considerable migration from the front section of the sampling tube was observed. When 46.7 ug of acrylic acid in methanol was spiked into an atmosphere ahead of two silica gel tubes mounted in series, and humid air was drawn through the system for four hours at a 0.1 L/min flow rate, only 15% of the total analyte was retained on the front section of the first silica gel tube. (See Backup Data Section 4.9., Table 4.9.)

Differences in retention efficiency between two different lots of SKC silica gel tubes are also apparent from this data. The recently purchased lot 119 silica gel tubes are less effective in retaining acrylic acid in a humid atmosphere than the older SKC silica gel tubes which do not have a lot number designation. (See Backup Data Section 4.9., Table 4.9.) In addition to silica gel, several other solid sorbent materials were determined to be inadequate for sampling acrylic acid. Low desorption efficiencies were obtained for both charcoal and Porapak T sorbents using various ratios of methanol and water to desorb the spiked tubes. XAD-2 and XAD-4, both non-polar, styrene-divinyl benzene copolymers, gave 100% desorption efficiencies using methanol. However, neither of these two sorbents were totally effective in retaining acrylic acid when humid air was sampled. Six XAD-2 tubes retained an average of only 60% of 120 ug acrylic acid spikes when 80% relative humidity air was drawn through each tube for three hours at a 0.1 L/min flow rate. Although more effective in retaining acrylic acid than XAD-2, the higher surface area XAD-4 sorbent still lost an average of 20% of a 327 ug acrylic acid spike when 80% relative humidity air was drawn through duplicate sample tubes at a 0.1 L/min flow rate for 7.5 hours. Further studies on the collection of acrylic acid from air indicated that the solid sorbent, XAD-8, an acrylic ester polymer, was quite effective in collecting and retaining acrylic acid.

Amounts equivalent to twice the target concentration for a four-hour air sample (327 µg) could be spiked into an atmosphere ahead of the sampling tube and effectively collected and recovered after 80% relative humidity air is drawn through the tube for four hours at 0.1 L/min. No breakthrough onto a second tube mounted in series was observed for acrylic acid collected from a spiked atmosphere, even though 80% relative humidity air was drawn through the system for 8 hours. Similar results were observed when relatively dry laboratory air was sampled. (See Backup Data Section 4.5.)

Although no problems were encountered with the use of XAD-8 in sampling for acrylic acid, it should be noted that there exists a similar polymeric acrylic ester, XAD-7, which because of its higher surface area may be a more effective sampling media for low molecular weight, polar substances. (Ref. 5.5) However, based on the evaluation procedures performed to date, an XAD-8 sorbent packed tube is currently recommended as the sampling media for acrylic acid in air.

1.1.2. Toxic Effects (This section is for information only and should not be taken as the basis of OSHA policy).

Acrylic acid is an acute local irritant. Exposure to its vapors can produce an irritating effect to the skin, eyes, nasal and bronchial passages. (Ref. 5.3.) An exposure of 300 ppm for six hours per day for 20 days resulted in nasal irritation, lethargy, and weight loss in three male and three female rats. A one time, five-hour exposure at saturated conditions (6000 ppm) produced nose and eye irritation, respiratory impairment, and death in one of four exposed rats. (Ref. 5.6.)

A large variability in the LD_{50} value is reported for both rabbits and mice. LD_{50} values for a single skin application ranging from 295 mg/kg bw (body weight) to 950 mg/kg bw are reported in rabbits. Oral LD_{50} values in rats vary from 193 mg/kg bw to 3200 mg/kg bw. (Ref. 5.1.)

In a fetal rat toxicity study conducted by Singh, et al, a dose related increase in the incidences of skeletal abnormalities, reduced birth weights, and resorptions was observed with exposure of pregnant rats to acrylic acid. (Ref. 5.7.) The authors note however, that the effects observed by acrylic acid and several methacrylate esters were not as pronounced as was observed for phthalate ester treated rats in previous studies.

The International Agency for Research in Cancer (IARC) reports that there is no data available regarding the carcinogenic potential of acrylic acid, and recommends study in this area. (Ref. 5.1.)

The recommended target concentration of 2 ppm is based on the results of a recent industry sponsored subchronic-inhalation study of mice and rats. A slight focal degeneration of the olfactory mucosa was observed in a portion of the mice exposed to 5 ppm acrylic acid for 90 days. The 2 ppm level is a suggested TWA exposure limit of the Health and Safety Division of Rohm and Haas. (Ref. 5.8.)

1.1.3. Exposure

Exposure to acrylic acid vapors is primarily confined to production processes since most acrylic acid is used as a precursor in the production of a variety of different acrylates. The alkyl esters of acrylic acid are used to produce a number of products including acrylic fibers, emulsion and solution polymers, and surface coatings. Some of the free acid is used to produce polyacrylic acid, which has industrial uses as a thickener, flocculant, and binder. In 1976 three U.S. companies reported a production of 116.5 million kg of acrylic acid. (Ref. 5.1., 5.3.)

1.1.4. Physical Properties (Ref. 5.9. unless otherwise indicated)

M.W.:	72.06
Solubility:	Miscible in alcohol and ether. Soluble in acetone and benzene.
B.P.:	141°C at 760 mm
Flash Point:	155°F (Ref. 5.10.) Cleveland open cup.
Specific Gravity:	1.05 (20/4°C)
Color:	Clear, colorless (Ref. 5.10.)
Odor:	Pungent, irritating, odor resembling acetic acid. (Ref. 5.10.)
Formula:	$H_2C=CHCOOH$
Synonyms:	Acroleic acid, propenoic acid, ethylene carboxylic acid, propene acid, vinyl formic acid (Ref. 5.11.)

1.2. Limit defining parameters

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 5 ng per injection. This is the amount of analyte which will give a peak whose height is five times the amplitude of the baseline noise. (See Backup Data Section 4.1., Figure 4.2.).

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure is 1 µg per sample (0.014 ppm/0.042 mg/m^3). This is the amount of analyte spiked on the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (See backup data section 4.2.)

1.2.3. Reliable quantitation limit

The reliable quantitation limit is 1 µg per sample (0.014 ppm/0.042 mg/m^3). This is the smallest amount of analyte which can be quantitated within the requirements of 75% recovery and 95% confidence limits of ±25%. (See Backup Data Section 4.3.)

It must be recognized that the reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters. In this case, the limits reported on analysis reports will be based on the operating parameters used during the analysis of the samples.

1.2.4. Sensitivity

The sensitivity of the analytical procedure over a concentration range representing 0.5 to 2 times the target concentration based on the recommended air volume is 12,415 area units per µg/mL. The sensitivity is determined by the slope of the calibration curve. (See Backup Data Section 4.4., Figure 4.4.) The sensitivity will vary somewhat with the particular instrument used in the analysis.

1.2.5. Recovery

The average recovery from spiked samples over the range of 0.5 to 2 times the target concentration is 102%. (See Backup Data Section Table 4.7.) The recovery of analyte from the collection medium must be 75% or greater.

1.2.6. Precision (Analytical method only)

The pooled coefficient of variation obtained from eight replicate determinations of analytical standards at 0.5X, 1X and 2X the target concentration is 0.0085. (See Backup Data Section 4.6.)

1.2.7. Precision (Overall Procedure)

The overall procedure must provide results at the target concentration that are ±25% or better at the 95% confidence level. The average precision at the 95% confidence level for the ambient storage tests is ±14%. (See Backup Data Section Figure 4.8.1. and Table 4.8.1.) This includes an additional ±5% for sampling error.

1.3. Advantages

1.3.1. The sensitivity of the analytical method permits sampling times as short as 15 minutes.

1.3.2. HPLC analysis of acrylic acid is rapid, direct, and sensitive.

1.3.3. Reanalysis of samples is possible.

1.4. Disadvantages

The method has not been field tested at this time.

2. Sampling Procedure

2.1. Apparatus

2.1.1. A personal sampling pump which can be calibrated to within 5% of the recommended 0.1 L/min flow rate while the sampling tubes are in line.

2.1.2. Glass tubes of 4- to 5-cm length with a 4-mm ID and a 6-mm OD are packed with approximately 100 mg of XAD-8 solid sorbent of 16-50 mesh size. Small silanized glass wool plugs on each end of the tube are used to retain the sorbent. These packed XAD-8 tubes are currently available from the laboratory upon request.

April 6,1990

Dr. Rafael Moure
University of Lowell

METHOD FOR THE ANALYSIS OF ORGANIC ACIDS IN AIR

Dear Dr. Moure:

This is a brief description of the organic acids analysis method that we discussed on the phone earlier today. Formic, acetic, and acrylic acids can be collected simultaneously on silica gel tubes (700 mg front/300 mg back), with a flow of about 100 mL/min. The acids are then desorbed using de-ionized water (typically 10 mL), with a 1-hour extraction time (we use a flatbed shaker). We have typically seen recoveries in excess of 90%, but we always run some spiked tubes with our samples to confirm the recoveries.

The extraction solvent is then analyzed using high-performance liquid chromatography (HPLC). The column we have found to work the best is an Aminex HPX-87H ion exclusion column (7.8 x 300 mm), which is manufactured by Bio-Rad Laboratories (32 nd Street, Richmond, CA 94804, catalog # 125-0140). The eluent was 0.01 N H_2SO_4 at a flow of 1 mL/min. U.V. detection at 208 nm was used, which was fed into our laboratory data system. Retention times for formic, acetic and acrylic acids were about 8.4, 9.3, and 11.8 minutes, respectively. The limit of detection for formic and acetic acid was about 1 µg/mL in solution, while the LOD for acrylic acid was about 0.1 µg/mL. With a desorption volume of 10 mL and an air sample volume of about 20 L, the corresponding LOD's in air are around 0.2 ppm and 0.02 ppm, respectively. Some representative chromatograms are shown on the next page. If you have any further questions, please do not hesitate to give me a call.

Sincerely,

Patrick Murphy

Patrick Murphy
H&ES Analytical Chemistry
The Dow Chemical Company
1803 Building
Midland, MI 48674
(517) 636-0629

4. Aerosol Sampling
* Total Dust NIOSH -0600

NUISANCE DUST, RESPIRABLE

METHOD: 0600
ISSUED: 2/15/84

FORMULA: The respirable fraction of the dust mass, as specified by the American Conference of Governmental Industrial Hygienists [1]

OSHA: 5 mg/m³
NIOSH: no standard
ACGIH: 5 mg/m³

PROPERTIES: Penetrates the non-ciliated portions of the lung; quartz less than 1%

SYNONYMS: boron oxide (CAS #1303-86-2) and nuisance dusts [2], including alumina (CAS #1344-28-1), calcium carbonate (CAS #1317-65-3), cellulose (paper fiber; CAS #9004-34-6), glycerin mist (CAS #56-81-5), limestone (CAS #1317-65-3), etc.

SAMPLING

SAMPLER: CYCLONE + FILTER
(10-mm Dorr-Oliver cyclone + tared 5-µm PVC membrane)

FLOW RATE: 1.7 L/min

VOL-MIN: 75 L @ 5 mg/m³
-MAX: 1000 L @ 5 mg/m³

SHIPMENT: routine

SAMPLE STABILITY: indefinitely

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 10 mg/m³ (lab and field)

BIAS: depends on dust size distributions [3]

OVERALL PRECISION (s_r): 0.043 to 0.145 (lab); 0.144 to 0.227 (field) [4]

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHING)

ANALYTE: mass of respirable dust fraction

BALANCE: 0.01 mg sensitivity or better; use same balance before and after sample collection

CALIBRATION: National Bureau of Standards Class M weights

RANGE: 0.3 to 2 mg per sample

ESTIMATED LOD: 0.2 mg per sample

PRECISION: 68 µg with 0.01-mg sensitivity balance [5]

APPLICABILITY: The method measures the mass concentration of any non-volatile respirable dust. Besides inert dusts [1], the method is recommended for respirable coal dust, which has an OSHA PEL = 2.4 mg/m³. The method may be biased where the respirable fraction is defined by the British Medical Research Council's criteria or the MRE horizontal elutriator [4].

INTERFERENCES: Larger than respirable particles (over 10 µm) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in the sample are known to be caused by inverting the cyclone assembly. Heavy dust loadings, charged particles, fibers and water-saturated dusts also interfere with the cyclone's size-selective properties.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported with backup pad in a two-piece, 37-mm cassette filter holder held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm Dorr-Oliver nylon cyclone.
   c. Sampling head holder: this holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Personal sampling pump, 1.7 L/min ± 5%, with flexible connecting tubing.
   NOTE: Pulsation in the pump flow must be within ± 20% of the mean flow.
3. Balance, analytical, with sensitivity of at least 0.01 mg. A more sensitive balance will be necessary for substances with PEL's below 1 mg/m^3.
4. Static neutralizer, e.g., Po-210; replace nine months after the production date.
5. Environmental chamber for balance, e.g., 20 °C ± 0.3 °C and 50% ± 5% RH.
6. Vacuum desiccator.

SPECIAL PRECAUTIONS: None.

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Dry filters and backup pads under vacuum in the vacuum desiccator for at least 15 min.
2. Release the vacuum, remove the desiccator cover, and equilibrate the filters in the environmental chamber for at least 1 hr.
3. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
4. Weigh the filters in the environmental chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing;
   b. Handle the filter with forceps (nylon forceps if further analyses will be done); and
   c. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
5. Place the weighed filters on top of the backup pads in the filter cassette bottom sections and allow to stand an additional 8 to 16 hrs in the environmental chamber.
6. Reweigh the filters. If this tare weight differs by more than 0.01 mg from the first tare weight obtained in step 4 above, discard the filter.
   NOTE: Insert a rod through the outlet hole of the filter cassette bottom section to raise the backup pad and filter so that the filter can be grasped with forceps.
7. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry, and mark with the same number as the backup pad.
8. Remove the cyclone's grit cap and vortex finder before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separati n characteristics of the cyclone might be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
9. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

10. Calibrate each personal sampling pump to 1.7 L/min with a representative sampler in line.
11. Sample at 1.7 L/min for 45 min to 8 hrs (76 to 816 L). Do not exceed 5 mg dust loading on the filter.

    NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit over-sized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

12. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
13. Remove the top and bottom plugs from the filter cassette. Place the filter cassettes in a vacuum desiccator under vacuum for at least 15 min, followed by equilibration for at least 1 hr in the environmental chamber.
14. Remove the filter cassette band, pry open the filter cassette, and remove the filter by inserting a rod in the outlet hole of the filter cassette. Handle the filters very gently by the edge to avoid loss of dust.

    NOTE: If the filter sticks to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

15. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Bureau of Standards Class M weights.
16. Take two to four replicate samples for every batch of field samples for quality assurance on the sampling procedures. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [7] or in the field [8]. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. Calculate precision from these replicates and record s_r on control charts. Take corrective action when the precision is out of control [7].

MEASUREMENT:

17. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloaded, leakage, wet, torn, etc.).

CALCULATIONS:

18. Calculate the concentration of respirable nuisance dust, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) + B}{V} \cdot 10^3, \ mg/m^3$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B = mean change in field blank filter weights between tare and post-sampling (mg) (+ or -).

EVALUATION OF METHOD:

1. Bias. In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust criterion. The theory for calculating bias is developed by Bartley and Breuer [3]. For this method, the bias, therefore, depends on the ACGIH criterion for respirable dust, the cyclone's penetration curve at 1.7 L/min flow rate, and the size distribution of the ambient dust. Based on the cyclone's penetration curves for non-pulsating flow measured with a monodisperse aerosol by Caplan, Doemeny and Sorenson [9], the bias in this method is shown in Figure 1.

   For dust size distributions in the shaded region, the bias in this method lies within the $\pm$ 0.10 criterion established by NIOSH for method validation. Bias larger than $\pm$ 0.10 would, therefore, be expected for many workplace aerosols, especially those with small mass median diameters. However, bias within $\pm$ 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

   Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [10] showed that cyclone samples with pulsating flow can have negative bias as large as -0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias is less than -0.02 for most dust size distributions encountered in the workplace.

   Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [11] have found electrostatic biases as large as -50%, and show that cyclones made with graphite-filled nylon eliminate the problem.

2. Precision. In a recent review [4], the overall cyclone precision is shown to be most sensitive to two factors: the analytical precision and the sampling procedures, particularly the quality control system used in the maintenance and calibration of samplers. Theoretically, the variance for the overall precision is the sum of the variances from the sampling and analysis. The analytical variance depends on the dust loading on the filter. For the dust loading in an 8-hr sample above 1.5 mg/m^3, Bowman, et al. [4] find that the empirically determined sampling error dominates this analytical error.

   Because of the effects of the environment, precision estimates for dust samplers are much more variable than those reported for gas and vapor sampling. In laboratory tests with 0.01 mg sensitivity balances, the overall precision of a single respirable dust sample has relative standard deviations (s_r) from 0.043 to 0.145 over concentrations ranging from 0.5 to 5 mg/m^3. In the laboratory studies where the dust concentrations in the test chamber are more carefully controlled, the estimated s_r is less than 0.091, which is the target precision value for a bias equal to $\pm$ 0.10 in the NIOSH validation criteria.

   In the field tests with 0.01 mg sensitivity balances, precision estimates range from 0.144 to 0.227 over concentrations ranging from 1 to 10 mg/m^3. Whether the larger s_r values in field tests are due to sampler performance or to more inhomogeneous dust concentrations in the field tests cannot be determined from existing data.

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[3] Bartley, D. L. and G. M. Breuer. Analysis and Optimization of the Performance of the 10-mm Cyclone, Am. Ind. Hyg. Assoc. J., 43, 520-528 (1982).

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METHOD WRITTEN BY: Joseph Bowman, Ph.D., CIH, NIOSH/DPSE.

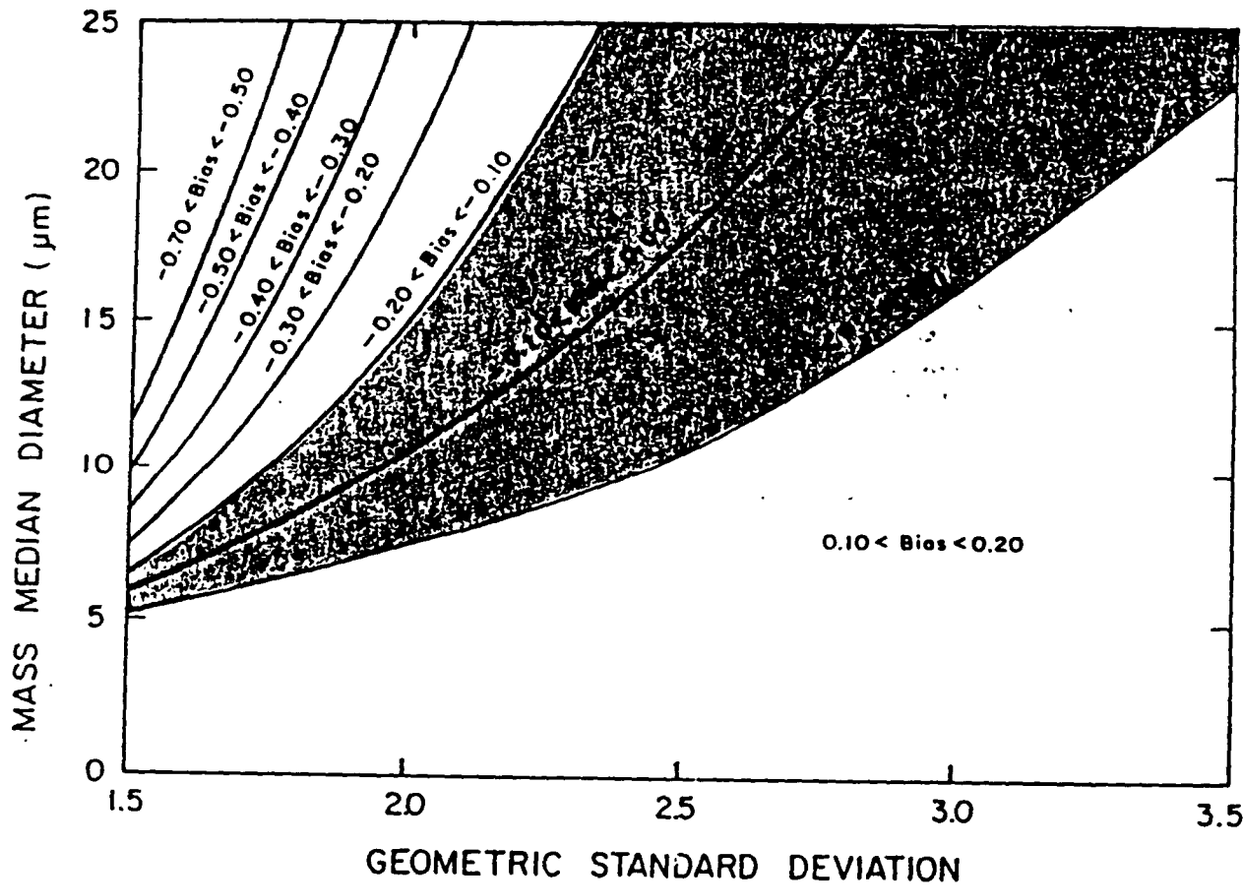

Figure 1. Bias in respirable dust determination.

CTL032333

4. Aerosol Sampling
* Benzene Soluble Particulate NIOSH - 5023

FORMULA: various organic-soluble compounds [1,2,3]
M.W.: various

COAL TAR PITCH VOLATILES

METHOD: 5023
ISSUED: 5/15/85

OSHA: 0.2 mg/m³ (benzene-solubles)
NIOSH: 0.1 mg/m³/10 hr (cyclohexane-solubles) [2,3]
ACGIH: 0.2 mg/m³ (benzene solubles) [4]

PROPERTIES: liquid; d ~1.06 g/mL @ 38 °C; 60 to 85% distills @ ≤355 °C [5]; creosote distills @ 270 to 395 °C [2]

SYNONYMS: benzene-solubles, cyclohexane-solubles, coal tar pitch volatiles (CAS #8007-45-2), creosote from coal tar.

SAMPLING

SAMPLER: FILTER (2-µm, 37-mm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 500 L @ 0.2 mg/m³
-MAX: 2400 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

FIELD BLANKS: 10% (≥2) of samplers

ACCURACY

RANGE STUDIED: not studied

BIAS: unknown

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: GRAVIMETRIC

ANALYTE: organic-solubles (includes anthracene, benzanthracene, benzo(a)pyrene, carbazole, chrysene, phenanthrene, pyrene and others [1,2,3,4])

EXTRACTION: benzene, cyclohexane or other appropriate solvent; ultrasonic 20 min

CALIBRATION: National Bureau of Standards Class M weights

RANGE: 0.1 to 2 mg per sample

ESTIMATED LOD: 0.05 mg per sample [6]

PRECISION (s_r): 0.02 at 1.35 mg [6]; 0.23 for blanks [6]

APPLICABILITY: The working range is 0.1 to 2 mg/m³ for a 1000-L air sample. The method is useful for air monitoring of coke oven emissions, petroleum combustion products such as diesel emissions, and petroleum asphalt fumes. The method may be applied to bulk samples. The method is non-specific and measures all substances in the sample which are soluble in the solvent selected and which can be desorbed from particulate matter present on the filter.

INTERFERENCES: Changes in temperature or humidity during pre- and post-collection weighing affect accuracy. Losses may occur due to volatilization of collected aerosol during or after sampling.

OTHER METHODS: This method modifies and combines P&CAM 217 [7] and the criteria document method [2].

REAGENTS:

1. Solvent: Benzene,* cyclohexane or other solvent, reagent grade.
2. Dichromic acid cleaning solution.
3. Acetone, reagent grade.
4. Hexane.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: PTFE laminated membrane filter, 2-µm pore size, 37-mm diameter (Zeflour, Membrana Inc., Pleasanton, CA or equivalent) backed by a gasket (37 mm OD, 32 mm ID) cut from a cellulose support pad in plastic filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Ultrasonic bath.
4. Microbalance, readable to 1 µg, with NBS Class M weights.
5. Environmental chamber for balance, e.g., 20 °C ±0.3 °C and 50% ±5% relative humidity.
6. Weighing cups, PTFE, 2-mL, approximate tare weight 60 mg, in metal rack.
7. Vacuum oven.
   NOTE: Keep the interior of the vacuum oven dust-free for maximum sensitivity, reproducibility, and accuracy.
8. Forceps.
9. Test tubes, PTFE-lined, screw cap, 13 mm x 100 mm.*
10. Filter, 0.5-µm (Millex-SR, Millipore Corp., Bedford, MA or equivalent).
11. Pipets, 1- and 5-mL.*

*Rinse with distilled water, acetone, and hexane; dry.

SPECIAL PRECAUTIONS: Benzene and coal tar pitch volatiles are suspect carcinogens [1,2,3,4].

SAMPLING:

1. Calibrate each sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample volume of 500 to 2400 L. Do not exceed a filter loading of ca. 2 mg total particulate.
3. Replace caps in cassette and ship to laboratory.

SAMPLE PREPARATION:

4. Transfer filter carefully using forceps to test tube. Add 5.0 mL solvent via pipet. Cap the tube.
   NOTE 1: Cyclohexane is recommended as solvent because of the carcinogenic potential of benzene [2].
   NOTE 2: This extraction is also applicable to bulk samples (ground and sieved to ca. 250 µm). Extract 250 mg bulk sample with 5.0 mL solvent.
5. Place tube upright in beaker containing water to the same level as the liquid in the tube. Place beaker and tube in ultrasonic bath. Sonicate for 20 min.
6. Filter solution through a 0.5-µm filter into a clean, preweighed weighing cup. Discard the filter.
   NOTE: An aliquot of the solution may be taken at this step if other analyses (e.g., polynuclear aromatic hydrocarbons) are to be performed on the sample. Apply the appropriate aliquot factor in calculations.

CALIBRATION AND QUALITY CONTROL:

7. Zero the microbalance on the 1.0 mg range and calibrate per balance manufacturer's directions.
   NOTE: Perform weighings at constant temperature and relative humidity.
8. Process three blank filters through the extraction and measurement procedures.

MEASUREMENT:

9. Transfer via pipet a 1.0-mL aliquot of sample extract to a preweighed weighing cup.
10. Place weighing cup in vacuum oven preheated to 40 °C. Apply vacuum until pressure in the oven is 7 to 27 kPa (50 to 200 mm Hg). Allow solvent to evaporate for 2 hrs. Releas vacuum by slowly opening release valve which has an in-line filter to remove room dust.
11. Equilibrate the weighing cup to the temperature and relative humidity of the balance room for at least 30 min. Weigh the weighing cup to the nearest microgram.

CALCULATIONS:

12. Determine the mass of organic-soluble residue found in the sample, W (µg), and in the average media blank, B (µg).
13. Calculate concentration, C, of organic-solubles in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 5}{V}, \quad mg/m^3.$$

EVALUATION OF METHOD:

Several benzene extracts of samples of aluminum reduction plant emissions were combined to give a solution containing 1.35 mg of benzene-soluble material per sample; nine aliquots of this solution gave residue weights with a relative standard deviation of 0.02. Benzene extracts of six blank filters gave residue weights with a relative standard deviation of 0.23 [7].

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METHOD REVISED BY: B. R. Belinky, NIOSH/DPSE.

CTL032337

4. Aerosol Sampling
* Lead NIOSH - 7082

FORMULA: Pb

LEAD

METHOD: 7082
ISSUED: 2/15/84

M.W.: 207.19 (Pb); 223.19 (PbO)

OSHA: 0.05 mg/m³
NIOSH: 0.05 mg/m³ [1]
ACGIH: 0.15 mg/m³; STEL 0.45 mg/m³

PROPERTIES: soft metal;
d 11.3 g/cm³; MP 327.5 °C;
valences +2, +4 in salts

SYNONYMS: vary depending upon the chemical form (elemental lead and lead compounds except alkyl lead); CAS #1317-36-8 (PbO); CAS #7439-92-1 (Pb).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 200 L @ 0.05 mg/m³
-MAX: 1200 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.13 to 0.4 mg/m³ [2];
0.15 to 1.7 mg/m³ (fume) [3]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.072 [2];
0.068 (fume) [3]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: lead

ASHING: conc. HNO_3, 6 mL; 140 °C

FINAL SOLUTION: 10% HNO_3, 10 mL

FLAME: air-acetylene, oxidizing

WAVELENGTH: 283.3 nm

BACKGROUND CORRECTION: D_2 or H_2 lamp

CALIBRATION: Pb^{++} in 10% HNO_3

RANGE: 10 to 200 µg per sample [3,8]

ESTIMATED LOD: 2.6 µg per sample [9]

PRECISION (s_r): 0.03 [2]

APPLICABILITY: The working range is 0.025 to 0.5 mg/m³ for a 400-L air sample. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.

OTHER METHODS: This method combines and replaces P&CAM 173 [8] and S341 [7,9] for lead. Method 7300 (ICP-AES) is an alternate analytical method.Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [4] and the lead criteria document [1]; P&CAM 191 (ASV) [5]; and P&CAM 214 (graphite furnace-AAS) [6].

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 10% (w/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O_2 (w/w), reagent grade.
4. Calibration stock solution, 1000 µg Pb/mL. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable ≥ one year.
5. Air, compressed, filtered.
6. Acetylene.
7. Distilled or deionized water.

EQUIPMENT:

1. Sampler: Cellulose ster filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic Absorption Spectrophotometer with an air-acetylene burner head.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for air and acetylene.
6. Beakers, Phillips, 125 mL, or Griffin, 50 mL with watchglass covers.*
7. Volumetric flasks, 10- and 100-mL.*
8. Assorted volumetric pipets as needed.*
9. Hotplate, surface temperature 140° C.
10. Bottles, polyethylene, 100-mL.

*Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 hrs for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [9]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3, and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.
   NOTE: If PbO_2 is not present in the sample, the 30% H_2O_2 need not be added [3,9].
5. Heat on hotplate (140 °C) until most of the acid has evaporated.
6. Repeat two more times using 2 mL conc. HNO_3 and 1 mL 30% H_2O_2 each time.
7. Heat on 140 °C hotplate until a white ash appears.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO_3. Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. HNO_3.
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.
    NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M Na_2EDTA to each flask before dilution to volume: $CO_3^{=}$, $PO_4^{\equiv}$, I^-, F^-, CH_3COO^-. If Ca^{++} or $SO_4^{=}$ are present in 10-fold excess, make all standards and samples 1% (w/w) in La^{+++} [8].

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards covering the range 1 to 20 µg Pb/mL (1 t 200 µg Pb per sampl) by adding aliquots f calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% HNO_3. Store the working standards in polyethylene bottles and prepare fresh weekly.
12. Analyze the working standards together with the blanks and samples (steps 17 and 18).
13. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
14. Aspirate a standard for every 10 samples to check for instrument drift.
15. Check recoveries with at least one spiked media blank per 10 samples.
16. Use method of additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.
    NOTE: An alternate wavelength is 217.0 nm [10]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D_2 or H_2 continuum background correction mandatory at that wavelength.
18. Aspirate standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of lead in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S241 [7] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m^3 for a 180-L air sample, using generated atmospheres of lead nitrate [2]. Recovery in the range 18 to 72 µg Pb per sample was 98%, and collection efficiency of 0.8-µm mixed cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 µg Pb per sample gave the results [3,9]:

Species	Digestion Method	Analytical Recovery, %
Pb metal	HNO_3 only	92 ± 4
Pb metal	HNO_3 + H_2O_2	103 ± 3
PbO	HNO_3 only	93 ± 4
PbS	HNO_3 only	93 ± 5
PbO_2	HNO_3 only	82 ± 3
PbO_2	HNO_3 + H_2O_2	100 ± 1
Pb in paint*	HNO_3 only	95 ± 6
Pb in paint*	HNO_3 + H_2O_2	95 ± 6

*Standard Reference Material #1579, U.S. National Bureau of Standards.

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 μm [3]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was >97 ± 2%. Overall precision, s_r, was 0.072 for lead nitrate aerosol [2,7] and 0.068 f r Pb fume [3,9].

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[5] Ibid, P&CAM 191.
[6] Ibid, P&CAM 214.
[7] Ibid., V. 3, S341, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[8] Ibid, V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1979).
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[10] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).

METHOD REVISED BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE; S341 originally validated under NIOSH Contract CDC-94-74-45; additional studies under NIOSH Contract 210-79-0058.

5. Hydrochloric Acid NIOSH - 7903

INORGANIC ACIDS

Methods Research Branch

Analytical Method

Analyte:	Inorganic acids (Table I)	Method No.:	P&CAM 339
		Range:	Table I
Matrix:	Air		
		Precision:	0.06-0.10
Procedure:	Silica gel tube collection, eluent desorption, ion chromatography		
Date Issued:	8/18/81		
Date Revised:		Classification:	D (Operational)

1. Synopsis

1.1 A known volume of air is drawn through a silica gel sampling tube to collect the analyte. The samples are desorbed in an aqueous solution of 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 with heat. Solutions of samples and standards are analyzed by means of an ion chromatograph.

2. Working Range, Sensitivity, and Detection Limit

2.1 For H_3PO_4, H_2SO_4, HNO_3, and HBr, the working range is based on a 48-L air sample and on a 15-L air sample for HCl. Refer to Table I.

2.2 The sensitivity is expressed as µg per sample per mm chart deflection at a conductance setting of 10 µmhos full scale.

2.3 With a 10-mL final solution volume and the instrumental parameters stated in the method, the lowest analytically quantifiable level (LAQL) is stated as µg/sample at 10% relative standard deviation. This lower limit may be extended through use of a more sensitive conductivity meter setting.

3. Interferences

3.1 Possible interferences in the method are SO_2 for H_2SO_4 and NO_2 for HNO_3. Their collection potential on silica gel and reduction during desorption have not been investigated.

3.2 Chlorine or hypochlorite ion may interfere with chloride up to 50% of its initial concentration, and bromine may give an interference of approximately 30% of its original concentration as determined from spiked samples. The collection potential of these substances on silica gel has not been investigated.

4. Precision and Accuracy

4.1 The precision is expressed as percent relative standard deviation for the overall sampling and analytical method over the range stated for each acid (Table I).

4.2 The collection efficiencies for each of the acids are based on samples at three concentration levels, 0.2, 1 and 2 times the OSHA permissible exposure limits.

5. Advantages and Disadvantages

5.1 The advantage of ion chromatography over other methods is its capability of separating the ions such that each of the acid anions may be identified and measured in a single sample.

5.2 The method is specific for the acid anions. Different oxidation states of the acids have different retention times, e.g., NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}.

5.3 The sampling device is a solid sorbent collection tube and involves no liquids.

5.4 The sampling device will collect five inorganic acids in both particulate and vaporous forms.

5.5 Because identification is based on retention time, interferences may not be easily identified.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Personal sampling pumps capable of operation at 0.2 L/min and calibrated to an accuracy of ±5% with a representative sampling tube in line.

6.1.2 Silica gel tubes. 7-mm o.d./4.8 mm i.d. glass tubes approximately 10 cm in length packed with 400 mg of 20/40 mesh washed silica gel in the front section and 200 mg in the backup section. Polyurethane foam plugs are placed between the sorbent sections and at the end. The front section of silica gel is held in place with a 5-mm diameter plug of thick glass fiber filter.

The silica gel is washed by the following procedure: Approximately a 200-mL volume of silica gel is placed in a 1-L beaker. 500-600 mL of deionized water is added slowly with stirring. When the exothermal reaction has subsided, the silica gel is heated in a 100 °C water bath for approximately 30 minutes with occassional stirring, decanted, and rinsed four to five times with deionized water. It is heated again in deionized water for 15-30 minutes, decanted, and rinsed thoroughly with deionized water. The silica gel is then dried overnight in a 100 °C oven until free flowing. If a blank of the silica gel shows any impurities, the washing procedure is repeated. Approximately 90% of the resulting silica gel will be 20/40 mesh.

6.1.3 Barometer.

6.1.4 Thermometer.

6.1.5 Hygrometer.

6.1.6 Stopwatch.

6.2 Ion chromatograph with a standard or fast run anion precolumn and separator column, a standard suppressor column, and conductimetric detector (Dionex Corp., Sunnyvale, CA, or equivalent).

6.3 Strip chart recorder.

6.4 Electronic integrator or some other suitable means of determining peak height (optional).

6.5 Centrifuge tubes, 15-mL, graduated.

6.6 Micropipettes with disposable tips for preparing standards.

6.7 Volumetric flasks, 100-mL and 25-mL or other convenient sizes for preparing standard solutions.

6.8 Syringes, 10-mL, polyethylene with luer tip.

6.9 In-line filter holders (Swinnex-type) with 25-mm membrane filters, 0.8 µm pore size, or Acrodisc in-line filters.

6.10 Parafilm.

6.11 Water bath maintained at 100 °C.

7. Reagents

Whenever possible, reagents used should be ACS reagent grade or better.

7.1 Deionized, filtered water. Conductivity grade deionized water with specific conductance of 10 µmho/cm or less is needed for the preparation of eluents and other solutions used in the ion chromatograph. The water must be filtered before use to avoid plugging valves in the chromatograph.

7.2 Silica gel, 3/8 mesh, grade 01, thoroughly washed with deionized water (Sec. 6.1.2).

7.3 Sodium carbonate, Na_2CO_3.

7.4 Sodium bicarbonate, $NaHCO_3$.

7.5 Potassium chloride, KCl.

7.6 Monopotassium phosphate, KH_2PO_4.

7.7 Potassium sulfate, K_2SO_4.

7.8 Sodium nitrate, $NaNO_3$.

7.9 Sodium bromide, NaBr.

7.10 Stock standard solutions (1000 µg/mL). Dissolve salt in deionized, filtered water in a 100-mL volumetric flask, and dilute to volume with deionized, filtered water.

7.10.1 Chloride (1000 ppm Cl^-). Dissolve 0.2103 g KCl/100 mL.

7.10.2 Phosphate (1000 ppm PO_4^{3-}). Dissolve 1.433 g KH_2PO_4/100 mL.

7.10.3 Sulfate (1000 ppm SO_4^{2-}). Dissolve 0.1814 g K_2SO_4/100 mL.

7.10.4 Nitrate (1000 ppm NO_3^-). Dissolve 0.13707 g $NaNO_3$/100 mL.

7.10.5 Bromide (1000 ppm Br^-). Dissolve 0.1288 g NaBr/100 mL.

7.11 Eluent (0.003 M $NaHCO_3$/0.0024 M Na_2CO_3). Dissolve 1.008 g $NaHCO_3$ and 1.0176 g Na_2CO_3 in 4 L of deionized, filtered water.

8. Procedure

8.1 Cleaning of Equipment. Glassware and plasticware should be washed in detergent and thoroughly rinsed with deionized water. Acid cleaning is not recommended.

8.2 Collection and Shipping of Samples

8.2.1 Each personal sampling pump must be calibrated with a representative collection tube in line to assure accurately known sample volumes.

8.2.2 Immediately before sampling, break the ends of the collection tube to provide an opening of at least one half of the internal diameter of the tube.

8.2.3 Insert the tube in the sampling device with the glass fiber filter plug at the inlet. Place tube in a vertical position during sampling to minimize channeling through the sorbent.

8.2.4 Collect the sample at 0.2 Lpm. The air being sampled should not pass through any hose or tubing before entering the collection tube. A sample size of 48-L is recommended.

8.2.5 Record the temperature, relative humidity, and pressure of the air being sampled. If the pressure reading is not available, record the elevation.

8.2.6 After sampling, label the collection tubes appropriately and cap the ends with plastic caps.

8.2.7 With each batch of up to 10 samples submit one blank collection tube which has been subjected to the same handling except that no air has been drawn through it.

8.3 Analysis of Samples

8.3.1 Place the silica gel and glass fiber plug from the front section of the collection tube into a 15-mL graduated centrifuge tube. (The backup section is analyzed separately.)

8.3.2 Add 5-6 mL of eluent solution (Section 7.7) and heat in a 100 °C water bath for 10 minutes. Allow to cool and dilute to a 10-mL volume with eluent. Cover with Parafilm and shake vigorously.

8.3.3 Pour the contents into a 10-mL plastic syringe fitted with an in-line filter and collect the filtrate in a second syringe or autosampler vial.

8.3.4 Inject 100-µL aliquots of the filtered sample into the ion chromatograph and record the sample identity and instrumental conditions. Typical operating conditions for inorganic acids are:

Eluent:	0.003 M $NaHCO_3$/0.0024 M Na_2CO_3
Flow Rate:	138 mL/hr (30% pump capacity)
Columns:	Standard Anion precolumn
	Standard Anion separator
	Standard Anion suppressor
Conductivity Meter Setting:	10 µmho full scale
Injection Volume:	100 µL
Recorder Speed:	30 cm/hr.

8.3.5 Measure and record peak height of each peak. The use of peak height is recommended over peak area for ion chromatography.

9. Calibration and Standardization

9.1 From the 1000 µg/mL acid stock solutions in Section 7.10, prepare mixed working standards in the concentrations of 0.5, 1, 2, 5, 10, 15, and 20 µg/mL in eluent solution (Section 7.7). The use of eluent eliminates the water dip in the chromatogram which occurs immediately before the elution of the chloride peak. These standards should be prepared fresh weekly and stored in polyethylene bottles.

9.2 With each set of samples analyzed, a complete calibration curve should be constructed. Plot peak height versus concentration.

10. Calculation

10.1 Read the concentration of each sample and blank from the calibration curve obtained in Section 9.2. Calculate the net concentration of each acid anion found

$$C_1 = C_2 - B$$

where: C_1 = acid anion concentration from air sample (µg/mL)
C_2 = total acid anion found on silica gel tube (µg/mL)
B = acid anion concentration from blank (µg/mL).

10.2 Calculate the concentration of acid in air sample.

10.2.1 Acid concentration in mg/m^3

$$C_A = \frac{F\ C_1\ D}{V}$$

where: C_A = acid concentration in air (mg/m^3)
C_1 = anion concentration in solution (µg/mL)
D = final volume of desorbed sample (mL)
V = volume of air sampled (L)
F = factor for converting anion to acid.

Acid	F
H_3PO_4	1.032
H_2SO_4	1.021
HNO_3	1.016
HBr	1.0125
HCl	1.028

10.2.2 Vapor-forming acid concentration in ppm. One gram molecular weight of a gas occupies 24.45 L at 25 °C and 760 mm Hg pressure

$$C_B = K \times C_A \times \frac{760 \times T}{298 \times P}$$

where: C_B = acid concentration in air (ppm)
C_A = acid concentration in air (mg/m^3)
T = absolute temperature at which the sample was taken (°K = °C + 273)
P = air pressure at which the sample was taken (mm Hg).

$$K = \frac{\text{vol. acid}}{\text{g-mol. wt. acid}}$$

Acid	K
HNO_3	0.3881
HBr	0.3022
HCl	0.6699

11. References

11.1 Cassinelli, M. E. and Taylor, D. G., Monitoring for Airborne Inorganic Acids, Symposium on Measurement and Control of Chemical Hazards in the Workplace Environment, ACS Symposium Series (1980).

11.2 Cassinelli, M. E., Ion Chromatographic Determination of Hydrogen Chloride - Hydrogen Bromide Mixtures, IMDS, MRB, Technical Report (1979).

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Appendix D

Calibration Sampling Equipment

APPENDIX D

Calibration of Sampling Equipment

(OSHA Procedure (8), Industrial Hygiene OSHA Technical Manual, 1990)

1. Procedures for Calibration of Pump-Collector Tube System (Organic Vapor Collection) --Using Electronic Bubble Meter Method:

   (1) Allow the pump to run 5 minutes prior to voltage check and calibration.

   (2) Assemble the charcoal tube holder, using the appropriate tube for the sampling method. Compress charcoal tube by using a mechanical press or other means of applying pressure. Use shrink tape around charcoal tube to cover joints and prevent leakage. If a tube adaptor is using , care should be taken to ensure that it does not come in contact with the back-up pad.

NOTE : When calibrating with a bubble meter , the use of tube adaptors can cause moderate to severe pressure drop at high flow rates in the sampling train, which will affect the calibration result . If adaptors are used for sampling , then they should be used when calibrating.

CAUTION: Nylon adapters can restrict air flow due to plugging over time.Stainlesssteel adapters are preferred.

   (3) Connect the collection device, tubing , pump and calibration apparatus as shown in Figure 1 and 2 charcoal tube and cyclone samplers, respectively.

(4) A visual inspection should be made of all Tygon tubing connections.

(5) Wet the inside of the electronic flow cell with the supplied soap solution by pushing on the button several times.

(6) Turn on the pump and adjust the pump rotameter, if available, to the appropriate flow rate setting.

(7) Press the button on the electronic bubble meter. Visually capture a single bubble and electronically time the bubble . The accompanying printer will automatically record the calibration reading in liters per minute.

(8) Repeat step 7 until two reading are within 5% .

(9) Repeat the procedures described above for all pumps to be used for sampling. The same charcoal tube may be used for all calibrations involving the same sampling methods.

2. Procedure for Calibration of Pump-Cassette Filter System (Particulate - total dust). --Using Electronic Bubble Meter Method:

(1) Allow the pump to run 5 minutes prior to voltage check and calibration.

(2) Assemble the polystyrene cassette filter holder, using the appropriate filter for the sampling method. Compress cassette by using a mechanical press or other means of applying pressure. Use shrink tape around cassette to cover joints and prevent leakage. If a cassette adaptor is using , care should be taken to ensure that it does not come

in contact with the back-up pad.

NOTE : When calibrating with a bubble meter , the use of cassette adaptors can cause moderate to severe pressure drop at high flow rates in the sampling train, which will affect the calibration result . If adaptors are used for sampling , then they should be used when calibrating.

CAUTION: Nylon adapters can restrict air flow due to plugging over time. Stainless steel adapters are preferred.

(3) Connect the collection device, tubing , pump and calibration apparatus as shown in Figure 1 and 2 cassette and cyclone samplers, respectively.

(4) A visual inspection should be made of all Tygon tubing connections

(5) Wet the inside of the electronic flow cell with the supplied soap solution by pushing on the button several times.

(6) Turn on the pump and adjust the pump rotameter, if available, to the appropriate flow rate setting.

(7) Press the button on the electronic bubble meter. Visually capture a single bubble and electronically time the bubble . The accompanying printer will automatically record the calibration reading in liters per minute.

(8) Repeat step 7 until two reading are within 5% .

(9) Repeat the procedures described above for all pumps to be used for sampling. The same cassette and filter may be used for all calibrations involving the same sampling methods.