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**INVESTIGATION OF
ODOROUS EMISSIONS
FROM A FUEL ETHANOL PLANT**

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April 1989

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INVESTIGATION OF ODOROUS EMISSIONS
FROM A FUEL ETHANOL PLANT

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CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	i
LIST OF TABLES	iii
LIST OF FIGURES	iv
ACRONYMS AND INITIALISMS	v
ABSTRACT	vi
1. INTRODUCTION	1
2. CHARACTERIZATION OF ODOR COMPONENTS	6
2.1 Source Terms	7
2.1.1 Sampling	7
2.1.2 Analysis	16
2.2 Ambient Species	18
2.2.1 Sampling	19
2.2.2 Analysis	23
3. RESULTS AND DISCUSSION	24
3.1 Source Terms	24
3.2 Ambient Species	44
3.3 Discussion	45
4. REFERENCES	48
APPENDIX A--DESCRIPTIONS OF ANALYTICAL METHODS USED	A-1
APPENDIX B--SUMMARY OF METEOROLOGICAL DATA RECORDED BY THE NATIONAL WEATHER SERVICE OFFICE AT SOUTH BEND, INDIANA DURING SAMPLING TRIPS	B-1

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Analysis of samples collected at the NECI evaporator vent	28
2	Summary of analytical results, source term samples	31
3	Analysis of samples collected at the QUAD pilot plant during operation at NECI	42
4	Workplace and ambient air quality standards for specified organic compounds	42

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Location of the New Energy of Indiana (NECI) plant	2
2	Locations of potential odor sources within the NECI plant	8
3	Diagram of sampling train for source term emissions sampling	9
4	Configuration of the QUAD pilot plant system and associated sampling points	13
5	Diagram of sampling train for ambient air quality samples	21
6	Decrease in the relative amount of total chromatographable organics condensed by impinger	38
7	Decrease in relative amount of benzene collected on solid sorbent	39
8	Relative changes in the amount of tetrachloroethylene . . .	40

ACRONYMS AND INITIALISMS

BOD	Biochemical Oxygen Demand
CEASE	Committee of Environmentalists Against the Stench of Ethanol
DDGS	Distillers Dried Grains with Solubles
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
GC/MS	Gas Chromatography/Mass Spectrometry
INEL	Idaho National Engineering Laboratory
NECI	New Energy Company of Indiana
NEPA	National Environmental Policy Act
NWS	National Weather Service
ppm(v)	parts per million by volume (e.g., ml/m ³)
TVA	Tennessee Valley Authority

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ABSTRACT

Oak Ridge National Laboratory (ORNL) staff conducted source and ambient air quality sampling and analysis to characterize odorous emissions from a fuel ethanol plant constructed in part with a loan guaranteed by the U.S. Department of Energy. The 52 million gallon (197 million liter) per year plant, which is located in South Bend, Indiana, became operational in October 1984, and shortly thereafter was cited by local citizens as a source of odor in the community. In October 1985, a suit was filed against the plant that would enjoin the plant from producing an odor during operation. If the suit were successful, the plant could be forced to close, and the company would default on its loan of \$127 million, 90% of which is guaranteed by DOE. DOE's Office of Alcohol Fuels formed a technical advisory committee in October 1985 to characterize the problem and to identify possible solutions. As part of the committee, ORNL was charged with conducting source and ambient air quality sampling to identify the sources of odor within the plant, to determine the general types of chemical compounds producing the odor, and to perform sampling and analysis that will help determine the effectiveness of pollution control equipment for reducing the odor.

Analysis of samples taken at the plant has determined that the most likely cause of the odor is the exhaust stacks from the five rotary-kiln, steam-fed dryers for producing distillers dried grains with solubles. A variety of organic compounds are emitted from these stacks, including aromatics, acids, aldehydes, and higher alcohols. The compounds appear to be normal by-products of a whole-grain fermentation process. Furfural and phenylethanol occur in condensates from the gases at concentrations of about 1000 parts per million (ppm). A few compounds, such as benzaldehyde, methylbenzene alcohol and furfural alcohol, occur at concentrations of 100 to 300 ppm. The remaining compounds occur at concentrations of a few ppm to a few parts per billion. Most of the compounds in the gases are odiferous

to varying degrees and many of them, independent of concentration in the gases, contribute to the complex odor spectrum observed. The compounds have a wide range of physical and chemical properties. Some of the compounds can be removed by cooling the vent gases or by scrubbing the exhaust gas with water, but the resulting gas retains about the same chemical profile and also retains a strong odor. Scrubbing with sodium hydroxide solution is more effective, but likewise, the odor is not entirely eliminated. Effective scrubbing and venting to the atmosphere would probably require a two-component solution that would provide chemical transformation of the odiferous compounds. Source testing of a pollution control pilot plant using sodium hydroxide and sodium hypochlorite scrubbing indicates that it should be effective in reducing the odor. Based on a comparison with worker protection standards and international ambient air quality standards, compounds emitted by the pilot plant should have minimal, if any, effects on human health. As a result of this work, the U.S. Department of Energy is prepared to consider a loan to the New Energy Company of Indiana for the purchase of such an odor control system.

1. INTRODUCTION

The Energy Security Act (Public Law 96-294, June 1980) provided for federal loans, loan guarantees, price guarantees and purchase agreements promoting expansion of the fuel alcohol industry in the United States to help reduce the need for imported petroleum. The Office of Alcohol Fuels was established within the Department of Energy (DOE) to implement these provisions of P.L. 96-294. At the beginning of the loan guarantee program, 57 applications were submitted to DOE; these were screened for potential viability, which reduced the number to eleven.

The federal decision of whether or not to grant loan guarantees to these eleven applicants was subject to the provisions of the National Environmental Policy Act (NEPA) of 1969 (Public Law 91-190), which requires consideration of environmental factors in federal decisionmaking. In the Fall of 1981, the loan guarantee environmental assessment program was established at Oak Ridge National Laboratory (ORNL) to assess the environmental impacts of ten fuel ethanol plants (one loan guarantee applicant withdrew before the assessment work began). Environmental assessments were completed for the original ten projects in the Spring of 1982; no significant impacts were identified for any of the projects, and consequently the NEPA process terminated with the publishing of Findings of No Significant Impacts for the projects.

To date, three of the original projects have received loan guarantees and have come to fruition. The first to be constructed and to begin operation is the New Energy Company of Indiana (NECI) facility located in South Bend, Indiana. Construction of the New Energy plant was completed in October 1984. The plant was operating at about 2/3 capacity by approximately December 1984, and reached full capacity around May, 1985. The \$185 million plant was built with a \$127 million loan, 90% of which is guaranteed by the U.S. Department of Energy. As shown in Figure 1, the plant is located in the southwest corner of the City of South Bend, Indiana.

The NECI plant is a corn-based, dry-milling fuel ethanol plant with an annual capacity of about 52 million gallons (197 million liters). Coal combustion is used to provide process heat, and wastewater is discharged to a municipal treatment plant. Corn is delivered to the plant by truck, and

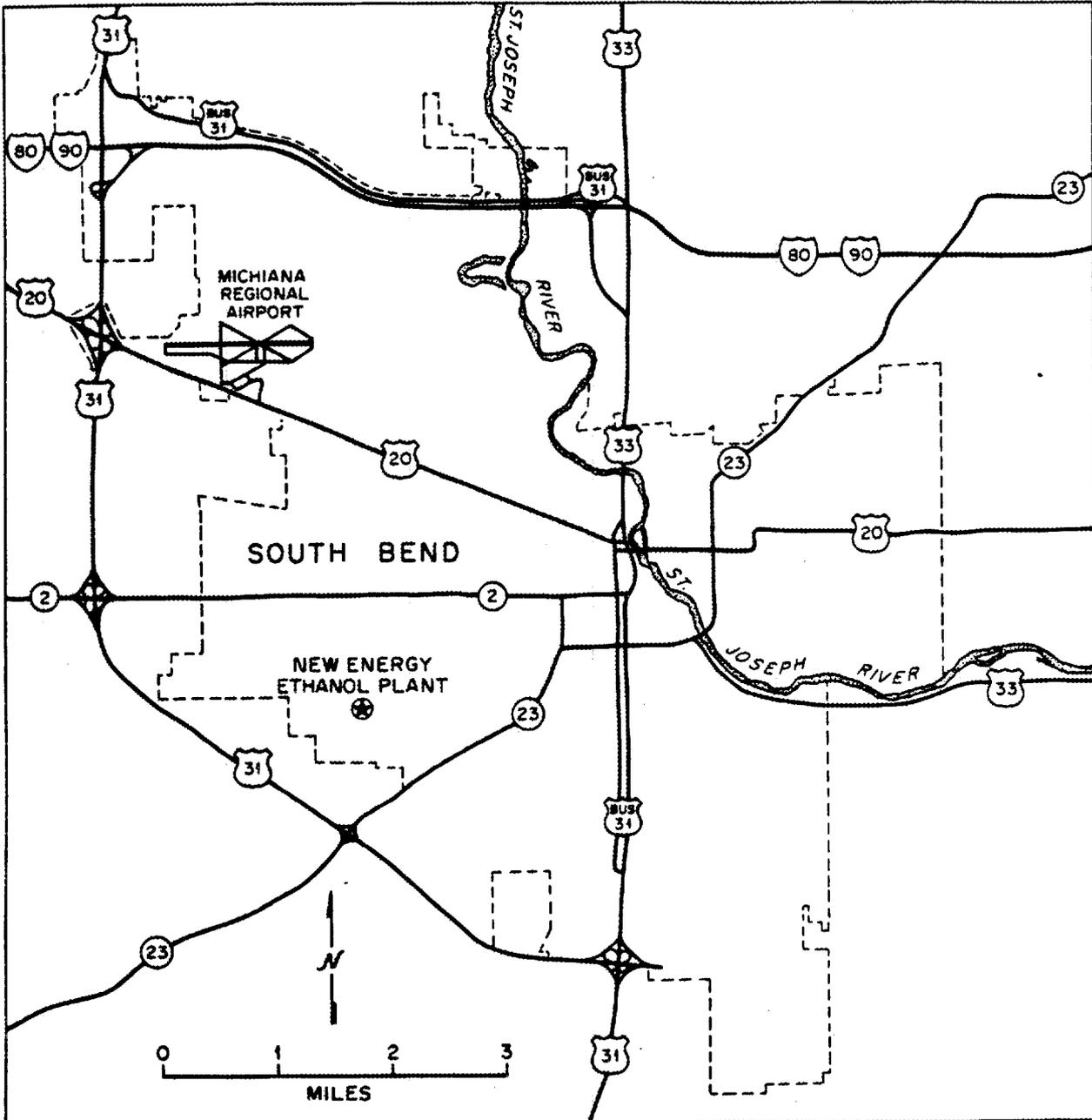


Figure 1. Location of the New Energy of Indiana (NECI) plant.

is milled with onsite hammer mills. A mash is prepared from milled corn, enzyme, lime, water, and steam, using standard techniques to liquefy and saccharify the cornstarch (Elmore et al. 1982). The mash is transferred to fermentation tanks, and yeast is added (in using sugar as an energy source, the yeast cells produce ethanol and carbon dioxide as by-products). After all of the sugar has been oxidized, the fermented mash (called beer) is sent to the beer column, where ethanol is separated from the remainder of the material (called stillage). The ethanol is distilled further in a rectifying column to produce 95% ethanol, and is then dehydrated with benzene to achieve high-purity ethanol (>99.5% by weight). This ethanol is then denatured with unleaded gasoline before being shipped offsite. The stillage is sent to centrifuges and mechanical evaporators to concentrate the dissolved residues to about 50% solids. The evaporator concentrate is mixed with the wet-cake from the centrifuges and is fed to five steam-heated, rotary kiln driers. The drier product, distillers dried grains with solubles (DDGS), is sold as animal feed.

Shortly after the plant became operational, citizens downwind of the plant began to complain about an odor. The odor has been described as a "brewery odor" similar to the smell of "burning sugar;" it was first reported by the local news media in January 1985. The odor became widely recognized as a problem by the citizens of South Bend and neighboring communities during the Spring of 1985. A combination of compounds has been believed to be contributing to the odor, but uncertainty has existed regarding the individual constituents or classes of compounds. The odor reportedly has been detected as far as 20 miles (32 km) downwind of the plant, but appears to remain within a narrow few hundred-yard (- meter) wide band at all distances, regardless of meteorological conditions. The situation has been exacerbated by the plant's location relative to South Bend: the plant is sited in the southwestern corner of the city, resulting in the odor often passing directly through the center of South Bend because of prevailing winds from the southwest (SW). The DDGS dryer stacks were considered the most likely sources of the odor, due to the high volume of discharged effluent and due to the similarity of the odor near the stacks to that observed in the community.

In late Spring of 1985, city and county officials began working with NECI personnel to identify solutions to the problem. In May 1985, NECI

contracted with Gabriel Laboratories of Chicago, Illinois to collect grab samples of the exhaust from one of the DDGS driers (#513) and to analyze the condensable organics and the gaseous organics to determine if known odiferous compounds exist in the exhaust. A number of such compounds were detected in the condensable fraction, including aldehydes (acetaldehyde and furfural, among others), acids (butyric and isobutyric acids, among others), and some "unknowns" that were probably higher alcohols (Gabriel Laboratories, 1985). No gaseous organics were detected using the charcoal tubes, probably because they could not be effectively desorbed from the tubes for analysis (Gabriel Laboratories, 1985). NECI also arranged for another firm to conduct a demonstration during the Summer of 1985 in which a chemical "deodorant" was added to the DDGS stack effluent in an effort to mask the odor. A consensus of people smelling the ambient air downwind of the stack felt the odor was not appreciably improved or masked. Lastly, the Davy McKee Corporation, which built the New Energy plant, designed an odor control system consisting of a water-based scrubber to capture the odorous compounds followed by a closed loop system to recycle the effluent. The system was estimated to cost about \$3-5 million, and was not guaranteed to be successful.

Some local citizens, dissatisfied with the slow progress in solving the problem, organized into a group named the Committee of Environmentalists Against the Stench of Ethanol (CEASE). In the Summer of 1985, they collected thousands of signatures on petitions protesting the odor. In the Fall of 1985, they filed suit against NECI to enjoin the plant from operating in conjunction with producing an odor.

From a regulatory standpoint, the odorous emissions were not violating any provisions of the loan guarantee or any environmental regulations, and therefore DOE legally could not force NECI to control the odor under the loan guarantee. There are no federal, state or local regulations governing the odor emissions. The odor could be controlled under local nuisance ordinances if it could be proved that the odor was a public nuisance. The U.S. Environmental Protection Agency (EPA) could only get involved if the odor was proven or suspected to be a health hazard.

NECI was unable to provide the needed capital for the Davy-McKee system. They also could not obtain a business loan to pay for the equipment, because under legally enforceable terms of their loan agreement, the

company could not incur any further debt on its own without approval by DOE. The agency was unwilling to authorize a loan of this magnitude as authorized by Public Law 99-190 (Joint Resolution, December 19, 1985) unless additional facts could be gathered that would allow a thorough evaluation of the potential effectiveness of the system in reducing the odor.

Because of the growing seriousness of the problem, i.e., the lawsuit could close the NECI plant, which in turn would cause the company to default on its loan, DOE in October 1985 organized a special multi-organizational task force to evaluate the problem and to recommend solutions. The task force was composed of members of DOE, ORNL, Tennessee Valley Authority (TVA), Idaho National Engineering Laboratory (INEL), and EPA. TVA members functioned in the leading role due to their expertise in biomass-related projects in general and in monitoring the NECI project for DOE. INEL became involved because of technical monitoring work for other DOE alcohol fuels projects, and provided biochemical engineering support related to potential contamination in the process cycle. EPA provided recommendations concerning procedures for sampling and analysis.

Section 2 of this document describes the source and ambient air quality sampling and analysis performed by ORNL at the NECI plant. The overall sampling protocol is first described, followed by a description of the specific methods and techniques that were used. Section 3 presents the analytical results and discusses their relevance to solving the NECI odor problem.

2. CHARACTERIZATION OF ODOR COMPONENTS

ORNL's role in the task force was to conduct source and ambient air quality sampling and analysis to provide as many facts as possible regarding the odor problem. DOE's action on the problem would be based on the analyses and recommendations provided by the task force.

In general, it was desired to use established methods, procedures and techniques for sampling and analysis, and to use EPA methods wherever possible. Because of the nature of the sampling, few of the EPA sampling methods, which generally deal with the criteria pollutants, were directly applicable. In these cases, the most similar EPA method was modified as needed. EPA approved analysis methods were in general directly applicable.

Based on the results of the Gabriel Laboratories report, and on inspections made during a site visit in October 1985, it became apparent that any ambient sampling would be concerned with the capture of gaseous organic compounds, and that any source term sampling would be concerned with the same, but usually in the presence of a moisture-rich stream. Given these conditions, it was decided to use an overall sampling and analysis strategy that was broad in scope initially, and that narrowed in scope with successive sampling campaigns until the desired level of information was obtained. It was also decided to emphasize source-term sampling for the characterization of possible odor-producing compounds. Ambient samples would then be examined for any potential candidates detected in the source streams.

The goal of the sampling and analysis was threefold: (1) identify the major potential odor sources within the NECI plant; (2) characterize the principal chemical constituents of emissions from these sources; and (3) identify the types of chemical compounds present in the NECI plume. Achieving the first goal would identify the sources to be examined in detail. The second goal would provide key information needed to select the appropriate type of odor control equipment. If any classes of compounds known to be hazardous to human health were found in the emission samples, then the ambient samples (third goal) would be examined to determine if these same compounds were added to the ambient air as a given air parcel passed over the NECI facility.

2.1 SOURCE TERMS

2.1.1 Sampling

During a site visit in October 1985, task force members toured the NECI plant to identify potential odor sources. Based on discussions with NECI engineers, examination of process flow diagrams and related information, and inspection of facilities within the plant, the following six sources were identified as potential sources of odorous emissions: the five DDGS drier stacks; the evaporator vent; the centrifuge vents; the cooker vents; the fermenter vents; and the wastewater surge pond. Criteria used in selecting these sources include the nature of the process occurring at the source, release characteristics (e.g., moisture content, velocity, height etc.), and sensory perception of the emissions (i.e., whether or not the odor was similar to that detected offsite). Figure 2 illustrates the location of each of these potential sources within the plant. These six sources were targeted for sampling.

In addition to visual inspections of these source areas, a number of experiments were performed on the drier stack to gather information needed to design a sampling train. Various configurations of pumps, organic compound collection devices (stainless steel traps packed with adsorbent), etc. were operated at a variety of flow rates. The samples collected from these trials were analyzed by gas chromatography at ORNL to determine the range of boiling points represented by the compounds in the exhaust stream; information on the moisture content of the stream and on the "loading" of the solid adsorbent used to collect organics was also obtained from analysis of these traps. This information was used to design the sampling train shown in Fig. 3.

The sampling train consisted of teflon tubing running from the odor source (stack, vent, etc.) to a condenser and then to a bubbler that was packed in ice. The bubbler was partially filled with a liquid to collect condensate from the moisture-laden stack effluents. The tubing continued to a second bubbler and a wide-mouth odor collection trap made of glass and filled with a sorbent named Tenax™, and finally to an AC pump which drew in the sample at a high flow rate. The second bubbler, which was empty, served

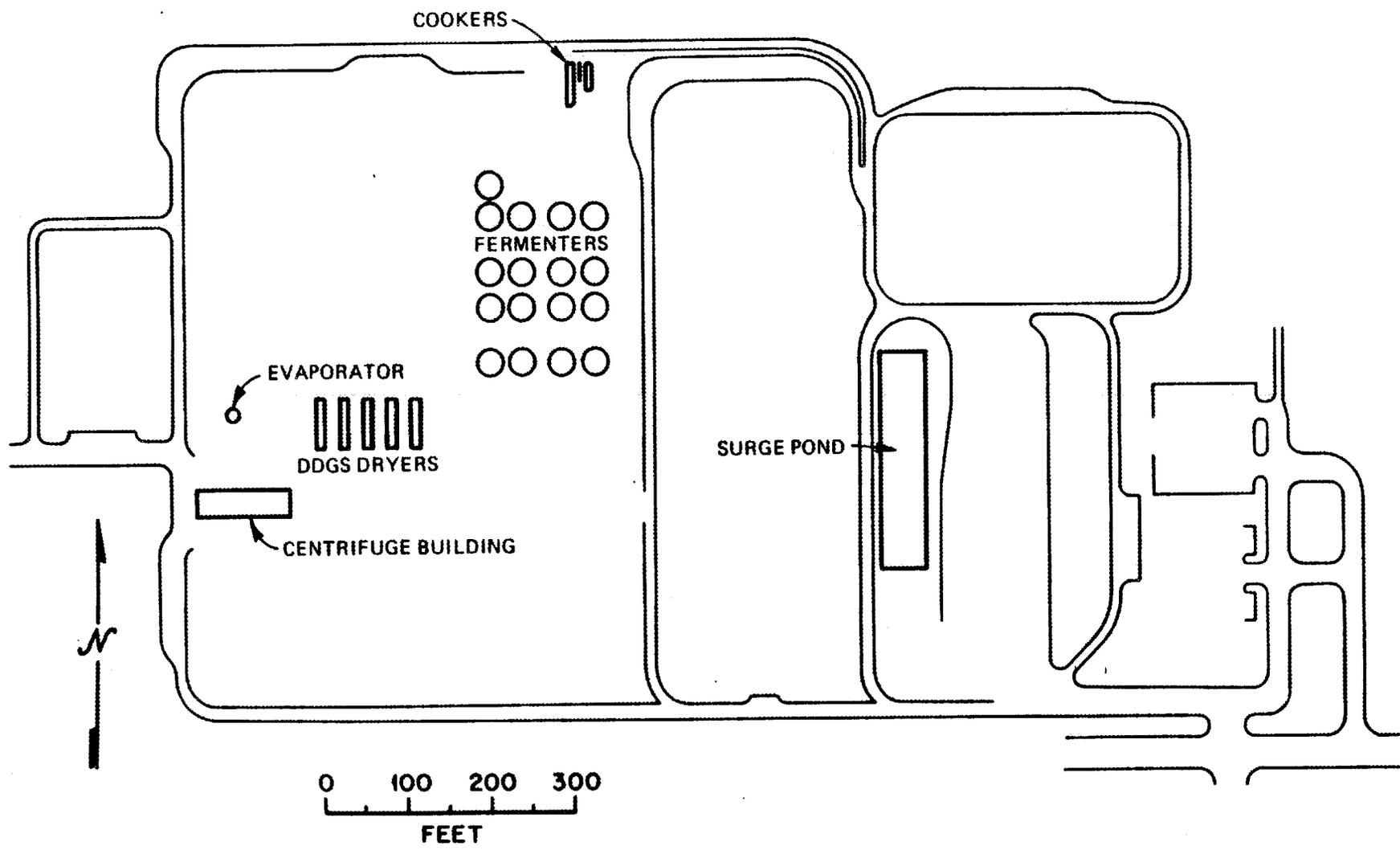


Figure 2. Locations of potential odor sources within the NECI plant.

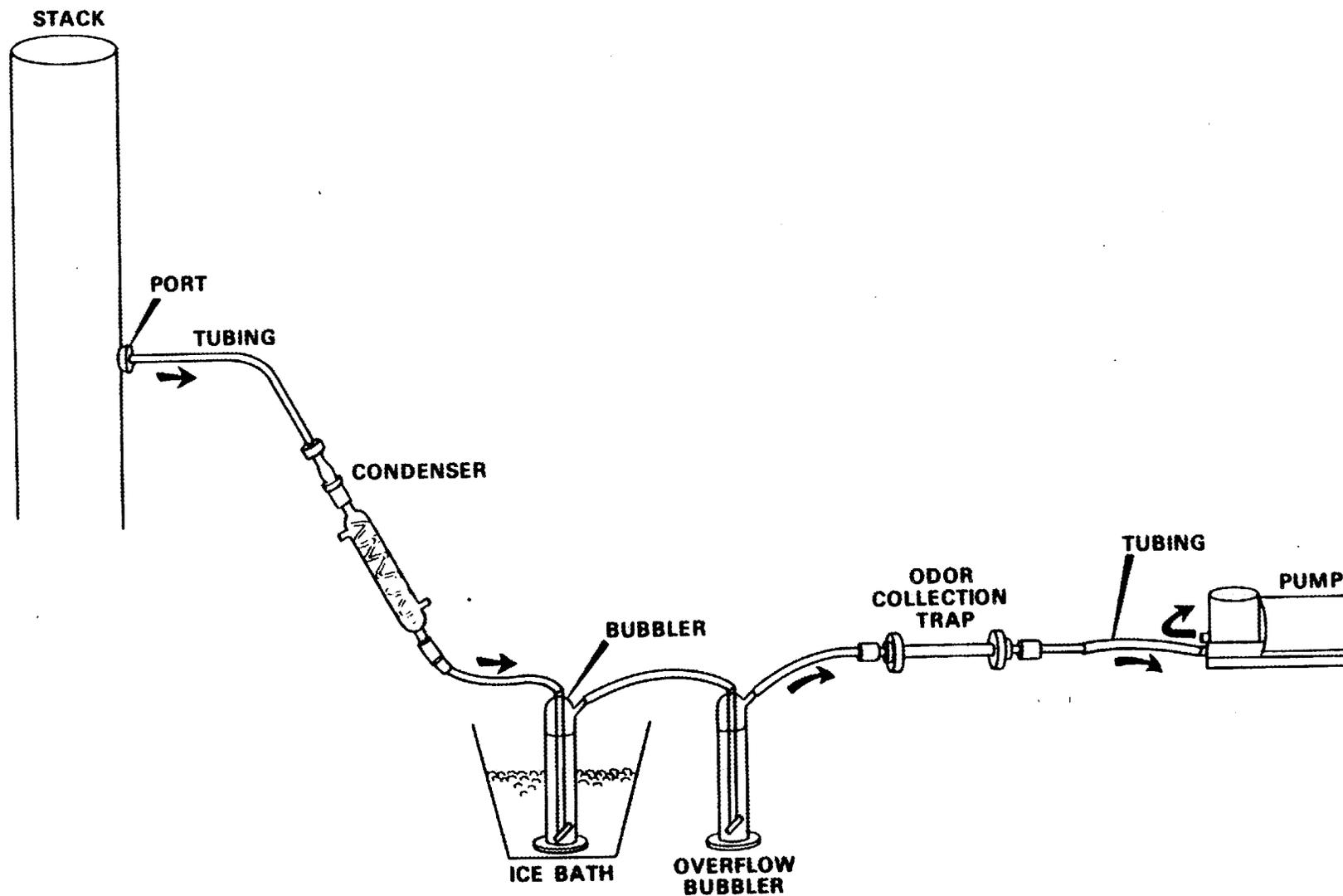


Figure 3. Diagram of sampling train for source term emissions sampling.

to prevent contamination of the wide-mouth trap in case of condensate overflow from the first bubbler. Tenax™ was used since it proved to be very efficient in adsorbing the types of compounds which were of interest to the investigation.

Source sampling began in November 1985 at the middle DDGS dryer stack (#513). This stack was chosen because it is the same one used by Gabriel Laboratories in their 1985 study (Gabriel Laboratories, 1985).

Three trials were conducted using the configuration shown in Figure 3. The first two trials started with 50 ml of distilled water in the first bubbler, while the final trial began with 50 ml of sodium hydroxide. In each trial, sampling was performed until 50 ml of condensate collected in the first bubbler (for a total of 100 ml of liquid). This was accomplished in approximately 30 minutes for each trial. In the sodium hydroxide sample, the color of the liquid in the first bubbler changed from clear to yellow during sample collection. An eight-second sample was also collected in a narrow stainless steel trap drawn directly from the stack port by the pump. A longer sampling period in this configuration would have overloaded the sorbent with condensate.

Other sources were sampled using sampling trains without provisions for moisture removal, since the sources were not as laden with condensable moisture as the DDGS dryer stacks. In these situations, the sampling train consisted of a pair of narrow stainless steel traps packed with Tenax™ and attached in series to an AC powered pump. The leading trap was usually located about two feet (60 cm) from the vent. A cooker vent and a fermenter vent each were sampled for an hour using this configuration. Two sets of traps with battery-powered pumps were installed at the edge of the surge pond to sample for several hours.

NECI personnel collected a sample from an experimental apparatus that was installed at another DDGS dryer stack. The apparatus was designed to simulate the proposed Davy-McKee closed loop system on a small scale. The sample was included with the others for analysis at ORNL.

Lastly, two solid samples were obtained for analysis. Grab samples of the wet cake/syrup mixture fed to the dryers, and the DDGS product, were obtained, and were placed in double sealed plastic bags, and then placed in stainless steel containers. The rationale here was to determine if the

compounds found coming out of the dryer stack were found in the dryer feed; if not, then perhaps they were being formed in the dryer.

In response to the request of the New Energy Task Force, additional source term sampling was conducted during two days in January, concentrating on the six potential sources: the DDGS dryer stacks, surge pond, cooker vents, fermenter vents, evaporator vent, and centrifuge vents (Figure 2).

The middle DDGS dryer stack (#513) was again sampled. The configuration for the sampling train was the same as that used in November. Two trials were performed at this source: the first started with 50 ml of distilled water in the bubbler, and the second began with 50 ml of sodium hydroxide. Flow calculations were performed for this configuration. In each trial, sampling was performed until 50 ml of condensate collected in the bubbler (for a total of 100 ml of liquid). This was accomplished in approximately 45 minutes for the first trial and 20 minutes for the second trial. The color of the liquid in the sodium hydroxide trial changed from clear to pale yellow.

The evaporator vent stack was sampled using the same sampling train, and two trials were again conducted with distilled water and sodium hydroxide. It became quickly obvious that a tremendous flow of condensate was venting from the evaporator stack; only two minutes were required to collect 50 ml of condensate in the distilled water trial, and only three minutes were needed in the sodium hydroxide trial. The liquid's color in the sodium hydroxide trial changed from clear to a deep yellow.

A cooker vent was again sampled, using the sampling train with the bubblers, since enough condensable moisture was believed to be available; indeed, 50 ml of condensate were obtained after 50 and 35 minutes for distilled water and sodium hydroxide, respectively. For this source, the color of the liquid in both trials remained clear.

Sampling was performed on top of a fermenter tank which was filling and nearing capacity. This tank was selected in order to maximize potential emissions for the sampling train. A trial with distilled water was attempted at the vent, but condensate was not collecting in the bubbler. Several attempts to enhance condensation were unsuccessful; only about four drops of condensate were collected. Therefore, due to the lack of moisture emanating from the vent, a trial with sodium hydroxide was not tried.

The centrifuge vents were not readily accessible. However, a sampling port was available at the conveyor leading to the vents. Two trials were performed at the port with distilled water and sodium hydroxide. In both of the trials, approximately ten minutes were required to collect 50 ml of condensate.

A number of potential odor control systems were identified by TVA. A system similar to the proposed Davy-McKee design was evaluated by visual inspection at the Hiram Walker distillery located in Windsor, Ontario. Source term sampling and analysis were not permitted, however. Vendors of commercially available odor control systems were also contacted in regards to submitting proposals for odor control at the NECI plant. One proposal for an odor abatement system, submitted by QUAD Environmental Technologies Corporation of Highland Park, Illinois, included an offer of a demonstration using a pilot system. The New Energy Task Force agreed to the demonstration and requested that air sampling be conducted by ORNL staff at several locations in the flow stream of the pilot system. Fig. 4 depicts the configuration of the QUAD pilot system.

Source term sampling was performed during two days in March at four ports in the flow stream: (1) between the DDGS dryer stack and the heat exchanger (condenser), (2) between the heat exchanger and the outside air inlet, (3) between the air inlet and the QUAD pilot system, and (4) at the effluent stack of the QUAD system. The four ports allowed comparisons to be made regarding the effectiveness of the system by using results from the first port as a baseline. Air sampling was conducted when the QUAD system was spraying sodium hydroxide alone, sodium hypochlorite alone, and the combination of the two compounds, in order to evaluate the relative efficiency of the three variations. Two independent runs were made for each case at Ports 3 and 4; Ports 1 and 2 were sampled less frequently, since the results at these upstream locations should be unaffected by variations of the QUAD system. In addition, three grab samples of condensate in the flow stream were taken: (1) at a drain from the heat exchanger (grab sample A), (2) at a drain between the outside air inlet and the QUAD system (grab sample B), and (3) at a drain from the QUAD system (grab sample C).

The QUAD system was connected to the middle DDGS dryer stack (#513), which is the same stack previously sampled. Cyclones had recently been

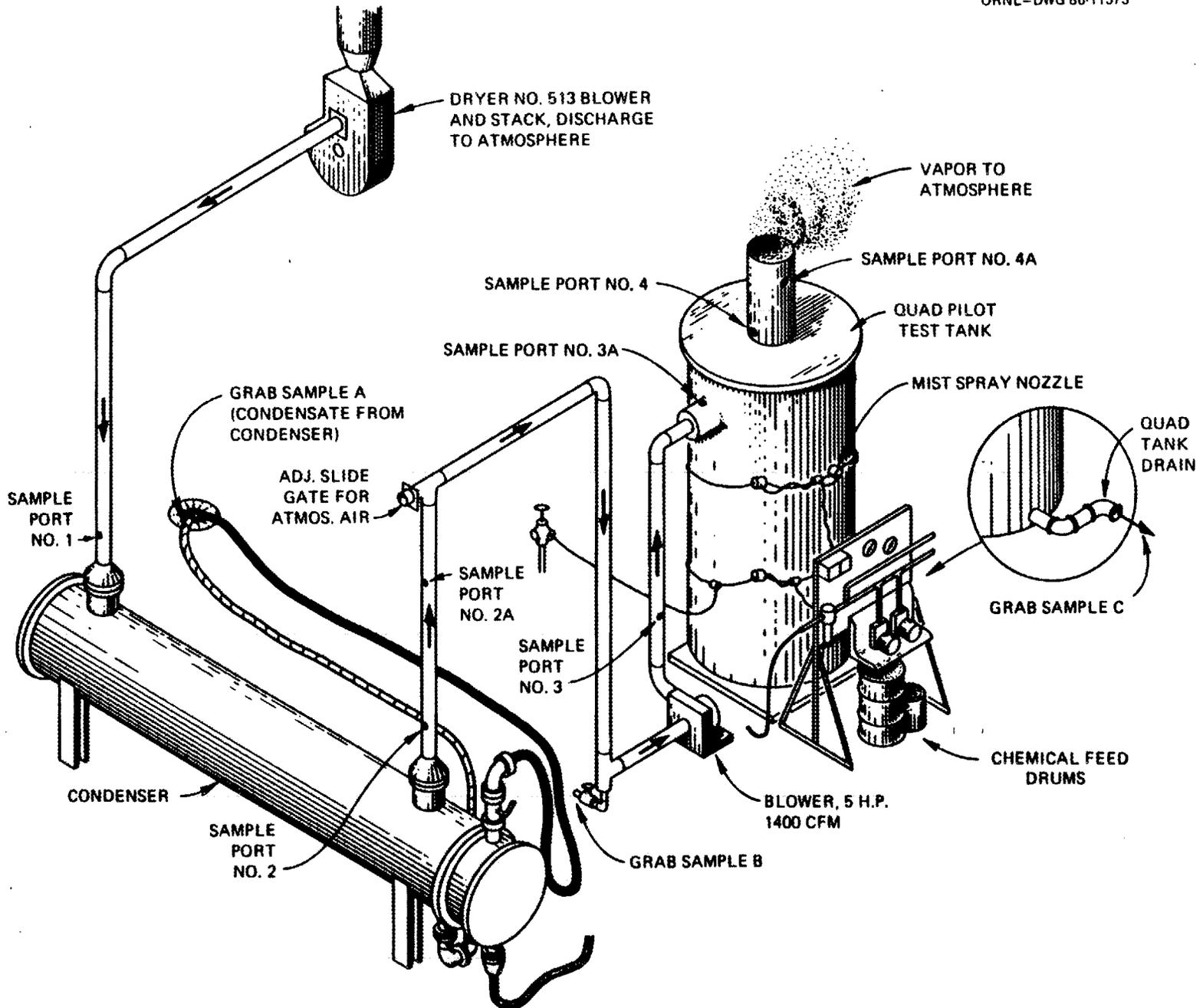


Figure 4. Configuration of the QUAD pilot plant system and associated sampling points.

installed at all of the DDGS dryer stacks to remove particulates; the cyclones did not appear to have any effect on the odor. The configuration for the sampling train was the same as used before for source sampling: a condenser, two bubblers, a wide-mouth odor collection trap, and an AC pump. Teflon tubing was used exclusively. Two complete sets of glassware and pumps were utilized so that two ports could be sampled simultaneously.

Ports 1 and 2 were sampled with the QUAD system spraying sodium hydroxide and sodium hypochlorite through nozzles in the upper ring of the system. The lower ring was not used because of insufficient pressure. All sampling conducted during the two days started with 50 ml of distilled water in the bubbler. Sampling was performed until 50 ml of condensate collected in the bubbler (for a total of 100 ml of liquid). This was achieved in approximately 15 minutes at Port 1 and 30 minutes at Port 2. Flow calculations were performed for both sampling trains.

The sampling trains were moved to sample Ports 3 and 4 with conditions at the QUAD system remaining constant. Very little condensate collected in the bubblers at these two ports because the effluent was diluted by the addition of cooler, drier air from the outside air intake between Ports 2 and 3 in the flow stream. The ports were sampled for two hours with a total accumulation of 65 ml in each bubbler.

The next variation in sampling consisted of stopping the flow of sodium hypochlorite so that only sodium hydroxide was being sprayed in the QUAD system. Ports 3 and 4 were again sampled under this variation. A large degree of foaming was observed in the bubbler of the sampling train at Port 4. The amount of condensate collected remained quite consistent with the previous set, however. Sampling was stopped after two hours with a sum of 60 ml in the bubbler at Port 3 and 55 ml at Port 4.

Ports 3 and 4 were sampled again, this time with only sodium hypochlorite being sprayed in the QUAD system. The ports were sampled for two hours with a total accumulation of 60 ml in the bubbler at Port 3 and 65 ml at Port 4. Flow calculations were again performed for both sampling trains to ensure consistency with previous measurements.

The next set of sampling was conducted using both sodium hydroxide and sodium hypochlorite spray in the QUAD system. Prior to sampling, two new ports were drilled into the flow stream: Port 3A which was slightly downstream and around a 90 degree turn from Port 3, and Port 4A which was

immediately downstream from Port 4 near the mouth of the QUAD stack. In addition, the inlet tubing of the sampling train within the flow stream at each of the ports was turned 90 degrees so that it faced into the flow rather than perpendicular to the flow. These two modifications were performed in attempts to increase the rate of condensate collection in the bubblers. However, two hours of sampling revealed no appreciable change in the rate: 60 ml of liquid was contained in the bubbler at Port 3A and 65 ml at Port 4A.

Sampling was repeated at Ports 3A and 4A with one change to the QUAD system: enough pressure was available to permit sodium hydroxide and sodium hypochlorite spray to both upper and lower rings of the system, thereby doubling the flow of these compounds. Two hours of sampling resulted in a total accumulation of 65 ml in the bubbler at Port 3A and 70 ml at Port 4A.

The sampling trains were returned to Ports 1 and 2 for another set of sampling. Condensate was quickly collecting in the bubblers at these ports. A total of 125 ml was obtained in 25 minutes at Port 1, and 130 ml in 20 minutes at Port 2.

Sampling was conducted with a single sampling train at Port 1. The sampling train was modified slightly by replacing the wide-mouth trap with a narrow stainless steel trap which was filled with charcoal. The purpose of this modification was to obtain a sample which could be analyzed for low-boiling compounds that are not normally detected by a gas chromatograph because they desorb quickly from the Tenax™ used in traps, but which would be held longer by the charcoal in the trap. A five-minute sample was required; the bubbler contained 65 ml of liquid at the end of the five minutes.

In addition to the air source term sampling, samples were also collected from the wastewater discharge points of the pilot plant. These were used to help evaluate the impact of odor control system operation on NECI wastewater characteristics.

All source term samples were numbered, noted in a log book and placed in locked cases for transportation to ORNL via commercial airline (checked baggage). The inventory of each case was verified upon opening the case at ORNL. Samples were then transferred to ORNL's Analytical Chemistry Division using EPA-recommended chain of custody procedures (EPA 1977b).

2.1.2 Analysis

Analysis of the source term samples was performed by ORNL's Analytical Chemistry Division at Oak Ridge. Initially, a methodology was employed for the first set of samples in which screening techniques were used to identify groups of compounds which were suspect and rule out others for which no further analysis was needed. Selected samples from each sampling expedition were thoroughly examined for a variety of organic compounds. In general, the protocols were designed to detect a wide range of volatile or semivolatile organic compounds, and whenever possible standard methods (such as those recommended by EPA) were employed (see Appendix A for a brief description of analysis methods).

All volatile organic determinations made on samples in a liquid form were accomplished using a purge and trap sampling technique at ambient temperature. For such analysis by gas chromatography/mass spectrometry (GC/MS), EPA Method 8240 (EPA 1984a) was followed. When liquid samples were analyzed for volatile organic compounds by gas chromatography, Method 8010 (EPA 1984a) was followed.

Liquid samples (condensates) were also analyzed for semivolatile organic compounds. After sample preparation the analysis was accomplished according to Method 8270 (EPA 1984a) or according to Method 625 (EPA 1984b). Because the liquid samples generated in this work were of limited volume (usually 60 to 150 ml), techniques for extraction of semivolatile organic compounds were adapted to accommodate the reduced sample size. Thus, 35-ml aliquots of sample were extracted with 3-ml portions of methylene chloride using a Mixxor¹ separating system. Each sample was extracted three times at pH 10 and three times at pH 2. Both the basic and acidic extract were combined when semivolatile organics were analyzed by Method 8270. The acidic and basic extracts were separately concentrated and analyzed when Method 625 was employed. Concentration to a final volume of 1 ml was accomplished on a Kuderna-Danish concentration apparatus.

Samples obtained on solid sorbents (Tenax™ traps) were analyzed by thermal desorption techniques. These traps were desorbed by heating while

¹"Mixxor" is a trademark of Lidex Corporation, U.S. Patent No. 4454231.

purging with a stream of pure helium flowing in the opposite direction of sampling. The entire desorbed sample was subsequently introduced onto a column of a gas chromatograph. In the case of a packed column, the sample was desorbed directly onto the column. When a capillary column was employed, the desorbed sample was cryothermally focused before the chromatography process was initiated. Detection was by either flame ionization or mass spectrometry. Samples were also obtained on wide-mouth solid sorbent traps containing Tenax™. Homogeneous portions of these traps were thermally desorbed in a manner similar to the smaller traps.

The pH of some of the samples from the QUAD pilot system was analyzed. This was done to evaluate potential effects of the effluent stream on the material durability of the odor control system.

Some solid samples [wet cake/syrup (dryer feed) and DDGS] were also analyzed for organic components. The solid samples were prepared by sorbent extraction according to Method 8240 (EPA 1984a). Following concentration of the extract, it was analyzed in the same manner as other samples for semivolatiles.

The lack of emission or ambient air quality regulatory standards for specific organic compounds (condensable and volatile) made the evaluation of the results of the analysis difficult. For liquid samples, it was decided to examine the condensable and volatile components for the presence of EPA priority pollutants, which is a list of 129 designated toxic substances. Although not strictly applicable to air emissions cases [i.e., they are promulgated under the authority of the Federal Water Pollution Control Act (Public Law 92-500)] the presence of these compounds in NECI air source terms will at least give some idea of the potential harmfulness of the odorous emissions.

There were also attempts to define the nature of the compound or compounds giving rise to the odor by "sniff" tests on the effluent from a gas chromatograph and by breakthrough tests on Tenax™. In the "sniff" tests the chromatogram of a headspace sample was characterized and then an identical sample was chromatographed with the column disconnected. The effluent from the column was then monitored by frequently "sniffing" and noting the times that odors were detected. In the Tenax™ breakthrough studies, odorous headspace above a condensate was drawn through a known

weight of Tenax™ with a helium carrier at a known flow rate. The breakthrough volume of the odor was noted and related to the breakthrough volume for compounds of known volatility.

The liquid wastewater samples obtained from the QUAD pilot system were analyzed for five-day biochemical oxygen demand (BOD) using standard methods.

All data generated from these samples were reported through the data management system of the Analytical Chemistry Division of Oak Ridge National Laboratory. Thus, a hard copy has been archived along with a microfiche copy and a tape copy.

2.2 AMBIENT SPECIES

The initial approach for ambient sampling involved upwind and downwind ambient stations to sample gaseous compounds. A comparison of sample analyses from these stations was hoped to identify compounds which were being added by the NECI plant; the technique to be utilized involved simply subtracting background constituents found at the upwind station from those at the downwind station to identify new compounds.

A network of possible sites for the upwind and downwind sampling stations was designed during a "familiarization" trip. The network consists of thirteen sites configured in a circle with a radius of about three miles (5 km) to reflect the distance of downtown South Bend, where many of the complaints were registered, from the plant which formed the center of the circle. Sites were selected based on several criteria such as adequate exposure, flat terrain, distance from local emission sources (e.g., diesel fumes from trucks), and instrument security. The network was developed in advance to save time in site selection (one upwind and one downwind site) during a particular sampling expedition.

"Small-scale" sampling was performed during another familiarization trip to the NECI plant. Two ambient sampling stations were installed within the plant near the fence perimeter; the stations were positioned at opposite ends of the plant to sample conditions upwind and downwind of the sources. The goal of this sampling was to learn as much as possible regarding effective sampling procedures such as preferred sorbents, odor collection

traps, sample flow volumes, and sampling periods. Information learned from this experience proved useful in developing methodology and procedures for ambient sampling.

The ambient sampling was difficult to implement and operate effectively for several reasons. The odor plume was not easily detectable "by nose" at a distance of three miles (5 km) from the plant on days with considerable atmospheric mixing. On other occasions, the odor plume was so thin in width at the ground that it could travel between two sites in the network with little or no detection "by nose" at those sites. Also, a slight wind shift during the sampling period could shift all or most of the odor away from a downwind site at that distance. In addition, temporary emission sources (e.g., an idling vehicle) occasionally arrived at a site. Finally, analyses from ambient sampling conducted using sites in the network were inconclusive in identifying compounds contributing to the odor plume; the complexity of the analyses dampened the effectiveness of the simple technique of subtracting upwind constituents from downwind constituents.

A suggestion was made at a New Energy Task Force meeting that during ambient sampling, the upwind station should be sited as close as possible to the NECI plant to positively identify contributions at the downwind station as originating at the plant rather than at another source. Otherwise, if another source was between the upwind and downwind stations, then additional compounds detected at the downwind site could not be linked to the plant as easily. Although few other sources were within the circle of the network and were not expected to pose a problem, the suggestion was accepted. With this approach, however, care would have to be taken in selecting the upwind site to ensure that the plant itself would not affect the upwind sampling station.

2.2.1 Sampling

Ambient sampling began in November 1985, before the New Energy plant became equipped with cyclones to remove particulates prior to the air venting from the DDGS dryer stacks. The cyclones were installed to meet air permit conditions for particulate emissions, and were not expected to alleviate the odor, but background measurements were desired before their installation in case they did help.

During the trip, meteorological observations and projected conditions were studied at the National Weather Service (NWS) Office at South Bend before and during sampling. Appendix B contains a record of meteorological data from the NWS office which is applicable to sampling on this and later trips. Potential sites were examined downwind of the plant based on projected wind directions. Several approaches to sampling were discussed, and a strategy was selected for this trip based on the number of odor collection traps and pumps available.

Ambient sampling was performed during the daylight hours of two days. Sampling during the familiarization trip revealed that four to eight hours of ambient sampling would provide an effective sample. During the first day, sampling stations were established at upwind and downwind sites located approximately three miles (5 km) west and one mile (2 km) ENE of the plant, respectively. Selection of the downwind site was attempted at a distance of three miles (5 km), but the odor was not detected because of considerable mixing in the atmosphere. The odor was strong at the site chosen.

Three sets of narrow, odor collection traps made of stainless steel and filled with Tenax™ were installed at each location. Each set was connected to a battery-powered pump drawing air at a high flow rate through one trap or through two traps in series. In the latter configuration, the second trap served to measure the efficiency of the first trap in adsorbing compounds. A filter between the traps and the pump served to protect the pump from dust or other particulates. Figure 5 illustrates the configuration for a set of two traps. Three sets were needed primarily for replication. Flow calculations were performed for each set, which was standard procedure at all ambient stations during both installation and retrieval.

The samples were retrieved from the sites at the end of the day. Because of the cold temperature [the afternoon maximum was 30 degrees F (-1 degrees C)], several of the pumps had ceased due to battery failure. Diesel fumes from a nearby idling truck were detected at the downwind site upon return, thus making the identification of ethanol plant odorous compounds from the samples difficult.

A gradual wind shift predicted for the second day posed somewhat of a problem in keeping a downwind site within the odor plume. A downwind sampling station was established first in order to allow time to add another downwind site later if necessary. Three sets of traps were installed in the

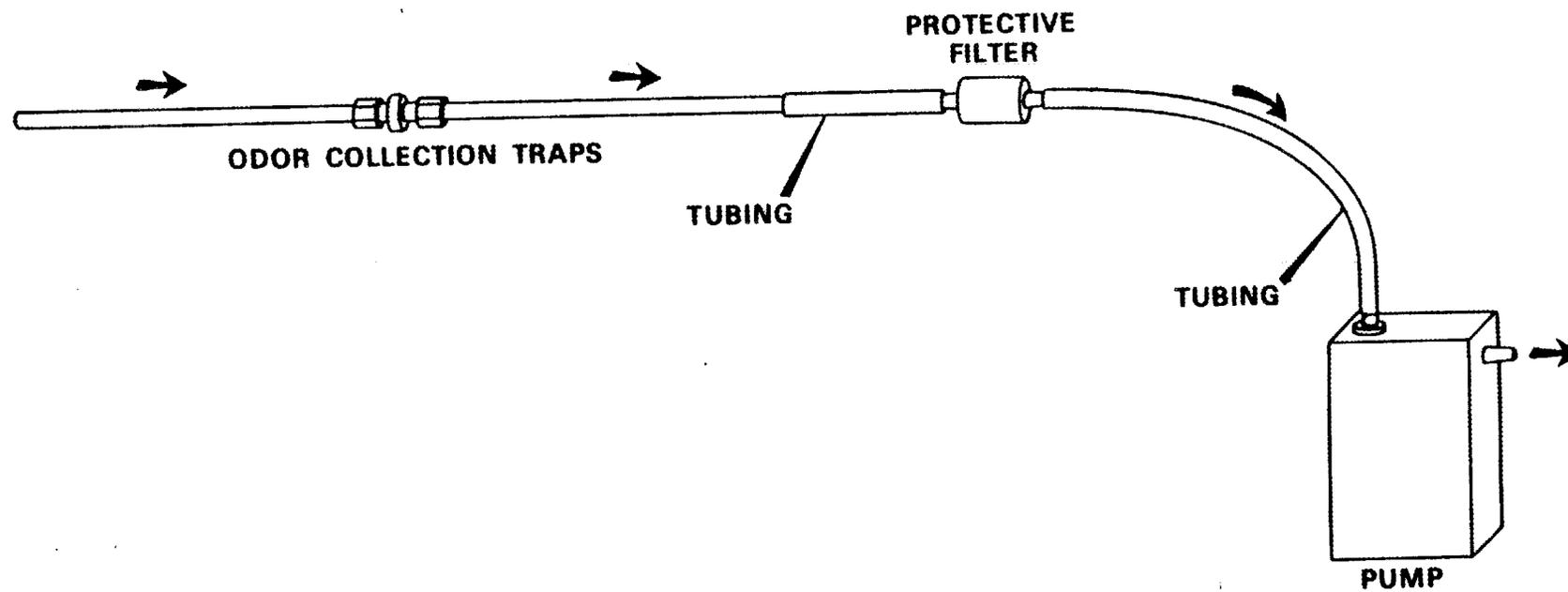


Figure 5. Diagram of sampling train for ambient air quality samples.

odor plume about 1.5 miles (2.5 km) south-southwest (SSW) of the plant. An upwind station with three sets of traps was set up at a site located approximately four miles (6 km) north-northeast (NNE) of the plant. When the odor vanished from the downwind site due to the wind shift, the station was kept operating and a new sampling station with three sets of traps was established within the odor plume about two miles (3 km) WSW of the plant.

Upon collection of the samples from the upwind and two downwind sites, it was again noted that some of the pumps had quit due to the cold temperature [the afternoon maximum was 35 degrees F (2 degrees C)]. The odor was still evident at the second downwind site upon collection of the samples. The odor plume at ground level was noticed to remain quite thin in width (as judged by the olfactory senses), even at a distance of several miles (several km), an observation noted in a variety of meteorological conditions.

Limited ambient sampling was also conducted in January 1986. A downwind sampling station was installed approximately 0.25 miles (0.4 km) southeast (SE) of the DDGS dryer stacks. A strong odor was detected at the downwind site, which was in a cleared corn field beyond the plant perimeter. Three sets of narrow stainless steel traps were installed, each set consisting of a battery-powered pump drawing air through two traps in series. Flow calculations were performed for each set.

An upwind sampling station was established at a site approximately 0.25 miles (0.4 km) west (W) of the DDGS dryer stacks. The site was in an open area upwind of the plant railroad tracks. Three sets of traps were installed, and flow calculations were performed. The distance from the plant to each of the ambient sampling stations was minimized to comply with the previously mentioned suggestion made at a task force meeting. Analyses of ambient samples during this trip could possibly be compared with analyses of previous ambient samples to determine effects of distance from the plant on results.

The ambient samples were collected at the end of the day, approximately eight hours after installation of the sampling stations. All but one of the pumps had quit because of the cold temperature [the highest temperature during the period was 34 degrees F (1 degree C)]. A strong odor was still evident at the downwind site upon retrieval of the samples.

In March, one ambient sampling station was established approximately 0.25 miles (0.4 km) downwind of the DDGS dryer stacks. The site for the

station was a cleared field immediately outside the plant perimeter on the ENE side. The wind was generally from the WSW, but was fluctuating greatly with much atmospheric mixing. The odor was apparent about 50% of the time during station installation. The station consisted of a battery-powered pump drawing air through a single narrow stainless steel trap which was filled with charcoal. Charcoal was used in lieu of Tenax™ to check for low-boiling compounds. The pump operated continuously during the 2.5 hours of sampling. Upon retrieval of the trap, the odor was no longer present because the wind had shifted to a westerly direction.

All ambient samples were numbered, noted in a log book, sealed in stainless steel cans, and placed in a transport case that was then locked for shipment to ORNL as checked baggage on commercial airlines. The inventory of each case was verified upon opening the case at ORNL. Samples were then transferred to ORNL's Analytical Chemistry Division (ACD) using EPA-recommended chain of custody procedures (EPA 1977a).

2.2.2 Analysis

The Tenax™ traps containing the ambient samples were analyzed by thermal desorption gas chromatography. No identification of specific compounds nor quantitation of the amounts of particular species was attempted, primarily due to the fact that no priority pollutants were found in the source term samples. Also, the large number of organic compounds present in the samples would have made detailed sample analysis time-consuming and expensive. In general, the front trap of a two-trap sample train was analyzed for each of an upwind and downwind station for a particular sampling day. Not all of the ambient samples collected were analyzed. Those not analyzed were placed in cold storage for analysis at a later date if required.

3. RESULTS AND DISCUSSION

"In most cases, the exact nature of the pollutants responsible for the odor is, as yet, unknown. In the gas chromatographic analysis of such samples, using the flame ionization detector only, a feeling of futility is inevitable when inspecting the gas chromatogram which registered the presence of very many species." (Dravnieks 1972)

3.1 Source Terms

Analysis of source term samples was performed for samples collected from the NECI plant during all three sampling expeditions.

The three condensate samples collected from the DDGS dryer stack (#513) in November 1985 were thoroughly analyzed by gas chromatography and GC/MS. Following the protocol for Method 8270 (EPA 1984a), no priority pollutants were observed in these samples. However, the condensate did contain many organic compounds. Some compounds tentatively identified in one or more of these condensate samples were furfural, benzaldehyde, phenyl ethanol, isomers of hydroxymethylacetophenone, methylfuraldehyde, furfural alcohol, butyrolactone, and phenylacetaldehyde. In short, the vapor from the dryer stack contained many condensable organic compounds. In addition, the samples extracted from these condensates showed many additional organic components when gas chromatographic analysis was preceded by derivatization. Derivatization is a procedure designed to convert difficult-to-chromatograph compounds with active hydrogen(s) into more readily chromatographable compounds. The results indicated that many such compounds were present in the stack.

Volatile samples collected on Tenax™ which were associated with the dryer stack were also analyzed by GC/MS. These volatile samples were first screened for the presence of volatile priority pollutants normally determined by Method 8240 (EPA 1984a) and none were found (see Appendix A for descriptions of the methods). However, these analyses showed the presence of several volatile compounds containing oxygen. Some of the tentatively identified compounds included acetone, 2-butanone, furfural, and benzaldehyde. In addition, two volatile samples collected off the plant

site were also analyzed. Both contained hexane (a component of gasoline) and one contained methylene chloride, benzene, and toluene. However, the most significant point to be made concerning these off-site samples is that neither contained furfural or benzaldehyde -- two of the principle components of the samples associated with the dryer stack.

The November 1985 samples were collected on Tenax™ in the narrow stainless steel traps from the cooker and fermenter vents. All samples were analyzed using EPA protocol for priority pollutants. No priority pollutants were observed. Gas chromatography using flame ionization detection was conducted for one trap from each of the vents. The profiles were quantified with respect to the following targeted compounds: hexane, methylene chloride, toluene, benzene, benzaldehyde, and isobutanol. Only one of the compounds was found in each sample, each at a very low concentration after normalizing for the total air volume drawn through the sample. Benzaldehyde was identified in the sample from the cooker vent at a concentration of 3×10^{-4} ug/ml. Hexane was identified in the fermenter vent sample at a concentration of 2×10^{-6} ug/ml. Another sample from the cooker vent was analyzed using gas chromatography/mass spectrometry techniques which produced one major peak that was identified as ethanol.

Analysis of the surge pond sample by thermal desorption GC indicated the presence of about 25 organic compounds. Of principal interest is the fact that none of the major peaks detected in the surge pond sample were found in the downwind ambient sample collected in the offsite odor plume; this suggests that the surge pond is not a principal contributor to the off-site odor. This conclusion is supported by the observation that the surge pond is an intermittent source; during the January sampling trip, the pond was mostly dry, and the remaining liquid in the pond was frozen, yet the odor is fairly continuous. For these reasons, it was decided that no additional sampling of the surge pond or analysis of collected samples were warranted.

The conclusions to be drawn from these analyses of the November 1985 samples are four-fold:

1. The vapor stream associated with the DDGS dryer stack (#513) contains significant amounts of organic compounds. Many of these compounds contain oxygen.

2. None of the priority pollutants appear to be present in this vapor stream in significant quantity.
3. The principal components of this stream were not detected in the off-site samples.
4. The cooker vents, fermenter vents and wastewater surge pond are probably not major contributors to the off-site odor, and no additional sampling or analysis of samples already collected would be needed.

From the January 1986 sampling expedition, six samples were thoroughly analyzed. These six consisted of two condensate samples (distilled water and sodium hydroxide condensing media) collected from the evaporator vent stack; two volatile samples on Tenax™ collected in conjunction with the condensed samples; and two solid samples which were dryer feed and DDGS. Analysis of the evaporator stack samples was emphasized since the evaporator was considered to be a major potential source, and results could be compared with previously obtained results from the DDGS dryer stack. Several miscellaneous tests involving headspace analyses and direct analysis of the condensates were also carried out.

The two condensate samples were extracted at pH 2 and pH 10 and the extracts were not combined (as was done for the extracts in the prior samples), in order to get a more detailed analysis for potential acidic constituents. The resulting four sample extracts were analyzed according to Method 625 (EPA 1984b) in order to quantitatively determine any priority pollutants. None were found. Subsequently, the extracts were derivatized to increase the chromatographability of polar compounds and analyzed by gas chromatography with detection by chemical ionization mass spectrometry (to obtain molecular weight information) and by conventional electron impact mass spectrometry.

Results indicated the presence of the same classes of compounds which were found in the dryer stack. Numerous organic compounds were identified with many containing oxygen. The major component was phenylethanol. Other compounds tentatively identified included alkyl-substituted benzene, alcohols, ethers, hydroxymethylacetophenone, and furfural. These condensate samples were also analyzed for volatile organic compounds. The major components found were ethanol, methylbutanol, dimethyl disulfide, and furfural. Benzene, chloroform, methylene chloride, and toluene, which are priority pollutant volatile compounds, were identified at the part-per-billion level in these condensates.

The Tenax™ traps backing the condensate samples were found to contain several volatile organic compounds including methylene chloride, tetrachloroethylene, benzene, toluene, hexane, 2-butanone, benzaldehyde, furfural, and isobutanol. Of these, benzaldehyde, furfural, and isobutanol were targeted as compounds to be examined in more detail, primarily because they are classified as odorous compounds (Amoore and Hautala 1983; Hellman and Small 1974; Kirk-Othmer 1978).

The three targeted compounds were quantified by gas chromatography. The absorbed amounts were adjusted by the air volume passing through the traps to derive concentrations of the compounds in the air. Actual concentrations were probably slightly higher since these values assume that the traps were completely efficient in capturing the compounds. Table 1 displays the results.

Of the three odorous compounds examined by quantitative analysis, none were found to be regulated by emissions standards or ambient air quality standards in the United States. Thus, to evaluate the potential human health impacts from measured levels of these compounds in the emissions from NECI, worker exposure standards in the United States and ambient air quality standards established to protect public health in other countries were used. For benzaldehyde, no worker exposure levels or international ambient air quality standards were located; the literature reports that the compound is non-toxic, with a mild narcotic effect from vapors (Kirk-Othmer 1978). Furfural levels in the workplace are limited to 2 ppm (v) or less, averaged over a full work shift (Amoore and Hautala 1983). International ambient air quality standards for furfural range from 0.013 to 0.06 ppm(v) [short-term] (Newill 1977). Isobutanol standards in the workplace are reported as 50 ppm(v); no international ambient air quality standards for this compound were located.

In order to allow a direct comparison of these standards with the measured levels in the NECI samples, the values in Table 1 must be reduced to account for dispersion in the atmosphere. This was done using effluent release characteristics, meteorological data collected at the South Bend Airport, and the EPA-approved atmospheric dispersion model ISCST (EPA 1986). Atmospheric dilution results in predicted ambient levels of about 1×10^{-5} of the original source concentrations given in Table 1. In addition, the units given must be converted to match those of the standards. Using the molecular weights of the listed compounds, and the molar volume of

Table 1. Analysis* of samples collected at the NECI evaporator vent

Trap following condensate collection in distilled water:

Targeted Compounds	Adsorbed Amount (mg)	Sample Air Volume (l)	Concentration in Air (ug/ml)
Benzaldehyde	1.44	1.50	0.96
Isobutanol	1.11	1.50	0.74
Furfural	1.61	1.50	1.08

Trap following condensate collection in sodium hydroxide:

Targeted Compounds	Adsorbed Amount (mg)	Sample Air Volume (l)	Concentration in Air (ug/ml)
Benzaldehyde	0.04	2.25	0.02
Isobutanol	0.04	2.25	0.02
Furfural	0.05	2.25	0.02

* Gas chromatography

an ideal gas (22.4 l) the values in Table 1 can be converted from ug/ml to ppm(v). Upon adjusting the values in Table 1 for atmospheric dilution and converting units, predicted ambient levels of all three compounds are found to be well below appropriate standards, and thus should have minimal, if any, health effects.

Note that the concentrations in the trap downstream of the bubbler with sodium hydroxide are dramatically reduced by a factor of 50 with respect to concentrations in the trap following the bubbler with distilled water. This finding indicates that the sodium hydroxide solution is an effective medium for trapping these organic compounds. Corroborating evidence is found in the dramatic color change of the sodium hydroxide solution as condensate collected from the evaporator vent stack. The color changed from clear to a deep yellow, indicating a chemical transformation. The distilled water sample, on the other hand, remained clear. It can be concluded that an odor control system which utilizes sodium hydroxide should markedly reduce concentrations of odor-causing compounds such as benzaldehyde, furfural, and isobutanol.

Note that it is not being assumed that these compounds are solely responsible for the odor; rather, it is assumed that they are the major components of a complex mixture of organic compounds that is responsible for the odor. By tracking the effect of various odor control technologies on these compounds, one can get some idea of the potential effectiveness of said technologies in reducing the overall odor problem.

The solid samples from the dryer were extracted according to Method 3540 (EPA 1984a) and subjected to the same analytical procedures as the condensate extracts. Results showed that these extracts contained significant amounts of oxygen-containing organic compounds including furfural, phenylacetic acid, vanillin, acetovanillin, alcohols, glycols, ketones, ethers, and lactones. No semivolatile priority pollutants were detected by the standard protocol (Method 625). No furfural or benzaldehyde were found in the headspace above these solid samples even after heating.

In conclusion, the results of the analysis of the January 1986 samples collected indicated the same major constituents found previously: the evaporator vent stack was found to be discharging the same classes of compounds as the DDGS dryer stack. More detailed analyses were carried out including separate evaluation of acid and base fractions, headspace analysis, and specific direct procedures to detect low molecular weight

acids. With these additional results, the picture became quite clear that the principal organic constituents in the process vapor stream were furfural, benzaldehyde, and phenylethanol. There were hundreds of other minor organic constituents that could not be specifically associated with the prevailing odor. Results also indicated that any content of low molecular weight organic acids was minimal. Table 2 summarizes the results of the November 1985 and January 1986 sampling trips. Source of the samples, sampling procedures, analysis methods, and organics identified are given; for some compounds, approximate concentrations are also listed.

A select group of samples was analyzed from the entire set of samples taken in March 1986 to evaluate the effectiveness of the QUAD pilot system. Due to temporal and financial constraints, efforts focused on one set of samples (condensate collected in the bubbler and the associated wide-mouth odor collection trap) obtained at each of the four ports. The set of samples which was thoroughly analyzed at Port 4 was collected with the QUAD system spraying both sodium hypochlorite and sodium hydroxide through both upper and lower rings of the system. Thus, any chemical transformation caused by the system should have peaked in this configuration which was analyzed. Limited analysis was also performed for other samples at Port 4 to confirm findings. Samples analyzed at each port are identified as follows:

- Port 1. Volatile and condensate samples before any system treatment.
- Port 2. Volatile and condensate samples after the stream had passed through a condenser.
- Port 3. Volatile and condensate samples after the stream had passed through a condenser and had been diluted with air.
- Port 4. Volatile and condensate samples after the stream had passed through a condenser, been subjected to air dilution, and received final chemical treatment.

In addition, three liquid samples were analyzed:

- Liquid A: liquor sampled after the condenser.
- Liquid B: liquor sampled after air dilution.
- Liquid C: liquor sampled after final chemical treatment.

Thorough analytical procedures were carried out on each of the samples. Condensate and liquid samples were analyzed for both volatile and semivolatile organic compounds. The acid and base extracts were treated

Table 2. Summary of analytical results, source term samples

Source	Sampling Procedure	Analysis Method	Compound Identification	Concentration (ug/ml)		
DDGS Dryer Stacks	Dist. Water Condensate	Bubbled with Helium (GC/MS)	Dimethyl ether			
			Isobutanol			
			Furfural			
			Hexane	6		
					Methylene Chloride	5
			Extraction (GC/MS)	Furfural	>>1000	
		Furanmethanol		20		
		Benzaldehyde		90		
		Methylethylfuran		5		
		Methylfuraldehyde		30		
		Methylthiopropanol		30		
		Phenylacetaldehyde		10		
		Benzene ethanol		>1000		
		Methylbenzene alcohol		80		
		Furanylpentanone		10		
		Methoxyphenyl propanone		10		
		Dimethylbenzoic acid		60		
		Hydroxymethoxy benzaldehyde		5		
					Phenyl ethanol,	>1000
					Hydroxymethylacetophenone	
		Furfural alcohol		100		
		Butyrolactone	200			
		Thymol	100			
	Direct Injection (GC)	Acetic acid	0.2			
		Isobutyric acid	0.5			

Table 2. Summary of analytical results, source term samples (continued)

Source	Sampling Procedure	Analysis Method	Compound Identification	Concentration (ug/ml)
		Headspace (GC)	Acetaldehyde Isobutyraldehyde Furfural Propionaldehyde	
	NaOH Condensate	Extraction (GC/MS)	Furfural Hydroxymethylacetophenone	
	Dist. Water Wide Trap	(GC/MS)	Acetone Butanone Butane-dione Furfural Benzaldehyde Ethanol	0.001
		(GC/FID)	Hexane Toluene Methylene chloride Isobutanal	0.00004 0.00003 0.001 0.001
	NaOH Wide Trap	(GC/MS)	Acetone Butanone Butane-dione Furfural Benzaldehyde Ethanol	
Cooker Vent	Narrow Trap	(GC/FID)	Benzaldehyde	0.0003

Table 2. Summary of analytical results, source term samples (continued)

Source	Sampling Procedure	Analysis Method	Compound Identification	Concentration (ug/ml)
Fermenter Vent	Narrow Trap	(GC/FID)	Hexane	0.000002
Evaporator Stack	Dist. Water Condensate	Bubbled with Helium (GC/MS)	Methylene chloride Ethanol Methylpropylaldehyde Methylethylketone Ethyl acetate Methylbutanal Dimethyl disulfide Furaldehyde, (furfural)	
		Extraction (GC/MS)	Phenylethanol Phenylethylacetate Di-t-butyl phenol Alcohols Esters Furaldehyde (furfural) Diethylphthalate Ethers C6H14O2 Alkyl substituted benzenes Methyl styrene	
	NaOH Condensate	Bubbled with Helium (GC/MS)	Methylene chloride Ethanol Methylpropylaldehyde Methylethylketone Methylbutanal Dimethyl disulfide	

Table 2. Summary of analytical results, source term samples (continued)

Source	Sampling Procedure	Analysis Method	Compound Identification	Concentration (ug/ml)
		Extraction (GC/MS)	Phenylethanol Alcohols Benzyl alcohol Di-t-butyl phenol Esters Di-butylphthalate Dimethyl benzoquinone Hydroxymethylacetophenone Decanoic acid Ethyl phenyl phenyl ether Furanaldehyde (furfural) Alkyl substituted benzenes	
	Dist. Water Wide Trap	(GC/MS)	Methylene chloride Tetrachloroethylene Benzene Toluene Methylethyl ketone Ketone	
		(GC/FID)	Benzaldehyde Isobutanol Furfural	0.96 0.74 1.07
	NaOH Wide Trap	(GC/MS)	Methylene chloride Tetrachloroethylene Benzene Toluene Hexane C2 hexanonone	

Table 2. Summary of analytical results, source term samples (continued)

Source	Sampling Procedure	Analysis Method	Compound Identification	Concentration (ug/ml)
			Methyl propylaldehyde C5 furan C6H12O2	
		(GC/FID)	Benzaldehyde Isobutanol Furfural	0.02 0.02 0.02
DDGS Dryer Feed	Solid Sample	(GC/MS)	Furfural Phenyl acetic acid Vanillin Acetovanillin Phthalates Esters Alcohols Glycols C3 triols Ketone Ethers Lactones	
DDGS Dryer Dried Solid (Out)	Solid Sample (grab)	(GC/MS)	Furfural Phenylacetic acid Vanillin Acetovanillin Phthalates	

Table 2. Summary of analytical results, source term samples (continued)

Source	Sampling Procedure	Analysis Method	Compound Identification	Concentration (ug/ml)
DDGS Dryer Dried Solid (cont.)	Solid Sample (grab)	(GC/MS)	Esters Alcohols Glycols C3 triols Ketone Ethers Lactones	

separately. Samples were analyzed for all organic priority pollutants. No semivolatile priority pollutants were found. Because some of these samples now included contact with a chemical treatment that could cause compounds to become chlorinated, a hexane extract was prepared for each liquid sample. This extract was examined by capillary gas chromatography with flame ionization detection and with electron capture detection. The chromatograms indicated that the chemical treatment changed many of the compounds. For example, the mass spectral analysis showed rather conclusively that the phenylethanol was converted to chlorophenylethanol.

However, these chromatograms also indicated that the total organic chemical content was greatly decreased by this system. Figure 6 shows the change in total chromatographic area (area under all chromatographic peaks) for the condensate extracts from the various sampling ports. Based on this estimate, approximately 95% of the organics in the vapor were condensed by this treatment system. In fact, no furfural was found in the condensed samples associated with Port 4 or Liquid C. It seems likely that the furfural underwent polymerization during the chemical treatment.

The volatile hydrocarbons associated with this system showed a similar trend as evidenced by the reduction of levels of benzene through the system (Figure 7). Furfural in the gas phase was reduced by a factor of 30. However, the relative amount of some chlorinated compounds increased in this system; for example, Figure 8 shows tetrachloroethylene increasing by a factor of six between Port 1 and Port 4. This is probably not surprising because the chemical treatment associated with Port 4 should result in some chlorination capability. In fact, the concentration of chloroform associated with the condensate collected at Port 4 was around 200 ppb.

As an attempt to interpret the significance of this concentration, a comparison can be drawn with chloroform concentrations in drinking water. Although the comparison is somewhat questionable since concentrations of chloroform in the gaseous effluent may differ significantly from the collected sample of condensate, a crude analogy may be derived. Several studies (Federal Register, 1979) have determined mean, median, and extreme values of chloroform concentrations in drinking water. The mean values in the studies ranged between 35 and 83 ppb. Median values varied between 21 and 59 ppb. Extreme values ranged between no concentration detected and 540 ppb. Therefore, one would not expect chloroform associated with this system

ORGANICS IN CONDENSATE, QUAD PILOT PLANT

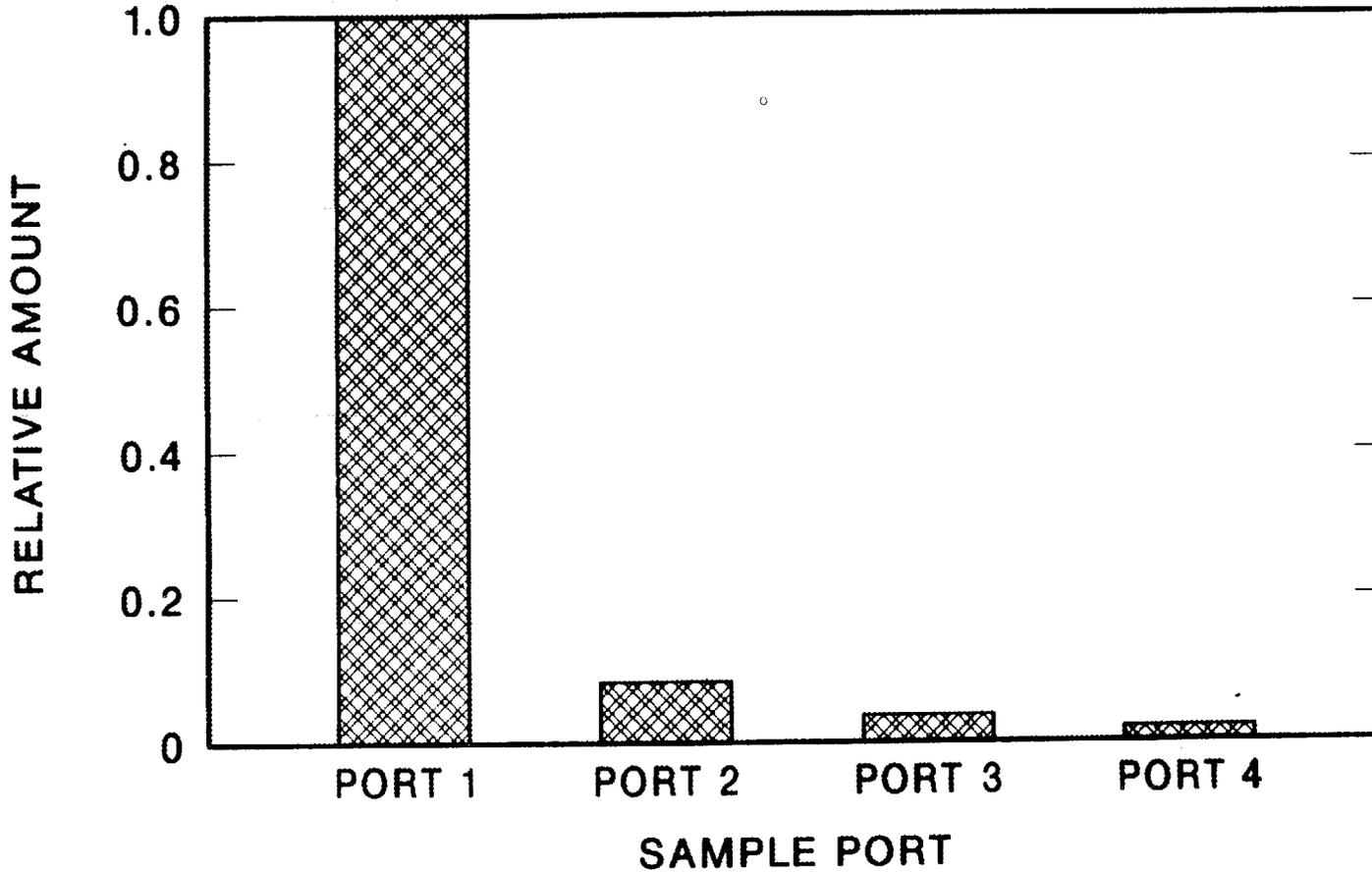


Figure 6. Decrease in the relative amount of total chromatographable organics condensed by impinger. (Value assigned to Port 1 is 1.0).

BENZENE IN VAPOR PHASE, QUAD PILOT PLANT

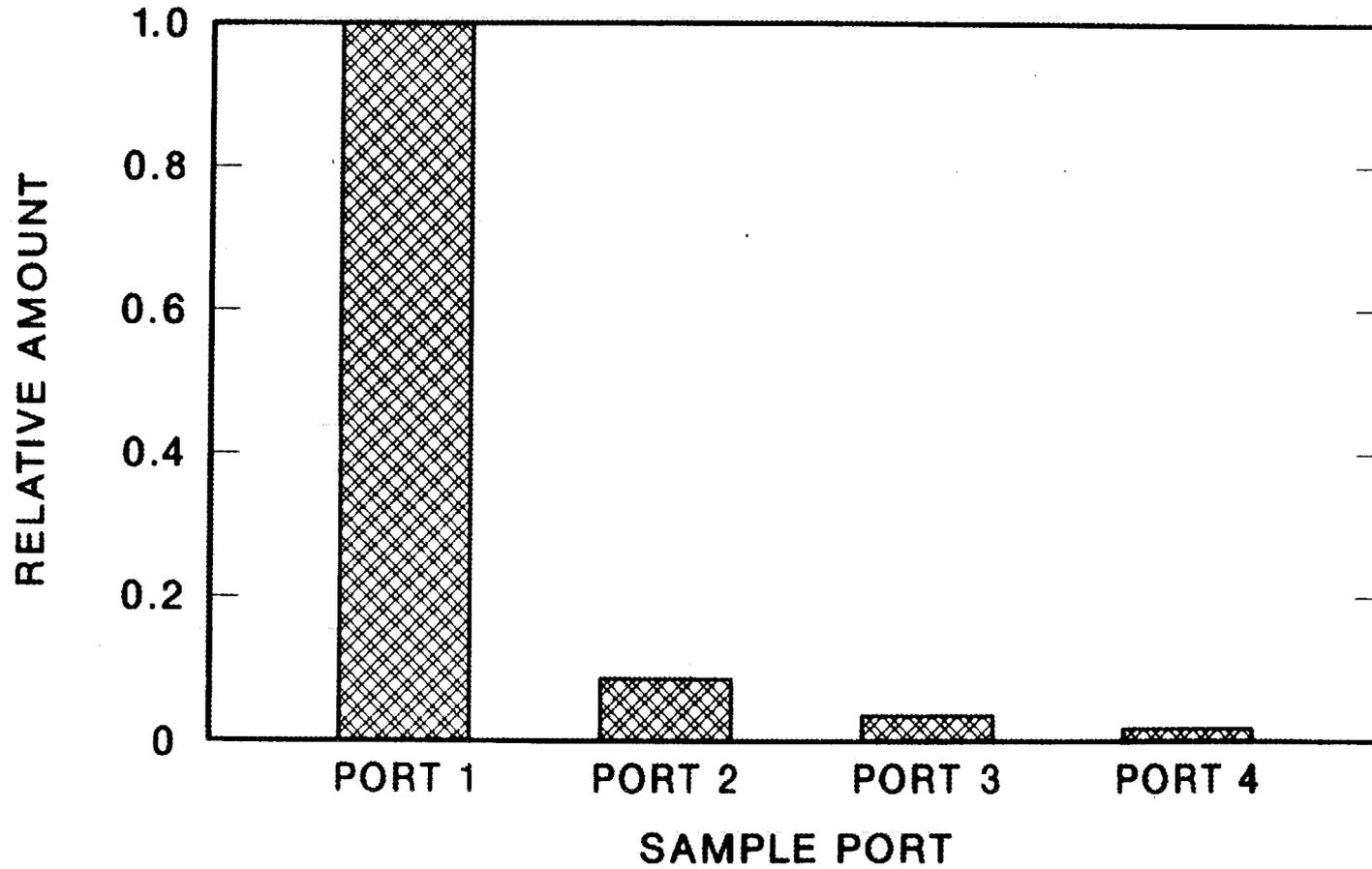


Figure 7. Decrease in relative amount of benzene collected on solid sorbent. (Value assigned to Port 1 is 1.0).

TETRACHLOROETHYLENE IN VAPOR, QUAD PILOT PLANT

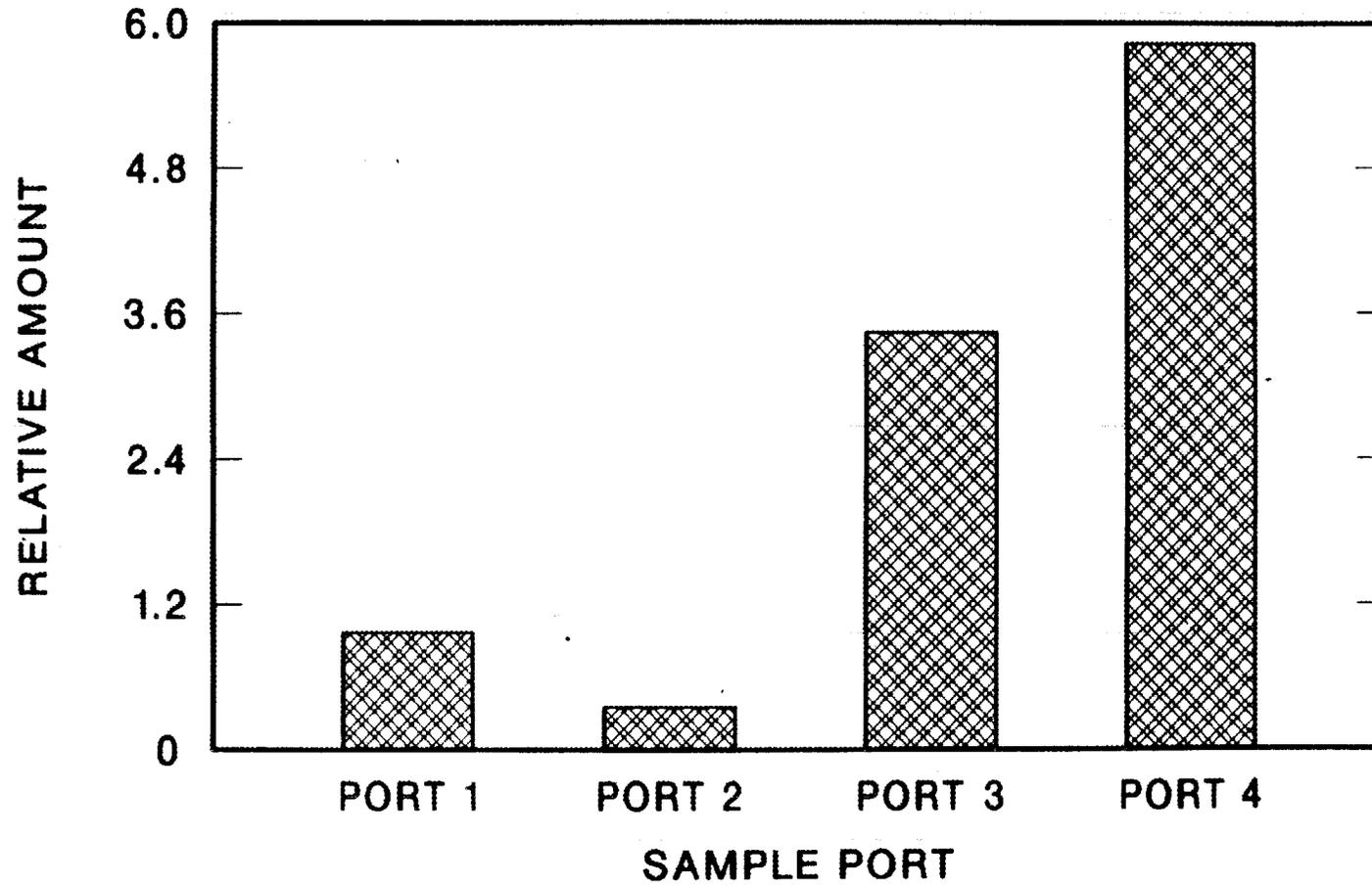


Figure 8. Relative changes in the amount of tetrachloroethylene (Port 1 assigned value of 1.0).

to create an air quality problem, especially when considering the dilution capacity of the atmosphere and the lability of chloroform in the presence of air and light. This conclusion is reinforced by noting that West Germany has promulgated an ambient air quality standard for chloroform of 6,000 ppb for a 30-minute averaging period (Newill, 1977).

Table 3 lists concentrations of several targeted compounds in the air stream passing through the traps of the sampling train at the four ports of the QUAD pilot system. As was the case in evaluating the emissions from a water-based and/or sodium hydroxide-based scrubber system, no ambient air quality or emissions standards applicable to this source type are available for judging the significance of the levels reported in Table 3. Consequently, a similar approach to that used previously will be employed (i.e., comparison with worker protection standards and with international ambient air quality standards). Appropriate standards are listed in Table 4.

Using the same techniques as described previously for adjusting for atmospheric diffusion and for converting units, predicted ambient levels of key compounds from operation of the Quad odor control system would be well below standards set to protect human health, and thus should have minimal, if any, impact on public health in the NECI vicinity.

"Sniff" tests of the condensate samples were rated as follows: Port 1: 10; Port 2: 6; Port 3: 4; and Port 4: 2. On this scale, 10 is the most objectionable. Although subjective, this rating technique indicates that the system tended to substantially reduce the odor.

The pH of the samples was also tested, and results are summarized below:

<u>Port No.</u>	<u>Nominal (average) pH</u>
1	3.5
2	5
3	5.5
4	7.5

The results show that the upstream samples are quite acidic, which is to be expected given the presence of aldehydes and acids in the exhaust stream. The pH then increases in response to the removal of these compounds in the condenser, followed by treatment with caustic.

Biochemical oxygen demand results of the grab liquid samples (locations A, B & C on Figure 5) were 1980, 2100, and <5 mg O₂/L, respectively.

Table 3. Analysis of samples collected at the QUAD pilot plant during operation at NECI

Targeted Compounds	Concentration in Air (ug/l)			
	Sample Test #13 Port #1	Sample Test #14 Port #2	Sample Test #11 Port #3A	Sample Test #12 Port #4A
Methylene Chloride	10.94	8.18	1.12	0.25
Benzene	1.04	0.38	0.25	0.08
Trichloroethylene	1.25	0.22	0.05	0.56
Toluene	0.26	0.00	0.04	0.02
Tetrachloroethylene	0.42	0.16	1.49	2.49
Ethylbenzene	30.21	3.59	2.11	3.66
m-xylene	9.38	0.63	3.72	3.10

Table 4. Workplace and ambient air quality standards for specified organic compounds

Compound	Workplace Standard [ppm(v)]*	International Ambient Air Quality Standard [ppm(v)]**
Methylene Chloride	100	15
Benzene	10	0.46- 3.12
Trichloroethylene	50	0.74-15
Toluene	100	0.16-15
Tetrachloroethylene	50-100***	---
Ethylbenzene	100	.005-.014
m-xylene	100	0.14-15 [†]

*As given in Amoore and Hautala 1983.

**As given in Newill 1977; short-term (30 min exposure) standards.

***As given in Mackison, et al. 1980.

[†]Xylene (not specific to m-isomer).

These results indicate that the effluent from the first two drains had a greater organic content, and thus produced a higher demand for oxygen, than the effluent from the third drain (after final chemical treatment), in which most of the condensable organic compounds have been oxidized and have reacted with sodium hydroxide. As originally designed, the BOD of the overall NECI effluent discharge to the South Bend municipal treatment plant was about 300 mg/l (DOE 1982). For comparison, typical sewage has a BOD of about 100 mg O₂/l. Although the BOD from specific drains in the pilot plant discharge was higher than the typical discharge, the QUAD system should not add significantly to the existing wastewater burden of the NECI facility on the South Bend treatment plant.

In conclusion, the treatment system which was tested substantially reduced the organic chemical content of the vapor stream. One could estimate that more than 90% of the organic chemical burden was removed from the vapor stream. Based on "sniff" tests of the samples collected, this reduction may alleviate the odor problem.

In conjunction with reducing the odor, the abatement system will also produce other environmental impacts, but none are expected to be significant. First, the air emissions from the stack will contain chlorinated aliphatic organics; given the nature of the compounds and their expected levels, they should dissipate rapidly in the atmosphere. Secondly, the drains from the odor abatement system will add to the wastewater burden of the NECI plant; however, the increase in BOD₅ should not be large enough to require any additional pretreatment. Third, the system will involve the transportation, storage and handling of chemicals classified as hazardous to the NECI plant (e.g., sodium hydroxide, sodium hypochlorite). Hazardous chemicals are already used at the NECI plant, and the increment represented by the odor control system should not place a significant burden on the storage facilities, handling procedures and spill response capabilities currently in place at the NECI plant. Furthermore, it is clear from the results of the source term testing that a water-based system alone would not be adequate for effective odor removal, and that some type of chemical treatment is needed. Thus although these other environmental impacts of the odor abatement system were not evaluated in as much detail as the air emissions and odor reduction, they are not expected to be major problems.

The results suggest that an odor control system based on oxidation of organics in the exhaust to aldehydes and/or acids, followed by caustic scrubbing, should remove most of the odor-causing species from the gaseous effluent. A system based on water scrubbing only would also reduce the levels of the organic compounds, but not to the extent of the system described above.

3.2 Ambient Species

Analysis of the ambient samples collected during the November 1985, January 1986, and March 1986 sampling trips was confined to GC/FID analyses of some of the November and January samples.

At the outset of the project, the intent of the ambient sampling was to identify specific compounds present in the offsite odor plume that were contributed by the NECI plant. This information was intended to be obtained by comparing a gas chromatogram of a sample taken upwind of the plant against a chromatogram of a sample taken downwind of the plant within the odor plume. Variations in the types and levels of organic compounds in the ambient air could be attributed to the NECI plant, provided emissions from other sources in the area had little or no effect on the downwind sample.

The upwind and downwind chromatograms of the front traps from the November sampling indicate the presence of about 50-60 different organic compounds in each sample. A comparison of the two chromatograms indicates that they differ in some respects. For example, the downwind sample contained about four compounds that were present at levels significantly higher than in the upwind sample [the peak intensities ranged from 20% to 65% of full scale for these compounds given the same GC conditions (recorder attenuation)]. In addition, the levels of three compounds were increased markedly in the downwind sample over levels present upwind of the NECI plant.

In theory, quantification of the differences between the two chromatograms could have been accomplished by more detailed examination, such as computerized matching of peaks, and subsequent identification of the matched peaks. In practice, this was not attempted because of the large number of compounds present, and because information provided by this work would not be crucial to the overall goal of abating the odor problem.

Consequently, only qualitative results were obtained for the November ambient samples. These did show that the NECI plant altered the spectrum of organic compounds present in the air as it passed over the plant.

Analysis of the January 1986 samples was directed at determining whether or not specific compounds identified in the source term sampling were present in the odor plume downwind of the NECI plant. Specific targetted compounds were furfural and benzaldehyde. These were found in the downwind Tenax™ traps, but were also found in the samples taken upwind of the plant. In both cases, the levels detected were at the part per billion (ppb) range. Two explanations for these results are as follows: (1) the plant is the source of the compounds and eddies that formed around the plant caused the emissions to be detected "upwind" of the prevailing wind direction, or (2) the NECI plant is not the source, and these compounds were present in the ambient air upwind of the plant.

The results of the source term sampling suggest that no compounds of concern to human health were found in the air emissions from the NECI plant (with the exception of methylene chloride, which is most likely an artifact of the glassware used and not a by-product of the ethanol production process). Consequently, given the strategy developed at the outset of the project, there was little incentive to analyze the ambient samples in detail to determine the presence, and quantify the levels, of specific compounds of interest. The qualitative results obtained do indicate that the NECI plant changes the spectrum of organic compounds in the ambient air.

3.3 Discussion

Because the results as described up to this point were sufficient to allow evaluation of candidate odor control measures, no further analysis or quantification of the collected samples was attempted. Identifying a proposed solution to the problem did not hinge on identification and confirmation of every organic compound in the gas stream. Based on the results of this work, the U.S. Department of Energy is prepared to consider a loan to NECI, as provided by statutory authority, to purchase an odor control system at least as effective as the Quad pilot plant. In accordance with NEPA, the overall environmental impacts of this use of federal funds will be evaluated.

Engineering evaluations of the plant during the odor production could find no major operational problem or excursion that could be causing the odor. Consequently, the problem could occur at other fuel ethanol plants and raise similar objections with the public if the location of the plant with respect to prevailing winds and populated areas is similar to the situation at NECI.

The work conducted by ORNL and the rest of the task force thus accomplished the overall goal of identifying a solution to the problem. The sampling and analysis component of the overall task force effort in general achieved its goals as stated in the beginning of the report. Six process areas within the plant were identified as potential odor sources (DDGS drier stacks, evaporator vent, centrifuge vents, cooker vents, fermenter vents and wastewater surge pond), based on information gained during a site visit. Sampling of the air emissions from these sources, and subsequent analysis of the samples determined that the DDGS drier stacks and the evaporator vent were probably the major contributor to the offsite odor. A wide variety of oxygenated organic compounds were detected in most of the sources; the DDGS stack and evaporator vent effluents contained odorous compounds (e.g., furfural and derivatives, isobutanol, etc.) in levels markedly higher than those found in many of the other sources. Based on this information, a pilot odor reduction system using sodium hydroxide and sodium hypochlorite was designed and brought to the NECI plant for testing. Analysis of pilot plant process samples indicates that the odor can be removed by this type of system. Key compounds emitted by the odor control systems considered were evaluated with respect to human health standards to assess the significance of the levels observed in the exhaust streams; compounds at these levels are anticipated to have minimal, if any, adverse effects on human health. Lastly, the ambient samples showed that the NECI plant does noticeably change the spectrum of chromatographable organics in the ambient air upwind of the plant. The plant appears to add a few compounds in high levels not found in the upwind air, and it also increases the intensity of a few more compounds.

The ambient sampling component of ORNL's work was the only one not carried out to the extent envisioned at the outset of the project. The large number of chromatographable organic compounds found in both upwind and downwind samples made the identification of the effect of the NECI plant on

upwind air difficult. Furthermore, for the purpose of identifying a potential solution to the problem, the identification of the constituents in the offsite odor plume was not necessary. Lastly, no compounds of human health concern (priority pollutants) and attributable to the NECI plant were found in the source term samples, thereby obviating the need to analyze the ambient samples for these same compounds.

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APPENDIX A

DESCRIPTIONS OF ANALYTICAL METHODS USED

Sources: U.S. Environmental Protection Agency (EPA). 1984a. Test Methods for Evaluating Solid Waste - Physical/Chemical Methods. SW-846, 2nd Edition Revised, U. S. Environmental Protection Agency, April, 1984.

U.S. Environmental Protection Agency (EPA). 1984b. Federal Register, October 26, 1984, Part VIII, Environmental Protection Agency, 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule".

Environmental Protection Agency

Pt. 136, App. A, Meth. 625

METHOD 625 -- BASE/NEUTRALS AND ACIDS

1. Scope and Application

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Ben-zidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction step, α -BHC, γ -BHC, endosulfan I and II, and endrin are subject to decomposition. Hex-achlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. The preferred method for each of these parameters is listed in Table 3.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method^{2, 14} applicable to the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 16.1)¹ for each parameter is listed in Tables 4 and 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is serially extracted with methylene chloride at a pH greater than 11

and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitative analysis is performed using internal standard techniques with a single characteristic m/z.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

3.4 The packed gas chromatographic columns recommended for the basic fraction may not exhibit sufficient resolution for certain isomeric pairs including the following: anthracene and phenanthrene; chry-

sene and benzo(a)anthracene; and benzo(b)fluoranthene and benzo(k)fluoranthene. The gas chromatographic retention time and mass spectra for these pairs of compounds are not sufficiently different to make an unambiguous identification. Alternative techniques should be used to identify and quantify these specific compounds, such as Method 810.

3.5 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 6 and 7 give characteristic CI ions for most of the compounds covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged but not required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified** for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α -BHC, β -BHC, δ -BHC, γ -BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls (PCBs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composited sampling.

5.1.1 Grab sample bottle—1-L or 1-gt. amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used, before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three all macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid—liquid extractor—Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6841-10 or equivalent.)

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min of Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 GC/MS system:

5.6.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

Environmental Protection Agency

Pt. 136, App. A, Meth. 625

5.6.2 Column for base/neutrals—1.8 m long x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are provided in Section 13.1.

5.6.3 Column for acids—1.8 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are given in Section 13.1.

5.6.4 Mass spectrometer—Capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.6.5 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 12) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.6.6 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z and plotting such m/z 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 abundance in any EICP between specified time or scan number limits.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H₂SO₄ (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Stock standard solutions (100 µg/µL) standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. 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.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

6.8 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 8. Prepare a surrogate standard spiking solution containing each selected surrogate compound at a concentration of 100 µg/mL in acetone. Addition of 1.00 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 µg/L of each surrogate standard. Store the spiking solution at 4 °C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9 DFTPP standard—Prepare a 25 µg/mL solution of DFTPP in acetone.

6.10 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Table 4 or 5.

7.2 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 8. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use

Pt. 136, App. A, Meth. 625

40 CFR Ch. I (7-1-85 Edition)

one of the next two most intense m/z quantities for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and dilute to volume with acetone. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z (Tables 4 and 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_i)}{(A_i)(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_i = Area of the characteristic m/z for the internal standard.

C_i = Concentration of the internal standard ($\mu\text{g/L}$).

C_s = Concentration of the parameter to be measured ($\mu\text{g/L}$).

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_i , vs. RF.

7.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 20\%$, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to

evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

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

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 $\mu\text{g/mL}$ in acetone. Multiple solutions may be required. PCBs and multicomponent pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available

from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 $\mu\text{g/L}$ by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery (\bar{X}) in $\mu\text{g/L}$, and the standard deviation of the recovery (s) in $\mu\text{g/L}$, for each parameter using the four results.

8.2.5 For each parameter 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 parameters of interest 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, the system performance is unacceptable for that parameter.

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

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters 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 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in

Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 $\mu\text{g/L}$ or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 $\mu\text{g/L}$.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 $\mu\text{g/L}$, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (\bar{X}) using the equation in Table 7, substituting the spike concentration (T) for C ; (2) calculate overall precision (S) using the equation in Table 7, substituting \bar{X} for \bar{X} ; (3) calculate the range for recovery at the spike concentration as $(100 \bar{X}/T) \pm 2.44(100 S/T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being si-

Pt. 136, App. A, Meth. 625

40 CFR Ch. I (7-1-85 Edition)

multaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Section 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_i) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_i) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (\bar{P}) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices* should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All sampling must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.* Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

10. Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When sample volumes of 2 L are to be extracted, use 250, 100, and 100-mL volumes of methylene chloride for the serial extraction of the base/neutrals and 200, 100, and 100-mL volumes of methylene chloride for the acids.

10.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to $\text{pH} > 11$ with sodium hydroxide solution.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical

methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 11.3.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

10.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60-mL aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extracts as the acid fraction.

10.6 For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.7 For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

10.9 Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride

to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of acetone or methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap vials and labeled base/neutral or acid fraction as appropriate.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel in Section 10.3, a continuous extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH > 11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and using a pipet, add 1.00 mL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50 to 100-mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 h. Allow to cool, then detach the distilling flask. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

11.5 Charge a clean distilling flask with 500 mL of methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Ex-

tract for 24 h. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP.¹⁰ Each day that benzidine is to be determined, the tailing factor criterion described in Section 12.4 must be achieved. Each day that the acids are to be determined, the tailing factor criterion in Section 12.5 must be achieved.

12.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)

Mass Range: 35 to 450 amu

Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

12.3 DFTPP performance test—At the beginning of each day, inject 2 μ L (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 9 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test for base/ neutrals—At the beginning of each day that the base/neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. Inject 100 ng of benzidine either separately or as a part of a standard mixture that may contain DFTPP and calculate the tailing factor. The benzidine tailing factor must be less than 3.0. Calculation of the tailing factor is illustrated in Figure 13.¹¹ Replace the column packing if the tailing factor criterion cannot be achieved.

12.5 Column performance test for acids—At the beginning of each day that the acids are to be determined, inject 50 ng of pentachlorophenol either separately or as a part of a standard mix that may contain DFTPP. The tailing factor for pentachlorophenol must be less than 5. Calculation of the tailing factor is illustrated in Figure 13.¹¹ Replace the column packing if the tailing factor criterion cannot be achieved.

13. Gas Chromatography/Mass Spectrometry

13.1 Table 4 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction. Table 5 summarizes the recommended gas chromatographic operating conditions for the acid fraction. Included in these tables are reten-

tion times and MDL that can be achieved under these conditions. Examples of the separations achieved by these columns are shown in Figures 1 through 12. Other packed or capillary (open-tubular) columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 The internal standard must be added to sample extract and mixed thoroughly immediately before it is injected into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

13.4 Inject 2 to 5 μ L of the sample extract or standard into the GC/MS system using the solvent-flush technique.¹² Smaller (1.0 μ L) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μ L.

13.5 If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

14. Qualitative Identification

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification:

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

14.1.2 The retention time must fall within ± 30 s of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within $\pm 20\%$ of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5. Use the base peak m/z for internal and surrogate standards. If the

sample produces an interference for the primary m/z , use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)^4}{(A_n)(RF)(V_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_n = Area of the characteristic m/z for the internal standard.

I_s = Amount of internal standard added to each extract (μg).

V_s = Volume of water extracted (L).

15.2 Report results in $\mu\text{g/L}$ without correction for recovery data. All QC data obtained should be reported with the sample results.

16. Method Performance

16.1 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.¹ The MDL concentrations listed in Tables 4 and 5 were obtained using reagent water.¹² The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

16.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5 to 1300 $\mu\text{g/L}$.¹⁴ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

17. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD)

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

17.1.1 Concentrate the base/neutral extract to a final volume of 0.2 ml.

17.1.2 Adjust the temperature of the base/neutral column (Section 5.6.2) to 220 °C.

17.1.3 Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

17.1.4 Inject 5 to 7 μL of the base/neutral extract. Collect SIM data for a total of 10 min.

17.1.5 The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

17.1.6 For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, calculate and retain the relative abundances of each of the three masses.

17.2 False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

17.3 Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can be obtained only from a properly equipped laboratory through the use of EPA Method 613 or other approved alternate test procedures.

REFERENCES

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Pt. 136, App. A, Meth. 625

40 CFR Ch. I (7-1-85 Edition)

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14. "EPA Method Study 30, Method 625, Base/Neutrals, Acids, and Pesticides," EPA 600/4-84-053, National Technical Information Service, PB84-206572, Springfield, Virginia 22161, June 1984.

TABLE 1.—BASE/NEUTRAL EXTRACTABLES

Parameter	STORET No.	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Aldrin	39330	309-00-2
Benzo(a)anthracene	34526	56-55-3
Benzo(b)fluoranthene	34230	205-99-2
Benzo(k)fluoranthene	34242	207-08-9
Benzo(a)pyrene	34247	50-32-8
Benzo(ghi)perylene	34521	191-24-2
Benzyl butyl phthalate	34292	85-68-7
β -BHC	39338	319-85-7
δ -BHC	3425910399-86-8	
Bis(2-chloroethyl) ether	34273	111-44-4
Bis(2-chloroethoxy)methane	3427810111-91-1	
Bis(2-ethylhexyl) phthalate	39100	117-81-7
Bis(2-chloroisopropyl) ether*	34283	108-60-1

TABLE 1.—BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	STORET No.	CAS No.
4-Bromophenyl phenyl ether*	34636	101-55-3
Chlordane	39350	57-74-9
2-Chloronaphthalene	34581	91-58-7
4-Chlorophenyl phenyl ether	34641	7005-72-3
Chrysene	34320	218-01-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dibenzo(a,h)anthracene	34556	53-70-3
Di-n-butylphthalate	39110	84-74-2
1,3-Dichlorobenzene	34566	541-73-1
1,2-Dichlorobenzene	34536	95-50-1
1,4-Dichlorobenzene	34571	106-46-7
3,3'-Dichlorobenzidine	34631	91-94-1
Dieldrin	39380	60-57-1
Diethyl phthalate	34336	84-66-2
Dimethyl phthalate	34341	131-11-3
2,4-Dinitrotoluene	34611	121-14-2
2,6-Dinitrotoluene	34626	606-20-2
Di-n-octylphthalate	34596	117-84-0
Endosulfan sulfate	34351	1031-07-8
Endrin aldehyde	34366	7421-93-4
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachloroethane	34396	87-72-1
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Isophorone	34408	78-59-1
Naphthalene	34696	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodi-n-propylamine	34428	621-64-7
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
Toxaphene	39400	8001-35-2
1,2,4-Trichlorobenzene	34551	120-82-1

* The proper chemical name is 2,2'-oxybis(1-chloropropane).

TABLE 2.—ACID EXTRACTABLES

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-3
2,4-Dinitrophenol	34616	51-28-1
2-Methyl-4,6-dinitrophenol	34657	534-52-7
2-Nitrophenol	34591	88-77-1
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-1
Phenol	34694	108-95-1
2,4,6-Trichlorophenol	34621	88-19-1

Environmental Protection Agency

Pt. 136, App. A, Meth. 625

TABLE 3.—ADDITIONAL EXTRACTABLE
PARAMETERS *

Parameter	STORET No	CAS No	Method
Benzidine	39120	92-87-5	605
β -BHC	39337	319-84-6	608
δ -BHC	39340	58-89-8	608
Endosulfan I	34361	959-98-8	608
Endosulfan II	34356	33213-65-9	608

TABLE 3.—ADDITIONAL EXTRACTABLE
PARAMETERS *—Continued

Parameter	STORET No	CAS No	Method
Endrin	39390	72-20-8	608
Hexachlorocyclopentadiene	34386	77-47-4	612
N-Nitrosodimethylamine	34438	62-75-9	607
N-Nitrosodiphenylamine	34433	86-30-6	607

* See Section 1.2.

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC
MASSES FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Reten- tion time (min)	Method detection limit ($\mu\text{g/L}$)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Second- ary	Second- ary	Meth- ane	Meth- ane	Meth- ane
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachloroethane	8.4	1.6	117	201	199	199	201	203
Bis(2-chloroethyl) ether*	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether*	9.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propylamine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	65	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	209
Isophorone	11.9	2.2	82	95	138	139	167	178
Naphthalene	12.1	1.6	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	65	107	137
Hexachlorocyclopentadiene*	13.9		237	235	272	235	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	181
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141			
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Diethyl phthalate	20.1	1.9	149	177	150	177	223	251
N-Nitrosodiphenylamine*	20.5	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.9	284	142	249	284	286	288
β -BHC*	21.1		183	181	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
δ -BHC*	22.4		183	181	109			
Phenanthrene	22.8	5.4	178	179	176	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β -BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ -BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.9	66	263	220			
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I*	26.4		237	339	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	248	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin*	27.9		81	263	82			
Endosulfan II*	28.6		237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzidine*	28.8	44	184	92	185	185	213	225
4,4'-DDT	29.3	4.7						
Endosulfan sulfate	29.8	5.6	237	165				
Endrin aldehyde			272	387	422			
			67	345	250			

Pt. 136, App. A, Meth. 625

40 CFR Ch. I (7-1-85 Edition)

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	Reten- tion time (min)	Method detec- tion limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Second- ary	Second- ary	Meth- ane	Meth- ane	Meth- ane
Butyl benzyl phthalate.....	29.9	2.5	149	91	206	149	299	327
Bis(2-ethylhexyl) phthalate 1D30.6.....	2.5	149	167	279	149			
Chrysene.....	31.5	2.5	228	226	229	228	229	257
Benzo(a)anthracene.....	31.5	7.8	228	229	226	228	229	257
3,3'-Dichlorobenzidine.....	32.2	16.5	252	254	126			
Di-n-octyl phthalate.....	32.5	2.5	149					
Benzo(b)fluoranthene.....	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene.....	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene.....	36.4	2.5	252	253	125	252	253	281
Indeno(1,2,3-cd) pyrene.....	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h)anthracene.....	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene.....	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethylamine ^a			42	74	44			
Chlordane ^c	19-30		373	375	377			
Toxaphene ^c	25-34		159	231	233			
PCB 1016 ^c	18-30		224	260	294			
PCB 1221 ^c	15-30	30	190	224	260			
PCB 1232 ^c	15-32		190	224	260			
PCB 1242 ^c	15-32		224	260	294			
PCB 1248 ^c	12-34		294	330	262			
PCB 1254 ^c	22-34	36	294	330	362			
PCB 1260 ^c	23-32		330	362	394			

^a The proper chemical name is 2,2'-bis(1-chloropropane).^b See Section 1.2.^c These compounds are mixtures of various isomers (See Figures 2 through 12). Column conditions: Supelcoport (100/120 mesh) coated with 3% SP-2250 packed in a 1.8 m long x 2 mm ID glass column with helium carrier gas at 30 mL/min. flow rate. Column temperature held isothermal at 50 °C for 4 min., then programmed at 8 °C/min. to 270 °C and held for 30 min.

TABLE 5.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR ACID EXTRACTABLES

Parameter	Reten- tion time (min)	Method detec- tion limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Second- ary	Second- ary	Meth- ane	Meth- ane	Meth- ane
2-Chlorophenol.....	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol.....	6.5	3.6	139	65	109	140	168	122
Phenol.....	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol.....	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol.....	9.8	2.7	162	164	98	163	165	167
2,4,6-Trichlorophenol.....	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol.....	13.2	3.0	142	107	144	143	171	183
2,4-Dinitrophenol.....	15.9	4.2	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol.....	16.2	24	198	182	77	199	227	239
Pentachlorophenol.....	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol.....	20.3	2.4	65	139	109	140	168	122

Column conditions: Supelcoport (100/120 mesh) coated with 1% SP-1240DA packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min. flow rate. Column temperature held isothermal at 70 °C for 2 min. then programmed at 8 °C/min. to 200 °C.

TABLE 6.—OC ACCEPTANCE CRITERIA—METHOD 625

Parameter	Test conclusion (µg/L)	Limits for s (µg/L)	Range for x(µg/L)	Range for P, P ₁ (Percent)
Acenaphthene.....	100	27.6	60.1-132.3	47-145
Acenaphthylene.....	100	40.2	53.5-126.0	33-145

TABLE 6—QC ACCEPTANCE CRITERIA—METHOD 625—Continued

Parameter	Test conclusion ($\mu\text{g/L}$)	Limits for s ($\mu\text{g/L}$)	Range for \bar{X} ($\mu\text{g/L}$)	Range for P, P _i (Percent)
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
μ -BHC	100	31.5	41.5-130.6	24-149
δ -BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether*	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.8-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.8-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26-155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Dichlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4)

\bar{X} = Average recovery for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4)

P, P_i = Percent recovery measured (Section 8.3.2, Section 8.4.2)

D = Detected; result must be greater than zero.

Note: 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.

* The proper chemical name is 2,2'-oxybis(1-chloropropane).

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, S _s (µg/L)	Overall precision, S (µg/L)
Acenaphthene.....	0.96C + 0.19	0.15X̄ - 0.12	0.21X̄ - 0.67
Acenaphthylene.....	0.89C + 0.74	0.24X̄ - 1.06	0.26X̄ - 0.54
Aldrin.....	0.78C + 1.66	0.27X̄ - 1.28	0.43X̄ + 1.13
Anthracene.....	0.80C + 0.68	0.21X̄ - 0.32	0.27X̄ - 0.64
Benzo(a)anthracene.....	0.88C - 0.60	0.15X̄ + 0.93	0.26X̄ - 0.28
Benzo(b)fluoranthene.....	0.93C - 1.80	0.22X̄ + 0.43	0.29X̄ + 0.96
Benzo(k)fluoranthene.....	0.87C - 1.56	0.19X̄ + 1.03	0.35X̄ + 0.40
Benzo(a)pyrene.....	0.90C - 0.13	0.22X̄ + 0.48	0.32X̄ + 1.35
Benzo(ghi)perylene.....	0.98C - 0.86	0.29X̄ + 2.40	0.51X̄ - 0.44
Benzyl butyl phthalate.....	0.66C - 1.68	0.18X̄ + 0.94	0.53X̄ + 0.92
β-BHC.....	0.87C - 0.94	0.20X̄ - 0.58	0.30X̄ - 1.94
δ-BHC.....	0.29C - 1.09	0.34X̄ + 0.86	0.93X̄ - 0.17
Bis(2-chloroethyl) ether.....	0.86C - 1.54	0.35X̄ - 0.99	0.35X̄ + 0.10
Bis(2-chloroethoxy)methane.....	1.12C - 5.04	0.16X̄ + 1.34	0.26X̄ + 2.01
Bis(2-chloroisopropyl) ether.....	1.03C - 2.31	0.24X̄ + 0.28	0.25X̄ + 1.04
Bis(2-ethoxyethyl) phthalate.....	0.84C - 1.18	0.26X̄ + 0.73	0.36X̄ - 0.67
4-Bromophenyl phenyl ether.....	0.91C - 1.34	0.13X̄ + 0.66	0.16X̄ + 0.66
2-Chloronaphthalene.....	0.89C + 0.01	0.07X̄ + 0.52	0.13X̄ + 0.34
4-Chlorophenyl phenyl ether.....	0.91C + 0.53	0.20X̄ - 0.94	0.30X̄ - 0.46
Chrysene.....	0.93C - 1.00	0.28X̄ + 0.13	0.33X̄ - 0.09
4,4'-DDD.....	0.56C - 0.40	0.29X̄ - 0.32	0.66X̄ - 0.96
4,4'-DDE.....	0.70C - 0.54	0.26X̄ - 1.17	0.39X̄ - 1.04
4,4'-DDT.....	0.79C - 3.28	0.42X̄ + 0.19	0.65X̄ - 0.58
Dbenzo(a,h)anthracene.....	0.88C + 4.72	0.30X̄ + 8.51	0.59X̄ + 0.25
Di-n-butyl phthalate.....	0.59C + 0.71	0.13X̄ + 1.16	0.39X̄ - 0.60
1,2-Dichlorobenzene.....	0.80C + 0.28	0.20X̄ + 0.47	0.24X̄ - 0.39
1,3-Dichlorobenzene.....	0.86C - 0.70	0.25X̄ + 0.88	0.41X̄ - 0.11
1,4-Dichlorobenzene.....	0.73C - 1.47	0.24X̄ + 0.23	0.29X̄ + 0.36
3,3'-Dichlorobenzidine.....	1.23C - 12.65	0.28X̄ + 7.33	0.47X̄ + 3.45
Dieldrin.....	0.82C - 0.16	0.20X̄ - 0.16	0.26X̄ - 0.07
Diethyl phthalate.....	0.43C + 1.00	0.28X̄ + 1.44	0.52X̄ - 0.22
Dimethyl phthalate.....	0.20C + 1.03	0.54X̄ + 0.19	1.05X̄ - 0.92
2,4-Dinitrotoluene.....	0.92C - 4.81	0.12X̄ + 1.06	0.21X̄ + 1.50
2,6-Dinitrotoluene.....	1.06C - 3.60	0.14X̄ + 1.26	0.19X̄ + 0.35
Di-n-octyl phthalate.....	0.78C - 0.79	0.21X̄ + 1.19	0.37X̄ + 1.19
Endosulfan sulfate.....	0.39C + 0.41	0.12X̄ + 2.47	0.63X̄ - 1.03
Endrin aldehyde.....	0.76C - 3.86	0.18X̄ + 3.91	0.73X̄ - 0.62
Fluoranthene.....	0.81C + 1.10	0.22X̄ - 0.73	0.28X̄ - 0.60
Fluorene.....	0.90C - 0.00	0.12X̄ + 0.26	0.13X̄ + 0.61
Heptachlor.....	0.87C - 2.97	0.24X̄ - 0.56	0.50X̄ - 0.23
Heptachlor epoxide.....	0.92C - 1.87	0.33X̄ - 0.46	0.28X̄ - 0.64
Hexachlorobenzene.....	0.74C + 0.66	0.18X̄ - 0.10	0.43X̄ - 0.52
Hexachlorobutadiene.....	0.71C - 1.01	0.19X̄ + 0.92	0.26X̄ - 0.49
Hexachloroethane.....	0.73C - 0.83	0.17X̄ - 0.67	0.17X̄ + 0.80
Indeno(1,2,3-cd)pyrene.....	0.78C - 3.10	0.29X̄ - 1.46	0.50X̄ - 0.44
Isophorone.....	1.12C + 1.41	0.27X̄ - 0.77	0.33X̄ - 0.26
Naphthalene.....	0.76C + 1.58	0.21X̄ - 0.41	0.30X̄ - 0.68
Nitrobenzene.....	1.09C - 3.05	0.19X̄ - 0.92	0.27X̄ - 0.21
N-Nitrosodi-n-propylamine.....	1.12C - 6.22	0.27X̄ - 0.68	0.44X̄ - 0.47
PCB-1260.....	0.81C - 10.86	0.35X̄ - 3.61	0.43X̄ - 1.82
Phenanthrene.....	0.87C - 0.06	0.12X̄ - 0.57	0.15X̄ - 0.25
Pyrene.....	0.84C - 0.16	0.16X̄ - 0.06	0.15X̄ - 0.31
1,2,4-Trichlorobenzene.....	0.94C - 0.79	0.15X̄ - 0.85	0.21X̄ - 0.39
4-Chloro-3-methylphenol.....	0.84C + 0.35	0.23X̄ - 0.75	0.29X̄ - 1.31
2-Chlorophenol.....	0.78C - 0.29	0.18X̄ - 1.46	0.28X̄ - 0.97
2,4-Dichlorophenol.....	0.87C - 0.13	0.15X̄ - 1.25	0.21X̄ - 1.28
2,4-Dimethylphenol.....	0.71C + 4.41	0.16X̄ - 1.21	0.22X̄ - 1.31
2,4-Dinitrophenol.....	0.81C - 18.04	0.38X̄ - 2.36	0.42X̄ - 26.24
2-Methyl-4,6-dinitrophenol.....	1.04C - 28.04	0.10X̄ - 42.29	0.26X̄ - 23.17
2-Nitrophenol.....	1.07C - 1.15	0.16X̄ - 1.94	0.27X̄ - 2.60
4-Nitrophenol.....	0.61C - 1.22	0.38X̄ - 2.57	0.44X̄ - 3.24
Pentachlorophenol.....	0.93C - 1.99	0.24X̄ - 3.03	0.30X̄ - 4.31
Phenol.....	0.43C - 1.26	0.26X̄ - 0.73	0.35X̄ - 0.64
2,4,6-Trichlorophenol.....	0.91C - 0.18	0.16X̄ - 2.22	0.22X̄ - 1.87

X' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L
 S_s = Expected single analyst standard deviation of measurements at an average concentration found of X, in µg/L

Environmental Protection Agency

Pt. 136, App. A, Meth. 625

S = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{X} , in $\mu\text{g/L}$.
 C = True value for the concentration, in $\mu\text{g/L}$.
 \bar{X} = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.
 * The proper chemical name is 2,2'-oxybis(1-chloropropane).

TABLE 8.—SUGGESTED INTERNAL AND SURROGATE STANDARDS

Base/neutral fraction	Acid fraction
Aniline-d ₆	2-Fluorophenol.
Anthracene-d ₁₀	Pentafluorophenol.
Benzo(a)anthracene-d ₁₂	Phenol-d ₆ .
4,4'-Dibromobiphenyl.....	2-Perfluoromethyl phenol.
4,4'-Dibromooctafluorobiphenyl.....	
Decafluorobiphenyl.....	
2,2'-Difluorobiphenyl.....	
4-Fluorobenzine.....	
1-Fluoronaphthalene.....	
2-Fluoronaphthalene.....	
Naphthalene-d ₈	
Nitrobenzene-d ₅	
2,3,4,5,6-Pentafluorobiphenyl.....	
Phenanthrene-d ₁₂	
Pyridine-d ₅	

TABLE 9.—DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
51	30-60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40-60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5-9 percent of mass 198.
275	10-30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17-23 percent of mass 442.

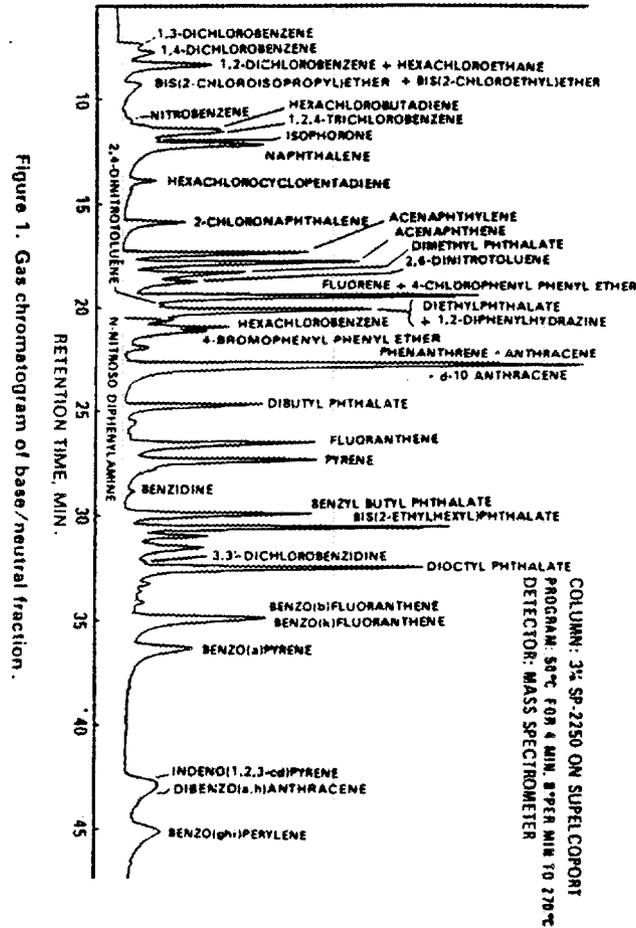


Figure 1. Gas chromatogram of base/neutral fraction.

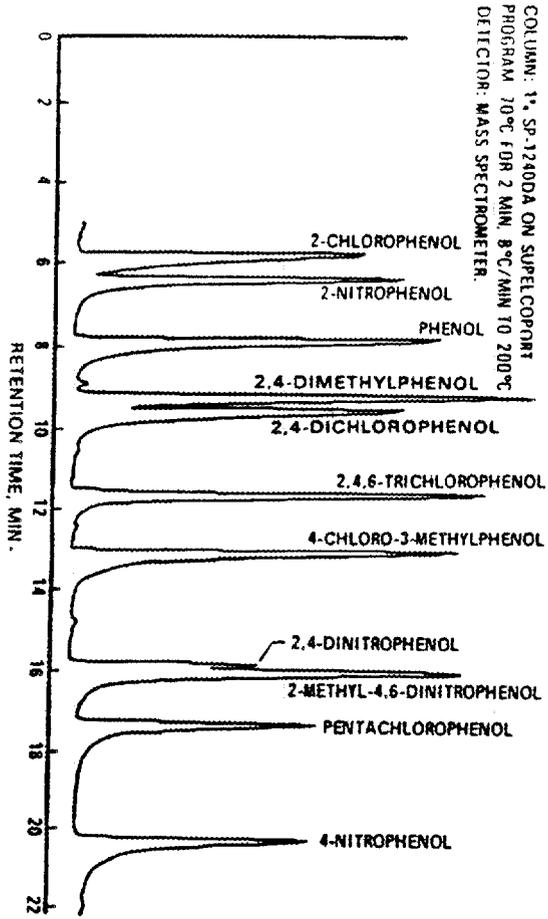


Figure 2. Gas chromatogram of acid fraction.

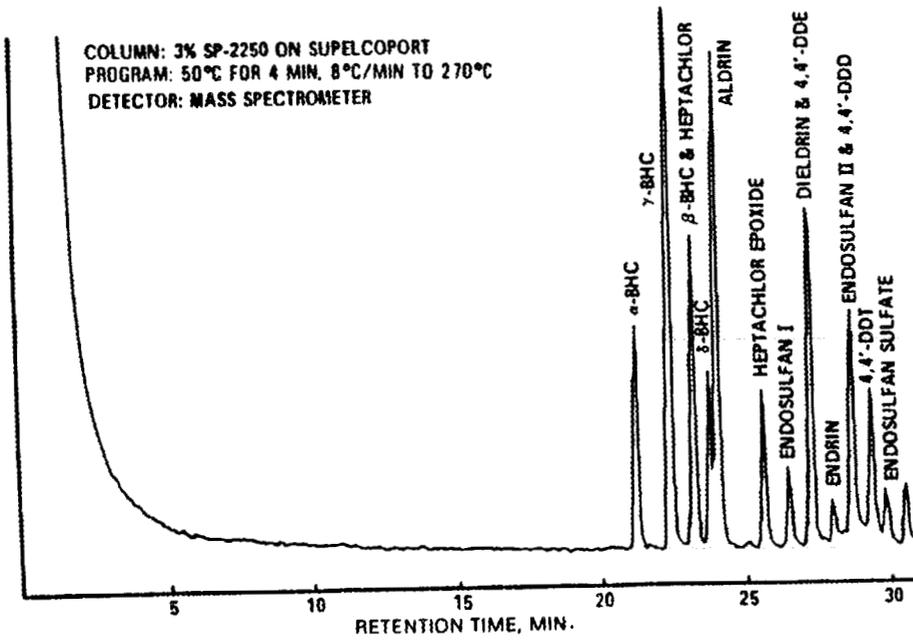


Figure 3. Gas chromatogram of pesticide fraction.

Environmental Protection Agency

Pt. 136, App. A, Meth. 625

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

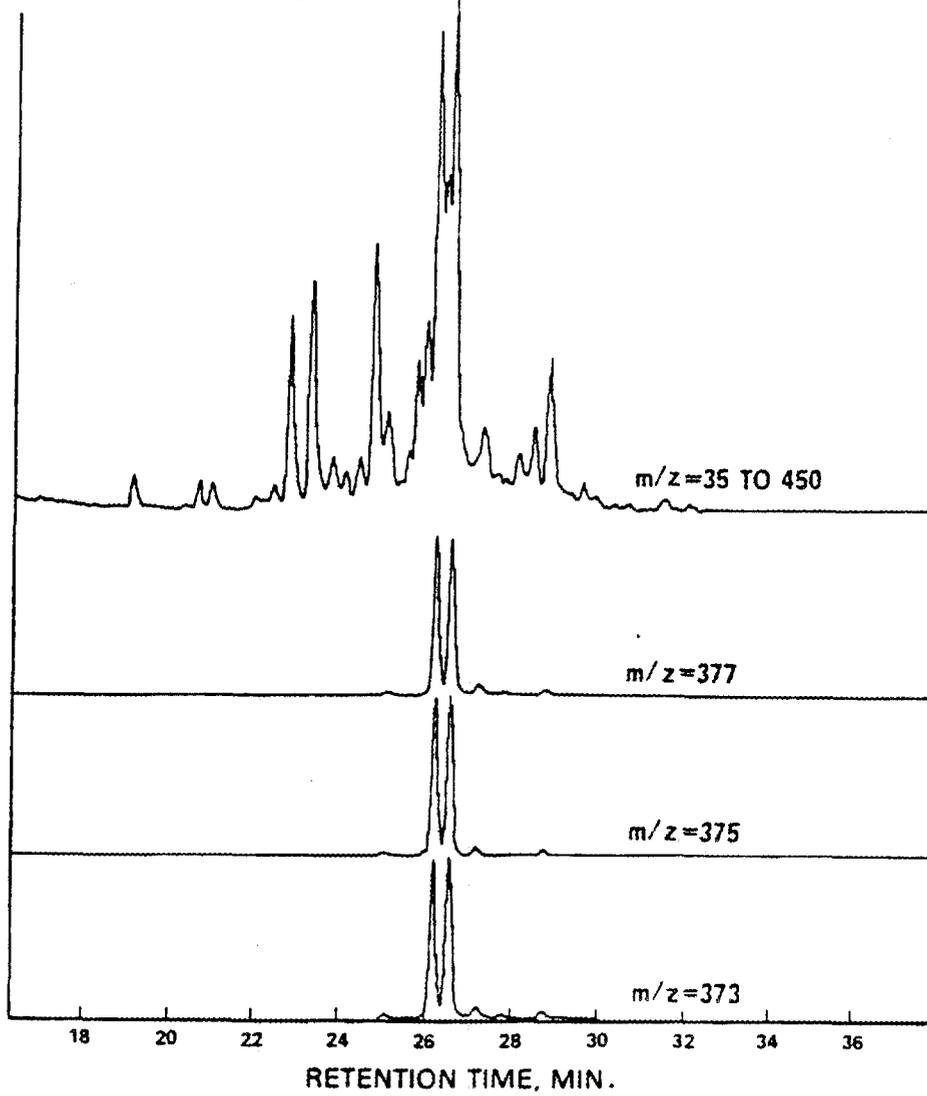


Figure 4. Gas chromatogram of chlordane.

Pt. 136, App. A, Meth. 625

40 CFR Ch. I (7-1-85 Edition)

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

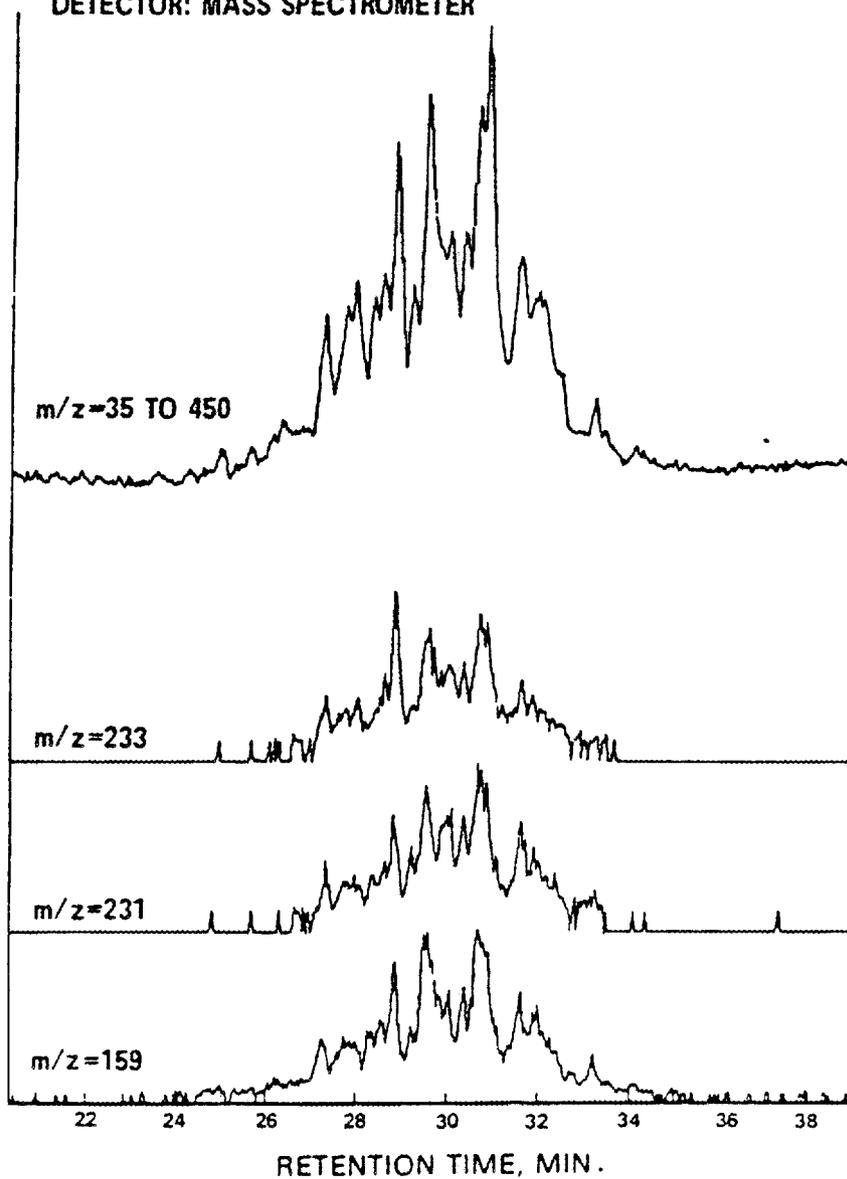


Figure 5. Gas chromatogram of toxaphene.

Environmental Protection Agency

Pt. 136, App. A, Meth. 625

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

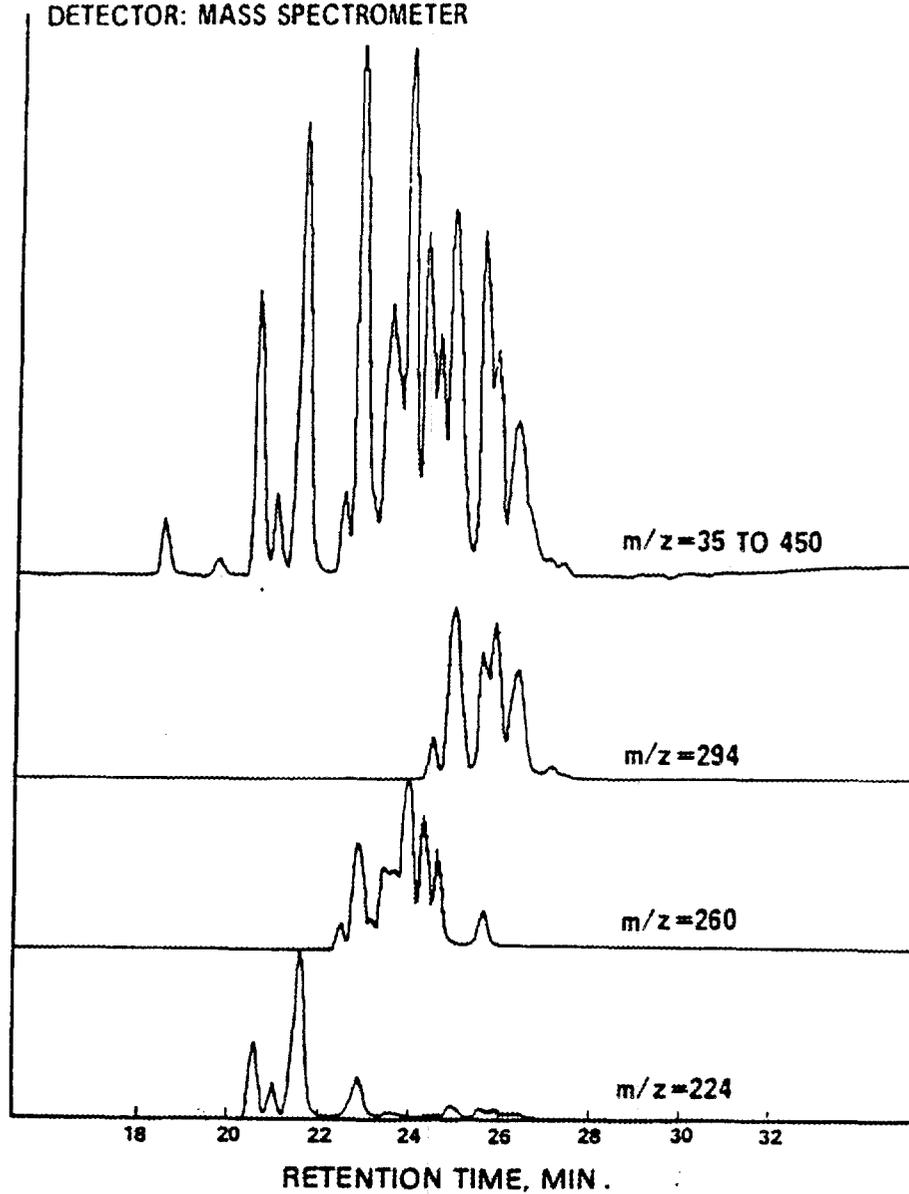


Figure 6. Gas chromatogram of PCB-1016.

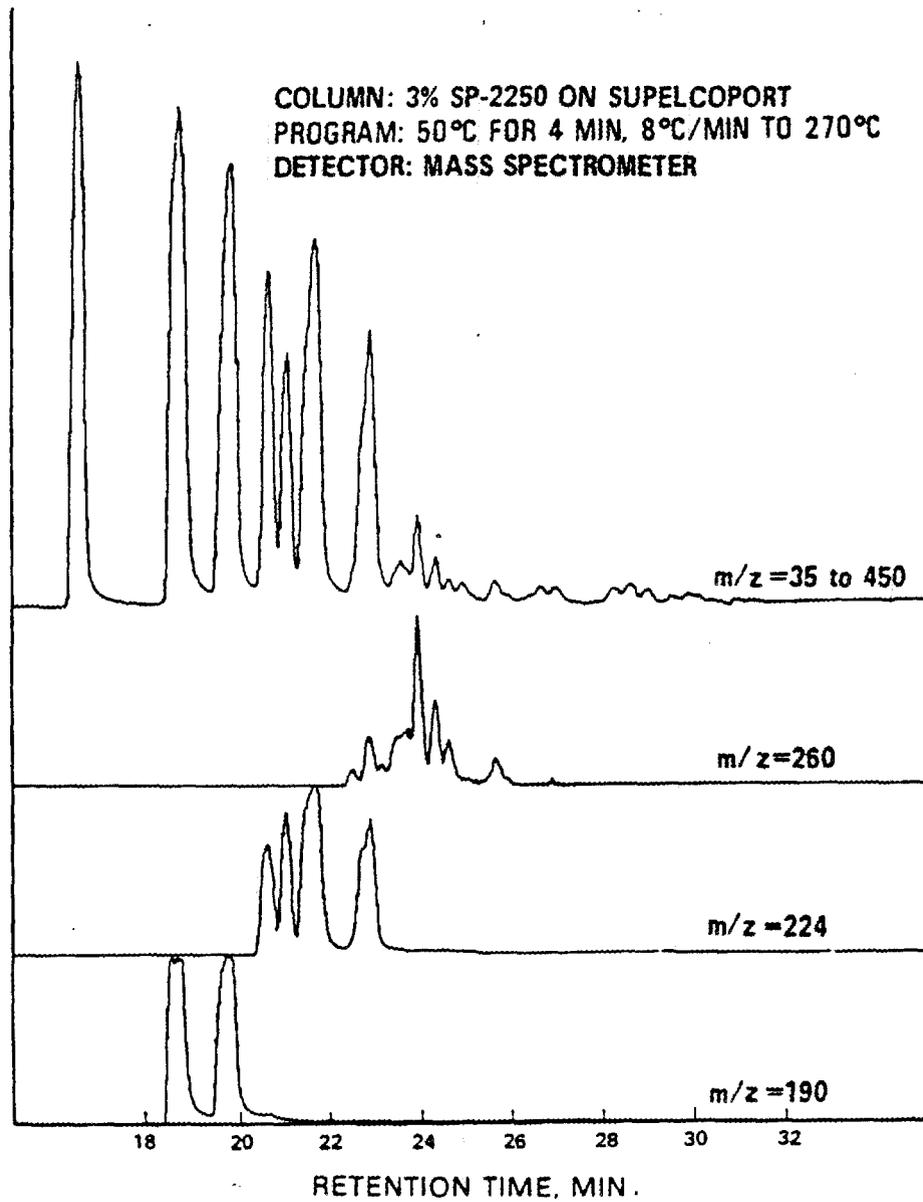


Figure 7. Gas chromatogram of PCB-1221.

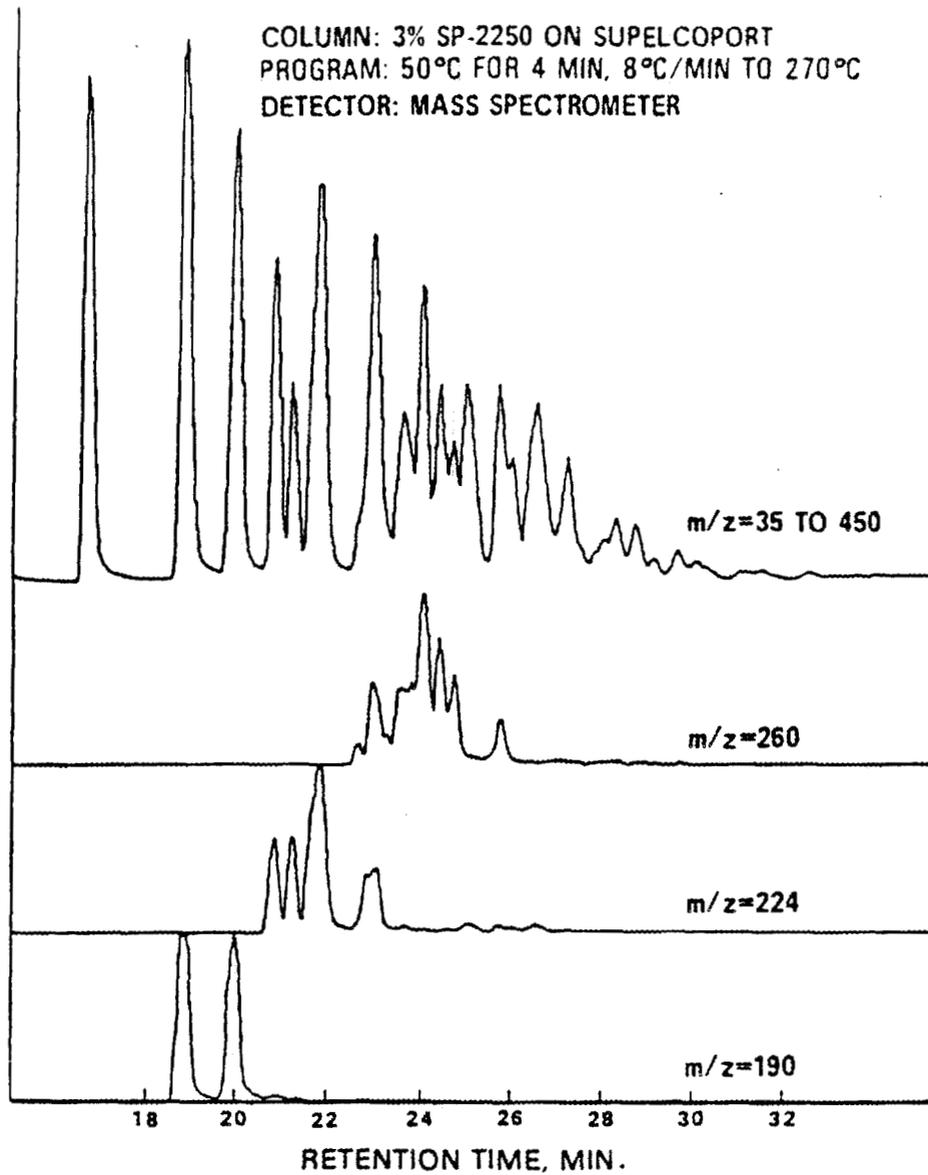


Figure 8. Gas chromatogram of PCB-1232.

Pt. 136, App. A, Meth. 625

40 CFR Ch. I (7-1-85 Edition)

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

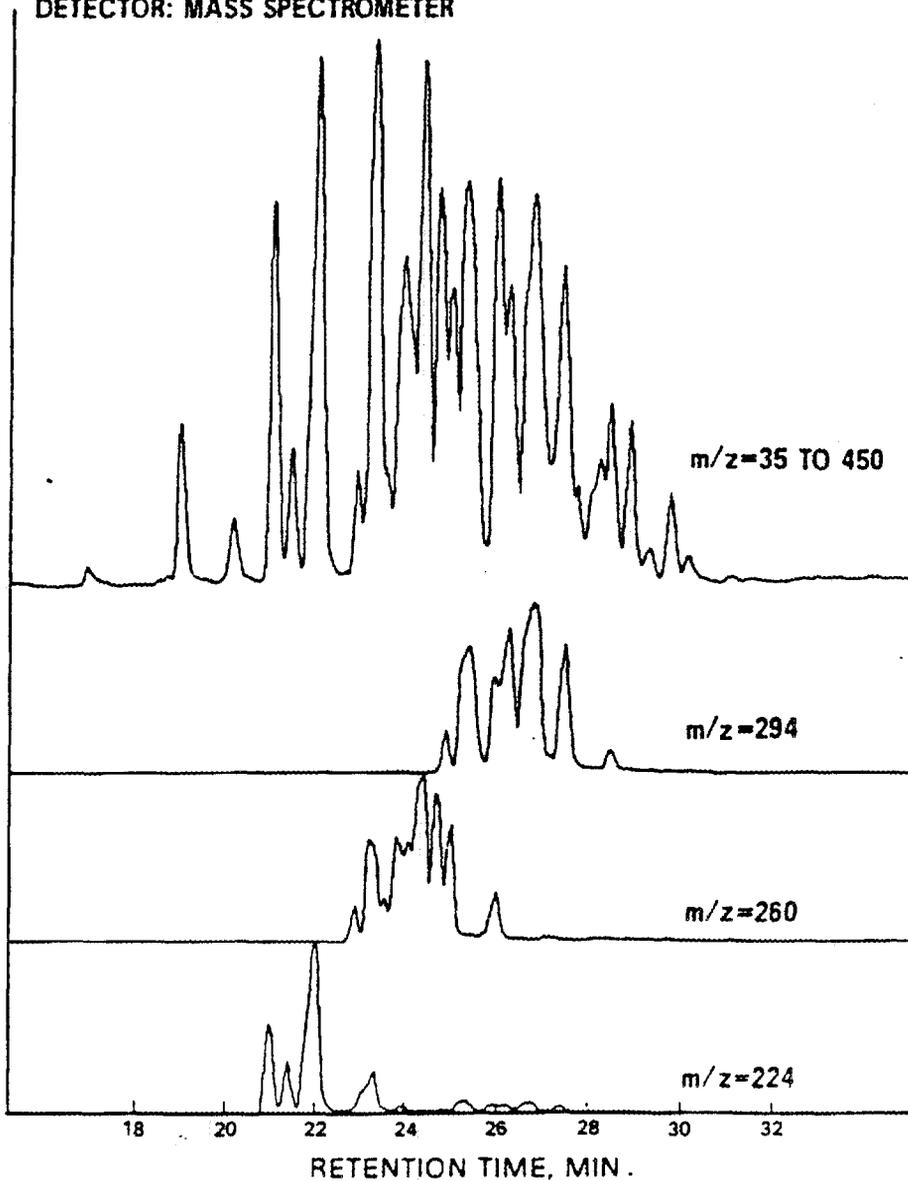


Figure 9. Gas chromatogram of PCB-1242.

Environmental Protection Agency

Pt. 136, App. A, Meth. 625

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

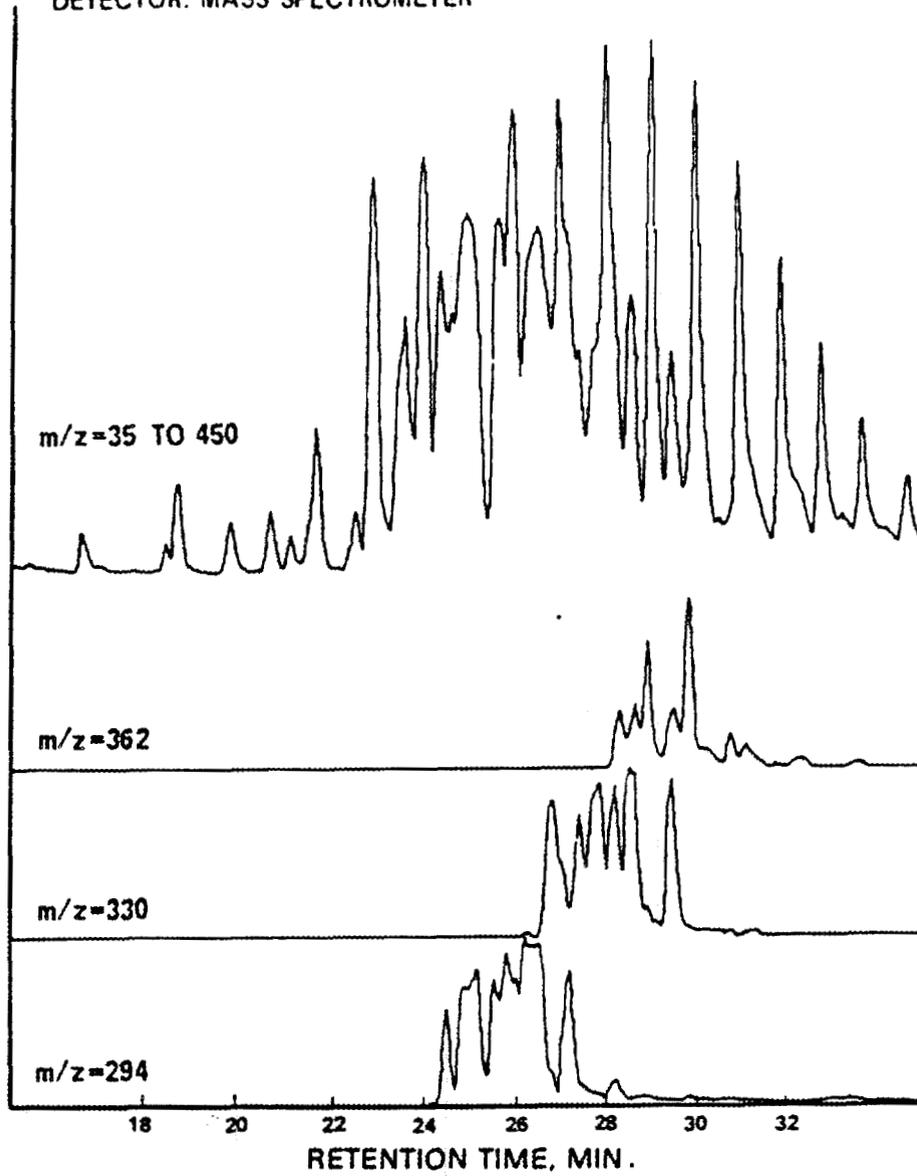


Figure 10. Gas chromatogram of PCB-1248.

Pt. 136, App. A, Meth. 625

40 CFR Ch. I (7-1-85 Edition)

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

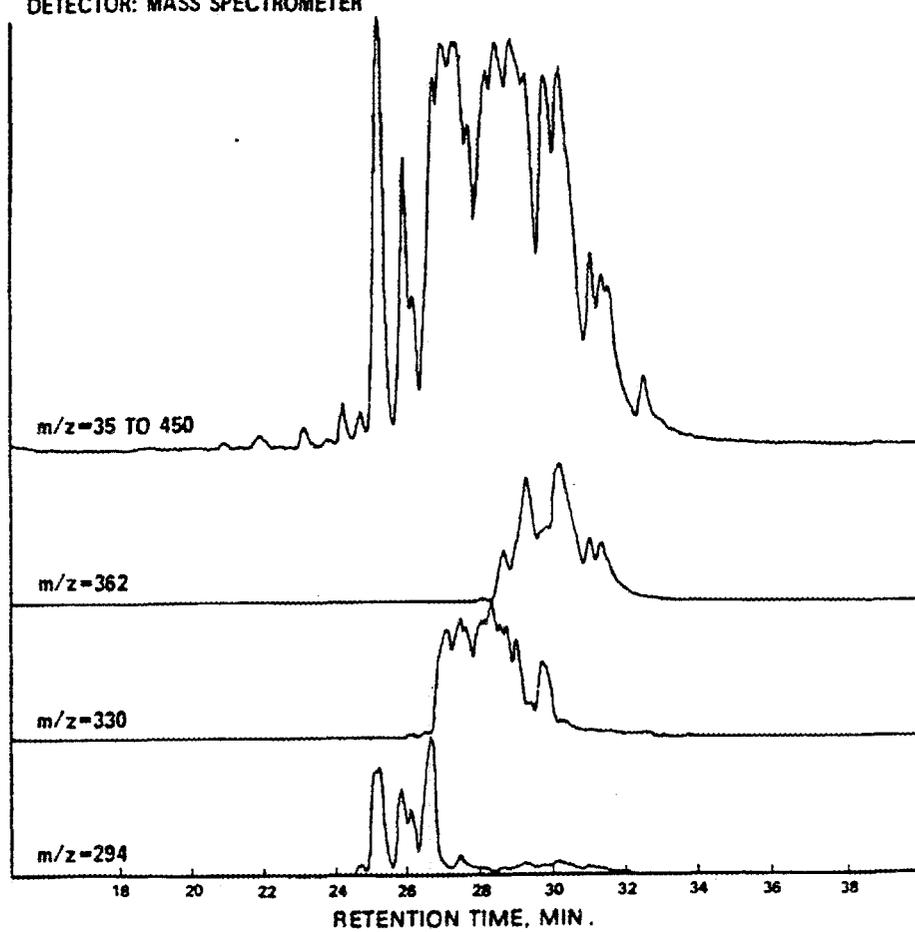


Figure 11. Gas chromatogram of PCB-1254.

Environmental Protection Agency

Pt. 136, App. A, Meth. 625

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN. 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

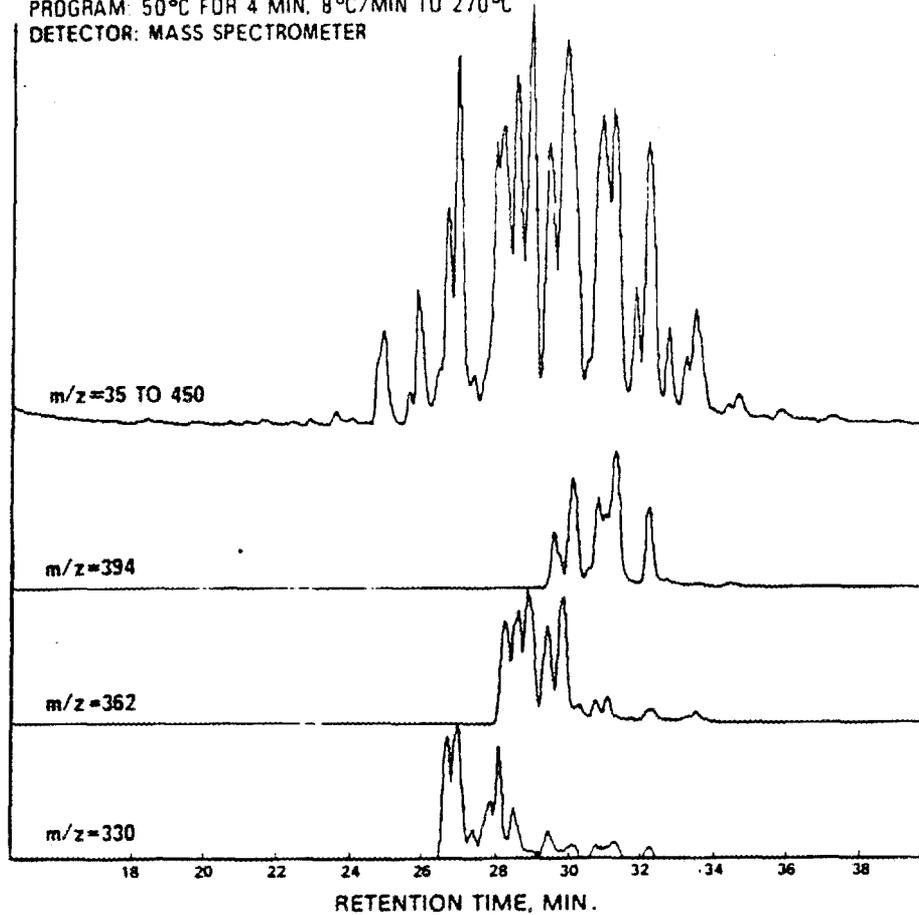
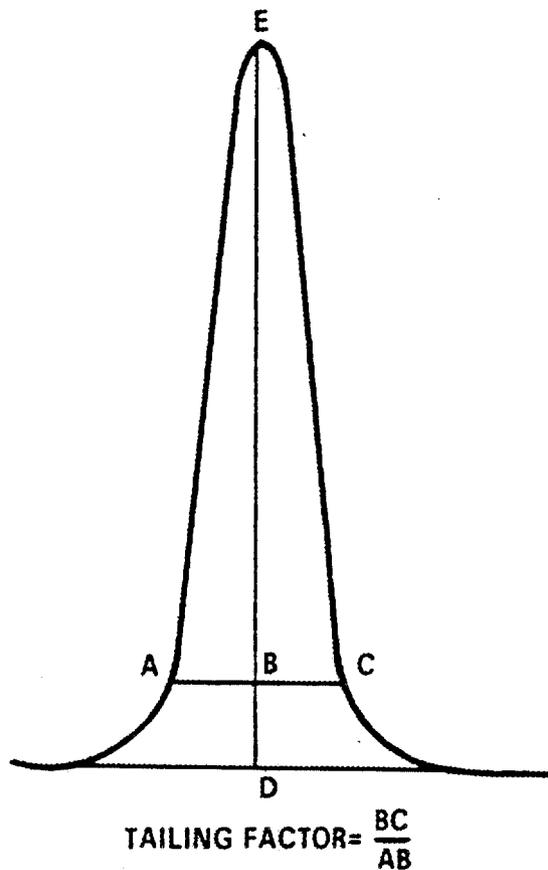


Figure 12. Gas chromatogram of PCB-1260.



Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm
Therefore: Tailing Factor = $\frac{12}{11} = 1.1$

Figure 13. Tailing factor calculation.

METHOD 3540

SOXHLET EXTRACTION1.0 Scope and Application

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils and sludges. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

2.0 Summary of Method

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. Methylene chloride should be employed when a solvent is not specified. The extract is then dried and concentrated, and either cleaned up further or analyzed directly by the appropriate measurement technique.

3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

4.0 Apparatus and Materials

4.1 Soxhlet extractor: 40-mm I.D., with 500-ml round-bottom flask.

4.2 Kuderna-Danish apparatus with three-ball Snyder column.

4.3 Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.

4.4 Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.

4.5 Boiling chips: Approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.6 Rheostat controlled heating mantle.

2 / WORKUP TECHNIQUES - Organic

5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical methods that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Soil samples: Soil samples shall be extracted using either of the following solvent systems.

5.4.1 Toluene/Methanol, 10:1 v/v ACS reagent grade only.

5.4.2 Acetone/Hexane, 1:1 v/v ACS reagent grade only.

5.5 Methylene chloride: Pesticide quality or equivalent.

6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

7.0 Procedure

7.1 Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

7.2 Place 300 ml of the extraction solvent into a 500-ml round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

7.3 Allow the extract to cool after the extraction is complete. Rinse the condenser with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

2 / ORGANIC ANALYTICAL METHODS - GC

3.0 Interferences

3.1 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105° C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

4.0 Apparatus and Materials

4.1 Vial with cap: 40-ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C before use.

4.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at

105° C for 30 min before use. NOTE: Do not heat the TFE seals for extended periods of time (i.e., more than 1 hr) because the silicone layer slowly degrades at 105° C.

4.3 Sample introduction apparatus for Methods 5020 and 5030.

4.4 Gas chromatograph: Analytical system complete with programmable gas chromatograph suitable for on-column injection or purge-and-trap sample introduction and all required accessories, including HSD or FID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

4.5 GC columns:

Column 1: 8-ft x 0.1-in. I.D. stainless steel or glass column packed with 1% SP-1000 on Carbopac B 60/80 mesh.

Column 2: 6-ft x 0.1-in. I.D. stainless steel or glass column packed with n-octane on Porasil-L 100/120 mesh.

4.6 Detector: Electrolytic conductivity (HSD).

4.7 Syringes: 5-ml glass hypodermic with Luerlok top (2 each).

4.8 Microsyringes: 10, 25, 100 μ l.

4.9 Two-way syringe valve with Luer ends (3 each).

4.10 Syringe: 5 ml, gas-tight with shutoff valve.

4.11 Bottle: 15-ml screw-cap, with teflon cap liner.

5.0 Reagents

5.1 Activated carbon: Filtrasorb 200 (Calgon Corp.) or equivalent.

5.2 Organic-free water: Generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr.

5.3 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids or gas cylinders as appropriate. Because of the toxicity of many of the compounds

4 ORGANIC ANALYTICAL METHODS - GC

being analyzed, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.3.1 Place about 9 ml of methyl alcohol into a 10-ml ground-glass-stoppered volumetric flask. Allow to stand about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Add the assayed reference material

5.3.2.1 Liquids: Using a 100- μ l syringe, immediately add an amount of assayed reference material to the flask, then reweigh. Be sure that the reference material falls directly into the alcohol without contacting the neck of the flask.

5.3.2.2 Gases: To prepare standards from any of the organic compounds that boil below 30° C, fill a 5-ml valved gas-tight syringe with the reference standard to the 5-ml mark. Lower the needle to 5 mm above the methyl alcohol meniscus. Slowly inject the reference standard above the surface of the liquid (the heavy gas will rapidly dissolve into the methyl alcohol).

5.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μ g/ μ l from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can 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 at 4° C and protect from light.

5.3.5 Prepare fresh standards weekly for those compounds whose boiling point is less than or equal to 30° C and for the 2-chloroethyl-vinyl ether. All other standards must be replaced after 1 month, or sooner if comparison with check standards indicate a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the prepared aqueous calibration standards will completely bracket the working range of the analytical system. Secondary dilution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards, available from the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, can be used to determine the accuracy of calibration standards.

5.5 Calibration standards: In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 μ l of alcoholic standards into 100 ml of reagent water.

5.5.2 Use a 25- μ l Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask.

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr unless preserved, stored, and sealed according to 6.1 and 6.3.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers (see Apparatus, Sections 4.1 and 4.2) having a total volume of at least 25 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Solid and semisolid samples are to be taken in the same way. Assure that no solid material interferes with sealing of the glass vial. Maintain the hermetic seal on the sample bottle until time of analysis.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle attached or with no needle. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the enclosed end of the barrel of a glass hypodermic syringe.

6 / ORGANIC ANALYTICAL METHODS - GC

6.3 The samples must be iced or refrigerated from the time of collection until extraction. If the sample may contain free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 ml will suffice for up to 5 ppm Cl₂) to the empty sample bottles just prior to shipping to the sampling site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 min.

6.4 All samples must be analyzed within 14 days of collection.

7.0 Procedures

7.1 The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1: Set helium gas flow at 40 ml/min flow rate. Set column temperature at 45° C for 3 min, then program an 8° C/min temperature rise to 220° C and hold for 15 min.

Column 2: Set helium gas flow at 40 ml/min flow rate. Set column temperature at 50° C for 3 min, then program a 6° C/min temperature rise to 170° C and hold for 4 min.

7.2 Calibration

7.2.1 By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.2.2) or the internal standard technique (Section 7.2.3).

7.2.2 External standard calibration procedure

7.2.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µl of one or more secondary dilution standards to 100, 500, or 1,000 ml of reagent water or the matrix under study. A 25-µl syringe should be used for this operation. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.2.2.2 Analyze each calibration standard according to the procedure being used (direct aqueous injection, headspace, or purge-and-trap) and tabulate peak height or area responses against the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (less than 10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.2.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Because of these limitations, no internal standard that would be applicable to all samples can be suggested. The compounds recommended for use as surrogate spikes have been used successfully as internal standards, because of their generally unique retention times.

7.2.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.2.2.1.

7.2.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4.

7.2.3.3 Analyze each calibration standard according to appropriate methods (direct injection, 5020, 5030), adding the internal standard spiking solution directly to an aliquot of the sample or, in the case of purge-and-trap, to the syringe. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

8 / ORGANIC ANALYTICAL METHODS - GC

where:

A_S = Response for the parameter to be measured

A_{IS} = Response for the internal standard

C_{IS} = Concentration of the internal standard

C_S = Concentration of the parameter to be measured

If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_S/A_{IS} against RF.

7.2.3.4 The working calibration curve or RF must be verified on each working day by measuring one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, either the test must be repeated using a fresh calibration standard, or a new calibration curve must be prepared for that compound.

7.3 Gas chromatographic analysis

7.3.1 Introduce volatile compounds to the gas chromatograph using direct injection, headspace (Method 5020), or purge-and-trap (Method 5030).

7.3.2 Table 1 summarizes the estimated retention times for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.3.3 Calibrate the system immediately prior to conducting any analysis and recheck for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

TABLE 1. ESTIMATED RETENTION TIMES FOR SOME HALOGENATED VOLATILE ORGANICS

Compound	Retention time (min)		Estimated detection limit ^a (µg/l)
	Col. 1	Col. 2	
Bis(2-chloroethoxy)methane			
Bis(2-chloroisopropyl)ether			
Bromobenzene			
Bromodichloromethane	13.7	14.6	0.10
Bromoform	19.2	19.2	0.20
Carbon tetrachloride	13.0	14.4	0.12
Chloroacetaldehyde			
Chlorobenzene	24.2	18.8	0.25
Chloroethane	3.33	8.68	0.52
Chloroform	10.7	12.1	0.05
1-Chlorohexane			
2-Chloroethyl vinyl ether	18.0		0.13
Chloromethane	1.50	5.28	0.08
Chlorotoluene			
Dibromochloromethane	16.5	16.6	0.09
Dibromomethane			
1,2-Dichlorobenzene	34.9	23.5	0.15
1,3-Dichlorobenzene	34.0	22.4	0.32
1,4-Dichlorobenzene	35.4	22.3	0.24
Dichlorodifluoromethane			
1,1-Dichloroethane	9.30	12.6	0.07
1,2-Dichloroethane	11.4	15.4	0.03
1,1-Dichloroethylene	8.0	7.72	0.13
trans-1,2-Dichloroethylene	10.1	9.38	0.10
Dichloromethane	6.5		
1,2-Dichloropropane	14.9	16.6	0.04
trans-1,3-Dichloropropylene	15.2	16.6	0.34
1,1,2,2-Tetrachloroethane	21.6		0.03
1,1,1,2-Tetrachloroethane			
Tetrachloroethylene	21.7	15.0	0.03
1,1,1-Trichloroethane	12.6	13.1	0.03
1,1,2-Trichloroethane	16.5	18.1	0.02
Trichloroethylene	15.8	13.1	0.12
Trichlorofluoromethane	7.18		
Trichloropropane			
Vinyl chloride	2.67	5.28	0.18

^aUsing purge-and-trap method (503U). See also Section 8.3.

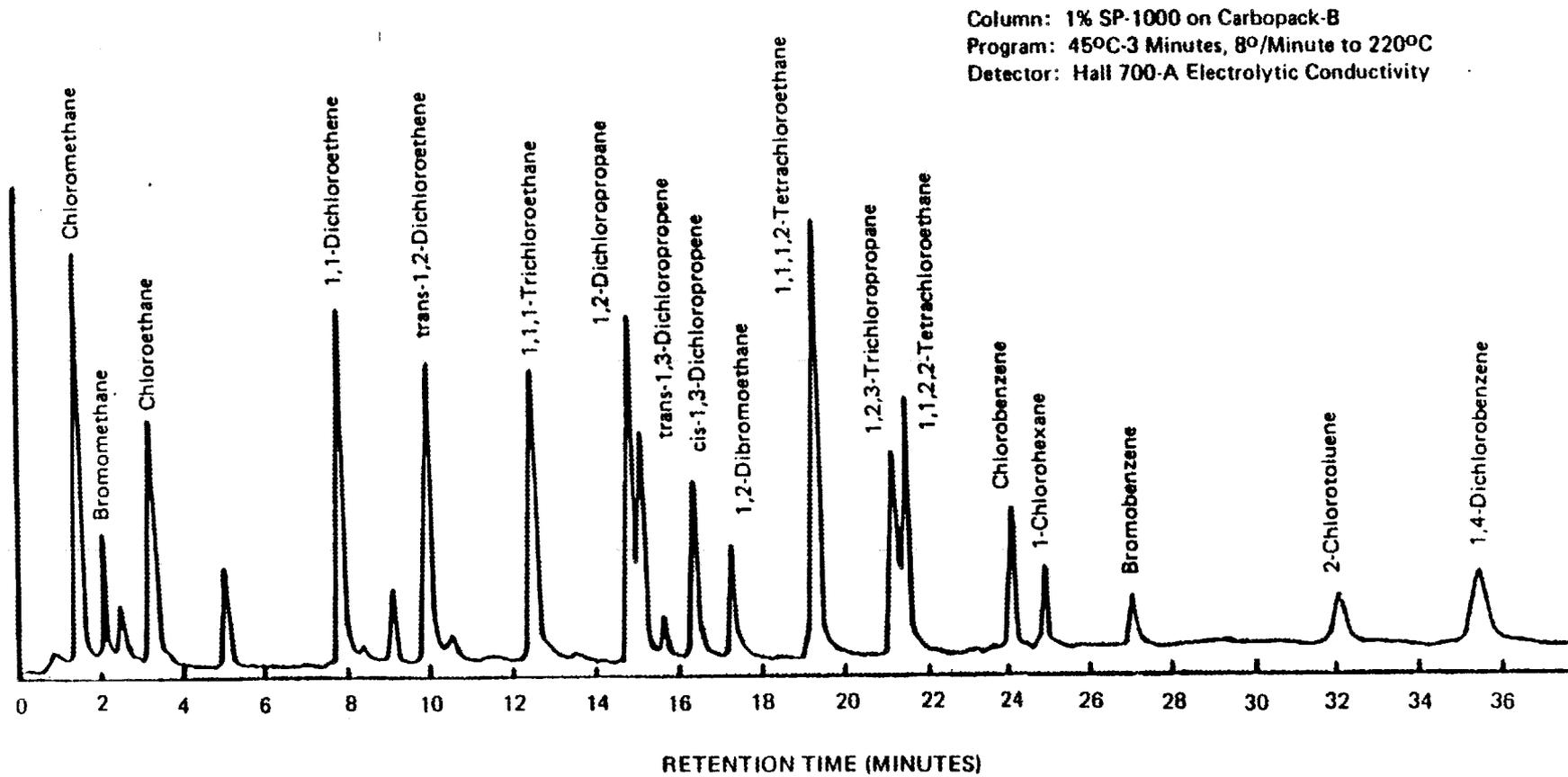


Figure 1. Gas Chromatogram of halogenated volatile organics.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased and the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.3 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 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.

8.4 In a single laboratory, using reagent water and wastewaters spiked near or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.
2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.
3. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635 (in preparation).

12 / ORGANIC ANALYTICAL METHODS - GC

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range ($\mu\text{g/l}$)	Number of analyses	Matrix types
Bromodichloromethane	100.9	5.0	0.43-46.7	21	3
Bromoform	89.5	9.0	1.45-50	20	3
Carbon tetrachloride	82.5	25.6	0.55-50	19	3
Chlorobenzene	93.9	8.9	2.21-50	20	3
Chloroethane	91.5	22.4	3.95-50	21	3
2-Chloroethylvinyl ether	96.3	9.9	4.39-133	20	3
Chloroform	101.7	20.6	0.44-50	20	3
Chloromethane	91.4	13.4	0.55-23.9	21	3
Dibromochloromethane	98.3	6.5	0.75-93.0	21	3
1,2-Dichlorobenzene	102.0	2.0	4.89-154	21	3
1,3-Dichlorobenzene	91.6	4.3	2.94-46.7	21	3
1,4-Dichlorobenzene	97.5	9.3	2.99-51.6	21	3
1,1-Dichloroethane	102.3	5.5	0.44-46.7	21	3
1,2-Dichloroethane	97.8	4.8	0.44-46.7	21	3
1,1-Dichloroethylene	101.1	21.7	0.37-50	19	3
trans-1,2-Dichloroethylene	91.0	19.3	0.44-98.0	20	3
1,2-Dichloropropane	97.7	8.8	0.29-39.0	21	3
trans-1,3-Dichloropropylene	73.5	17.2	0.43-50	20	3
1,1,2,2-Tetrachloroethane	91.9	15.0	0.46-46.7	21	3
Tetrachloroethylene	94.1	18.1	0.50-35.0	21	3
1,1,1-Trichloroethane	75.1	12.5	0.37-29.0	21	3
1,1,2-Trichloroethane	91.0	25.1	0.45-50	21	3
Trichloroethylene	106.1	7.4	0.38-46.7	21	3
Vinyl chloride	101.9	11.4	0.82-32.3	21	3

METHOD 8240

GC/MS METHOD FOR VOLATILE ORGANICS1.0 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 groundwater, 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.

1.2 The detection limit of Method 8240 for an individual compound is approximately 1 µg/g (wet weight) in waste samples. For samples containing more than 1 mg/g of total volatile material, the detection limit is proportionately higher.

1.3 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.

2.0 Summary of Method

2.1 The volatile compounds are introduced to the gas chromatograph by direct injection, the Headspace Method (Method 5020), or the Purge-and-Trap Method (Method 5030). Method 5030 should be used for groundwater analysis. 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 can be dispersed in methanol or polyethylene glycol (PEG) to dissolve the volatile organic constituents. A portion of the methanolic or PEG solution is combined with water in a specially designed purging chamber. An inert gas is then 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.

2.3 An aliquot of each sample must be spiked with an appropriate standard to determine percent recovery and detection limits for that sample.

2 / ORGANIC ANALYTICAL METHODS - GC/MS

2.4 Table 1 lists detection limits that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min) Column 1 ^a	Method detection limit ($\mu\text{g/l}$)
Chloromethane	2.3	ND
Bromomethane	3.1	ND
Vinyl chloride	3.8	ND
Chloroethane	4.6	ND
Methylene chloride	6.4	2.8
Trichlorofluoromethane	8.3	ND
1,1-Dichloroethene	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethene	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
trans-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
cis-1,3-Dichloropropene	17.2	ND
2-Chloroethylvinyl ether	18.6	ND
Bromoform	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	ND
1,2-Dichlorobenzene	35.0	ND
1,4-Dichlorobenzene	35.4	ND

ND = not determined.

^aColumn conditions: Carbowack B (60/80 mesh) coated with 1% SP-1000 packed in a 6-ft by 2-mm I.D. glass column with helium carrier gas at a flow rate of 30 ml/min. Column temperature is isothermal at 45° C for 3 min, then programmed at 8° C per minute to 220° and held for 15 min.

3.0 Interferences

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the particular waste or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences under the conditions of the analysis by running method blanks. Method blanks are run by analyzing organic-free water in the normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A field blank prepared from organic-free 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-level and low-level samples are sequentially analyzed. To reduce cross contamination, the purging device and sample syringe should be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

3.4 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.2.

4.0 Apparatus and Materials

4.1 Sampling equipment

4.1.1 Vial: 25-ml capacity or larger, equipped with a screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry for 1 hr at 105° C before use.

4.1.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water and dry at 105° C for 1 hr before use.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are now commercially available.

4 / ORGANIC ANALYTICAL METHODS - GC/MS

4.2.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous head space 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 purging chamber, illustrated in Figure 1, meets these design criteria.

4.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 2.5 mm. The trap must be packed to contain the following minimum lengths-of-adsorbents: 1.0 cm of methyl-silicone-coated packing (Section 5.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 5.3.1), and 8 cm of silica gel (Section 5.3.3). The minimum specifications for the trap are illustrated in Figure 2.

4.2.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec. The polymer section of the trap should not be heated higher than 180° C and the remaining sections should not exceed 220° C. The desorber design, illustrated in Figure 2, meets these criteria.

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

4.3 Gas chromatograph/mass spectrometer system

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

4.3.2 Column: 2-m x 2-mm I.D. stainless steel or glass, packed with 1% SP-1000 on 60/80 mesh Carboxpack B or equivalent.

4.3.3 Mass spectrometer: Capable of scanning from 40 to 250 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet or introduced in the purge-and-trap mode.

4.3.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Section 9) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

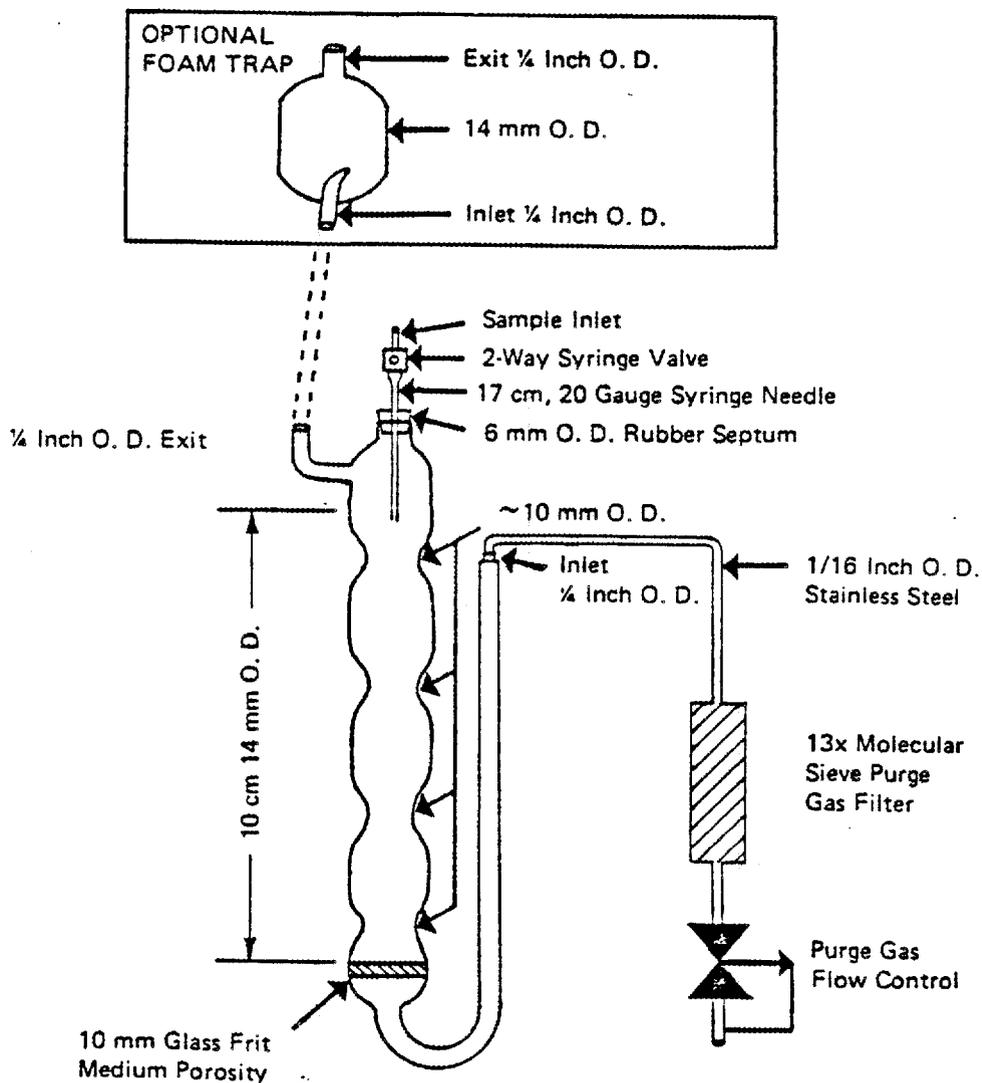


Figure 1. Purging chamber.

6 / ORGANIC ANALYTICAL METHODS - GC/MS

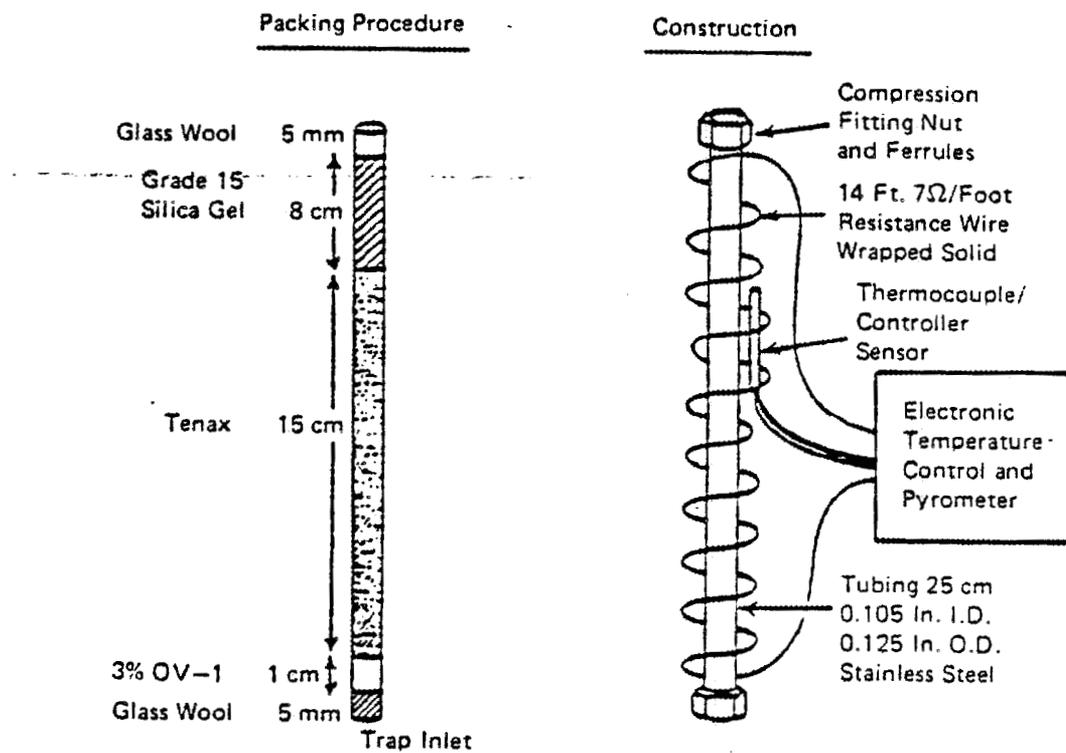


Figure 2. Trap packings and construction to include desorb capability.

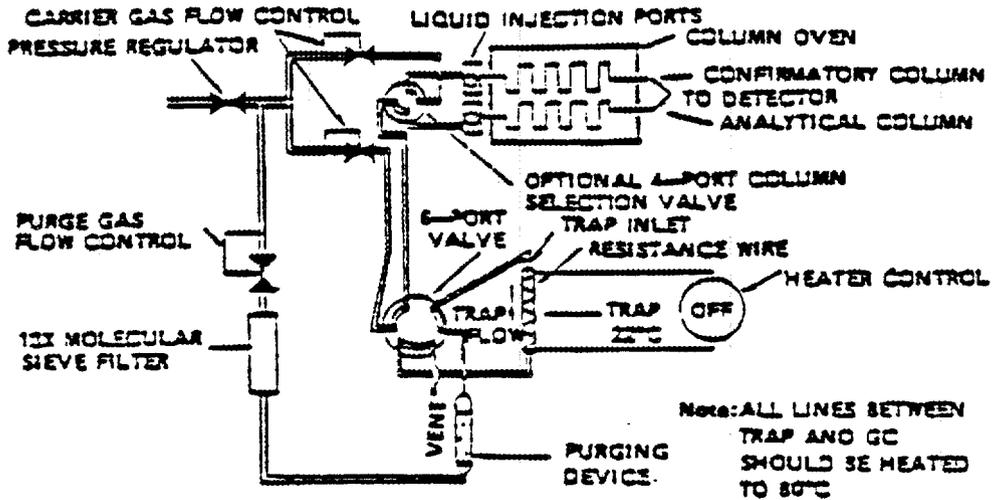


FIGURE 3. Schematic of purge and trap device - purge mode

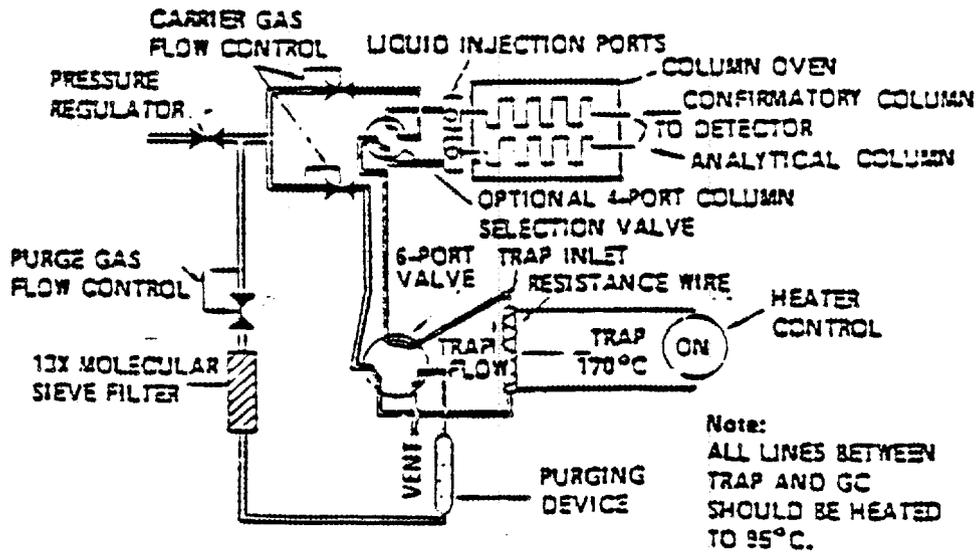


Figure 4. Schematic of purge and trap device - desorb mode

4.5 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.6 Micro syringes: 10- μ l, 25- μ l, 100- μ l, 250- μ l, and 1000- μ l. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.7 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation.

4.8 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.9 Syringe valve: 2-way, with Luer ends (2 each) (Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting, or equivalent).

4.10 Syringe: 5-ml, gas-tight with shut-off valve.

4.11 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.12 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.13 Rotary evaporator: equipped with Teflon-coated seals (Buchi Rotavapor R-110, or equivalent).

4.14 Vacuum pump: mechanical, two-stage.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300, or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

10 / ORGANIC ANALYTICAL METHODS - GC/MS

5.1.4 Reagent water may also be purchased under the name "HPLC water" from several manufacturers (Burdick and Jackson, Baker and Waters, Inc.).

5.2 Reagent PEG: Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferences are not observed at the method detection limit for compounds of interest.

5.2.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG 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 vacuum is maintained at less than 10 mm Hg for at least 1 hr 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.

5.2.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

5.3 Trap materials

5.3.1 2,6-Diphenylene oxide polymer: 60/80-mesh Tenax, chromatographic grade or equivalent.

5.3.2 Methyl silicone packing: 3 percent OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.3.3 Silica gel, Davison Chemical (35/60 mesh), grade-15 or equivalent.

5.3.4 Prepared trapping columns may be purchased from several chromatography suppliers.

5.4 Methanol: Distilled-in-glass quality or equivalent.

5.5 Calibration standards; stock solutions (2 mg/ml): Stock solutions of calibration standards may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions of individual compounds in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn by analysts when handling high concentrations of these materials.

5.5.1 Place about 9.8 ml of methanol in a 10-ml ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material as described below.

5.5.2.1 Liquids: Using a 100- μ l syringe, immediately add 2 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.

5.5.2.2 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 a 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 rapidly dissolves in the methanol.

5.5.3 Reweigh, dilute to volume, stopper, then mix by gently inverting the flask several times. Calculate the concentration in μ g/ μ l per microliter 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.

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

5.5.5 Prepare fresh standards weekly for gases or for reactive compounds such as 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

5.6 Calibration standards; secondary dilution solutions: Using stock solutions described in Section 5.5, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the methanol or aqueous PEG calibration solutions prepared as described in Section 6.3.2 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards from them.

5.7 Surrogate standards: Surrogate standards may be added to samples and calibration solutions to assess the effect of the sample matrix on recovery efficiency. The compounds employed for this purpose are 1,2-dibromotetrafluoroethane, bis(perfluoroisopropyl) ketone, fluorobenzene, and m-bromobenzotrifluoride. Prepare methanolic solutions of the surrogate standards using the procedures described in Sections 5.5 and 5.6. The

12 / ORGANIC ANALYTICAL METHODS - GC/MS

concentrations prepared and the amount of solution added to each sample should be those required to give an amount of each surrogate in the purging device that is equal to the amount of each internal standard added, assuming a 100% recovery of the surrogate standards.

5.8 Internal standards: In this method, internal standards are employed during analysis of all samples and during all calibration procedures. The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. However, for general use, D₄-1,2-dichloroethane, D₆-benzene, and D₅-ethylbenzene are recommended as internal standards covering a wide boiling point range.

5.9 4-Bromofluorobenzene (BFB): BFB is added to the internal standard solution or analyzed alone to permit the mass spectrometer tuning for each GC/MS run to be checked.

5.10 Internal standard solution: Using the procedures described in Sections 5.5 and 5.6, prepare a methanolic solution containing each internal standard at a concentration of 12.5 µg/ml.

5.11 Sodium monohydrogen phosphate: 2.0 µ in distilled water.

5.12 n-Nonane and n-dodecane, 98+% purity.

5.13 N-Hexadecane, distilled-in-glass (Burdick and Jackson, or equivalent).

6.0 Sample Collection, Handling, and Preservation

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples must be stored in Teflon-lined screw cap vials. Sample containers should be filled as completely as possible so as to minimize headspace or void space. Vials containing liquid sample should be stored in an inverted position.

6.3 All samples must be iced or refrigerated from the time of collection to the time of analysis, and should be protected from light.

7.0 Procedure

7.1 Calibration

7.1.1 Assemble a purge-and-trap device that meets the specifications in Section 4.2 and connect the device to a GC/MS system. Condition the trap overnight at 180° C by backflushing 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.

7.1.2 Operate the gas chromatograph using the conditions described in Section 7.3.5 and operate the mass spectrometer using the conditions described in Section 7.3.2.

7.1.3 Calibration procedure

7.1.3.1 Conduct calibration procedures using a minimum of three concentration levels for each calibration standard. One of the concentration levels should be at a concentration near but above the method detection limit. The remaining two concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3.2 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. To the purging device, add 5.0 ml of reagent water or reagent water/PEG solution. This solution is prepared by taking 4.0 ml of reagent water or reagent PEG and diluting to 100 ml with reagent water. The reagent water/PEG solution 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 a 20-gauge needle. Next, using a 10- μ l or 25- μ l micro-syringe equipped with a long needle (see Section 4.6), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (see Section 5.6). Add the aliquot of calibration solution directly to the reagent water or reagent water/PEG solution in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe be sure that the end of the syringe needle is well beneath the surface of the reagent water or water/PEG solution. Similarly, add 20 μ l of the internal standard solution (see Section 5.10). Close the 2-way syringe valve at the sample inlet.

7.1.3.3 Carry out the purge and analysis procedure as described in Section 7.3.4. Tabulate the area response of the primary characteristic ion against concentration for each compound

14 / ORGANIC ANALYTICAL METHODS - GC/MS

including the internal standards. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

where:

A_s = Area of the primary characteristic ion for the compound to be measured

A_{is} = Area of the primary characteristic ion of the internal standard

C_{is} = Concentration of the internal standard

C_s = Concentration of the compound to be measured.

The internal standard selected for the calculation of the RF of a compound and subsequent quantification of the compound is generally the internal standard that has a retention time closest to that of the compound. It is assumed that a linear calibration plot will be obtained over the range of concentrations used. If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , versus RF.

7.1.3.4 The RF must be verified on each working day. The concentrations selected should be near the midpoint of the working range. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within $\pm 20\%$ of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for BFB (see Table 2).

7.2.2 The BFB performance test requires the following instrumental parameters:

Electron Energy: 70 volts (nominal)

Mass Range: 40 to 250 amu

Scan Time: to give approximately 6 scans per peak but not to exceed 3 sec per scan.

7.2.3 Bleed BFB vapor into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of BFB given in Table 1. A solution containing 20 ng of BFB may be injected onto the gas chromatographic column in order to check the key ion criteria.

7.2.4 The peak intensity of D₆-benzene is used to monitor the mass spectrometer sensitivity. The peak intensity for D₆-benzene observed during each sample analysis must be between 0.7 and 1.4 times the D₆-benzene peak intensity observed during the applicable calibration runs. For example, if the peak intensity of D₆-benzene observed during calibration was 355,000 area counts, then each subsequent sample or blank must give a D₆-benzene peak intensity of between 250,000 and 500,000 area counts. If the D₆-benzene peak intensity is outside the specified range, the sample must be reanalyzed. If the peak intensity is again outside the specified range, the analyst must investigate the cause of the variability in sensitivity and correct the problem.

7.3 Sample extraction and analysis

7.3.1 The analytical procedure involves extracting the non-aqueous sample with methanol or polyethylene glycol (PEG) and analyzing a portion of the extract by a purge-and-trap GC/MS procedure. The amount of the extract to be taken for the GC/MS analysis is based on the estimated total volatile content (TVC) of the sample. The TVC is estimated by extracting the sample with n-hexadecane and analyzing the n-hexadecane extract by gas chromatography.

7.3.2 The estimated TVC is based on the total area response relative to that of n-nonane for all components eluting prior to the retention time of n-dodecane. The response factor for n-nonane and the retention time of n-dodecane are determined by analyzing a 2- μ l aliquot of an n-hexadecane solution containing 0.20 mg/ml of n-nonane and n-dodecane.

7.3.2.1 The GC analyses are conducted using a flame ionization detector and a 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100-200 mesh Chromosorb W-HP. The column temperature is programmed from 80° C to 280° C at 8°/min and held at 280° for 10 min.

7.3.2.2 Determine the area response for n-nonane and divide by 0.2 to obtain the area response factor. Record the retention time of n-dodecane.

7.3.2.3 Add 1.0 g of sample to 20 ml of n-hexadecane and 2 ml of 2.0 M Na₂HPO₄ contained in a 50-ml glass centrifuge tube and cap securely with a Teflon-lined screw cap. Shake the mixture vigorously for one minute. If the sample does not disperse

16 / ORGANIC ANALYTICAL METHODS - GC/MS

during the shaking process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate phase separation.

7.3.2.4 Analyze a 2- μ l aliquot of the n-hexadecane supernatant using the conditions described in Section 7.3.2.1. Determine the total area response of all components eluting prior to the retention time of n-dodecane and subtract the corresponding area of an n-hexadecane blank. Using the area response factor determined for n-nonane in Section 7.3.2.2, calculate the TVC as follows:

$$\text{TVC} = \frac{\text{TAR}_{\text{sample}} - \text{TAR}_{\text{blank}}}{\text{n-Nonane Area Response Factor}} \times 20$$

where:

TVC = total volatile content of the sample in mg/g

TAR_{sample} = total area response obtained for the sample

TAR_{blank} = total area response obtained for a blank.

7.3.3 The transfer of an aliquot of the sample for extraction with methanol or PEG should be made as quickly as possible to minimize loss of volatiles from the sample.

7.3.3.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent methanol or PEG. Weigh the capped centrifuge tube and methanol or PEG on an analytical balance.

7.3.3.2 Using an appropriate implement (see Section 4.4), transfer approximately 2 g of sample to the methanol or PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the methanol or PEG as quickly as possible. Take care not to touch the sample-transfer implement to the methanol or PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.3.3.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

7.3.3.4 The sample extract may be stored for future analytical needs. If this is desired, transfer the solution to a 10-ml screw cap vial with Teflon cap liner. Store at -10 to -20°C , and protect from light.

7.3.4 Reagent water, internal standard solution, and the sample extract are added to a purging chamber that is connected to the purge-and-trap device and that has been flushed with helium during a 7-min trap reconditioning step (see Section 7.3.4.4). The additions are made using an appropriately sized syringe equipped with a 15-cm 20-gauge needle. Open the syringe valve of the sample inlet (shown in Figure 1) and insert the needle through the valve.

7.3.4.1 Add 5.0 ml of reagent water or aqueous sample to which 20.0 μl of the internal standard solution has been added (see Section 5.10) to the purging chamber. Insert the needle of the syringe well below the surface of the water for the addition of the internal standard solution. If the sample is aqueous go to Section 7.3.5.

7.3.4.2 Add an aliquot of the sample extract from Section 7.3.3.4. The total quantity of volatile components injected should not exceed approximately 10 μg . If the total volatile content (TVC) of the sample as determined in Section 7.3.1.4 is 1.0 mg/g or less, use a 200- μl aliquot of the sample extract. If the TVC is greater than 1.0 mg/g, use an aliquot of the sample extract that contains approximately 10 μg of total volatile components; the volume (in μl) of the aliquot to be taken can be calculated by dividing 200 by the TVC. If the TVC is greater than 20 mg/g, take a 500- μl aliquot of the sample extract and dilute to 10 ml with PEG. In this case calculate the aliquot volume (in μl) of the undiluted extract to be taken by dividing 4,000 by the TVC. If the TVC is less than 1.0 mg/g and greater sensitivity is desired, use a large purging chamber containing 25 ml of reagent water and use a 1.0-ml aliquot of the sample extract.

7.3.4.3 Close the 2-way syringe valve at the sample inlet.

7.3.5 The sample in the purging chamber is purged with helium to transfer the volatile components to the trap. The trap is then heated to desorb the volatile components which are swept by the helium carrier gas onto the GC column for analysis.

7.3.5.1 Adjust the gas (helium) flow rate to 40 ± 3 ml/min. Set the purging device to purge, and purge the sample for 11.0 ± 0.1 min at ambient temperature.

18 / ORGANIC ANALYTICAL METHODS - GC/MS

7.3.5.2 At the conclusion of the purge time, adjust the device to the desorb mode, and begin the GC/MS analysis and data acquisition using the following GC operating conditions:

Column: 6-ft x 2-mm I.D. glass column of 1% SP-1000 on Carbo-pack B (60-80 mesh).

Temperature: Isothermal at 45° C for 3 min, then increased at 8° C/min to 220° C, and maintained at 220° C for 15 min.

Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 180° C while backflushing the trap with helium at a flow rate of 30 ml/min for 4 min. If this rapid heating requirement cannot be met, the GC column must be used as a secondary trap by cooling it to 30° C or lower during the 4-min desorb step and starting the GC program after the desorb step.

7.3.5.3 Return the purge-and-trap device to the purge mode and continue acquiring GC/MS data.

7.3.5.4 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution and distilled water, and then dried at 105° C.

7.3.5.5 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected when the trap is heated to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.3.6 If the response for any ion exceeds the working range of the system, repeat the analysis using a correspondingly smaller aliquot of the sample extract described in Section 7.3.2.3.

7.4 Qualitative identification

7.4.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.4.1.1 The characteristic ions of each compound of interest must maximize in the same or within one scan of each other.

7.4.1.2 The retention time must fall within ± 30 sec of the retention time of the authentic compound.

7.4.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within $\pm 20\%$ of the relative intensities of these ions in a reference mass spectrum. Reference spectra may be generated from the standards analyzed by the analyst or from a reference library. All reference spectra generated from standards must be obtained from an appropriately tuned mass spectrometer.

7.5 Quantitative determination

7.5.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion, as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used. Generally, the base peak of the mass spectrum is used.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of the data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.1.3 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

20 / ORGANIC ANALYTICAL METHODS - GC/MS

8.2.1 Analyze four aliquots of the unspiked check sample according to the method in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methanol at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples by adding the spiking solution to the PEG used for the extraction. Analyze the spiked aliquots according to the method in Section 7.3.

8.2.4 Calculate the average percent recovery, R , and the standard deviation of the percent recovery, s , for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery, $s/R \times 100$, must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= R + 3s \\ \text{Lower Control Limit (LCL)} &= R - 3s\end{aligned}$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standards to monitor spike recoveries. The spiking level used should be that which will give an amount in the purge apparatus that is equal to the amount of the internal standard assuming a 100% recovery of the surrogate standards. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be

qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Four surrogate standards, namely 1,2-dibromodifluoroethane, bis(perfluoroisopropyl) ether, fluorobenzene, and m-bromobenzotrifluoride, are recommended for general use to monitor recovery of volatile compounds varying in volatility and polarity.

8.5 Each day, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.8 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 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.

8.9 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

22 / ORGANIC ANALYTICAL METHODS - GC/MS

TABLE 3. ACCURACY AND PRECISION FOR PURGEABLE ORGANICS

Parameter	Reagent Water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Benzene	99	9	98	10
Bromodichloromethane	102	12	103	10
Bromoform	104	14	105	16
Bromomethane	100	20	88	23
Carbon tetrachloride	102	16	104	15
Chlorobenzene	100	7	102	9
Chloroethane	97	22	103	31
2-Chloroethyl vinyl ether	101	13	95	17
Chloroform	101	10	101	12
Chloromethane	99	19	99	24
Dibromochloromethane	103	11	104	14
1,1-Dichloroethane	101	10	104	15
1,2-Dichloroethane	100	8	102	10
1,1-Dichloroethene	102	17	99	15
trans-1,2-Dichloroethene	99	12	101	10
1,2-Dichloropropane	102	8	103	12
cis-1,3-Dichloropropene	105	15	102	19
trans-1,3-Dichloropropene	104	11	100	18
Ethyl benzene	100	8	103	10
Methylene chloride	96	16	89	28
1,1,2,2-Tetrachloroethane	102	9	104	14
Tetrachloroethene	101	9	100	11
Toluene	101	9	98	14
1,1,1-Trichloroethane	101	11	102	16
1,1,2-Trichloroethane	101	10	104	15
Trichloroethene	101	9	100	12
Trichlorofluoromethane	103	11	107	19
Vinyl chloride	100	13	98	25

Samples were spiked between 10 and 1000 µg/l.

METHOD 8270

GC/MS METHOD FOR SEMIVOLATILE ORGANICS:
CAPILLARY COLUMN TECHNIQUE1.0 Scope and Application

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including 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.

1.3 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8270 for determining an individual compound is approximately 1 µg/g (wet weight). For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8270 is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), sonication (Method 3550), or soxhlet extraction (Method 3540). If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

2 / ORGANIC ANALYTICAL METHODS - GC/MS

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon luer lock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2- μ m Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100- μ l (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control ($\pm 2^\circ$ C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to ± 0.1 pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

4 / ORGANIC ANALYTICAL METHODS - GC/MS

4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column: 30-m x 0.25-mm bonded-phase silicone-coated fused silica capillary column (J&W Scientific DB-5 or equivalent).

4.15.3 Mass spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA^a

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

^aJ.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. *Analytical Chemistry* 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS. The fused silica column may also be inserted directly into the MS source housing.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot 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 abundance in any EICP between specified time or scan number limits.

4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 nm.

4.16.6 Strip chart recorder.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic (K_3PO_4): Granular (ACS).

5.3 Phosphoric acid (H_3PO_4): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous (Na_2SO_4): Powder (ACS).

6 / ORGANIC ANALYTICAL METHODS - GC/MS

5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

5.6 D₁₀-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D₃-phenol, D₈-naphthalene, D₁₀-phenanthrene, D₁₂-chrysene, and D₁₂-benzo(a)pyrene. D₁₂-perylene may be used in place of D₁₂-benzo(a)pyrene.

5.9 Column performance standards: D₃-phenol, D₅-aniline, D₅-nitrobenzene, and D₃-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.0 Procedure

7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must use D₃-phenol, D₈-naphthalene, D₁₀-phenanthrene, D₁₂-chrysene and D₁₂-benzo(a)pyrene. D₁₂-perylene may be substituted for D₁₂benzo(a)pyrene. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards,

and a mass spectrometer tuning standard may be included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D₃-phenol, D₈-naphthalene, D₁₂-chrysene, and D₁₂-benzo(a)pyrene. D₁₂-perylene may be substituted for D₁₂-benzo(a)pyrene. D₁₀-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar neutral compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D₅-phenol or D₃-phenol, D₅-aniline, D₅-nitrobenzene, and D₃-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

8 / ORGANIC ANALYTICAL METHODS - GC/MS

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

A_S = Response for the parameter to be measured.

A_{IS} = Response for the internal standards.

C_{IS} = Concentration of the internal standard in $\mu\text{g/l}$.

C_S = Concentration of the compound to be measured in $\mu\text{g/l}$.

If the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_S/A_{IS} , against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within $\pm 20\%$ of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

- Maximum Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50 $\mu\text{g/ml}$ of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% absolute abundance from that observed during the analysis of the

calibration solution, then the analysis in question is considered invalid. The instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

7.3 Sample extraction

7.3.1 Samples may be extracted by Methods 3510, 3540, or 3550, or by the following procedure. The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with CH_2Cl_2 and analyzed. Solids and semisolids are extracted by Methods 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.3.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weigh 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to 7.0 ± 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M H_3PO_4 , the amount of 4 M H_3PO_4 needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization

to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2- μ m Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \quad (\text{Eq. 1})$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \quad (\text{Eq. 2})$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene

chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as described in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3

12 / ORGANIC ANALYTICAL METHODS - GC/MS

was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.5)}} \times \frac{10}{V_c(7.3.8)} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 3})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 4})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.7)}} \times \frac{V_F}{V_{\text{GPC}}(7.3.7)} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 5})$$

where:

V_s = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_c(7.3.8)$ = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_F(7.3.7)$ = Final volume of concentrate in Section 7.3.7

V_{GPC} = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl

phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVC of the concentrate as described in Section 7.3.6.

7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Section 7.3.8 by GC/MS using a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial column temperature hold: 40° C for 4 min

Column temperature program: 40-270° C at 10 degrees/min

Final column temperature hold: 270° C (until Benzo(ghi)perylene has eluted)

Injector temperature: 290° C

Transfer line temperature: 300° C

Injector: Grob-type, splitless

Sample volume: 1-2 µl

Carrier gas: Hydrogen (preferred) at 50 cm/sec or helium at 30 cm/sec

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Qualitative identification

7.6.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

14 / ORGANIC ANALYTICAL METHODS - GC/MS

7.6.1.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.1.2 The retention time must fall within +15 sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within +20% of the relative intensities of these ions in a reference mass spectrum.

7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu\text{g/g} = \frac{\mu\text{g of Int. Std.}}{\text{g of sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{\text{RF}} \quad (\text{Eq. 6})$$

where:

$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}}$ = internal standard concentration factor calculated in Section 7.3.8.

A_s = Area of the primary characteristic ion of the compound being quantified

A_{is} = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in $\mu\text{g/g}$ without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (s) for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery ($s/R \times 100$) must be less than 20 for all compounds to be measured and all surrogate compounds.

16 / ORGANIC ANALYTICAL METHODS - GC/MS

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

$$\text{Upper Control Limit (UCL)} = R + 3s$$

$$\text{Lower Control Limit (LCL)} = R - 3s$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP.
- Response factors of column performance standards and retention time standards.
- Relative retention time of column performance standards and retention time standards.
- Peak area intensity of the internal standard, e.g., D₁₀-phenanthrene.

METHOD 8270

GC/MS METHOD FOR SEMIVOLATILE ORGANICS:
CAPILLARY COLUMN TECHNIQUE

1.0 PREPARATION OF STANDARD SOLUTIONS

1.1 Internal standard solution: The internal standards recommended are 1,4-dichlorobenzene-d₄, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂. Other compounds may be used as internal standards as long as the requirements given in Section 5.1.2 are met. Dissolve 200 mg of each compound in 50 ml of methylene chloride. For complete dissolution, 5 to 10% benzene may be used with the methylene chloride. The resulting solution will contain each standard at a concentration of 4,000 ng/μl. Each 1-ml sample extract undergoing analysis should be spiked with 10 μl of the internal standard solution resulting in a concentration of 40 ng/μl of each internal standard. Store at 4°C or less when not being used.

1.2 GC/MS tuning standard: A methylene chloride solution containing 50 ng/μl of decafluorotriphenylphosphine (DFTPP) and of phenanthrene-d₁₀ should be prepared. This standard may contain other compounds from the calibration standard to verify GC column performance. Store at 4°C or less when not being used.

1.3 Calibration standards: Calibration standards at a minimum of three concentration levels should be prepared (five levels are recommended). One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples or should define the working range of the GC/MS system. Each standard should contain each compound of interest for detection by this method (e.g., some or all of the compounds listed in Tables 1, 2, and 3 may be included). Each 1-ml aliquot of calibration standard should be spiked with 10 μl of the internal standard solution prior to analysis. All standards should be stored at 4°C or less and should be freshly prepared as required (perhaps every 6 months at a minimum).

1.4 Surrogate standards: The recommended surrogate standards are phenol-d₆, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d₅, 2-fluorobiphenyl, and p-terphenyl-d₁₄. Two additional surrogates, one base/neutral and one acid, may be added. It is suggested that the acid compounds (the first three listed above) be prepared at a concentration of 100 μg/ml and the base/neutral surrogates at 50 μg/ml. Addition of 1.0 ml of the surrogate standard to 1,000 ml of sample is the recommended spiking level. The surrogate standard should be stored at 4°C and should be checked frequently for stability. Each sample undergoing extraction prior to GC/MS analysis must be spiked with the surrogate standard before actual extraction occurs.

8270 / 2

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE HSL COMPOUNDS

Parameter	Primary Ion	Secondary Ion(s)
N-Nitrosodimethylamine	42	74, 44
Phenol	94	65, 66
Aniline	93	66
Bis(2-chloroethyl) Ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Benzyl Alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
Bis(2-chloroisopropyl) Ether	45	77, 79
4-Methylphenol	108	107
N-Nitrosodipropylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	122	107, 121
Benzoic Acid	122	105, 77
Bis(2-chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-Methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl Phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	139	109, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	89	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethyl Phthalate	149	177, 150
4-Chlorophenyl-phenyl Ether	204	206, 141

(continued)

TABLE 1. (continued)

Parameter	Primary Ion	Secondary Ion(s)
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenyl Ether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Di-n-butyl Phthalate	149	150, 104
Fluoranthene	202	101, 100
Benzidine	184	92, 185
Pyrene	202	101, 100
Butylbenzyl Phthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Bis(2-ethylhexyl) Phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-octyl Phthalate	149	-
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277

8270 / 4

TABLE 2. CHARACTERISTIC IONS FOR PESTICIDES/PCBs

Parameter	Primary Ion	Secondary Ion(s)
Alpha-BHC	183	181, 109
Beta-BHC	181	183, 109
Delta-BHC	183	181, 109
Gamma-BHC (Lindane)	183	181, 109
Heptachlor	100	272, 274
Aldrin	66	263, 220
Heptachlor Epoxide	353	355, 351
Endosulfan I	195	339, 341
Dieldrin	79	263, 279
4,4'-DDE	246	248, 176
Endrin	263	82, 81
Endosulfan II	337	339, 341
4,4'-DDD	235	237, 165
Endrin Aldehyde	67	345, 250
Endosulfan Sulfate	272	387, 422
4,4'-DDT	235	237, 165
Methoxychlor	227	228
Chlordane	373	375, 377
Toxaphene	159	231, 233
Aroclor-1016	222	260, 292
Aroclor-1221	190	224, 260
Aroclor-1232	190	224, 260
Aroclor-1242	222	256, 292
Aroclor-1248	292	362, 326
Aroclor-1254	292	362, 326
Aroclor-1260	360	362, 394
Endrin Ketone	317	67, 319

TABLE 3. CHARACTERISTIC IONS FOR SURROGATES AND INTERNAL STANDARDS
FOR SEMIVOLATILE COMPOUNDS

Parameter	Primary Ion	Secondary Ion(s)
<u>Surrogates</u>		
Phenol-d ₆	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d ₅	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl-d ₁₄	244	122, 212
<u>Internal Standards</u>		
1,4-Dichlorobenzene-d ₄	152	150, 115
Naphthalene-d ₈	136	68
Acenaphthene-d ₁₀	164	162, 160
Phenanthrene-d ₁₀	188	94, 80
Chrysene-d ₁₂	240	120, 236
Perylene-d ₁₂	264	260, 265

8270 / 6

1.5 Matrix spike standards: Matrix spike standards should be prepared from acid and base/neutral compounds which will be representative of the compounds being investigated. The suggested base/neutral compounds are 1,2,4-trichlorobenzene, acenaphthene, 2,4-dinitrotoluene, di-n-butylphthalate, pyrene, N-nitroso-di-n-propylamine, and 1,4-dichlorobenzene. The suggested acid compounds are pentachlorophenol, phenol, 2-chlorophenol, 4-chloro-3-methylphenol, and 4-nitrophenol. Separate acid and base/neutral spiking standards should be prepared in methanol and should contain each base/neutral compound at 100 µg/ml and each acid compound at 200 µg/ml. Addition of 0.5 ml of each standard to 1,000 ml of sample is the recommended spiking level. Standards should be stored at 4°C or less and should be checked frequently for stability.

2.0 SAMPLE PRESERVATION

2.1 See Sample Handling and Preservation in the introductory material to the Organic section.

3.0 SAMPLE PREPARATION

3.1 The procedures for preparation of the sample are given in Methods 3510, 3520, 3540, 3550, and _____. Prior to sample extraction, the surrogate standard must be spiked into each sample. If matrix spike samples are required, the matrix spiking solution must be added to the sample prior to extraction. The concentrated extracts obtained from using the above methods will be analyzed by the following procedure.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph/Mass Spectrometer data system:

4.1.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

4.1.2 Column: 30-m x 0.25-mm I.D. (or 0.32-mm I.D.) silicon-coated fused silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 4 when 1 µl of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

TABLE 4. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA^a

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

^aJ.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

8270 / 8

4.1.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

4.1.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot 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 abundance in any EICP between specified time or scan number limits.

5.0 ANALYSIS PROCEDURE

5.1 Initial calibration:

5.1.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 50-ng injection of DFTPP. Analyses should not begin until all these criteria are met. The GC/MS tuning standard should also be used to assess GC column performance.

5.1.2 The internal standards selected in Section 1.1 should permit most of the components of interest in a chromatogram to have retention times of 0.080 to 1.20 relative to one of the internal standards (e.g., see Table 5). Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 3). If interferences are noted, use the next most intense ion as the quantitation ion, i.e., for 1,4-dichlorobenzene- d_4 use M/Z 152 for quantitation.

5.1.3 Analyze 1 μ l of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Tables 1, 2, and 3). Calculate response factors (RF) for each compound 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_x = Concentration of the compound being measured (ng/ μ l)

C_{is} = Concentration of the specific internal standard (ng/ μ l).

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING HSL ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d ₄	Naphthalene-d ₈	Acenaphthene-d ₁₀	Phenanthrene-d ₁₀	Chrysene-d ₁₂	Perylene-d ₁₂
N-Nitrosodimethyl-amine	Nitrobenzene	Hexachlorocyclopentadiene	4,6-Dinitro-2-methylphenol	Benzidine	Di-n-octyl Phthalate
Phenol	Isophorone	2,4,6-Trichlorophenol	N-nitrosodiphenylamine	Pyrene	Benzo(b)fluoranthene
Aniline	2-Nitrophenol	2,4,5-Trichlorophenol	4-Bromophenyl-phenyl Ether	Butylbenzyl Phthalate	Benzo(k)fluoranthene
Bis(2-chloroethyl) Ether	2,4-Dimethylphenol	2-Chloronaphthalene	Hexachlorobenzene	3,3'-Dichlorobenzidine	Benzo(a)pyrene
2-Chlorophenol	Benzoic Acid	2-Nitroaniline	Pentachlorophenol	Benzo(a)anthracene	Indeno(1,2,3-cd)pyrene
1,3-Dichlorobenzene	Bis(2-chloroethoxy)methane	Dimethyl Phthalate	Phenanthrene	Bis(2-ethylhexyl) Phthalate	Dibenz(a,h)anthracene
1,4-Dichlorobenzene	2,4-Dichlorophenol	Acenaphthylene	Anthracene	Chrysene	Benzo(g,h,i)perylene
Benzyl Alcohol	1,2,4-Trichlorobenzene	3-Nitroaniline	Di-n-butyl Phthalate	Terphenyl-d ₁₄ (surr)	
1,2-Dichlorobenzene	Naphthalene	Acenaphthene	Fluoranthene		
2-Methylphenol	4-Chloroaniline	2,4-Dinitrophenol			
Bis(2-chloroisopropyl) Ether	Hexachlorobutadiene	4-Nitrophenol			
4-Methylphenol	4-Chloro-3-methylphenol	Dibenzofuran			
N-Nitroso-di-n-propylamine	2-Methylnaphthalene	2,4-Dinitrotoluene			
Hexachloroethane	Nitrobenzene-d ₅ (surr)	2,6-Dinitrotoluene			
2-Fluorophenol (surr)		Diethyl Phthalate			
Phenol-d ₆ (surr)		4-Chlorophenyl-phenyl Ether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			
		2,4,6-Tribromophenol (surr)			

Surr = surrogate compound.

8270 / 10

5.1.4 The average response factor (RF) should be calculated for all compounds. The percent relative standard deviation (% RSD = $100[S/\overline{RF}]$) should be calculated for each compound. If the % RSD is less than 20%, the RF for a compound may be assumed to be constant over the working range of the GC/MS and the average RF may be used for subsequent calculations (i.e., quantitation of samples). Alternatively, the results can be used to generate a calibration curve of response ratios, A_x/A_{is} versus RF.

5.2 Daily GC/MS calibration:

5.2.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 4. These criteria must be demonstrated each 12-hr shift.

5.2.2 The initial calibration curve for each compound of interest should be checked and verified once every 12 hr of analysis time. This is accomplished by analyzing one or more of the calibration standards. The response factors calculated from the check calibration standard(s) should be within +20% of the response factor generated in the initial calibration (Section 5.1.4). If the deviation is greater than +20%, recalibration of the GC/MS must occur (Sections 5.1.3 and 5.1.4).

5.2.3 The internal standard responses and retention times in the check samples must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the initial calibration, the chromatographic system must be inspected for malfunctions and corrections made as required. If the EICP area for any internal standard 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 made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

5.3 GC/MS analysis:

5.3.1 Spike the 1-ml extract obtained from sample preparation (Section 3.0) with 10 μ l of the internal standard solution.

5.3.2 Analyze the 1-ml extract by GC/MS using a 30-m x 0.25-mm (or 0.32-mm) silicone-coated fused silica capillary column. The recommended GC/MS operating conditions to be used are as follows:

Electron energy: 70 volts (nominal)
Mass range: 35 to 450 amu
Scan time: 1 sec per scan
Initial column temperature and hold time: 40°C for 4 min
Column temperature program: 40-270°C at 10°/min
Final column temperature hold: 270°C (until benzo[g,h,i]perylene
has eluted)
Injector temperature: 250-300°C
Transfer line temperature: 300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
Sample volume: 1-2 µl
Carrier gas: Hydrogen (preferred) at 50 cm/sec or helium at
30 cm/sec.

5.3.3 If the response for any ion exceeds the working range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/µl of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

5.3.4 Perform all qualitative and quantitative measurements as described in Section 5.4. Store the extracts at 4°C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

5.4 Data interpretation:

5.4.1 Qualitative analysis:

5.4.1.1 A target compound (e.g., those listed in Tables 1, 2, and 3) shall be identified by comparison of the sample mass spectrum to 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. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of the sample component at the same GC relative retention times (RRT) as the standard component; and (2) correspondence of the sample component and standard component mass spectra.

8270 / 12

1. The sample RRT must compare within ± 0.06 RRT units of the RRT of the standard component. The RRT should be assigned by using the EICP for ions unique to the compound of interest.
2. The requirements for qualitative verification by comparison of a sample mass spectrum to a standard reference mass spectrum are as follows:
 - a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.
 - b. The relative intensities of ions specified above must agree within $\pm 20\%$ between the standard and sample mass spectra.
 - c. Ions greater than 10% in the sample spectrum which are not present in the standard spectra must be considered and accounted for by the analyst.

5.4.1.2 For samples which contain components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity of performing this type of identification will be determined by the type of analyses being conducted (e.g., for CLP requirements, up to 20 substances of greatest apparent concentration not listed in the Hazardous Substance List must be tentatively identified). All requirements specified for identification of target compounds (Section 5.4.1.1) apply to identification of noncalibrated components in the sample.

5.4.2 Quantitative analysis:

5.4.2.1 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).

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

Water

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

where:

- A_x = Area of characteristic ion for compound being measured
 I_s = Amount of internal standard injected (ng)
 V_t = Volume of total extract taking into account dilutions
 (i.e., a 1-to-10 dilution of a 1-ml extract will give
 $V_t = 10,000 \mu\text{l}$)
 A_{is} = Area of characteristic ion for the internal standard
 RF = Response factor for compound being measured (Sections
 5.1.3 and 5.1.4)
 V_o = Volume of water extracted (ml)
 V_i = Volume of extract injected (μl).

Sediment/Soil (on a dry-weight basis)

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

where:

- $A_x, I_s, V_t, A_{is}, RF, V_i$ = same as for water
 W_s = weight of sample extracted in grams
 $D = (100 - \% \text{ moisture in sample})/100$

5.4.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas 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 one. The concentration obtained should be reported indicating that the value is an estimate and indicating which internal standard was used to determine concentration.

5.4.2.4 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

8270 / 14

5.4.2.5 Calculate the recovery of each surrogate in each sample (including blanks and spikes). The recovery of matrix spike compounds, if used, should be corrected for sample contributions. These recoveries should be reported in the final data package.

6.0 INTERFERENCES

6.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being analyzed.

6.2 Laboratory contamination may affect sample analyses and, therefore, all precautions stipulated in the sample preparation procedures must be followed (e.g., clean glassware, use of high-purity solvents, etc.).

7.0 QUALITY ASSURANCE

7.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

7.2 Surrogate standards must be spiked into all samples to monitor continuing laboratory performance. Matrix spikes and process blanks should be analyzed on a routine basis (it is recommended that a minimum of 20% QC be adopted). Process blanks should be analyzed to determine the level of laboratory contamination prior to analysis and should therefore be performed on each set of samples on a per-extraction-method basis. Matrix spikes will be used to assess the accuracy of the analytical methods (extraction and detection) and should be performed on a per-extraction-method basis.

7.3 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should perform analysis of standard reference materials and should participate in relevant performance evaluation studies.

APPENDIX B

SUMMARY OF METEOROLOGICAL DATA RECORDED BY THE NATIONAL WEATHER
SERVICE OFFICE AT SOUTH BEND, INDIANA DURING SAMPLING TRIPS

SOUTH BEND, IN

November 20, 1985

SURFACE WEATHER OBSERVATIONS

<u>Time (EST)</u>	<u>Temperature (°F)</u>	<u>Dew Point (°F)</u>	<u>Wind Direction (Degrees)</u>	<u>Wind Speed (Knots)</u>
0053	36	29	250	22, Gust: 31
0152	33	27	260	20, Gust: 32
0252	30	23	250	22, Gust: 30
0353	27	19	240	17, Gust: 22
0451	25	19	240	14
0551	24	17	250	15, Gust: 23
0650	23	15	260	16, Gust: 24
0751	23	15	230	15, Gust: 20
0849	22	13	230	15, Gust: 20
0951	23	14	260	10
1021			250	14, Gust: 20
1048	25	13	260	15
1148	26	13	260	16
1248	25	12	230	15
1348	28	13	260	13 Gust: 21
1448	29	15	240	15 Gust: 21
1544	30	15	240	15
1647	28	16	240	10
1751	26	17	260	10
1847	25	17	240	08
1936			240	09
1947	25	18	240	08
2046			250	09
2050	25	18	250	09
2143			260	10
2147	26	18	260	08
2247	26	18	240	09
2347	27	19	290	11

SOUTH BEND, IN

November 21, 1985

SURFACE WEATHER OBSERVATIONS

<u>Time (EST)</u>	<u>Temperature (°F)</u>	<u>Dew Point (°F)</u>	<u>Wind Direction (Degrees)</u>	<u>Wind Speed (Knots)</u>
0052	27	18	300	09
0150	27	18	300	09
0251	27	19	300	11
0352	25	18	320	09
0451	25	19	340	08
0550	25	19	350	05
0651	25	19	350	06
0720			350	06
0750	24	19	360	04
0814			010	04
0850	26	19	360	04
0950	28	20	010	08
1050	30	20	020	07
1136			020	06
1150	32	20	050	10
1250	33	20	350	07
1350	34	20	050	07
1450	35	20	040	06
1550	35	19	050	07
1648	34	19	060	09
1750	31	20	060	08
1847	31	20	060	10
1947	31	20	080	09
2050	31	20	070	10
2147	31	21	080	12
2247	31	21	080	14
2347	31	22	060	12
2356				

SOUTH BEND, IN

January 21, 1986

SURFACE WEATHER OBSERVATIONS

<u>Time (EST)</u>	<u>Temperature (°F)</u>	<u>Dew Point (°F)</u>	<u>Wind Direction (Degrees)</u>	<u>Wind Speed (Knots)</u>
0048	27	25	150	08
0148	27	25	150	09
0248	27	25	140	08
0348	27	24	160	07
0448	26	24	140	07
0548	27	24	120	09
0648	27	24	120	10
0748	29	25	120	10
0836			150	12
0852	30	27	130	12
0950	34	29	140	16, Gust: 23
1051	38	31	140	13, Gust: 20
1150	41	32	150	17, Gust: 22
1253	45	34	170	19, Gust: 30
1350	46	35	160	14, Gust: 25
1452	50	37	170	14, Gust: 23
1549	51	38	180	17, Gust: 22
1648	50	39	180	12
1750	50	40	190	09
1850	48	40	180	09
1948	50	42	210	14
2051	48	43	250	14
2142			240	15
2150	40	36	270	16
2248	37	33	270	16
2348	37	32	260	18, Gust:
27				

SOUTH BEND, IN

January 22, 1986

SURFACE WEATHER OBSERVATIONS

<u>Time (EST)</u>	<u>Temperature (°F)</u>	<u>Dew Point (°F)</u>	<u>Wind Direction (Degrees)</u>	<u>Wind Speed (Knots)</u>
0048	37	32	250	14, Gust: 21
0150	36	32	250	13
0248	36	32	250	17, Gust: 24
0349	36	31	250	15, Gust: 23
0448	35	32	270	17, Gust: 23
0548	34	32	280	19, Gust: 25
0626			290	16, Gust: 24
0648	34	32	290	16
0748	34	32	310	14
0805			320	16
0815			330	14
0850	34	30	340	13
0952	34	28	340	13, Gust: 22
1040			330	15, Gust: 22
1050	34	27	340	13, Gust: 20
1150	34	27	320	16
1249	33	27	320	15, Gust: 21
1350	33	26	310	12
1450	32	24	310	15
1548	31	23	310	13
1637			310	10
1648	31	23	330	08
1748	29	22	320	05
1848	27	22	340	04
1948	25	22	010	03
2048	25	21	350	03
2148	23	21	250	03
2248	23	21	000	00
2348	22	20	000	00

SOUTH BEND, IN

March 25, 1986

SURFACE WEATHER OBSERVATIONS

<u>Time (EST)</u>	<u>Temperature (°F)</u>	<u>Dew Point (°F)</u>	<u>Wind Direction (Degrees)</u>	<u>Wind Speed (Knots)</u>
0049	51	30	180	11
0149	52	30	180	13
0252	52	32	190	13
0351	54	33	200	15
0451	53	34	200	14
0549	51	35	210	12
0648	51	36	210	09
0748	54	37	200	11
0851	60	38	210	15, Gust: 25
0953	63	39	220	17, Gust: 27
1051	66	38	230	21
1150	69	37	220	18, Gust: 31
1250	71	34	220	22, Gust: 33
1350	73	35	220	19, Gust: 29
1450	73	34	210	20, Gust: 33
1549	73	36	210	24, Gust: 36
1653	73	35	210	25, Gust: 34
1750	71	38	210	17, Gust: 27
1851	69	37	210	16, Gust: 22
1953	66	39	210	12
2052	65	39	220	12
2154	65	38	200	18, Gust: 24
2249	64	38	200	17, Gust: 24
2353	63	38	210	16, Gust: 24

SOUTH BEND, IN

March 26, 1986

SURFACE WEATHER OBSERVATIONS

<u>Time (EST)</u>	<u>Temperature (°F)</u>	<u>Dew Point (°F)</u>	<u>Wind Direction (Degrees)</u>	<u>Wind Speed (Knots)</u>
0050	63	39	220	16, Gust: 26
0149	61	39	210	18
0250	60	39	220	15
0351	59	39	220	12
0450	60	39	220	15
0550	60	39	220	15
0650	59	39	240	12, Gust: 22
0750	48	45	290	10
0813			280	07
0842			290	08
0850	47	46	290	11
0949	45	45	250	06
1029			220	06
1046	47	46	230	07
1148	51	48	240	10
1227			270	11
1248	56	45	260	11
1350	57	41	260	10
1448	60	42	260	11
1548	61	41	260	15, Gust: 21
1651	59	40	240	10
1751	59	32	300	17, Gust: 23
1852	55	32	300	12
1950	49	31	310	12, Gust: 21
2050	40	30	360	14, Gust: 19
2152	37	28	340	13
2259	37	27	340	12
2317	37	27	350	11
2354	36	27	330	11

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