QUALITY ASSURANCE PROJECT PLAN

FOR

Red River Flood - Disaster Response
Grand Forks, North Dakota
Environmental Monitoring

Indoor Air Monitoring
for
Residential Exposure
to
Hydrocarbons from Home-Heating Fuel Oil Spills

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A. PROJECT TASK ORGANIZATION

Flooding of the Red River Valley has created extensive damage to residential, commercial and public property in the vicinity of Grand Forks, North Dakota. On April 7, 1997, the President declared a major disaster in the State of North Dakota due to extensive residential, commercial, and agricultural destruction in the flooded area. Pursuant to Public Law 93-288 as amended by PL 100-707 (the "Stafford Act") EPA Region VIII was activated on April 25, 1997, under Emergency Support Function #10 (ESF #10) to ***"assist the State with household hazardous waste, retail/wholesale hazardous waste, and agricultural waste collection, biological monitoring support, and indoor air monitoring support"***. Detailed descriptions of the flood damage may be obtained from a variety of sources including Federal Response Plan (FRP) documentation available from the Federal Emergency Management Agency (FEMA) and through various Emergency Support Functions (ESFs) provided by other responding Federal and State agencies.

On February 5, 1998 FEMA established an additional mission assignment (EPA-02) for USEPA under ESF #10 to be implemented in coordination with the US Public Health Service/Centers for Disease Control and Prevention (ESF #8). This additional mission assignment directs EPA to "***provide technical assistance to FEMA and assess public health risk from fuel oil contamination inside residences due to 1997 Spring floods, to determine if any immediate health threat exists***".

This Quality Assurance Plan and Sampling Analysis Plan describes the technical approach to be used for effecting EPA's additional mission assignment.

A4 Project Management

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A5 PROBLEM DEFINITION and BACKGROUND

Problem: The uncontrolled flood-related release of residential heating fuel and household, commercial, and agricultural hazardous materials has resulted in Federal Response Plan (FRP) actions by the Environmental Protection Agency (EPA) to assess and abate these hazards to human health and the environment. On February 5, 1998, USEPA was directed by the Federal Emergency Management Administration (FEMA) to assess the magnitude of possible hydrocarbon exposures in residential homes impacted by flood-related spills of household heating oil (#2 fuel oil) and to determine in cooperation with the USPHS Centers for Disease Control and Prevention (CDCP) whether an immediate public health risk associated with these exposures exists (mission assignment EPA-02, 2/5/98).

Approach: This sampling plan describes the efforts planned by EPA to monitor indoor air quality and characterize chemical hazards to residents in homes known to have flood-related fuel oil spills. This plan also describes the rationale for choosing sampling locations and quality assurance and control procedures planned for this sampling activity. At FEMA's request, these efforts will be coordinated and coupled with efforts to protect public health in Grand Forks and other areas involved in the Red River Flood of spring 1997 under ESF #8. Efforts will be made to coordinate this sampling program with ongoing surveillance programs established by the State, county, and local hospital staff under funding from the Robert Wood Johnson Foundation.

The approach to exposure assessment addressed herein describes a biased sampling plan which will net screening information regarding the residential exposure to fuel oil hydrocarbons. This plan is not designed to assess the number of homes affected or to determine the range of exposures presently occurring due to spilled fuel oil.

Risk Assessment. This quality assurance project plan (QAPP) has been designed to produce analytical data for the purpose of qualitatively and quantitatively defining the potential exposure and related hazards to residents living in homes where fuel oil was spilled. This limited screening study is appropriate only for obtaining information on potential hazard that is site-specific and the results of the study can only support one of two possible conclusions regarding health **hazards** (and not necessarily for further quantifying extent or range of exposures occurring at this time). If successful, this screening investigation should allow users of this information to assess whether:

1. Air concentrations of mixed hydrocarbons (from #2 fuel oil) collected in severely impacted homes are essentially the **same** as background (homes with fuel oil heaters which were not flooded) levels;

   If so, then conclude: *no significant flood-related exposures are likely, thus no flood-related hazard exists at this time from spilled fuel oil.*

2. Concentrations of mixed hydrocarbons (from #2 fuel oil) collected in severely impacted homes are substantially **higher** than background levels;

   If so, then conclude: *flood-related exposures to mixed hydrocarbons from home heating oil are elevated in indoor.*

Interpretation. Chemical analyses to assess possible exposure via the inhalation pathway, when compared with adequate background concentrations, will determine the potential (or lack of potential) flood-related immediate threat under **present** post-flood conditions. Potential immediate threat will be established through comparison of potential expousre concentrations of fuel oil hydrocarbons measured within selected homes with a range of health-based criteria established by the Environmental Protection Agency in cooperation with the US Public Health Service-Centers for Disease Control and Prevention.

A6 PROJECT TASK DESCRIPTION

This project consists of a three part process to define the magnitude of possible exposures to residential fuel oil spills and to judge through standard risk assessment procedures the health consequences of present and possible future exposures to these hydrocarbon compounds.

Step #1 Exposure Questionnaire:

The first step in this process involves administration of a questionnaire (**Appendix E1**) to home owners or tenants of homes believed to have been impacted by fuel oil spills. The questionnaire will confirm the existence of detectable fuel oil odors in homes previously impacted and establish the subjective reaction of the respondent. The questionnaire will also establish the willingness of the homeowner to participate in quantitative chemical analysis for the presence of fuel oil constituents in indoor air of the home and other basic exposure-related information. Homeowners who use #2 fuel oil for heating but whose homes were not flooded will also be polled and asked their willingness to participate in the indoor air sampling as the "control" group. The data collected from this questionnaire will be used to establish sets of homes for quantitative analysis for hydrocarbons in indoor air. These sets will be broken into groups based upon the nature of the response from the responder. Those responders indicating a strong odor remaining in the home, will be segregated into a "high exposure" group. Those individuals who report low or absent fuel oil odor will be segregated into moderate and low groups depending upon their response. This method of dose grouping is subjective and may not yield empirical low, moderate, and high dose groups. Participants will only be placed in empirical low, moderate, and high categories after final results are available from the analytical measurements.

Step #2: Toxicological analysis:

Coordinated development of a toxicological benchmark or range of benchmarks for inhalation of hydrocarbons derived from #2 fuel oil and or fuel oil constituents will be set in cooperation with the Centers for Disease Control and Prevention. This step will involve a thorough literature review and assessment of all available toxicological data on the effects of hydrocarbon exposure to #2 fuel oil as well as to specific constituents of #2 fuel oil such as benzene, ethyl benzene, xylenes, toluene, etc. Additionally, a review of the toxicological literature on related chemical mixtures such as jet fuels will be conducted. This toxicological literature will establish a range of toxicological benchmarks to be used in the comparison with exposure data to be collected in homes impacted by spilled fuel oil. A separate deliverable will provide the basis for the toxicological benchmark chosen and a list of the literature and other pertinent information reviewed for the purpose of establishing the range of toxicological benchmarks used.

Step #3: Exposure-based indoor air monitoring:

During the last weekend in February, 1998, sample teams (3 teams of 2 individuals each) will collect air samples in homes of volunteer residents who meet the desired criteria (estimated exposure level or control group and willingness to participate in the sampling effort). Approximately 41 homes will be sampled using two distinct sampling media. The first is a charcoal tube and the second is a multi-bed thermal desorption tube. In both cases, a known volume of air is pulled through the tube with an air pump. Samples will be collected for approximately 5 hours in each home and the sample tubes will be sent to approved commercial

laboratories under strict chain-of-custody for analysis. A carbon disulfide extraction will be performed on the charcoal tube samples and the resulting extract will be analyzed via gas chromatography fitted with a flame ionization detector (GC/FID). The thermal desorption tube will be analyzed via GC/mass spectrometry, using thermal desorption (TD) technology. Procedures for calibration of personal air pumps, sampling procedures and analytical quantification are detailed in standard operating procedures (SOPs) established for this sampling effort (See appendices). This analysis will allow positive identification on hydrocarbon constituents at reporting levels lower than the health-based limits established in step #2 of this process.

Table 1: Summary of Target Air Samples*

	High Exposure Group (N)	Medium Exposure Group (N)	Low Exposure Group (N)	Control (non-flooded, fuel oil heated homes) (N)
Air Sampling	20	7	7	7
Quality control duplicate samples	2	1	1	1

***These sample numbers are estimates only. The actual number of samples may vary based upon availability, access, and professional judgement.**

A7 QUALITY OBJECTIVES and CRITERIA for MEASUREMENT DATA

Two types of objectives are identified in this QAPP: general objectives and data quality objectives (DQOs). General objectives are statements of practical goals that, if realized, will substantially contribute to achieving the purpose of the study. Development of DQOs is a process that is intended to ensure that task objectives are clearly defined and that data collected are appropriate and of sufficient quality to satisfy the objectives.

General Objective #1: *to characterize constituents of indoor air at flood-damaged residences where fuel oil was spilled relative to appropriate (fuel oil heated but not flood-damaged) non-damaged control areas.*

Null Hypothesis: Exposures to volatile and semi-volatile organic carbons components are the same or similar in both flood-damaged and non flood-damaged residences where #2 fuel oil was used for domestic heating.

General Objective #2: *to compare airborne fuel oil concentrations in flood-damaged homes with toxicological benchmark values used to determine whether an immediate health threat exists due to flood-related fuel oil spills.*

Null Hypothesis: There is no possibility or very low possibility that homes with spilled fuel oil exceed the toxicological threshold established by the health agencies for immediate threat under residential exposure conditions.

Data Quality Objective Process

The DQO process can be an iterative process which is designed to focus on the decisions that must be made and to help ensure that the site activities acquire data are logical, scientifically defensible, and cost effective. The DQO process is intended to:

- Ensure that task objectives are clearly defined
- Determine anticipated uses of the data
- Determine what environmental data are necessary to meet these objectives
- Ensure that the data collected are of adequate quantity and quality for the intended use

The three stages of the DQO process are identified below and a discussion of how they have been applied in the chemical characterization study described herein. The three stages are undertaken in an interactive and iterative manner, whereby all the DQO elements are continually reviewed and re-evaluated until there is reasonable assurance that suitable data for decision making will be attained.

- Stage I - Identify Decision Types: Stage I defines the types of decisions that will be made by identifying data uses, evaluating available data, developing a conceptual model, and specifying objectives for the project. The conceptual model facilitates identification of decisions that may be made, the end use of the data collected, and the potential deficiencies in the existing information. The conceptual model includes exposure to indoor chemical hazards from inhalation as a pathway for human health risk.

- Stage II - Identify Data Uses/Needs: Stage II stipulates criteria for determining data adequacy. This stage involves specifying the quantity and quality of data necessary to meet the Stage I objectives. EPA's Data Useability for Risk Assessment Guidance (DURA) outlines general and specific recommendations for data adequacy. This includes identification of data uses and data types, and identification of data quality and quantity needs.

- Stage III - Design Data Collection Program: Stage III specifies the methods by which data of acceptable quality and quantity will be obtained to make decisions. This

information is provided in the SOPs. Stage III also details the rationale applied for selection of the proposed methodologies.

Through utilization of the DQO process, as defined in EPA guidance (EPA540-R-93-071 and -078, Sep 1993), this QAPP will use several terms that are specifically defined to avoid confusion that might result from any misunderstanding of their use. For each of the tasks identified within this QAPP, a "Task Objective" is specifically defined. The Task Objective is a concise statement of the problem to be addressed by activities under this task. For each Task Objective, a decision (or series of decisions) is identified which addresses the problem contained in the Task Objective.

For each decision, the data necessary to make the decision are identified and described. For all analytical data, quality assurance objectives are specified that describe the minimum quality of data necessary to support the specified decision or test the hypotheses. These quality assurance objectives are specified as objectives for precision, accuracy, representativeness, comparability, and completeness. In addition, data review and validation procedures are specified in the QAPP that evaluate how well the analytical data meet these quality assurance objectives and whether or not the data are of sufficient quality for the intended usage.

The following sections apply the DQO process to the Grand Forks, North Dakota Flood Disaster Response, Stage I and Stage II, where Stage I and Stage II identify decision types and data uses/needs for the SAP. Stage III provides the specific task objectives, decisions, and rationale for resolving the decisions necessary to complete this study.

DQO Stage I - Identifying Decision Types

Stage I of the DQO process identifies a primary question and secondary questions that need to be resolved at the completion of the sampling and analyses program.

- PRIMARY QUESTION: Are concentrations of airborne hydrocarbons either as individual constituents of #2 fuel oil or taken collectively as TPH higher than background levels?

- SECONDARY QUESTIONS: Is there evidence for a range of exposures within the sample population?

- SECONDARY QUESTIONS: Is there a reliable analytical method for conducting rapid screening of a large number of homes to determine the likelihood of threat due to fuel oil inhalation exposures?

DQO Stage II - Identifying Data Uses/Needs

Stage II of the DQO process identifies data uses and needs. The primary uses of data are:

- Compare site data (air concentrations of hydrocarbons or hydrocarbon constituents) to background levels of fuel oil #2 or its constituents.
- Make a qualitative or semi-quantitative estimate of the concentration ranges and of exposures to spilled home heating oil (#2 fuel oil) which may be occurring in the City of Grand Forks.
- Evaluate whether the portable PID is a plausible rapid indoor air sampling approach for determination of #2 fuel oil in air.

Stage II of the DQO process also determines what type and quality of data are needed to answer the questions developed in Stage I.

1. Organic carbon concentrations measured in indoor air from a sufficient number of flood-damaged homes formerly using home heating oil as a primary fuel source, collected with conventional methods (charcoal and multi-bed thermal desorption tubes) and appropriately analyzed to meet risk-based concentrations established by the health agencies.

2. A sufficient number of control homes (defined as homes which presently use #2 fuel oil heating systems but which were not damaged by the flooding that occurred in April 1997)

3. Laboratory methods for chemical quantitation limits should be well (target <½) below human health risk-based concentrations.

Within this QAPP, quantitative and qualitative limits are defined for precision, accuracy, representativeness, comparability and analytical completeness. Target reporting limits for chemical analytes are set as project goals based upon the lowest observable effect level for acute or chronic health effect. The actual method detection limits, reported by the analytical laboratory, are typically based on matrix, historical data, and comparison to EPA limits for CLP and other methods. The QA procedures outlined in this section are intended to ensure data quality and to administer corrective actions with the goal of producing data that satisfy the following requirements. General guidelines, policies, and procedures to achieve these objectives are presented below. Where additional, detailed, procedures are required to attain QA objectives and to describe specific methods, these are provided in the SOPs (see appendices). The following PARCC requirements apply to more standard chemical analytical analyses.

Precision: Precision is defined as the agreement between a set of replicate measurements without assumption or knowledge of the true value. It is a measure of agreement among individual measurements of the same property under prescribed similar conditions. Agreement is expressed as the relative percent difference (RPD) for duplicate measurements if the reported values are sufficiently above the method detection limit (MDL) (> 5 x MDL) or the absolute difference of two values near the MDL. Additionally, agreement is expressed as the range and standard deviation for larger numbers of replicates. The appropriate precision calculation will be reported for the required 10-20% field duplicates, and a defined MDL will be reported as per EPA guidance in CFR, part 136, Appendix B (7 method-replicates of a low-level [near MDL] standard, with MDL = 3 x SD).

The RPD for field duplicates should not exceed 20% or, alternatively, the absolute difference should not exceed 1 x MDL. However, these acceptance limits are arbitrary; therefore, a graphical comparison of the original and field duplicate samples should also be prepared. This comparison will include a linear regression and will report the calculated correlation coefficient (r).

$$RPD = \frac{|2(A - B)|}{A + B} \times 100\%$$

$$\text{Absolute difference} = |A - B|$$

Where:

A = original concentration value of an analyte
B = duplicate concentration value of an analyte

Accuracy: Accuracy is a measure of the closeness of individual measurements to the "true" value. Accuracy usually is expressed as a percentage of that value. For a variety of analytical procedures, standard reference materials traceable to or available from National Institute of Standards and Technology (NIST, formerly National Bureau of Standards) or other sources can be used to determine accuracy of measurements. Accuracy will be measured as the percent recovery (%R) of an analyte in a reference standard that span the limit of linearity for the method. Acceptance range for recoveries of blind standards will be arbitrarily set at 80-120% of the true value. Specific accuracy guidelines for other accuracy measurements are detailed in the SOPs (See appendices).

$$\%R = \frac{A}{B} \times 100\%$$

Where:

A = measured concentration value of an analyte
B = theoretical concentration value of an analyte

Ideally, precision and accuracy estimates should represent the entire measurement process, including sampling, analysis, calibration, and other components. From a practical perspective, these estimates usually represent only a portion of the measurement process that occurs in the analytical lab.

Representativeness: Representativeness is the degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, or an environmental condition. For this QAPP, data and samples representative of chemical exposures in the study and reference areas are to be collected from selectively chosen residences that are within and outside of the affected flood areas, respectively. The intent is to identify and sample a sub population which is likely to have higher levels of indoor exposure to airborne fuel oil hydrocarbons than the average population of flood-damaged (formerly fuel oil heated) homes.

Comparability: Data are comparable if site considerations, collection techniques, and measurement procedures, methods, and reporting are equivalent for the samples within a sample set. A qualitative assessment of data comparability will be made of applicable data sets. These criteria allow comparison of data from different sources. Comparable data will be obtained by specifying standard units for physical measurements and standard procedures for sample collection, processing, and analysis. Please see the attached SOPs for exact methodologies employed for sample collection and chemical analysis.

Completeness: Data are considered complete when a prescribed percentage of the total measurements and samples are obtained. Analytical completeness is defined as the percentage of valid analytical results requested, and >90% of analyzed samples should have results reported. For this sampling program, a minimum of 90 percent of the planned collection of individual residential samples and a minimum of 90 percent of related parameters (e.g., observations of physical characteristics of the sampled residential dwelling and followup questionnaire) must be obtained to achieve a satisfactory level of data completeness.

Method Detection Limits (applicable to chemical analyses only): MDLs are minimum values that can be reliably measured to identify the analyte as being present in the matrix, versus method quantitation limits which are the minimum values that can be quantitated with reasonable scientific confidence. The method will also have a maximum linear value in most situations, and analyses should occur within this limit of linearity range. The method detection levels established for the GC/FID and TD-GC/MS analytical methodologies to be employed for this effort are presented in the next section (**Section B**). A range of detection limits, acceptable for end use, were established in anticipation of variability in achievement of MDLs between different methodologies and analytical laboratories.

DQO Stage III – Design Data Collection Program

Stage III of the DQO process identifies the specific methods by which data of acceptable quality and quantity are obtained.

Task Objective: *to obtain defensible analytical data that provides quantification of fuel oil #2 and/or its constituents of indoor air in selected flood-damaged homes in Grand Forks, ND.*

Decisions: The following decisions must be made in order to meet the task objective.

- Determine the appropriate volume of air that must be pumped across the charcoal and thermal desorption tubes to allow for adequate mass of samples to be collected onto the tubes in order to meet project-specific MDLs.
- Determine the appropriate analytical methodologies required to provide sufficient quantitative data for end use.
- Evaluate analytical results to determine which of the analytical methods used for this screening-level risk assessment may be used if screening of large numbers of residences is required in the future.

There are two phases for data collection:

- Collection of field data at the residences of Grand Forks, ND.
- Collection of laboratory data analyzed from samples collected in the field.

Collection of Field Data: Certain information can only be collected at the residential homes, but its integration for final data evaluation is important. The following data will be collected in the field:

- Information collected during interviews with residents and visual and olfactory observations by the field team.
- Measurement of temperature in the location where samples are collected.
- Measurement of humidity in the location where samples are collected.
- Measurement of volatile organics taken in the location where samples are collected using a photoionziation detector (PID).

It is important for final evaluations of risk to have a record of humidity and temperature conditions in the homes. If differences in these parameters are observed among residences, final data users may determine that analytical results must be normalized to achieve

comparable evaluations. Likewise, documentation of observations of visual and olfactory evidence of residual fuel oil contamination by the sampling team will provide qualitative data for final risk evaluation.

Because this investigation is meant to perform a screening-level risk assessment on a sub-population of affected residents, it is desirable to integrate a number of methodologies that may identify the presence of heating oil in indoor air and evaluate the comparability of results. The relative accuracy and precision of results along with cost-effectiveness and speed of analysis should be weighed if future analyses in the Grand Forks area are required. Three methods have been chosen.

The first of these methods is a PID measurement taken in the location where samples on charcoal and thermal desorption media are collected. The PID will measure the quantity of volatile organics present in the indoor air.

Collection of Laboratory Data: The remaining two methods planned for quantification of fuel oil in indoor air will be determined at commercial laboratories.

- Quantification of benzene, toluene, ethylbenzene, xylenes (BTEX) and total petroleum hydrocarbons (TPH) as fuel oil #2 via GC/FID.

- Quantification of BTEX, TPH (as undecane), total volatile organic compounds (TVOCs) and tentatively identified compounds (TICs) via TD-GC/MS.

GC/FID: GC/FID is a reliable method for screening the analytes of interest. In addition, quantification of BTEX and TPH (as fuel oil) can be performed on a large number of homes because it is more cost-effective than TD-GC/MS. However, achievement of project-specific detection limits within the stipulated air volume (300 L) is not certain for benzene.

TD-GC/MS: This method was chosen because thermal desorption allows for achievement of project-specific MDLs within the stipulated air volume (15-24 L). Additionally, the mass spectrometer enables the quantification of 72 calibration volatile organic compounds and the tentative identification of additional compounds that may exist in the residences. It is of interest to this project to eliminate potential sources other than heating oil that may be present in the residences.

An inter-instrument comparison of results for TD-GC/MS versus GC/FID will be performed to evaluate sensitivity and selectivity of each method.

B. MEASUREMENT AND DATA ACQUISITION

B1 SAMPLING PROCESS DESIGN

Treatment groups: For this investigation, the City of Grand Forks has been selected as the target study area. Residential homes impacted by fuel oil spilled during flooding exist along the Red River corridor including Fargo, ND, Wapeton, ND and rural areas extending to the Canadian border. It is believed that fuel oil-damaged homes in Grand Forks are likely to be representative of homes impacted in other areas and that exposures and possible hazards associated with homes in Grand Forks may be extrapolated to other areas of interest.

The exposure questionnaire (**Appendix E1**) administered to residents known or suspected of having fuel oil contamination will serve as a primary tool for targeting homes for indoor air monitoring. Homes will be broken into groups based upon residents response on the exposure questionnaire (step 1). The objective will be to preferentially sample homes at the high end of the spectrum of possible exposures, although homes of lesser reported importance will also be sampled. Whether an individual home is indeed at the high end of the exposure spectrum will only be determined by the final analytical data collected following successful sampling.

Three site teams of two individuals each will be designated for the sampling effort. Appointments will be established which will allow placement of sampling tubes and air pumps followed by collection of these sampling devices following approximately 5 hours of air sampling. Portable communication devices (eg. cellular telephones or VHF radios) will be used by each team to remain in contact with homeowners and other sampling teams.

Sample Location: All samples will be taken in the basements of homes since it is here where the largest concentrations of heating oil are expected to exist. Air pumps will be placed in the center of the room at breathing zone height (between 4-6 feet above the floor) during air sampling.

Table 2 provides an example sampling schedule for residences in the City of Grand Forks. The finalized sampling schedule will be establish after all volunteer residents have been contacted and appointments for sampling confirmed.

Table 2: Proposed schedule for sampling indoor air of homes in Grand Forks for fuel oil related hydrocarbons.

TIME	Friday			Saturday			Sunday			Monday		
	Team A	Team B	Team C	Team A	Team B	Team C	Team A	Team B	Team C	Team A	Team B	Team C
8:00 AM				Drop (12)	Drop (13)	Drop (14)	Drop (23)	Drop (24)	Drop (25)	Drop (34)	Drop (35)	Drop (36)
:30												
9:00 AM	Drop (1)	Drop (2)	Drop (3)									
:30				Drop (15)	Drop (16)	Drop (17)	Drop (26)	Drop (27)	Drop (28)	Drop (37)	Drop (38)	Drop (39)
10:00 AM												
:30	Drop (4)	Drop (5)	Drop (6)									
11:00 AM				Drop (18)	Drop (19)	Drop (20)	Drop (29)	Drop (30)	Drop (31)	Drop (40)	Drop (41)	
:30					Dup		Dup			Dup		
12:00 PM	Drop (7)	Drop (8)	Drop (9)									
:30			Dup	Drop (21)		Drop (22)		Drop (32)	Drop (33)			
1:00 PM												
:30	Drop (10)	Drop (11)		Pickup (12)	Pickup (13)	Pickup (14)	Pickup (23)	Pickup (24)	Pickup (25)	Pickup (34)	Pickup (35)	Pickup (36)
2:00 PM												
:30	Pickup (1)	Pickup (2)	Pickup (3)									
3:00 PM				Pickup (15)	Pickup (16)	Pickup (17)	Pickup (26)	Pickup (27)	Pickup (28)	Pickup (37)	Pickup (38)	Pickup (39)
:30												
4:00 PM	Pickup (4)	Pickup (5)	Pickup (6)									
:30				Pickup (18)	Pickup (19)	Pickup (20)	Pickup (29)	Pickup (30)	Pickup (31)	Pickup (40)	Pickup (41)	
5:00 PM												
:30	Pickup (7)	Pickup (8)	Pickup (9)									
6:00 PM				Pickup (21)		Pickup (22)		Pickup (32)	Pickup (33)			
:30												
7:00 PM	Pickup (10)	Pickup (11)										
:30												
8:00 PM												
:30												
9:00 PM												

Sample size and characteristics: For this study, a target number of 41 residences will be sampled using charcoal and thermal desorption tubes and personal air monitoring pumps. Residences will be categorized based upon questionnaire responses into one of four possible groups. These groups will include: 1) homes where respondents report a strong odor of fuel oil (20 homes); 2) homes where odors from fuel oil are moderate or intermittent (7 homes); 3) homes where odors are no longer detectable by the resident (7 homes); and 4) control homes where fuel oil is used for heat but which were not impacted by the flooding during the spring of 1997 (7 homes). Because these sampling locations are dependent upon resident responses and participation, actual sampling stratification and locations may differ slightly from the above proposal. Professional judgement will be applied for determination of final sampling stratification and locations.

B2 SAMPLING METHODS REQUIREMENTS

The proposed sampling consists of the collection of approximately 41 samples and the required QA/QC (10-20%) samples including appropriate background samples collected in residential areas unaffected by the flooding. Samples of indoor air will be collected directly onto charcoal and thermal desorption tubes using standard personal air pumps with known air flow rate. Samples will be collected for approximately 5 hours in each home as necessary to assure attainment of analytical method detection limits required for risk-based decision making.

Sample locations within the residential area of Grand Forks will be determined by analysis of a questionnaire to be administered prior to field sampling. Test and control residences will be stratified based upon responses to questions asked on the questionnaire.

QA/QC samples will consist of field blanks, duplicate samples, blind QC standards and background samples collected within randomly selected residences who use fuel oil heating systems within unaffected areas. The following descriptions of the QC samples, planned for collection or submittal, are provided below.

Field blank - One field blank will be collected each day of sampling. Because sampling is planned to extend over 4 days, 4 field blanks will be collected for each type of analysis (GC/FID and TD-GC/MS) and submitted for analysis. A field blank is collected by opening and closing the tube caps in the field. No air is pumped across the tubes.

Field duplicates – One field duplicate will be collected for every 10 investigative samples obtained. Since 41 investigative samples are planned, 5 field duplicates will be collected for each type of analysis (GC/FID and TD-GC/MS) and submitted for analysis.

Blind Standard – One blind standard will be collected for approximately every 20 investigative samples obtained. Two blind standards will be prepared during the investigation and submitted for analysis. One blind standard will be submitted to each of the two laboratories to evaluate accuracy of analysis. The blind standard will contain known masses of BTEX and fuel oil #2.

Surrogate Standards – Surrogate standards are chemicals that are similar to analytes of interest, but are not expected to be found in the environment (e.g. fluorinated or deuterated compounds) that will be flash spiked onto the thermal desorption tubes prior to delivery to the field. These standards are used to evaluate system performance by reporting percent recoveries of surrogates.

Every reasonable effort will be made to adhere strictly to specified SOPs and laboratory guidelines. Where deviation from SOPs is unavoidable, documentation of the deviation and its potential impact on the outcome of the data collection effort will be recorded. Detailed field notes will record information pertinent to each sample collection and specific characteristics of the residence being sampled. **Appendix E2** presents the SOP for field sampling procedures. These field notes will be indexed and made available for review following sample collection.

Sampling methods:A variety of sampling devices were evaluated for their applicability for fuel oil analysis of grab samples, including: SUMMA® canisters, Tedlar® bags, charcoal and thermal desorption tubes. Although accurate results (results within 20% of known values) for grab air samples using SUMMA® canisters and Tedlar® bags are well-documented for light, volatile hydrocarbons, these sampling systems are unproven for heavier diesel range organics (DROs) such as fuel oil. Therefore, the sampling devices chosen for this class of organic compounds are absorption via charcoal and thermal desorption tubes. Collection of DROs onto carbon tubes requires a known volume of air be pumped across the tubes to allow absorption of hydrocarbons onto the media. The appropriate volumetric flow rate of air requires that the total collection time be approximately 5 hours per sample.

Sample Identification: The following protocol details the procedures for identification of investigative and QC samples. All samples will have the following format:

GF-H-C-001
GF-H-C-001-D
GF-H-TD-001
GF-H-TD-001-FB

Each portion of the sample ID provides a separate piece of information.

First Section: Project Location
GF – Grand Forks

Second Section: Project Name
H - Hydrocarbon Project

Third Section: Sampling Media
C – Charcoal Tube
TD - Thermal Desorption Tube

Fourth Section: Residential Location Number

001 - Residence #1
002 - Residence #2
041 - Residence #41

Fifth Section: QC Sample Identification

None- First tube collected
D - Duplicate tube
FB – Field blank

B3 Sampling, Handling and Custody Requirement

Documentation of sample collection, handling, and shipment will include completion of chain-of-custody forms in the field, use of field maps and field forms, and entry of data into a field logbook. A chain-of-custody form shall accompany every shipment of samples to the analytical laboratory. The purpose of the chain-of-custody form is to establish the documentation necessary to trace possession from the time of collection to final disposal.

The chain-of-custody form will have the following information:

- Project number
- Sampler's signature
- Date and time of sample collection
- Sample identification number
- Analytical parameters

The shipping forms or transmittal memo from EPA will describe:

- Number of containers
- Date and time of sample shipments

The labs will enter the following information upon receipt:

- Name of person receiving the sample
- Date of sample receipt
- Sample condition
- Temperature of samples upon receipt at the laboratory

All corrections to the chain-of-custody record will be marked out with a single line, initialed and dated by the person making the corrections. Each chain-of-custody form will include signatures of the appropriate individuals indicated on the form. The originals will accompany the samples to the laboratory, and copies documenting each custody change will be recorded and kept on file.

Chain-of-custody will be maintained until final disposition of the samples by the laboratory and acceptance of analytical results by EPA. One copy of the chain-of-custody will be kept by field personnel.

The field sampling technician will include the following information on the Field Form:

. Date
. Sampler's name
. Identification and location of sample
. External appearance
. Sample identification numbers (type of media, visible condition)

All required paper work, including sample container labels, chain-of-custody forms, custody seals and shipping forms will be fully completed in ink prior to shipping of the samples to the laboratory. Shipping from sample storage freezer to laboratory will be by overnight delivery.

Upon receipt, coolers containing the samples will be received by the laboratory sample custodian. The coolers will be opened and the contents inspected. Chain-of custody forms will be reviewed for completeness, and samples will be logged and assigned a unique laboratory sample number. Any discrepancies or abnormalities in samples will be noted.

The EPA Project Manager will maintain original log books and receive all data packages and reports.

B4 ANALYTICAL METHODS REQUIREMENTS

The proposed method of analysis for this evaluation of fuel oil #2 in air is based upon consideration of target detection limits for benzene, toluene, ethylbenzene and xylenes (BTEX) and for total petroleum hydrocarbons (TPH). These detection limits have been established to ensure that concentrations can be analyzed at levels below those which may cause adverse acute or chronic health effects in humans. Detection limit goals are provided below.

Parameter	Target Detection Limits	
	$\mu g/m^3$	ppbv
Benzene	0.2-5	0.06-1.6
Toluene	10-50	2.7-13
Ethylbenzene	50-100	12-23
Xylenes	10-50	2.3-11
TPH (based upon undecane)	20	3

B5 Quality Control Requirements

The project team organization ensures attainment of QA objectives by:

- Assigning responsibility for performing work according to specifications
- Providing oversight of quality-related activities for verification of conformance with specifications
- Defining the relationships between management and personnel performing quality-related work Corrective Action

The Project Manager will prepare a summary of quality-related activities and problems. This summary will be forwarded to EPA for inclusion in the project file. If deficiencies in the program are identified, the Project Manager will identify recommendations for corrective action.

Communications. Lines of communication between project personnel and project management staff will be appropriate to enable timely response to events that have the potential to affect data quality. Project personnel will be provided with a project contact list that includes telephone numbers for both routine communications and emergency notifications. Copies of all written communications and written summaries of all substantive telephone conversations will be placed in a permanent project file maintained by the EPA Project Manager.

Communications will also entail ensuring that information on sample collection, transportation, analysis, and storage; data acquisition, analysis, and reporting; personnel assignments and activities; and other information pertinent to the project are distributed to potentially affected personnel in a timely manner. Changes in procedures, equipment, personnel, or other program elements as a result of an accident or emergency that have the potential to affect data quality or achievement of overall program objectives will be communicated to the Project Manager in writing in a timely manner.

Laboratory Responsibilities. The laboratory and its staff will have the responsibility for processing all samples submitted according to the specific protocols for sample custody, holding times, analysis, reporting, and associated laboratory QA/QC. Laboratory spikes, duplicates, etc. will be performed.

B7 INSTRUMENT CALIBRATION and FREQUENCY

Air pumps and PID detectors will be tested and calibrated prior to then following the sample collection field exercise. See **Appendices E3 and E4** for calibration procedures. Digital thermometers and hygrometers do not require calibration everyday of use. These instruments are calibrated by the manufacturer.

SOPs will identify requirements needed to be met by the laboratories to meet adequate instrument calibration frequency, and QA/QC for raw data and reports.

C. ASSESSMENT OVERSIGHT

C1 ASSESSMENTS and RESPONSE ACTIONS

The EPA Scientific Support Coordinator will be on-site to oversee and inspect sampling activities.

D. DATA VALIDATION and USABILITY

D1 DATA REVIEW, VALIDATION and VERIFICATION REQUIREMENTS

Data validation will consist of a) establishing an absolute range, acceptance limits (screening criteria), and appropriate statistics for each data parameter, b) describing methods for determining the disposition of suspect data, and c) documenting final disposition of invalid or qualified data.

Direct comparison of individual residential sampling and analytical results with toxicological benchmark criteria will be used to estimate the likelihood of health effects due to inhalation of hydrocarbons at each residence.

If feasible, based upon sampling success, a **one-tailed t-test** will be used to compare the four groups (flood-damaged homes reported to have severe, moderate and low odor and control homes) (a two-tailed t-test is not used since any change in concentration of indoor fuel oil hydrocarbon concentrations is expected to be one direction above background levels as per EPA Risk Assessment Guidance). If there is statistical probability of $\alpha \leq 0.05$ for flood damaged residences being higher than reference areas, then reject the null hypothesis and conclude that significant difference exists between the two groups for a particular toxicologically-based benchmark concentration . Therefore, potential exposure of humans to this indoor air concentration of fuel oil hydrocarbons would not be able to be screened out. Conversely, if $\alpha \geq 0.05$ for all hydrocarbon contaminant combinations in a study that is reasonably well conducted with fairly homogeneous concentrations (i.e., no "hot-spots"), then the null hypothesis is accepted and exposure via the inhalation route is not consequential and is able to be screened out with no further evaluation being justifiable.

QA for data reduction and validation will ensure that the screening criteria are comprehensive, unambiguous, reasonable, and internally consistent; and that data validation activities are properly documented. Data discrepancy reports should be prepared describing any data problems observed and any data correction activities undertaken.

All data records should be cataloged and stored in their original form. Calibration adjustments and adjustments to reduce data to standard conditions for comparability will be clearly documented, and raw data clearly distinguished from "corrected" data (i.e., data to which calibration and standardization adjustments have been applied).

Raw data and adjustments will be entered into a computer database and/or spreadsheet for correction, statistical analysis, manipulation, formatting, and summarizing to reduce the potential for human error. All data will be placed into MS Windows-based software such as MS Office Access version 2.0 and Excel version 5.0, or newer.

D2 VALIDATION and VERIFICATION METHODS

Data reporting consists of communicating summarized data in a final form. QA for reporting consists of measures intended to avoid or detect human error and to correct identified errors. Such methods include specification of standard reporting formats and contents of measures to reduce data transcription errors. Data will undergo peer review by qualified reviewers capable of evaluating reasonableness of the data for the scientific design.

Reports: A report of all the summary study design characteristics, sample collections and analyses, data quality and results shall be presented by the analytical laboratories. Simple statistical tests of group treatment differences should be performed and presented as discussed above and will be conducted by EPA. All raw data and summary results of both data and summary statistics (means, standard deviations, ranges, etc.) should be tabulated by the laboratories. Results should be interpreted to qualitatively estimate the relative frequency of occurrence of toxicologic effects above reference levels. Study reports should be available within 14 days of receipt of acceptable laboratory results and reports.

Data will be reviewed by project managers, EPA and State epidemiologists, and by a peer review team (CDC/NIOSH) to assess data quality in accordance with DURA (1992) for this Federal Response Plan site.

QA records and project files will be maintained in accordance with standard project procedures. All QA records, logbooks, sample data forms, raw data summaries, and the like will be maintained until written directions for their disposal are provided.

D3 RECONCILIATION with DQOs

The project team will review any results which fall outside the DQOs and decide (per DURA 1992 and RAGS 1992) the extent of useability of results for risk assessment.

REFERENCES:

EPA. 1992. DURA Data Useability for Risk Assessment.

EPA. 1992. RAGS Risk Assessment Guidance for Superfund.

EPA. 1994. Requirements for Quality Assurance Project Plans for Environemntal Data Operations, Draft Interim Final QA/R-5 August, 1994.

EPA. 1994. Guidance for the Data Quality Objectives Process QA/G-4 September, 1994.

Appendix E1: Exposure Questionnaire

Appendix E1: Exposure Questionnaire:

QUESTIONNAIRE FOR SURVEY OF GRAND FORKS HOMES

The U.S. Environmental Protection Agency is conducting a survey to investigate the extent of heating oil spills in homes impacted by the recent flood along the Red River.

QUESTIONS:

Phone (Day):_____ **Phone (Eve):**_____

Name: _____

Address: _____

How many people currently live in your home?

☐

What are the ages and sex of the people living in your house?

#1) M / F ☐ **#2) M / F** ☐ **#3) M / F** ☐ **#4) M / F** ☐

#5) M / F ☐ **#6) M / F** ☐ **#7) M / F** ☐ **#8) M / F** ☐

Is anyone in your home currently pregnant or nursing?

_ YES - Nursing _ NO

_ YES - Pregnant

Did you have a fuel oil spill in your home during the flood?

_ YES -----(go to question 4)

_ NO -----(go to question 6)

4. **Please rate the immediately <u>post-flood</u> odor from the oil inside your house according to one of the following categories:**

No Odor

Low (occasional odor, but not a bother)

_ Moderate (frequent unpleasant odor, but no other effects)
Severe (odor plus irritation of eyes, lungs, etc.)

5. Please rate the current odor from the oil inside your house according to one of the following categories:

__ No odor remains
__ Low (occasional odor, but not a bother)
__ Moderate (frequent unpleasant odor, but no other effects)
__ Severe (odor plus irritation of eyes, lungs, etc.)

6. EPA will be collecting samples in the Grand Forks area in the near future. If asked, would you permit an air sample to be collected from inside your home? This would require a sampling team placing an air monitoring unit in your home, and returning approximately 3-4 hours later to retrieve it.

__ YES ----(go to Question 7)
__ NO ------ Thank you for participating

EPA is planning on sampling in late February, early March. If your home is selected, what day and time would be most convenient for you?

Monday	AM / PM	Friday	AM / PM
Tuesday	AM / PM	Saturday	AM / PM
Wednesday	AM / PM	Sunday	AM / PM
Thursday	AM / PM		

OTHER NOTES OR COMMENTS

Appendix E2: Standard Operating Procedures for Air Sampling

Standard Operating Procedures
for Indoor Air Sampling for Fuel Oil #2 at Homes in Grand Forks
using Personal Air Pumps and Sampling Tubes (Charcoal and Thermal Desorption)

1.0 Purpose

The protocols prescribed in this standard operating procedure (SOP) document the step-by-step procedures for implementing the indoor air sampling program for selected homes in Grand Forks, ND for the eventual quantification of heating oil present. There are two phases to this sampling program: 1) Set-up and installation of personal air pumps and sampling tubes; and 2) Pick-up of sampling equipment and tubes.

Sampling of fuel oil #2 in air samples will collected on two different sampling tubes: charcoal and multi-bed thermal desorption tubes. Additionally a reading using a hand-held photoionization detector (PID) will be taken at every home where quantification of fuel oil #2 is planned (approximately 41 homes). The objective of this procedure is to evaluate whether the PID can effectively quantify human health risk levels of fuel oil concentrations inside affected homes.

2.0 Calibration of Field Equipment and Instrumentation

2.1 Personal Air Pumps: The personal air pumps must be calibrated twice daily, once before using the pumps to collected air samples and immediately following completion of sampling. The calibration procedures are detailed in another SOP.

2.2 Photoionization Detector: The PID must be calibrated twice daily, once before any readings are taken in the homes and at the end of the day after the last reading has been taken. The calibration procedures are detailed in another SOP.

3.0 Set-up and Installation of Sampling Equipment

3.1 Equipment Set-up: The team leader will set up the sampling equipment in the basement of selected homes.

3.1.1 The calibrated pumps should be placed in the breathing zone (approximately 4-6 feet above the floor).

3.1.2 Using an indelible marker (eg. Sharpie), mark on the sampling tube the date and time the sampling begins. Also label the tube with the sample ID. See Section B2 of the quality assurance project plan (QAPP) for the procedures for identifying samples.

3.1.3 The charcoal tube will be placed into the low volume air pump. Note the arrows on the tube. This indicates the direction that the tube should be loaded. The arrows identify the direction of air flow across the tube.

3.1.4 The thermal desorption tube will be placed into the very low volume air pump.

Note the arrow on the tube. This indicates the direction that the tube should be loaded. The arrows identify the direction of air flow across the tube.

3.1.5 Set the flow rate for the low volume pump (charcoal tube) at 1L/min. Turn on the air pump and note the time in the logbook the sampling was begun.

3.1.6 Set the flow rate for the very low volume pump (thermal desorption tube) at 70 mL/min. Turn on the air pump and note the time in the field logbook the sampling was begun.

3.2 Preliminary Observations: While one team member is setting up the sampling equipment, the second team member will make notes and observations as detailed on the attached sample logbook page.

4.0 Pick-up of Sampling Equipment

4.1 Equipment Pick-up: One member of the Pick-up Team will take down the sampling equipment.

4.1.1 Turn off the low volume air pump (charcoal tube) and note the time in the field logbook sampling was stopped.

4.1.2 Turn off the very low volume air pump (thermal desorption tube) and note in the field logbook the time sampling was stopped.

4.1.3 Remove the charcoal and thermal desorption tubes from the air pumps.

4.1.4 Calibrate both the low volume and very low volume air pumps before leaving the sampling location.

4.1.5 Note samples IDs on chain-of-custody forms and prepare for submission to analytical labs.

4.2 Final Field Observations: While one team member is taking down the sampling equipment, the second team member will make notes and observations as detailed on the attached sample logbook page.

Field Logbook Page for Indoor Air Sampling Using Charcoal and Thermal Desorption Tubes

Project: Grand Forks - Hydrocarbon

Date Sampled:_____

Team Members:

Resident Name:_____

Phone Number:_____

Address:_____

_____

Interview Questions/Observations:

1) Do you and/or any other residents smoke inside the house? _____ Yes_____ No

If yes, what is the combined estimate the residents smoke indoors (packs/week)?

_____

2) What type of heating did you use prior to the flood (% of each type)?

___ Fuel Oil Furnace ____ Natural Gas ____ Fireplace/Wood Stove
___ Electric ____ Other (list)_____

3) What type of heating do you use now (post-flood) (% of each type)?

___ Fuel Oil Furnace ____ Natural Gas ____ Fireplace/Wood Stove
___ Electric ____ Other (list)_____

4) Have you done any cleanup of the oil? If so, what type?

5) How much time do you spend in the basement?

6) Basement Composition:

7) Notes:

Drop-Off Sampling Information:

VLV Pump Serial #:_____ Pre-calibration by: _____ Time:_____

LV Pump Serial #:_____ _____ Time:_____

Sample ID# charcoal tube:_____
TD tube: _____

Flow rates (L/min): VLV:_____ LV:_____

Time Sampling Begun:_____

PID Reading (ppm):_____
Temperature (° F/C):_____
Relative Humidity (%):_____

Notes:

Visual observations of heating oil sources or other sources of volatile compounds (gas cans, smoking, cooking,)

_____ Hydrocarbon staining
Approximate coverage: _____Floor _____Walls _____Ceiling

_____ Are gas cans or gas powered equipment visible?

_____ Are paint or solvent containers visible? (circle which are present)

Olfactory observation of heating oil or other sources (gas, smoke, cooking)

Fuel Oil Odor:
_____ Severe (3)
_____ Moderate (2)
_____ Slight (1)
_____ None observed (0)

Smoke Odor:
_____ Severe (3)
_____ Moderate (2)
_____ Slight (1)
_____ None observed (0)

Gasoline/Paint or Solvent Odor:
_____ Severe (3)
_____ Moderate (2)
_____ Slight (1)
_____ None observed (0)

Oily/Greasy Cooking Odor:
_____ Severe (3)
_____ Moderate (2)
_____ Slight (1)
_____ None observed (0)

Pick-up Sampling Information:

VLV Pump Serial #:_____ Post-calibration by: _____ Time:_____

LV Pump Serial #:_____ _____ Time:_____

Flow rates (L/min): VLV:_____ LV:_____

Time Sampling Ended:_____

Total Air Volume:_____

PID Reading (ppm):_____
Temperature (° F/C):_____
Relative Humidity (%):_____

Notes:

Does the pump/sampling equipment appear disturbed? ____ No ____ Yes
If yes, describe_____

Visual observations of heating oil sources or other sources of volatile compounds (gas cans, smoking, cooking,)

_____ Hydrocarbon staining
Approximate coverage: _____Floor _____Walls _____Ceiling

_____ Are gas cans or gas powered equipment visible?

_____ Are paint or solvent containers visible? (circle which are present)

Olfactory observation of heating oil or other sources (gas, smoke, cooking)

Fuel Oil Odor:
_____ Severe (3)
_____ Moderate (2)
_____ Slight (1)
_____ None observed (0)

Smoke Odor:
_____ Severe (3)
_____ Moderate (2)
_____ Slight (1)
_____ None observed (0)

Gasoline/Paint or Solvent Odor:
_____ Severe (3)
_____ Moderate (2)
_____ Slight (1)
_____ None observed (0)

Oily/Greasy Cooking Odor:
_____ Severe (3)
_____ Moderate (2)
_____ Slight (1)
_____ None observed (0)

ADDITIONAL NOTES FOR THIS RESIDENCE:

USE THIS PAGE ONLY FOR DUPLICATE SAMPLES

Drop Off Information:

VLV Pump Serial #:_____ Pre-calibration by: _____ Time:_____

LV Pump Serial #:_____ _____ Time:_____

Flow rates (L/min): VLV:_____ LV:_____

Sample ID# charcoal tube:_____
TD tube: _____

Time Sampling Begun:_____

PID Reading (ppm):_____
Temperature (° F/C):_____
Relative Humidity (%):_____

Proximity to Primary Sampler _____

Notes:

Pick-up Information:

VLV Pump Serial #:_____ Post-calibration by: _____ Time:_____

LV Pump Serial #:_____ _____ Time:_____

Flow rates (L/min): VLV:_____ LV:_____

Time Sampling Ended:_____

Total Air Volume:_____

PID Reading (ppm):_____
Temperature (° F/C):_____
Relative Humidity (%):_____

Notes:

Does the pump/sampling equipment appear disturbed? ____No ____Yes
If yes, describe_____

Designation: D 3686 – 89

Standard Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)[1]

This standard is issued under the fixed designation D 3686; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers a method for the sampling of atmospheres for determining the presence of certain organic vapors by means of adsorption on activated charcoal using a charcoal tube and a small portable sampling pump worn by a worker. A list of some of the organic chemical vapors that can be sampled by this practice is provided in Annex A1. This list is presented as a guide and should not be considered as absolute or complete.

1.2 This practice does not cover any method of sampling that requires special impregnation of activated charcoal or other adsorption media.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* A specific safety precaution is given in 9.4.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Atmospheric Sampling and Analysis[2]

D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method[2]

2.2 *NIOSH Standard:*

CDC-99-74-45 Documentation of NIOSH Validation Tests[3]

HSM-99-71-31 Personnel Sampler Pump for Charcoal Tubes; Final Report[3]

2.3 *OSHA Standard:*

CFR 1910 General Industrial OSHA Safety and Health Standard[4]

3. Terminology

3.1 For definitions of terms used in this method, refer to Terminology D 1356.

3.2 Activated charcoal refers to properly conditioned coconut-shell charcoal.

4. Summary of Practice

4.1 Air samples are collected for organic vapor analysis by aspirating air at a known rate through sampling tubes containing activated charcoal, which adsorbs the vapors.

4.2 Instructions are given to enable the laboratory personnel to assemble charcoal tubes suitable for sampling purposes.

4.3 Instructions are given for calibration of the low flow-rate sampling pumps required in this practice.

4.4 Information on the correct use of sampling devices is presented.

4.5 Practice D 3687 describes a practice for the analysis of these samples.

5. Significance and Use

5.1 Promulgations by the Federal Occupational Safety and Health Administration (OSHA) in 29 CFR 1910.1000 designate that certain organic compounds must not be present in workplace atmospheres at concentrations above specific values.

5.2 This practice, when used in conjunction with Practice D 3687, will provide the needed accuracy and precision in the determination of airborne time-weighted average concentrations of many of the organic chemicals given in 29 CFR 1910.1000, CDC-99-74-45 and HSM-99-71-31.

5.3 A partial list of chemicals for which this method is applicable is given in Annex A1, along with their OSHA Permissible Exposure Limits.

6. Interferences

6.1 Water mist and vapor can interfere with the collection of organic compound vapors. Humidity greater than 60 % can reduce the adsorptive capacity of activated charcoal to 50 % for some chemicals (1).[5] Presence of condensed water droplets in the sample tube will indicate a suspect sample.

7. Apparatus

7.1 *Charcoal Tube:*

7.1.1 A sampling tube consists of a length of glass tubing containing two sections of activated charcoal which are held in place by nonadsorbant material and sealed at each end.

7.1.1.1 Sampling tubes are commercially available. The tubes range in size from 100/50 to 800/400 mg, which means the tubes are divided into two sections with the front section

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[1] This practice is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres, and is the direct responsibility of Subcommittee D22.04 on Analysis of Workplace Atmospheres.

Current edition approved May 26, 1989. Published July 1989. Originally published as D 3686 – 78. Last previous edition D 3686 – 84.

[2] *Annual Book of ASTM Standards*, Vol 11.03.

[3] Available from the U.S. Department of Commerce, National Technical Information Service, Port Royal Road, Springfield, VA 22161.

[4] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20401.

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

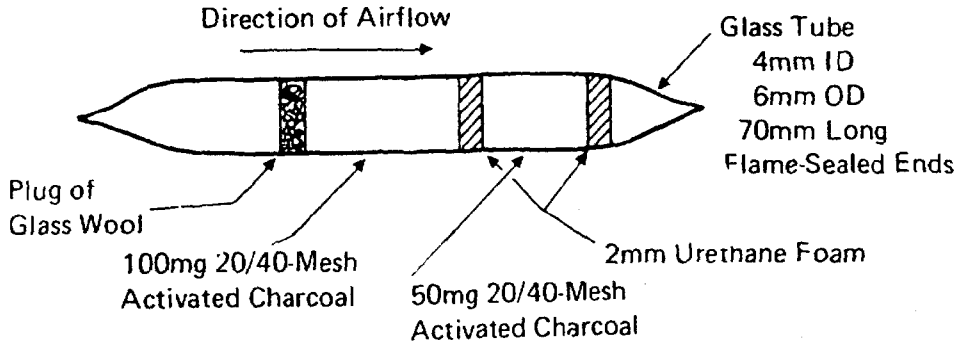

FIG. 1 Activated Charcoal Adsorption Sampling Tube

ontaining 100 to 800 mg of activated charcoal and the back ection containing 50 to 400 mg of activated charcoal. The 00/50-mg tube ((2, 3, 4) and Fig. 1) which is the one most requently used, consists of a glass tube, 70-mm long, 6-mm utside diameter, 4-mm inside diameter, and contains two ections of 20/40 mesh-activated charcoal but separated by a -mm section of urethane foam. The front section of 100 mg s retained by a plug of glass wool, and the back section of 50 ng is retained by either a second 2-mm portion of urethane oam or a plug of glass wool. Both ends of the tube are lame-sealed.

NOTE 1—Urethane foam is known to adsorb certain pesticides (5), or which this practice is contraindicated.

7.1.1.2 When it is desirable to sample highly volatile ompounds for extended periods, or at a high volume flow ate, a larger device capable of efficient collection can be sed, provided the proportions of the tube and its charcoal ontents are scaled similarly to the base dimensions, to rovide nominally the same linear flow rate and contact time vith the charcoal bed.

7.1.2 The back portion of the sampler tube, which may ontain between 25 and 100 % of the mass of activated char- oal present in the front section, adsorbs vapors that pene- rate the front section and serves as a warning that break- hrough may have occurred. (Annex A1 gives recommended naximum tube loading information for many chemicals.)

7.1.2.1 Should analysis of the back portion show it to ontain more than 20 % of the total amount of vapor col- ected (or 25 % of the amount found in the front section), the ossibility exists that solvent vapor penetrated both sections f charcoal, and the sample must be considered suspect. These percentages apply to 100/50-mg tubes. For other size ubes having disproportionate amounts of charcoal in the ront and back sections, the percentages used to indicate otential breakthrough must be adjusted to take into account lifferent ratios of charcoal. If results from the analysis of uspect samples are used to calculate vapor concentrations, he results must be reported as equal to or greater than the alculated concentrations. In such cases, the test must be epeated for confirmation of vapor concentration.

NOTE 2—Reportings from suspect samples would have significance when *health standards are clearly exceeded* and the amount by which hey are exceeded is academic. (See 9.5.)

7.1.3 The adsorptive capacity and desorption efficiency of different batches of activated charcoal may vary. Commer- ial tubes, if used, should be purchased from the same batch and in sufficient number to provide sampling capacity for a definite period of time. *Care must be taken to have enough tubes from the same batch for a given study.*

7.1.3.1 The desorption efficiency and contamination level of a batch of tubes should be determined, following the procedure outlined in Practice D 3687 for activated charcoal. A random selection of at least five charcoal tubes from a specified lot should be taken for these checks.

7.1.4 Pressure drop across the sampling tube should be less than 25 mm Hg (3.3 kPa) at a flow rate of 1000 mL/min and less than 4.6 mm Hg (0.61 kPa) at a flow rate of 200 mL/min.

7.1.5 Charcoal sampling tubes prepared in accordance with this practice and with sealed glass ends may be stored indefinitely.

7.2 *Sampling Pumps:*

7.2.1 Any pump whose flow rate can be accurately determined and be set at the desired sampling rate is suitable. Primarily though, this practice is intended for use with small personal sampling pumps.

7.2.2 Pumps having stable low flow rates (10 to 200 mL/min) are preferable for long period sampling (up to 8 h) or when the concentration of organic vapors is expected to be high. Reduced sample volumes will prevent exceeding the adsorptive capacity of the charcoal tubes. (Suggested flow rates and sampling times are given in Annex A1 for anticipated concentration ranges. Sample volumes are also discussed in 9.5.)

7.2.3 Pumps are available that will provide stable flow rates between ±5 %. Pumps should be calibrated before and after sampling. If possible, flow rates should be checked during the course of the sampling procedure.

7.2.4 All sampling pumps must be carefully calibrated with the charcoal tube device in the proper sampling position. (See Annex A2 for calibration procedure.)

8. Reagents

8.1 *Activated Coconut-Shell Charcoal*—Prior to being used to make sampling devices the charcoal should be heated in an inert gas to 600°C and held there for 1 h. Commercially available coconut charcoal (20/40 mesh) has been found to have adequate adsorption capacity. Other charcoals can be used for special applications.

9. Sampling with Activated Charcoal Samplers

9.1 *Calibration of the Sampling System*—Calibrate the sampling system, including pump, flow regulator, tubing to

be used, and a representative charcoal tube (or an equivalent induced resistance) with a primary or calibrated secondary flow-rate standard to ±5%.

9.1.1 A primary standard practice is given for the calibration of low flow-rate pumps in Annex A2 and Fig. A2.1.

9.2 Break open both ends of the charcoal tube to be used for sampling, ensuring that each opening is at least one half the inside diameter of the tube.

9.3 Insert the charcoal tube into the sampling line, placing the back-up section nearest to the pump. At no time should there be any tubing ahead of the sampling tubes.

9.4 For a breathing zone sample, fasten the sampling pump to the worker, and attach the sampling tube as close to the worker's breathing zone as possible. Position the tube in a vertical position to avoid channeling of air through the adsorber sections.

NOTE 3: **Warning**—Assure that the presence of the sampling equipment is not a safety hazard to the worker.

9.4.1 Turn on the pump and adjust the flow rate to the recommended sampling rate.

9.4.2 Record the flow rate and starting time or, depending on the make of pump used, the register reading.

9.5 *Sampling Volumes*—The minimum sample volume will be governed by the detection limit of the analytical method, and the maximum sample volume will be determined by either the adsorptive capacity of the charcoal or limitations of the pump battery.

9.5.1 One method of calculating required sample volumes is to determine first the concentration range, over which it is important to report an exact number, for example from 0.2 to 2 times the permissible exposure concentration, and then calculate the sample volumes as follows:

Minimum sample volume, m^3

$$= \frac{\text{minimum detection limit, mg}}{0.2 \times \text{permissible exposure limit, mg/m}^3}$$

Maximum sample volume, m^3

$$= \frac{\text{tube capacity for vapors, mg}}{2 \times \text{permissible exposure limit, mg/m}^3}$$

9.5.2 Select a sampling rate that, in the sampling time desired, will result in a sample volume between the minimum and maximum calculated in 9.5.1.

9.5.2.1 Generally a long sampling time at a low flow rate is preferable to short-term high-volume sampling. This is consistent with the fact that most health standards are based on 8-h/day time-weighted averages of exposure concentrations.

9.5.2.2 A sample flow rate of less than 10 mL/min, however, should not be used. Calculations based upon diffusion coefficients for several representative compounds indicate that sampling at less than 10 mL/min may not give accurate results.[6]

9.5.2.3 Approximate sample volumes and sample times are given in Annex A1.

9.5.3 When spot checks are being made of an environment, a sample volume of 10 L is adequate for determining vapor concentrations in accordance with exposure guidelines.

9.6 At the end of the sampling period recheck the flow rate, turn off the pump, and record all pertinent information: time, register reading, and if pertinent, temperature, barometric pressure, and relative humidity.

9.6.1 Seal the charcoal tube with the plastic caps provided.

9.6.2 Label the tube with the appropriate information to identify it.

9.7 At least one charcoal sampling tube should be presented for analysis as a field blank with every 10 or 15 samples, or for each specific inspection or field study.

9.7.1 Break the sealed ends off the tube and cap it with the plastic caps. Do not draw air through the tube, but in all other ways treat it as an air sample.

9.7.2 The purpose of the field blank is to assure that if the sampling tubes adsorb vapors extraneous to the sampling atmosphere, the presence of the contaminant will be detected.

9.7.3 Results from the field blanks shall not be used to correct sample results. If a field blank shows contamination, the samples taken during the test must be assumed to be contaminated.

9.8 *Calculation of Sample Volume:*

9.8.1 For sample pumps with flow-rate meters:

$$\text{Sample volume, mL} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled, mL/min,
t = sample time, min,
P_1 = pressure during calibration of sampling pump (mm Hg or kPa)
P_2 = pressure of air sampled (mm Hg or kPa)
T_1 = temperature during calibration of sampling pump (K), and
T_2 = temperature of air sampled (K).

9.8.2 For sample pumps with counters:

Sample volume, mL

$$V = \frac{(R_2 - R_1) \times V}{I} \times \frac{P_1}{760} \times \frac{298}{T_1 + 273}$$

where:

R_2 = final counter reading,
R_1 = beginning counter reading,
V = volume, (1) mL-count (1)
P_1 = barometric pressure, mm Hg,
T_1 = temperature, °C, and
V = total sample volume, mL.

10. Handling and Shipping of Samples Collected on Charcoal Sampling Tubes

10.1 There is a paucity of information on the possible fate of the many different chemical species that can be collected in activated charcoal and the variety of conditions to which these samples may be exposed. Good practice suggests the following:[7]

[6] Heitbrink, W. A., "Diffusion Effects Under Low Flow Conditions," American Industrial Hygiene Association Journal, Vol 44, No. 6, 1983, pp. 453–462.

[7] Two recent studies that present information pertinent to this section are:
Saalwaechter, A. T., et al, "Performance Testing of the NIOSH Charcoal Tube Technique for the Determination of Air Concentrations of Organic Vapors," *American Industrial Hygiene Association Journal*, Vol 38, No. 9, September 1977, pp. 476–486.
Hill, R. H., Jr., et al, "Gas Chromatographic Determination of Vinyl Chloride in Air Samples Collected on Charcoal," *Analytical Chemistry*, Vol 48, No. 9, August 1976, pp. 1395–1398.

.1 Samples should be capped securely and identified

.2 Samples collected in charcoal tubes should not be
n warm places or exposed to direct sunlight.

.3 Samples of highly vaporous or low-boiling mate-
uch as vinyl chloride, should be stored and transported
ice.

.4 At present there are no published test data on the
of conditions in aircraft cargo holds on capped
es. The preferred procedure is to carry the samples on

.5 Samples should be shipped as soon as possible,
under refrigeration until they are analyzed, and
zed if possible within 5 working days.

10.1.6 Migration or equilibration of the sampled material within the sampling tube during prolonged or adverse storage or handling could be interpreted as break-through. This can be prevented by separating the front and back sections immediately after sampling, by having each section in a separate tube and capping them separately.

10.1.7 In some situations, circumstances and facilities may permit making up calibration standards at the facility where the study is being made and submitting these standards as quality control checks. (See Practice D 3687 for recommended procedure for making up standards.)

10.1.8 Bulk solvent samples should never be shipped or stored with the collected air samples.

ANNEXES

(Mandatory Information)

A1. INFORMATION OF SOME ORGANIC COMPOUND VAPORS THAT CAN BE COLLECTED ON COCONUT-SHELL CHARCOAL (100/50 mg tubes)

Substance PEL ppm-mg/m³ [A]	Recommended Sampling Rate, mL/min to Detect Approximately 15 to 200 % of PEL in Time Given [B]			Recommended Maximum Tube Loading, mg [D]	Approximate Desorption Efficiency % [E]	Eluent	GC Column [F]	CV_T [G]
	2h	4h	8h					
ie, 1000–2400	10	C	C	9	86 ± 10	CS_2	3	0.082
itrile, 40–70	50	25	25	2.7				0.072
lcohol, 2–4.8	200	100	50	<0.4	89 ± 5	CS_2 + 5 % 2-propanol	2	0.11
l acetate, 100–525	50	25	10	15	86 ± 5	CS_2	4	0.051
nyl acetate, 125–650	50	25	10	15.5	91 ± 10	CS_2	4	0.071
yl alcohol, 100–360	50	25	10	10		CS_2 + 5 % 2-propanol	2	0.077
ne, 10–31.3	100	100	50		96	CS_2	1	0.060
l chloride, 1–5	—	200	200	<0.4	90 ± 5	CS_2	2	0.096
iene, 1000–2200	10	C	C	4		CS_2	1	0.058
oxy ethanol, 50–240	100	50	25		99 ± 5	methylene chloride + 5 % methanol	2	0.060
yl acetate, 150–710	50	25	10	15	95	CS_2	4	0.069
utyl acetate, 200–950	50	25	10	15	91 ± 5	CS_2	4	0.054
utyl acetate, 200–950	50	25	10	12.5	94 ± 5	CS_2	4	0.091
alcohol, 100–300	100	50	25	10.5	88 ± 5	CS_2 + 1 % 2-propanol	2	0.065
utyl alcohol, 150–450	50	25	10	6	93 ± 5	CS_2 + 1 % 2-propanol	2	0.066
utyl alcohol, 100–300	50	25	10	5	90 ± 5	CS_2 + 1 % 2-propanol	2	0.075
glycidyl ether, 50–270	100	50	25	11.5	86 ± 10	CS_2		0.074
-Butyl toluene, 10–60	100	50	25	2.5	100+	CS_2	2	0.067
hor, 2–12.5	200	100	50	13.4	98 ± 5	CS_2 + 1 % methanol	2	0.074
n disulfide, 20–60	200	100	50		95	benzene	8	0.059
n tetrachloride, 10–65	200	100	50	7.5	97 ± 5	CS_2	1	0.092
obenzene, 75–350	50	25	10	15.5	90 ± 5	CS_2	2	0.056
obromomethane 200–1050	25	10	C	9.3	94 ± 5	CS_2	2	0.061
oform, 50–240	100	50	25	11	96 ± 5	CS_2	1	0.057
ne, 50–245	50	25	10	11	100+	CS_2	2	0.059
hexane, 300–1050	25	10	C	6.3	100+	CS_2	3	0.066
hexanol, 50–200	100	50	25	10	99 ± 5	CS_2 + 5 % 2-propanol	2	0.080
hexanone, 50–200	100	50	25	13	78 ± 5	CS_2	2	0.062
hexene, 300–1015	25	10	C		100+	CS_2	3	0.073
tone alcohol, 50–240	100	50	25	12	77 ± 10	CS_2 + 5 % 2-propanol	2	0.101
hlorobenzene 50–300	50	25	10	15	85 ± 5	CS_2	6	0.067
ichloroethane, 100–405	50	25	10	7.5	100+	CS_2	2	0.057

A1 *Continued*

Substance PEL ppm-mg/m³ [A]	Recommended Sampling Rate, mL/min to Detect Approximately 15 to 200 % of PEL in Time Given [B]			Recommended Maximum Tube Loading, mg [D]	Approximate Desorption Efficiency % [E]	Eluent	GC Column [F]	CV_T [G]
	2h	4h	8h					
1,2-Dichloroethylene, 200–790	25	10	C	5.1	100+	CS_2	2	0.052
p-Dioxane, 100–360	100	50	25	13	91 ± 5	CS_2	1	0.054
Dipropylene glycol methyl ether, 100–600	25	10	C		75 ± 15	CS_2	2	0.064
2-Ethoxyethyl acetate, 100–500	50	25	10	19	74 ± 10	CS_2	4	0.062
Ethyl acetate, 400–1400	25	10	C	12.5	89 ± 5	CS_2	4	0.058
Ethyl acrylate, 25–100	200	100	50	<5	95 ± 5	CS_2	4	0.054
Ethyl alcohol, 1000–1885	C	C	C	2.6	77 ± 10	CS_2 + 1 % 2-butanol	2	0.065
Ethyl benzene, 100–435	200	100	50	16	100+	CS_2	2	0.041
Ethyl bromide, 200–890	100	50	25	7.1	83 ± 5	isopropanol	2	0.054
Ethyl butyl ketone, 50–230	50	25	10	<5.5	93 ± 5	CS_2 + 1 % methanol	2	0.086
Ethyl ether 400–1210	10	C	C	7.5	98 ± 5	ethyl acetate	3	0.053
Ethyl formate, 100–300	50	25	10	4.8	80 ± 10	CS_2	1	0.074
Ethylene bromide, 20–155	100	50	25	<10.7	93 ± 5	CS_2	2	0.077
Ethylene dichloride, 50–202.5	100	50	25	12	95 ± 5	CS_2	6	0.079
Glycidol, 50–150	100	50	25	22.5	90 ± 5	tetrahydrofuran	2	0.080
Heptane, 500–2000	10	C	C	12.5	96 ± 5	CS_2	6	0.056
Hexane, 500–1800	10	C	C	11	94 ± 5	CS_2	1	0.062
Isoamyl acetate, 100–525	50	25	10	16.5	90 ± 5	CS_2	4	0.056
Isoamyl alcohol, 100–360	50	25	10	10	99 ± 5	CS_2 + 5 % 2-propanol	2	0.065
Isobutyl acetate, 150–700	50	25	10	14	92 ± 5	CS_2	4	0.065
Isobutyl alcohol, 100–305	50	25	10	10.5	84 ± 10	CS_2 + 1 % 2-propanol	2	0.073
Isopropyl acetate, 250–950	25	10	C	13	85 ± 5	CS_2	4	0.067
Isopropyl alcohol 400–985	25	10	C	5.6	94 ± 5	CS_2 + 1 % 2-butanol	2	0.064
Isopropyl glycidyl ether, 50–240	100	50	25	10.5	80 ± 10	CS_2	2	0.067
Mesityl oxide, 25–100	100	50	25	4.8	79 ± 5	CS_2 + 1 % methanol	2	0.071
Methyl acetate, 200–610	25	10	C	7	88 ± 5	CS_2	1	0.055
Methyl acrylate, 10–35	200	100	50	<1.5	80 ± 10	CS_2	4	0.066
Methylal, 1000–3110	10	C	C	11.5	78 ± 10	hexane	3	0.06
Methyl amyl ketone, 100–465	50	25	10	7.5	80 ± 10	CS_2 + 1 % methanol	2	0.061
Methyl butyl ketone, 100–410	50	25	10	2.0	79 ± 10	CS_2	2	0.053
Methyl cellosolve, 25–80	100	50	25	10	97 ± 5	methylene chloride + 5 % methanol	2	0.068
Methyl cellosolve acetate, 25–120	100	50	25	5	76 ± 10	CS_2	4	0.068
Methyl chloroform, 350–1900	25	10	C	18	98+	CS_2	6	0.054
Methyl cyclohexane, 500–2000	10	C	C		95 ± 5	CS_2	1	0.052
Methyl ethyl ketone, 200–590	50	25	10	9.5	89 ± 10	CS_2	2	0.072
Methyl isobutyl carbinol, 25–105	200	100	50	5.7	99 ± 5	CS_2 + 5 % 2-propanol	2	0.080
α-Methyl styrene, 100–480	100	50	25	21	91 ± 5	CS_2	2	0.054
Methylene chloride, 500–1740	10	C	C	9.3	95 ± 5	CS_2	1	0.073
Naphtha (coal tar), 100–400	100	50	25	14.8	88 ± 5	CS_2	7	0.051
n-octane, 500–2350	10	C	C	15	93 ± 5	CS_2	1	0.060
Pentane, 1000–2950	10	C	C	9	96 ± 5	CS_2	1	0.055
2-Pentenone, 200–700	25	10	C		88 ± 5	CS_2	2	0.063
Perchloroethylene, 100–680	50	25	10	29	95 ± 5	CS_2	6	0.052
Petroleum distillates, 500–2000	10	C	C	12.3	96 ± 5	OS_2	6	0.052
Phenyl ether vapor, 1–7		200	200	0.6	90 ± 5	CS_2	2	0.070
Phenyl glycidyl ether, 10–59	100	50	25	12.5	97 ± 5	CS_2	2	0.057
n-Propyl acetate, 200–840	50	25	10	14.5	93 ± 5	CS_2	4	0.056
n-Propyl alcohol, 200–490	50	25	10	9	87 ± 5	CS_2 + 1 % 2-propanol	2	0.075
Propylene dichloride, 75–350	50	25	10	5	97 ± 5	CS_2	2	0.056
Propylene oxide, 100–240	25	10	C	2	90 ± 5	CS_2	3	0.085
Pyridine, 5–15	200	100	50	<7.3	70 ± 10	CS_2		0.059
Stoddard solvent, 500–2950	10	C	C	13	96 ± 5	CS_2	7	0.052
Styrene (monomer), 100–425	100	50	25	18	87 ± 5	CS_2	2	0.057
1,1,1,2-Tetrachloro-2,2-difluoroethane, 500–4170	10	C	C	19.5	100+	CS_2	2	0.069
1,1,1,2-Tetrachloro-1,2-difluoroethane, 500–4170	10	C	C	26	96 ± 5	CS_2	2	0.054
Tetrahydrofuran, 200–590	25	10	C	7.5	92 ± 5	CS_2	3	0.055
1,1,2-Trichloroethane, 10–55	100	50	25	5	96 ± 5	CS_2	6	0.057
Trichloroethylene, 100–535	100	50	25	21	96 ± 5	CS_2	6	0.082
1,1,2-Trichloro-1,2,2-trifluoroethane, 1000–7660	10	C	C	20	100+	CS_2	5	0.07
Turpentine, 100–560	50	25	10	13	96 ± 5	CS_2	7	0.055
Vinyl toluene, 100–480	100	50	25	17	85 ± 10	CS_2	2	0.058

A1 *Continued*

[A] *Substances*—The list does not contain all compounds for which the method is applicable. It lists only those for which reliable data could be obtained. PEL-Federal Permissible Exposure Limits, as given in the *Federal Register*, June 1974, and updated May 1976. These values, which may be either ceiling limits or 8-h/day average exposure limits, depending on the compound, are presented to give guidance in selecting sampling rates and times. These values are subject to change by the Federal Occupational Safety and Health Administration.

[B] *Recommended Sampling Rate*—The suggested sampling rates for the different sampling periods are sufficient to provide a tube loading of at least 0.01 mg when concentrations are 15 % of the PEL, but will not exceed the recommended tube loading when atmosphere are 200 % of the PEL. These figures are based on the 100-mg coconut-shell charcoal tubes described in this practice.

[C] Sample rates of less than 10 mL/min are not recommended. Shorter sampling periods are required.

[D] *Recommended Maximum Tube Loading*—These values are conservative, to allow for high humidity or the presence of other substances which reduce the normal tube capacity.

[E] *Approximate Desorption Efficiency*—These figures are given only as guides for carrying out system calibrations. Actual desorption efficiencies should always be determined at the time of analysis, and any significant deviation should be regarded as a possible indication of a systematic error in the analytical technique. The figure given for desorption efficiency is an average figure. The desorption efficiency for a compound will vary with the amount; in most cases, the desorption efficiency will be lower for reduced tube loadings.

[F] *Gas Chromatographic Columns*—key:

1—20-ft × 1/8 in: ss packed with 10 % FFAP on Chromosorb W AW
2—10-ft × 1/8 in: ss packed with 10 % FFAP on Chromosorb W AW
3—4-ft × 1/4 in: ss packed with 60/80 Porapak Q
4—10-ft × 1/8 in: ss packed with 5 % FFAP on Supelcoport
5—6-ft × 1/4 in: ss packed with 60/80 Porapak Q
6—10-ft × 1/8 in: ss packed with 10 % OV-101 on Supelcoport
7—6-ft × 1/8 in: ss packed with 1.5 % OV-101 on Chromosorb W AW
8—6-ft × 1/4 in: Glass column packed with 5 % OV-17 on Supelcoport

[G] CV_T—Coefficient of variation (that is, relative standard deviation) of the total (net) error in the method (including variability of the pump).

$$CV_T = (CV^2_{A+\overline{DE}} + CV_S^2 + CV_P^2)^{1/2}$$

where:

$CV_{A+\overline{DE}}$ = coefficient of variation of a single future assay including error in the desorption efficiency factor $\overline{DE}$,
CV_S = coefficient of variation due to sampling errors (not including variable of the pump) along with variability in true desorption efficiency from tube-to-tube, and
CV_P = coefficient of variation due to pump (CV_P = 0.05 assumed).

Acknowledgements: The information in this table comes from NIOSH Standards Completion Program.[8] We gratefully acknowledge NIOSH's contribution to this table, by making available previously unpublished CV_T data, and we acknowledge having used summaries of SCP data prepared by MDA Scientific, Inc., Park Ridge, IL, SKC Corp., Eighty-Four, PA, and Supelco, Inc., Bellefonte, PA.

[8] Taylor, D. G., Kupel, R. E., and Bryant, J. M., "Documentation of NIOSH Validation Tests," DHEW (NIOSH), Pub. No. 77-185. Available from National Technical Information Service, Springfield, VA 22161 (PB274-248).

A2. METHOD FOR CALIBRATION OF SMALL VOLUME AIR PUMPS

A2.1 Using a buret that approximately represents a 1-min sampling volume, assemble the apparatus as shown in Fig. A2.1 using any good soap bubble solution as a source of the film. Make sure all connections are tight.

A2.1.1 It is advisable to check the volume of burets used for calibrating sampling pumps by weighing the volume of water contained in the buret and calculating the true volume.

A2.1.2 Make sure the batteries of the pump are charged.

A2.2 Prime the surface of the cylinder with bubble solution by drawing repeated films up the tube until a single film travels to the desired mark.

A2.3 With a stop watch, time the travel of a single film from an initial zero mark to a selected volume mark. Note the time and repeat this procedure at least three times.

A2.4 Calculate the sampling rate of the pump, correcting the air volume to 25°C and 760 mm Hg (101.3 kPa), using the ambient barometric pressure.

A2.5 Replace the charcoal tube sampler with another one selected at random, and repeat the calibration sequence.

A2.5.1 Sampling tubes should consistently meet the pressure drop criterion given in 7.1.4.

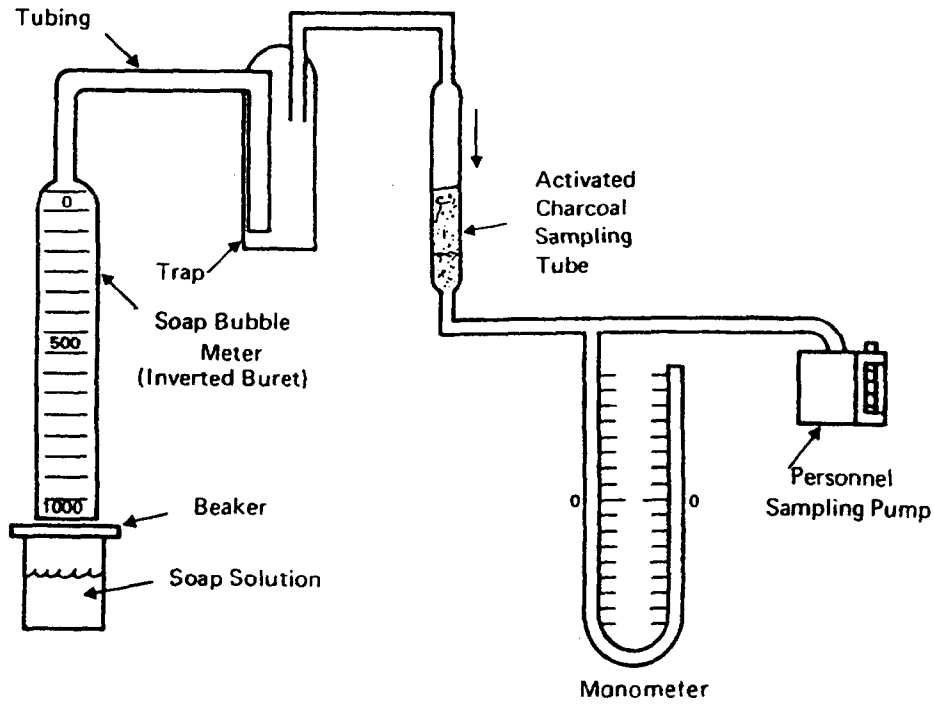

FIG. A2.1 Calibration Setup for Personnel Sampling Pump with Activated Charcoal Sampling Tube

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3) Otterson, E. J., and Guy, C. U., "A Method of Atmospheric Solvent Vapor Sampling on Activated Charcoal in Connection with Gas Chromatography," Transactions of the 26th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Philadelphia, 1964, pp. 37-46.

(4) Reid, F. H., and Halpin, W. R., "Determination of Halogenated and Aromatic Hydrocarbons in Air by Charcoal Tube and Gas Chromatography," *American Industrial Hygiene Association Journal*, July-August 1968, pp. 390-396.

(5) Turner, B. C., and Glotfelty, D. E., "Field Sampling of Pesticide Vapors with Polyurethane Foam," *Analytical Chemistry*, Vol 1977, pp. 7-10.

Appendix E3: Standard Operating Procedures for Calibration of Low Volume and Very Low Volume Personal Air Monitoring Pumps

Section 3
Theory of Operation

1. Primary Airflow Standard

To be a primary standard, all values must be absolute and measured as absolute. A primary standard airflow measurement is a volume divided by a time interval as performed by the Control Unit of the Gilibrator. The volume, V, is a measured volume of space between two infrared sensors. The time is that interval needed for a soap film bubble to traverse between the two sensors which bound the volume. Therefore, V/t, the volume per unit of time, becomes the airflow and is prime because all measurements are basic...volume and time. In today's technology, time is measured by an electronic clock whose accuracy exceeds that of volume measurements by orders of magnitude, hence, the control accuracy volume resides solely with volume measurements.

2. Bubble Generation and measurement

a) The Gilibrator consists of two elements, the Flow Cell Assembly and the Control Unit (base). The function of the Flow Cell Assembly is to generate a clean consistent bubble which traverses up the flow tube. Measurement of the traverse time is done by infrared sensor pairs which are mounted at the bottom and the top of the Sensor Block. The volume bound by these sensors is specifically adjusted to a volume standard by allowing the upper sensor blocks to move in unison so as to enable this calibration to be set accurately to a primary volume standard. A seconds function of the sensor block provides the interfacing code to define the cell volume as well as sensitivity adjustments for the optical sensor systems.

b) As the bubble traverses between the sensors, first one and then the second, sensors are tripped thereby providing the tme for the bubble traverse. This timing information is sent to the micro processor of the control base which in turn provides the crystal control time base for the system. The timing information along with the volumeinformation are then sent to the micro processor which in turn does the necessary mathematical calculations which allow the flow to be displayed directly on the LCD readout. In order to insure the highest accuracy possible, a Delete and Average function are provided on the Control Unit. The Delete allows for subtracting out an obvious malformed bubble and the average allows the user to obtain average information without pencil or paper. A printer interface allows connection of a Printer Module so that hard copy can be produced.

Section 4
Operating Procedures

1. Initial Set-up

This covers all steps necessary to bring the Gilibrator into operating status. This includes charging, cell mounting, installing soap solution, connecting the printer (optional) and connecting the sampling source.

A) Charging the Gilibrator for Operation

1. Prior to operation, plug the 120V charger into the wall and connect to the Charging Jack on the right side of the Control Unit. The unit's Charging LED will light indicating that the unit is charging properly. Allow to charge for 14 hours prior to operation.

B) Mounting the Flow Cell Assembly

1. Select the Flow Cell Assembly to cover the flow range required.

2. The bottom of the Flow Cell Assembly employs a quick mount feature. The base of the Flow Cell Assembly is positioned onto the mounting plate of the Control Unit.

3. Engage the pin of the cell assembly base into the mounting plate of the Control Unit (NOTE: When cell is properly engaged, the base of the cell will be flush to the mounting plate and the cell label will face the 3'oclock position - As observed from the top).

4. Grasp the bottom cell chamber and rotate clockwise until it clicks in. (CAUTION: Always engage & disengage the cell by grasping and rotating only the bottom cell chamber.) The cell assembly label will now face forward (6 o'clock position).

5. Insert the Control Unit's connector plug into the jack located at the back of the sensor block.

C) Adding the Gilibrator Soap Solution

1. Remove the Seal Tubing from the upper outlet boss of the upper cell. Fill dispenser bottle with soap solution. Using the rubber tubing as a funnel, add soap solution from the dispenser.

2. The amount of soap needed can be determined by depressing the Bubble Initiate button and holding it in the lower position. Continue to add only enough soap solution until the bottom of the ring generator is immersed in the solution.
Do Not Overfill!

3. After filling is completed, the rubber Seal Tubing may be removed completely. Recap soap solution for later use.
NOTE: If Flow Cell Assembly is not going to be used for a prolonged period of time, reinstall the rubber tubing between the

inlet and outlet bosses. This will prevent evaporation from occurring which may cause the solution's concentrations to alter.

D) Printer Connection (if applicable)

1. Connect printer cable to Printer Jack connector on The left side of the Control Unit. Be sure to properly match up connectors before connecting.

E) Connect the Sampler

1. Connect the air sampler to be calibrated to the upper outlet boss of the Flow Cell Assembly. An auxillary liquid trap between sampler and flow cell is recommended to prevent moisture carry over into the sampler during continuous calibration periods.

2. Operation

A) Conditioning the Flow Tube

1. Turn on the sampler . Depress the Bubble Initiate Button several times to wet the inner walls of the flow tube. You will not be able to initiate a timing bubble without first "Priming" the flow tube. The operator will develop a feel for bubble generation with practice.

B) Power Up

2. After the Flow Tube walls have been "primed", turn on the Power switch of the Gilibrator Control Unit (base) and the Printer Module if one is being used. Wait approximately 10 seconds while the system runs through it's check sequence. The Run LED will light at this time as well as a Lo Battery indication and a series of 5 dashes displayed on the LCD Readout. Do not operate the Gilibrator until the Run LED signal extinguishes. Ready operation is indicated by a series of 4 dashes.

C) Bubble Generation

1. For optimum bubble generation, depress the Bubble Generator button and hold to initiate 1 bubble up the flow tube. Release the button to initiate a second bubble up the flow tube. This will be the standard procedure to making clean, consistent bubbles at High and Medium flow ranges. At Low flow ranges depressing the button once will generate a clean bubble.

2. As the bubble rises up the tube, it will initiate the timing sequence as it passes the lower sensor (the Run LED will light) and culminate the timing sequence upon passing the upper sensors (the Run LED will extinguish). The timing information is then transmitted to the control unit which will perform all the necessary mathematics. A flow reading will appear on the LCD display.

Appendix E4: Standard Operating Procedures for Calibration of Field Photoionization Detector

SECTION III

Routine Maintenance

The routine maintenance of the 580B involves the calibration of the instrument, the cleaning of the lamp window, and he maintaining of charge on the battery. The following pages give instructions for routine maintenace. Figure 3.1 illustrates he detector assembly.

3.1 LAMP INSERTION AND REMOVAL

3.1.1 REMOVAL

NOTE: The 580B must be off while removing the lamp.

In order to remove the lamp the four screws which hold the case top and bottom together must first be loosened. The case bottom should be placed flat on the table and the top placed on its side next to the bottom.

The high voltage power supply is removed next by loosening the thumb screws on each side and then pulling the power supply towards the rear of the instrument (see figure 3.1). The lamp may now be removed by loosening the lamp nut.

3.1.2 INSERTION

Insertion of the lamp is accomplished by performing the above tasks in the reverse order. The lamp should be placed flat against the o-ring and the lamp nut fastened down in order to create a proper seal. The high voltage power supply should then be inserted and the thumb nuts fastened down. There are three pins protruding from the high voltage power supply which should fit snugly into connectors located beneath the detector. The lamp spring (mounted in the center of the high voltage power supply) should make contact with the lamp ring.

3.1.3 LAMP CLEANING

On occasion the lamp should be removed for cleaning. Cleaning of the lamp is accomplished by cleaning the lens surface of the UV lamp. This is accomplished by using the aluminum oxide scouring powder provided with the 580B.

The procedure for cleaning the lamp is as follows. First place a small amount of aluminum oxide scouring powder on the lens of the UV lamp. Next gently scour this lens with a soft tissue or cloth. Scour the lens in a rotary type motion. After scouring the lens surface gently blow the remaining powder from the lens. Throughly wipe the lamp lens with a clean tissue to remove the last traces of cleaning powder. The lamp is now able to be inserted into the detctor.

3.2 CALIBRATION

NOTE : Chapter four should be read before calibrating the 580B in order to gain a better understanding of the concepts behind calibration of the 580B.

The following is a brief discussion of calibration as it relates to different lamps. One of the parameters in the Parameters mode (see section 2.3) allows selection of lamp setting. The two types of lamps are the 10.0 eV and the 11.8 eV lamp. Whenever a new lamp is used the 580B must be calibrated. This is true even if the new lamp is the same type. For example the new and old lamp are both 10.0 eV. This is due to the fact that each lamp will have a slightly different sensitivity.

It is important to note that the 11.8 eV lamp will in general be less sensitive than the 10.0 eV lamp. This is true despite the higher energy level of the 11.8 eV lamp. The 11.8 eV lamp will however "see" certain gases which the 10.0 eV lamp will not. See table E.1 for a list of common organic vapors and their associated ionization potentials. Any questions regarding the use of the 580B should be directed to Thermo Environmental's Application Laboratory.

The 580B is quite simple to calibrate. A source of "zero air" and "span gas" are all that is needed to calibrate the 580B.

The zero air is introduced to the 580B in order to determine the "background" signal. The concentration of the span gas is then selected. The span gas is finally introduced to the 580B. The instrument makes all of the necessary calculations (including linearization) to arrive at a "calibration constant." When in the Run mode the signal is multiplied by the calibration constant in order to arrive at the current PPM.

$$\text{CALIBRATION CONSTANT} = \frac{\text{SPAN PPM}}{\text{SPAN ZERO SIGNAL}}$$

$$\text{PPM} = (\text{SPAN SIGNAL} - \text{ZERO SIGNAL})\ \text{CALIBRATION CONSTANT}$$

NOTE : The PPM is then multiplied by the RESPONSE FACTOR before being displayed. Chapter four explains the use of response factors when calibrating.

Section 2.4.6 gives a detailed explanation of which buttons to press in order to calibrate the 580B. The flow chart at the back of this manual may also be helpfull.

3.3 CHARGE

When there is a flashing "B" in the lower left corner of the display (while in the run mode) the battery is low. The battery is recharged by pluging the charger into the RUN/CHARGE plug at the rear of the 580B. The instrument runs while it is charging. The charger has an LED which indicates the amount of current being drawn. The LED gets brighter as more current is drawn. The LED can therefore be used as a rough indication of the charge on the battery.

2.4.5 LAMP SELECTION

The 580B will display:

LAMP

on the top line. The bottom line will alternate every two seconds between:

"RESET" TO CHG

and the currently selected lamp setting and its associated serial number.
i.e.

11.8eV 000000

By pressing the RESET switch, the 580B will display:

+/10eV −/11eV

on the bottom line. Pressing the +/INC switch will select the 10.0 eV lamp. Pressing the −/CRSR switch will select the 11.8eV lamp. In either case the 580B will then allow editing of the lamp serial number. The display will show:

SERIAL # 000000
"RESET"WHEN DONE

The +/INC switch will increment the number above the cursor and the −/CRSR switch will move the cursor. Pressing the RESET switch will return operation to the original lamp screen.

2.4.6 RESPONSE FACTOR SETTING

The current Response Factor setting will be displayed on the top line of the display. The Response Factor may be changed by simultaneously pressing the RESET switch with either the +/INC switch to increment the digit above the cursor or the −/CRSR switch to move the cursor.

The response factor is used to equate the response of one organic vapor with that of the calibration gas. The current reading is allways multiplied by the response factor in order to obtain the displayed concentration. A response factor of one will not change the displayed concentration.

2.4.7 CALIBRATION

The 580B will display:

"RESET" TO
CALIBRATE

The calibration mode may be entered by pressing the RESET switch.
The 580B will display:

RESTORE BACKUP
+ = YES

The previous calibration information may be restored by pressing the +/INC switch. The 580B will then return to the previous screen. If the backup is not desired, by pressing the −/INC switch the calibration routine will continue. The display will show:

ZERO GAS
RESET WHEN READY

Appendix E5: Standard Operating Procedures for GC/FID Analysis

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, BP 36 — 126 °C

METHOD: 1500
ISSUED: 2/15/84

OSHA, NIOSH, ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS:	benzene	n-heptane	n-octane
(Synonyms	cyclohexane	n-hexane	n-pentane
in Table 1)	cyclohexene	methylcyclohexane	toluene

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal,
100 mg/50 mg)

FLOW RATE, VOLUME: Table 3

SHIPMENT: no special precautions

SAMPLE STABILITY: at least 2 weeks

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable, 1 to 10 mL; ship in separate containers from samples

ACCURACY

RANGE STUDIED,
BIAS and OVERALL PRECISION (s_r): Table 3

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTES: hydrocarbons listed above
!
!DESORPTION: 1 mL CS_2; stand 30 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 250 °C
! -DETECTOR: 250 °C
! -COLUMN: see step 11
!
!CARRIER GAS: N_2 or He, 25 mL/min
!
!COLUMN: glass, 3.0 m x 2 mm, 20% SP-2100 on
! 80/100 mesh Supelcoport
!
!CALIBRATION: analytes in CS_2
!
!RANGE AND PRECISION (s_r): Table 4
!
!ESTIMATED LOD: 0.001 to 0.01 mg per sample
! with capillary column [1]
!

APPLICABILITY: This method is intended for determining the OSHA-regulated hydrocarbons included within the boiling point range of n-pentane through n-octane. It may be used for simultaneous measurements; however, interactions between analytes may reduce breakthrough volumes and change desorption efficiencies.

INTERFERENCES: At high humidity, breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers, and halogenated hydrocarbons, are likely interferences. If interference is suspected, use a more polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene and toluene [2]; S28, cyclohexane [3]; S82, cyclohexene [3]; S89, heptane [3]; S90, hexane [3]; S94, methylcyclohexane [3]; S311, benzene [4]; S343, toluene [4]; S378, octane [4]; and S379, pentane [4]. For benzene or toluene in complex mixture of alkanes ($\leq C_{10}$), Method 1501 (aromatic hydrocarbons) is more selective.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality with (optional) suitable internal standard.
2. Analytes, reagent grade.*
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1500-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, with pipet bulb.
6. Syringes, 5-, 10-, 25- and 100-µL.
7. Volumetric flasks, 10-mL

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (0.01 to 0.05 L/min for n-pentane) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11, 12 and 13).
   c. Prepare calibration graph (peak area of analyte vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11, 12 and 13).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control. Check for possible contamination during shipment of field samples by comparing results from field blanks and media blanks.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1500-1. Select appropriate column temperature:

	Approximate Retention Time (min), at Indicated Column Temperature			
Substance	40 °C	70 °C	100 °C	Programmed[a]
n-pentane	2.2	1.2		1.8
solvent (CS_2)	3.0	1.6		2.4
n-hexane	5.1	2.2		3.5
benzene[b]	7.7	3.2		4.5
cyclohexane[b]	8.4	3.4		4.7
cyclohexene	9.5	3.8		4.9
n-heptane	12	4.3		5.4
methylcyclohexane	14	5.2	2.2	5.9
toluene	17	6.5	2.6	6.5
n-octane	19	8.7	3.2	7.1

[a]Temperature program: 50 °C for 2 min, then 15 °C/min to 150 °C, 2-min final hold.
[b]Not completely resolved.

NOTE: Alternatively, column and temperature may be taken from Table 4.

12. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

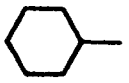
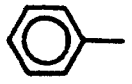
$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:
Precisions and biases (Table 3) were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions (Table 4) were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [12] provides more specific information.

REFERENCES:
[1] User check, UBTL, NIOSH Sequence #4213-L (unpublished, January 31, 1984).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 127 U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S28, S82, S89, S90, S94, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3., S311, S343, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] R. D. Driesbach, "Physical Properties of Chemical Compounds"; Advances in Chemistry Series, No. 15; American Chemical Society, Washington (1955).
[6] R. D. Driesbach, "Physical Properties of Chemical Compounds - II"; Advances in Chemistry Series, No. 22; American Chemical Society, Washington (1959).
[7] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington, (1980); 29 CFR 1910.1000.
[8] Update Criteria and Recommendations for a Revised Benzene Standard, U.S. Department of Health, Education, and Welfare, (August 1976).
[9] Criteria for a Recommended Standard....Occupational Exposure to Alkanes (C5-C8), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-151 (1977).
[10] Criteria for a Recommended Standard....Occupational Exposure to Toluene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 73-11023 (1973).
[11] TLVs—Threshold Limit Values for Chemical Substances and physical Agents in the Work Environment with Intended Changes for 1983-84, ACGIH, Cincinnati, OH (1983).
[12] Documentation of the NIOSH Validation Tests, S28, S82, S89, S90, S94, S311, S343, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: R. Alan Lunsford, Ph.D., and Julie R. Okenfuss; based on results of NIOSH Contract CDC-99-74-45.

Table 1. Synonyms, formula, molecular weight, properties.

Name Synonyms	Structure	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	Vapor Pressure @ 25 °C (kPa)	Density @ 20 °C (g/mL)
benzene[a] CAS #71-43-2		C_6H_6	78.11	80.1	95.2	12.7	0.879
cyclohexane[a] CAS #110-82-7 hexahydrobenzene hexamethylene		C_6H_{12}	84.16	80.7	97.6	13.0	0.779
cyclohexene[a] CAS #110-83-8 tetrahydrobenzene		C_6H_{10}	82.15	83.0	88.8	11.8	0.811
n-heptane[b] CAS #142-82-5		C_7H_{16}	100.21	98.4	45.8	6.1	0.684
n-hexane[b] CAS #110-54-3		C_6H_{14}	86.18	68.7	151.3	20.2	0.659
methylcyclohexane[a] CAS #108-87-2		C_7H_{14}	98.19	100.9	46.3	6.2	0.769
n-octane[b] CAS #111-65-9		C_8H_{18}	114.23	125.7	14.0	1.9	0.703
n-pentane[b] CAS #109-66-0		C_5H_{12}	72.15	36.1	512.5	68.3	0.626
toluene[a] CAS #108-88-3 methylbenzene		C_7H_8	92.14	110.6	28.4	3.8	0.867

[a]Properties from [5].
[b]Properties from [6].

Table 2. Permissible exposure limits, ppm [7-11].

Substance	OSHA TWA	OSHA C	OSHA Peak	NIOSH TWA	NIOSH C	ACGIH TLV	ACGIH STEL	mg/m³ per ppm @ NTP
benzene*	10	25	50[b]	1		10	25	3.19
cyclohexane	300					300	375	3.44
cyclohexene	300					300		3.36
n-heptane	500			85	440	400	500	4.10
n-hexane[a]	500			100	510	50		3.52
methylcyclohexane	500					400	500	4.01
n-octane	500			75	385	300	375	4.67
n-pentane	1000			120	610	600	750	2.95
toluene	200	300	500[b]	100	200[c]	100	150 (skin)	3.77

[a]The ACGIH recommendation for other hexane isomers is: TLV 500, STEL 1000.
[b]Maximum duration 10 min in 8 hr.
[c]10-min sample.
*ACGIH: suspect carcinogen

Table 3. Sampling flowrate[a], volume, capacity, range, overall bias and precision [2-4, 12].

Substance	Sampling Flowrate (L/min)	Sampling Volume (L) VOL-NOM	Sampling Volume (L) VOL-MAX[b]	Breakthrough Volume at Concentration (L)	Breakthrough Volume at Concentration (mg/m³)	Range at VOL-NOM (mg/m³)	Overall Bias (%)	Overall Precision (s_r)
benzene	≤0.20	2[c]	30	>45	149.1	41.5 - 165	0.8	0.059
cyclohexane	≤0.20	2.5	5	7.6	1650	510 - 2010	5.4	0.060[d]
cyclohexene	≤0.20	5	7	10.4	2002	510 - 2030	9.0	0.073
n-heptane	≤0.20	4	4	6.1	4060	968 - 4060	-6.5	0.056
n-hexane	≤0.20	4	4	5.9	3679	877 - 3679	-3.8	0.062
methylcyclohexane	≤0.20	4	4	6.1	3941	940 - 3941	5.5	0.052
n-octane	≤0.20	4	4	6.5	4612	1050 - 4403	-5.2	0.060
n-pentane	≤0.05	2	2	3.1	5640	1476 - 6190	-9.7	0.055
toluene	≤0.20	2[c]	8	11.9	2294	548 - 2190	3.8	0.052

[a]Minimum recommended flow is 0.01 L/min.
[b]Approximately two-thirds the breakthrough volume.
[c]10-min sample.
[d]Corrected value, calculated from data in [12].

Table 4. Measurement range, precision, and chromatographic conditions [2-4,12].

	Measurement[a]		Carrier		Column Parameters[b]			
Substance	Range (mg)	Precision (s_r)	Gas	Flow (mL/min)	t (°C)	Length (m)	Diameter (mm)	Packing[c]
benzene	0.09-0.35	0.036	N_2	50	115	0.9	3.2	A
cyclohexane	1.3 - 5.3[d]	0.024	N_2	50	210	1.2	6.4	B
cyclohexene	2.4 - 9.7[d]	0.021	N_2	50	205	1.2	6.4	B
n-heptane	4.08-16.3	0.016	He	30	80	3.0	3.2	C
n-hexane	3.56-14.5	0.014	He	30	52	6.1	3.2	D
methylcyclohexane	3.98-16.1	0.012	He	30	55	6.1	3.2	D
n-octane	4.75-18.9	0.009	He	30	52	6.1	3.2	D
n-pentane	2.98-11.8	0.014	He	30	52	6.1	3.2	D
toluene	1.13-4.51	0.011	N_2	50	155	0.9	3.2	B

[a] Injection volume, 5.0 µL; desorption volume, 1.0 mL, except cyclohexane and cyclohexene, 0.5 mL.

[b] All columns stainless steel. Diameter is outside dimension.

[c] A, 50/80 mesh Porapak P; B, 50/80 mesh Porapak Q; C, 10% OV-101 on 100/120 mesh Supelcoport; D, 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

[d] Corrected value, calculated from data in [12].

Designation: D 3687 – 89

Standard Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method[1]

This standard is issued under the fixed designation D 3687; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

Scope

1.1 This practice covers the applications of methods for e desorption and gas chromatographic determination of ganic vapors that have been adsorbed from air in sampling bes packed with activated charcoal.

1.2 This practice is complementary to Practice D 3686.

1.3 This practice is applicable for analysis of samples ken from workplace or other atmospheres, provided that e contaminant has been found amenable to collection on arcoal tubes and gas chromatographic analysis. A partial t of organic compounds for which this method is appli- ble is given in the appropriate Annex in Practice D 3686.

1.4 Components of multicomponent samples may mutu- ly interfere during analysis. Methods to resolve interfer- ces are given in Section 6.

1.5 *This standard may involve hazardous materials, oper- ions, and equipment. This standard does not purport to ddress all of the safety problems associated with its use. It is e responsibility of the user of this standard to establish ppropriate safety and health practices and determine the pplicability of regulatory limitations prior to use.* Specific ecautions are given in 8.1.4.2 and Annex A1.

Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Atmospheric Sampling and Analysis[2]

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)[2]

E 355 Practice for Gas Chromatography Terms and Relationships[3]

2.2 *NIOSH Standards:*

CDC-99-74-45 Documentation of NIOSH Validation Tests[4]

Manual of Analytical Methods, 2nd Ed.[4]

2.3 *OSHA Standard:*

29 CFR 1910 General and Industrial OSHA Safety and Health Standard[5]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this practice, refer to Definitions D 1356, and E 355.

3.1.2 *retention time* (RT)—time to elute a specific chemical from a chromatographic column, for a specific carrier gas flow rate, measured from the time the chemical is injected into the gas stream to when it appears at the detector.

3.1.3 *relative retention time* (RRT)—a ratio of RTs' for two chemicals for the same chromatographic column and carrier gas flow rate, where the denominator represents a reference chemical.

4. Summary of Practice

4.1 Organic vapors, which have been collected on activated charcoal and eluted therefrom with carbon disulfide or other appropriate desorbent, are determined by gas-liquid chromatography, using a flame ionization detector and other appropriate detectors.

4.2 Interferences resulting from the analytes having similar retention times during gas-liquid chromatography are resolved by improving the resolution or separation, such as by changing the chromatographic column or operating parameters, or by fractionating the sample by solvent extraction.

4.3 Peaks are identified using techniques such as GC/MS and dual column chromatography.

5. Significance and Use

5.1 Promulgations by the Federal Occupational Safety and Health Administration (OSHA) in 29 CFR 1910 designate that certain organic compounds must not be present in workplace atmospheres at concentrations above specified values.

5.2 This practice, when used in conjunction with Practice D 3686, will promote needed accuracy and precision in the determination of airborne concentrations of many of the organic chemicals given in 29 CFR 1910, CDC-99-74-45, and the Manual of Analytical Methods. It can be used to determine worker exposures to these chemicals, provided appropriate sampling periods are used.

5.3 A partial list of chemicals for which this method is

[1] This practice is under the jurisdiction of ASTM Committee D-22 on ampling and Analysis of Atmospheres, and is the direct responsibility of ubcommittees D 22.04 on Analysis of Workplace Atmospheres.

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[2] *Annual Book of ASTM Standards*, Vol 11.03.

[3] *Annual Book of ASTM Standards*, Vol 14.01.

[4] Available from the U.S. Department of Commerce, National Technical Information Service, Port Royal Road, Springfield, VA 22161.

[5] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

applicable is given in the appropriate Annex of Practice D 3686, along with their OSHA Permissible Exposure Limits.

6. Interferences

6.1 Any gas chromatographic separation that involves a mixture of polar and nonpolar compounds is confronted with serious problems due to peak superimposition. In many industrial operations, both nonpolar compounds, such as mixed aliphatic petroleum hydrocarbons, and polar substances, such as aromatic hydrocarbons, amines, oxygenated compounds and sometimes halogenated compounds, may be used and found in the workplace atmosphere. It is rarely the case that a single organic solvent vapor may be expected in a workplace atmosphere where organic solvents are being used.

6.2 Such interferences are frequently resolved by changing the type of column, length of column, or operating conditions, to improve resolution of separation of compounds.

6.3 General approaches which can be followed are given below:

6.3.1 Generally unknown samples are analyzed using at least two columns of different polarity.

6.3.2 As a general guide to practice, nonpolar substrates, such as the silicones, tend to separate according to the boiling points of the compounds, whereas polar column separations are influenced more by the polarity of the compounds.

6.3.3 A single wide bore capillary column can replace several specialized packed columns and provide better sample resolution in significantly less time. Application of these columns minimizes operational changes required to achieve peak resolution.

6.4 Selective solvent stripping techniques have been used successfully to make clean and fast separations of polar, nonpolar and oxygenated compounds. A general guideline is given in Annex A1 and detailed procedures are given in Refs (1) and (2).[6]

7. Apparatus

7.1 *Gas Chromatograph* (GC), having a flame ionization detector and either an isothermally controlled or temperature programmed heating oven.

7.2 A variety of packed and capillary columns are suitable. Two suitable packed columns are a 10 ft stainless steel column, ⅛ inch ID packed with 10 % free fatty acid phase (FFAP) substrate on 80/100 mesh acid washed Chromosorb W[7] and a nonpolar column containing 10 % methyl silicone substrate on the same support material in a similar column as given above. Alternatively, 35 % diphenyl, 65 % dimethyl polysiloxane and Carbowax 20 M[8] wide bore capillary columns (0.53 and 0.75 mm) may be used in place of the packed columns. These columns are available in 30 and 60 m lengths.

7.3 *Microsyringes*, two or more 10-µL volume.

7.4 *Vials*, 5-mL serum,[9] fitted with caps lined with TFE-fluorocarbon.

8. Calibration

8.1 *Preparation of Gas Chromatograph:*

8.1.1 Install the selected column.

8.1.2 Check the system for leaks as prescribed by GC manufacturer.

8.1.3 Select a carrier gas flow compatible with the detector and column selected for the separation.

8.1.4 Calibrate the chromatographic column to determine the relative retention times (RRTs') of the various compounds of interest.

8.1.4.1 Select a reference solvent which will serve as a benchmark.

8.1.4.2 Prepare a 0.05 % solution of this solvent (volume/volume) in chromatographic grade carbon disulfide (CS_2). When kept in a properly closed container (see 7.4) and refrigerated when not in use, some solutions will keep for several weeks (3).

NOTE 1: **Warning**—Carbon disulfide is toxic and explosive, as are many of the organic compounds to be analyzed. Work with these chemicals must be done in a properly operating laboratory hood.

8.1.4.3 Into a clean 10-µL syringe draw 2 µL of CS_2. Draw the CS_2 into the barrel of the syringe until the air bubble appears at the 1-µL mark. Check the nominal volume of CS_2; it should be about 2 µL. If it is not, repeat the process until the proper volume is present.

8.1.4.4 Draw 2 µL of 0.05 % benzene (or other reference chemical)[10] in CS_2 into the syringe and then into the barrel in accordance with 8.1.4.3. The barrel should now contain 2 µL of CS_2, a small bubble of air, and 2 µL of 0.05 % solution of benzene in CS_2.

NOTE 2—Two microlitres of an 0.05 % v/v solution of any solute in a solvent will contain, in micrograms, the numerical equivalent of the density of the solute. For example, 2 µL of an 0.05 % solution of benzene contains 0.879 µg of benzene. The practical density of benzene is 0.879 at 25°C.

8.1.4.5 Inject the contents of the syringe into the gas-chromatographic column. (See 8.1.4.3, 8.1.4.4, and 8.1.4.5 describing the solvent-flush technique referred to in this practice.) Start the chart recorder and mark the starting point on the strip chart. Injection by means of a GC autosampler is acceptable in most cases.

8.1.4.6 Permit the benzene to be eluted from the column so as to form a complete chromatogram.

8.1.4.7 The time between the injection of benzene onto the chromatographic column and peak maximum is the retention time (RT) for benzene.

8.1.4.8 Retention times may be determined manually by observing the time required for a compound to pass through the chromatographic column using a stop watch or by measuring the distance from the starting point to peak maximum shown on the strip chart. Alternatively an electronic integrator may be used to determine RTs'. Most modern gas chromatographs are equipped with electronic integrators that can

[6] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[7] "Chromosorb W," a trademark of the Johns-Manville Products Corp., or equivalent has been found satisfactory for this purpose.

[8] "Carbowax," a trademark of the Union Carbide Co., or equivalent has been found satisfactory for this purpose.

[9] A. H. Thomas Catalog No. 5569-E10 or equivalent has been found satisfactory.

[10] Benzene is used in this practice as the reference chemical for the purposes of illustration, but a less toxic chemical such as toluene could be used.

accurately measure RTs' within a hundredth of a minute.

8.1.4.9 For the same conditions of operation (carrier gas-flow rate, column temperature, column characteristics) the RT may be considered a constant.

8.1.4.10 It is an excellent practice to maintain a continuing record of RTs' for the reference compound in a laboratory log. This log record should include the date, the concentration and volume of the reference compound, the operating conditions of the gas chromatograph, the carrier gas flow rate, the recorder constants, and the degree of signal attenuation. It should also include the flow rate of air and hydrogen to the detector flame.

8.1.4.11 Prepare 0.05 % solutions (or other concentrations) of organic solvents of interest and develop a set of RTs' for them. It is preferable to run more than one analysis for each solvent.

8.1.4.12 Record both the RT and the detector response. For general analytical usage these data provide a quick means of ascertaining crude concentration levels. (When precise information is necessary, fresh standards are run to prepare a standard curve.)

TABLE 1 Relative Retention Times (RRTs') for a Group of Common Organic Compounds

NOTE—Column: 20-ft, ⅛-in. outside diameter, stainless steel column (20 m) packed with 10 % Carbowax on 80/100 mesh Chromosorb W. Oven: Isothermal at 95°C.

(All data relative to the Retention Time of Benzene = 1.000. RRTs' are a mean of three or more determinations.)

Compound	Mean RRT	Standard Deviation	Relative Standard Deviation, %
Acetone	0.676	0.014	2.1
Amyl acetate	2.156	0.047	2.18
Isoamyl acetate	2.228	0.107	4.8
Benzene	1.000		
Butanol	2.945	0.155	5.3
Isobutanol	2.146	0.935	43.6
2-Butanone (MEK)	0.930	0.085	9.14
Butyl acetate	1.739	0.026	1.5
Isobutyl acetate	1.37		
Carbon tetrachloride	0.74	0.014	1.9
Cellosolve	5.27		
Cellosolve acetate	6.51		
Chloroform	1.298	0.03	2.3
Ethanol	1.078	0.001	0.1
Ethyl acetate	0.812	0.027	3.3
Ethyl benzene	2.183	0.002	0.1
Ethylene chloride	1.408	0.33	23.4
Methyl acetate	0.639	0.015	2.4
Methanol	1.020	0.028	2.7
Methylene chloride	0.875	0.005	0.57
Methyl isobutyl ketone	1.382	0.009	0.7
Pentanol	5.11		
Perchloroethylene	1.335	0.019	1.4
Propanol	1.659	0.018	1.1
Isopropanol	1.033	0.0099	1.0
Propyl acetate	1.16	0.028	2.4
Isopropyl acetate	0.828	0.017	2.1
Styrene	4.467	0.270	6.0
Toluene	1.505	0.016	1.06
Trichloroethylene	1.162	0.03	2.6
Trimethyl benzene	3.72		
1,1,1-Trichloroethane	0.78		
m-Xylene	2.309	0.107	4.6
o-Xylene	2.964	0.058	1.96
p-Xylene	2.315	0.04	1.7

8.1.4.13 Using the RT of the reference compound as the denominator and the RT of the solute as the numerator, calculate the relative retention time (RRT). This parameter is a constant for a given set of operating conditions. It may be used for rapid and accurate qualitative analysis when there is no reason to believe that there are peak superimpositions. A separate laboratory log for RRTs' should be developed and maintained, using at least two columns of different polarities. (A list of such values is given in Table 1, for example only.) A gas chromatograph interfaced with a mass spectrometer provides the most positive means of peak identification.

8.1.4.14 It is good practice to ascertain periodically the relative standard deviation of this parameter for all solutes of interest.

8.1.5 The quantitative response of a GC detector may be determined by the peak height measurement or peak area integration using an electronic integrator or a Data System. A detailed description of these techniques can be found in Practice E 355.

8.2 For any compound of interest a set of standards should be prepared in the eluent to be used for the samples (usually CS_2). The concentration levels of the standards should be such as to embrace the concentration of the unknown quantity.

8.2.1 At least five standard solutions should be prepared.

8.2.2 At least three runs of each standard should be done.

8.2.3 When there is initial variability in the detector response of standards, so that the calculated relative standard deviation or the mean is greater than a value considered acceptable by the analyst (generally this should not exceed 5 % for a good chromatographic system), a series of at least five points should be run and at least five peaks per point measured. Outliers should be eliminated by the application of statistical methods (4). If the variability does not comply with the performance criteria described in this paragraph, check the stability system (flow, temperature, column, etc) before proceeding further.

8.2.4 A fresh set of standards should be prepared for each analytical series. Generally standards kept in properly closed vials, sealed with TFE-fluorocarbon lined screw caps, will keep for at least a week if refrigerated (5). Standards kept in containers capped by glass stoppers will not keep longer than a day and should be discarded after that time.

8.2.5 This practice does not recommend the use of small, standard-taper centrifuge tubes, sealed with standard taper stoppers, for preparation of either standards or samples. Carbon disulfide (CS_2) is highly volatile and will be lost from such vials. No attempt should be made to replace the evaporated loss by addition of CS_2 to a fixed volume line in such a container.

8.3 Desorption efficiencies for organic compounds trapped on activated charcoal must be determined for each batch of charcoal or charcoal samplers. For purpose of reference, reported desorption efficiencies for a number of organic compounds are given in the appropriate Annex of Practice D 3686.

8.3.1 Open a charcoal sampling tube of the same lot used for collecting the samples.

8.3.2 Inject a known amount (2 to 20 μL/100 mg charcoal)

of one or more solvents below the surface of and directly onto the activated charcoal, and cap the tube immediately. It is useful to chill the sampling tube during this operation, or to have chilled the capped tube and contents immediately prior to its being charged with solvent, since the heat of adsorption may be sufficient to volatilize some of the material and to cause loss. The amount injected should approximate realistically that quantity which would be found in 10 L of air containing the exposure limit designated in 29 CFR 1910.

8.3.3 Tubes should be prepared for each of the following amounts: 0.5, 1.0, and 2.0 times the amount determined in 8.3.2.

8.3.4 Let the tubes stand at room temperature for a minimum of 8 h.

8.3.5 Treat these charcoal tubes exactly as described in Section 9 of this practice, eluting the chemical with CS_2 (or other appropriate eluent) and analyzing the eluate for its contents.

8.3.6 The percentage of chemical recovered from the charcoal (calculated by dividing the quantity recovered by the quantity applied, times 100) is the desorption efficiency. The datum obtained for the analyte of concern should be corrected by using the decimal fraction of the determined desorption (elution) efficiency.

8.3.7 When the desorption efficiency of a chemical is less than 75 %, an alternative sampling and analytical method should be considered.

9. Procedure

NOTE 3: **Warning**—Perform in a properly ventilated fume hood.

9.1 Prepare a set of empty vials by placing appropriate labels on them, indicating the identification number and designating whether they will contain the front (F) of the sampler or the back-up (B) portion.

9.2 Remove the plastic caps from the sampling tubes, or score and break the tubes just above the plug.

9.3 Remove the plug of glass wool which holds the front portion of charcoal in place and transfer the charcoal to the appropriate vial and close the vial. (A crochet hook is a convenient device for removing the plugs from the samplers, or a hook can be fashioned from a fine (18 to 20-gage) steel wire or a 3-in. (76-mm) No. 20 hypodermic needle.)

9.4 Repeat the same procedure for the back-up portion.

9.5 Continue this process until all of the samples have been transferred appropriately to vials.

9.6 Fit a 1-mL hypodermic syringe with a 3 or 4-in. (76 or 100-mm) No. 20 or No. 22 hypodermic needle.

9.7 With this syringe transfer 1 mL of CS_2 to each of the vials, taking care to cap them securely after the CS_2 has been added.[11]

9.8 From time to time agitate the samples. Let the elution process continue for at least 30 min. A longer period of time is desirable (3). (Some methods given in the reference in 2.2.2 require up to 4 h.)

9.9 Using the solvent-flush technique described in 8.1.4.3, 8.1.4.4, and 8.1.4.5, accomplish the chromatography of the samples.

NOTE 4: **Caution**—Before beginning any analytical program, place a fresh septum into the injection port of the chromatograph. As a matter of good practice, replace the septum daily or when necessary. Septum failure is the most frequent cause of inconsistent detector response for a given standard or sample.

9.10 Repeat the analysis at least three times.

9.11 The volume parameters specified in 8.1.4.3, 8.1.4.4, and 8.1.4.5 should be maintained. Two microlitres of sample, followed by 2 µL of solvent-flush in the microsyringe, have been found practical and completely adequate for all needs by at least one compliance laboratory (5).

9.12 After the analytical series has been accomplished, the reference solvent should be run as a performance standard. (See 8.1.4.)

9.13 Data reduction, either by peak height, area, or mass measurement, may now be performed.

10. Calculation

10.1 *Determination of µg per Sample:*

10.1.1 The actual concentration, in micrograms of analyte per millilitre of sample solution, can be taken from a standard curve plotted on linear paper, where peak height (or peak area or mass) is plotted as the ordinate and concentration in micrograms per 1 mL of CS_2 as the abscissa. If the instrumental response is known to be linear (from the performance of the standards) a single concentration level may be chosen as a calculation constant, if desired.

10.1.2 From the standard curve, determine the micrograms of analyte standard equivalent to the peak area (or height) from a particular compound. When 1 mL of CS_2 has been used for desorption, no volume corrections are needed; the standard curve is based on µg/mL CS_2 and the volume of the sample injected is identical to the volume of the standard injected.

10.1.3 Ascertain whether the field blank has been contaminated. If the blank has been contaminated, the sampling series must be held suspect. (See appropriate paragraph of Practice D 3686.)

10.1.4 The total microgram amount found in the sample is corrected for desorption efficiency and laboratory blank as follows:

$$\mu g, \text{ corrected} = \frac{\mu g \text{ in sample} - \mu g \text{ in blank}}{\text{desorption efficiency}}$$

Sum quantities for front and back-up sections.

10.1.5 If the back-up section contains more than 25 % of that of the front section, discard the sample as unreliable (see 7.1.2.2 of Practice D 3686).

NOTE 5—A break-through to the back-up section of 25 % of that of the front section usually suggests that some of the contaminant in the sampled air was not retained by the charcoal, and the calculated airborne concentration results will be lower than the actual concentrations. In cases where the calculated airborne concentrations exceed the health standard, despite break-through, it is meaningful and proper to report the results as greater than the calculated value.

10.2 *Determination of Air Concentration:*

10.2.1 Correct air volume of the sample to standard temperature and pressure (see appropriate paragraph of Practice D 3686).

[11] The 1-mL volume of CS_2 is used when analyzing 150-mg charcoal tubes. If larger charcoal tubes are being analyzed, a proportionately larger volume of CS_2 should be used.

10.2.2 If the criteria for a proper sample have been met, ulate the concentration of solvent vapor in a cubic metre ir as follows:

$$\frac{\text{Total analyte (µg/sample)}}{\text{Sampled air volume (L/sample)}} = \frac{\mu g}{L} = \frac{mg}{m^3}$$

10.2.3 If it is desired to convert this value to parts per lion (v/v) in air:

$$ppm = 24.47 \times \frac{mg/m^3}{\text{molecular weight of solvent}}$$

11. Precision and Bias

11.1 Precision and bias in this type of analytical procedure are dependent upon the precision and bias of the analytical procedure for each solvent analyte of concern, and the precision and bias of the sampling process.

11.2 When the errors involving determination of desorption efficiency, sampling, analysis, and pump calibration are combined, the state of the art indicated a relative precision of ±15 % at the 95 % confidence level for most solvent vapors.

ANNEX

(Mandatory Information)

A1. SELECTIVE SOLVENT-STRIPPING TECHNIQUES

A1.1 Organic compounds are soluble, or react with a mber of solvents in a selective manner. Advantage of these enomena may be taken in the analysis of solvent systems CS_2 when there is peak overlap (1).

A1.2 The following criteria are generally useful:

A1.2.1 Certain amines and amides are water soluble. methylformamide is rapidly extracted from CS_2 with one ish of laboratory grade water (5).

A1.2.2 Oxygenated hydrocarbons such as esters, ketones, cohols, and ethers are extracted by a solution consisting of parts by volume of concentrated sulfuric acid and one of iosphoric acid (85 %). A volume of 0.5 to 1 mL of this lution is sufficient to effect a quantitative extraction of an xygenated hydrocarbon compound from CS_2 (1).

A1.2.3 Dimethyl sulfate will extract nitrated aromatic compound from a mixture of aromatics and alkyl hydrocarbon solvents in CS_2.

NOTE A1.1: **Warning**—Dimethyl sulfate is a suspected carcinogen and is extremely corrosive.

A1.2.4 A saturated solution of sodium metabisulfite will extract selectively acetone and methyl ethyl ketone from a mixture of oxygenated and other carbon compounds in CS_2 with one wash.

A1.2.5 A 10 % solution of hydroxylamine hydrochloride will extract selectively acetone, methyl ethyl ketone, isobutyl ketone, methyl propyl ketone and methyl butyl ketone from solution in CS_2 in three separate washes.

A1.3 The usual semimicrochemical techniques and precautions should be taken when such manipulations of the CS_2 eluate are undertaken, and cognizance should be taken of the fact that CS_2 is highly volatile.

REFERENCES

(1) Levadie, B., and MacAskill, S. M., "Analysis of Organic Solvents Taken on Charcoal Tube Samplers by a Simplified Technique," *Analytical Chemistry*, Vol 48, No. 1, 1976, pp. 76–78.

(2) Levadie, B., and MacAskill, S. M., addendum to Ref (1), Vol 48, No. 11, p. 1656.

(3) White, I. D., Taylor, D. G., Mauer, P. A., and Kupel, R. E., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in Industrial Atmosphere," *American Industrial Hygiene Association Journal*, Vol 31, 1970, p. 225.

(4) Dean, R. B., and Dixon, W. J., "Simplified Statistics for Small Numbers of Observations," *Analytical Chemistry*, Vol 23, 1951, pp. 636–638.

(5) Levadie, B., Vermont Division of Occupational Health Laboratory, Personal Communication on File at ASTM Headquarters, July 1976.

Appendix E6: Standard Operating Procedures for TD-GC/MS Analysis

Standard Operating Procedures
for the Analytical Determination of
Benzene, Toluene, Ethylbenzene, Xylenes and Total Petroleum Hydrocarbons
using Gas Chromatography/Mass Spectrometry

1.0 Applicability

The protocols prescribed in this standard operating procedure (SOP) are based upon EPA Method TO-1 and NIOSH Method 2549 and have been altered slightly to identify compounds of interest and to tighten the quality control (QC) associated with the method to meet project-specific requirements. Deviations from the prescribed method are noted in this SOP. This SOP is not meant to take the place of original methods, therefore, the details of the GC/MS analysis as presented in EPA TO-1 are required for this analysis. EPA Method TO-1 and NIOSH Method 2549 are attached. EPA Method TO-1 and NIOSH Method 2549 have been used for the characterization of environments containing mixtures of volatile organic compounds (VOCs). The sampling has been conducted using multi-bed thermal desorption tubes.

2.0 Interferences

2.1 In situations where high levels of humidity may be present on the sample, some of the polar volatile compounds may not be efficiently collected on the internal trap of the thermal desorber.

2.2 Compounds which coelute on the chromatographic column may present an interference in the identification of each compound. By appropriate use of background subtraction, the mass spectrometrist may be able to obtain more representative spectra of each compound and provide a tentative identification.

2.3 Contamination of the thermal desorption tubes is a common problem encountered with this method. For this reason, all tubes will be pre-heated/purged to remove potential residual contamination present on purchased tubes.

3.0 Equipment/Instrumentation

3.1 Sample tubes: The multi-bed sorbent tubes containing tenax, carbosieve and carbopack sorbents. (Manufactured by Dynatherm.)

3.2 Gas Chromatograph/Mass Spectrometer with Thermal Desorption System (GC/MS-TD): The GC will have an initial oven temperature of 40 °C, ramped for 30 minutes to a final oven temperature of 280 °C. Mass Spectrometer capable of scanning 30-440 m/z region with a scan rate of 1 scan/second. Equipped with a computerized data system for instrument control, data acquisition, data processing and data storage.

4.0 Reagents

4.1 Helium, high purity

4.2 Organic compounds of interest for mass spectral verification (benzene, toluene, ethylbenzene, xylenes, undecane, hexane, fuel oil #2 and full list of SW-846 8260 volatile organic compounds (VOCs)).

4.3 Solvents (99+% purity; low benzene; chromatographic grade) for preparing spiking solutions, liquid calibration standards (eg. carbon disulfide).

5.0 Standards

5.1 Liquid Standards: Prepare stock solutions by adding known amounts of analytes to 10-mL volumetric flasks containing high purity solvent (carbon disulfide). Solvents are chosen based on solubility for the analytes of interest and ability to be chromatographically separated. Highly volatile compounds should be dissolved in a less volatile solvent. Carbon disulfide is a good general purpose solvent, but will interfere with early-eluting compounds. For this reason, the instrument must be programmed so the carbon disulfide solvent is not displayed on the chromatography.

5.2 Tube Spiking: Fit Dynatherm attachment for flash preparation of calibration standards, performance evaluation standard spikes and surrogate spikes onto thermal desorption tubes. Attach clean thermal desorption tubes to the attachment so that the flow direction is the same as for sampling. Take an aliquot of the standard solution (liquid standards 0.1 to 2 µL) and flash onto a thermal desorption tube. Remove tube and submit for field investigation or analyze by thermal desorption using the same conditions as for field samples.

6.0 Holding Times and Storage

6.1 Thermal desorption tubes must be analyzed within 14 days of sampling.

6.2 Thermal desorption tubes may be transported from the field at ambient temperatures. If long-term storage is required at the laboratory, the tubes must be stored at –10 °C. This will not be the case for this project because turn-around-time will be 10 days from receipt of the samples at the laboratory.

7.0 Reporting Limits

For this project, the required reporting limits are also referred to as the method detection limits. The method detection limit (MDL) is a statistically defined value. The procedure for determination of the MDL is prescribed in the 40 Code of Federal Regulation (CFR), Chapter 1, Part 136, Appendix B. In summary, a standard for each analyte of interest is prepared with a concentration approximately the estimated limit of detection for the instrument. Seven replicates of this standard are prepared. A blank and 7 replicates are analyzed and a statistical evaluation is performed. The MDL is the value described by 3 standard deviations of the mean concentration for the seven replicates. The complete procedure for MDL determination is attached to this SOP.

The required project-specific reporting/method detection limits are presented in Table 1. A range of detection limits, acceptable for end use, were established in anticipation of variability in achievement of MDLs between different methodologies and analytical laboratories.

Table 1: Project Target Detection Limits

Target Detection Limits				
Parameter	**Low**		**High**	
	µg/m3	ppbv	µg/m3	ppbv
Benzene	0.2	0.06	5	1.6
Toluene	10	2.7	50	13
Ethylbenzene	50	12	100	23
Xylenes	10	2.3	50	11
TPH (based on undecane)	20	3	--	--

8.0 Instrument Set-up

8.1 The GC column will be fused silica bonded phased and have dimensions of 0.31 mm ID and 30 m in length. The GC temperature program will have an initial oven temperature of 40 °C, ramped for 30 minutes to a final oven temperature of 280 °C.

8.2 Helium purge flows and carrier gas flows are set at approximately 10 mL/min and 1-2 mL/min, respectively.

8.3 The MS and data system are set according to manufacturer's instructions. Electron impact ionization (70 eV) and an electron multiplier gain of approximately 5 x 10^4 should be employed.

9.0 Instrument Calibration

9.1 Instrument Tuning and Mass Standardization: Instrument tuning and mass standardization

of the MS system is performed according to manufacturer's instructions. Perfluorotributylamine is generally used for this purpose. The material is introduced directly into the ion source. The instrumental parameters (e.g. lens volatages, resolution, etc.) should be adjusted to give acceptable resolution and peak shape as well as the relative ion abundances shown in Table 2.

Table 2: Suggested Performance Criteria for Relative Ion Abundances

M/E	% Relative Abundance
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

If these approximate relative abundance cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. These alternate values must be repeatable on a day-to-day basis.

9.2 Initial Calibration: An acceptable initial calibration must be performed prior to the analysis of any investigative samples. The following steps must be successfully performed before analyzing any investigative samples.

9.2.1 Perform an initial calibration of the instrument using a range of 5 concentration levels and including the following compounds: benzene, toluene, ethylbenzene, xylenes, undecane, hexane, fuel oil #2 and the 72 SW-846 8260 VOCs. The concentration levels should be graduated along the linear range of the instrument for the compounds of interest and will begin with the minimum requested detection limit described in the Quality Assurance Project Plan (QAPP) and in Section 6.0 of this SOP. Introduction standards into the GC/MS system will be accomplished by thermal desorption of standards spiked onto thermal desorption tubes.

9.2.2 Data from calibration standards are used to calculate a response factor for each component of interest. Determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). A relative standard deviation (RSD) will be calculated using the 5 levels of each analyte. The RSD must not exceed 20% for any of the compounds of interest. Alternatively, a calibration curve of area versus concentration (in nanograms) may be constructed. The linear regression of this

curve must result in a correlation coefficient, $r \geq 0.995$.

$$RSD = \frac{\sigma}{x} \times 100\%$$

Where σ = standard deviation of the 5 response factors for each analyte
x = average response factor for the 5 levels of each analyte

9.2.3 If substantial nonlinearity is present in the calibration curve, a nonlinear least squares fit (quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

Where Y = peak area
X = quantity of analyte, nanograms
A,B, C = coefficients in the equation

9.2.4 Data processing for instrument calibration also involves determination of retention times and integrated characteristic ion intensities for each of the compounds of interest. Additionally, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectral to ensure proper instrumental performance.

9.3 Continuing Calibration: Investigative samples may be analyzed on days subsequent from the successful initial calibration. However, the instrument must be evaluated prior to each analytical batch to confirm that conditions have not altered significantly. The following steps must be successfully performed prior to the analysis of any investigative samples.

9.3.1 Tune the mass spectrometer according Section 8.1 of this SOP.

9.3.2 Analyze a continuing calibration verification (CCV). The CCV is typically the mid-range concentration standard containing all compounds of interest used for the initial calibration standard. The percent drift (% D) for each analyte may not exceed 20%.

$$\%\ D = \frac{A-B}{B} \times 100\%$$

Where A = Observed concentration value of the analyte
B = Theoretical value of the analyte.

10.0 Sample Preparation

10.1 Allow the sample tubes to equilibrate to room temperature prior to analysis. The long-

term storage caps must remain securely in place.

10.2 Analyze the "humidity test" sampler first to determine if humidity was high during sampling.

10.3 If high humidity is observed, dry purge the tubes with purified helium at 50 to 100 mL/min for a maximum of 3 L and at ambient temperature prior to analysis. Note this procedure in the analytical logbook and include this information in the case narrative provided with the analytical results.

11.0 Sample Analysis

11.1 Analyze at least one instrument blank prior to analyzing any investigative samples to ensure that the TD-GC/MS system produces a clean chromatographic background. Also, analyze an instrument blank after analysis of heavily concentrated samples to prevent any carryover in the system. If carry over is observed, perform instrument blanks until the contamination is flushed from the thermal desorption system.

11.2 Place the sampler (thermal desorption tube) onto the termal dersorber. Desorb in the reverse direction to the sampling flow.

11.3 Quantification of target analytes is general performed by 1) qualitatively determining the presence or absence of each compound of interest on the basis of a set of characterisitic ion and the retention time using a reverse-search software routine; 2) quantification of each identified component by integrating the intensityof a characterisitc ion and compring the value to that of the calibration standard; and 3) tentative identification of other components observed using a NIST library search software routine. Compounds not included in the calibration will be considered tentatively identified compounds (TICs) if the quality of match is 50 or greater.

11.4 Based upon estimated TD sample loading (determined by analysis of target analytes via GC/FID), samples will be split by flow regulation to achieve optimum GC column loading and optimal MS performance.

11.5 TVOC concentration will be estimated as the sum of calibrated VOC concentrations plus the sum of TICs, estimated as toluene. Additional TVOC concentration will be reported for calibrated VOC plus TOC as hexane and then as undecane.

11.6 TPH (as fuel oil #2) concentrations will be estimated as the sum of total peak response over the elution period (retention time) for fuel oil #2.

11.7 BTEX and other EPA 8260 listed VOC concentration will be calculated based on a point-to-point or best-fit through zero curve of the five point calibration standards.

12.0 Quality Control

12.1 Analyze a minimum of one instrument blank per analytical batch. Perform additional instrument blanks as necessary to eliminate carryover between analyses. The instrument blanks must be free of target analyte contamination. If target compounds are detected in the instrument blank, perform another instrument blank analysis.

12.2 Analyze surrogate recoveries on each investigative and QC sample. The surrogate compound will be either a fluorinated or deuterated compound. Historical data for typical surrogate recoveries will be established by the laboratory prior to submission of investigative samples. Because TD tubes are one-time analyses only, surrogate recoveries outside laboratory-established acceptance limits cannot be re-evaluated. Surrogate recoveries outside the acceptance limits will serve as indicators for potential problems in sampling and analysis.

13.0 References

EPA. 1984. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. 600/4-84-041.

EPA. 1986. Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods SW-846, 3rd Edition plus updates.

EPA. 1995. Title 40 Code of Federal Regulations, Chapter I, Part 136, Appendix B pp 882-884.

NIOSH. 1996. NIOSH Manual of Analytical Methods: Method 2549.

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING TENAX® ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 The document describes a generalized protocol for collection and determination of certain volatile organic compounds which can be captured on Tenax® GC (poly(2,6-Diphenyl phenylene oxide)) and determined by thermal desorption GC/MS techniques. Specific approaches using these techniques are described in the literature (1-3).

1.2 This protocol is designed to allow some flexibility in order to accommodate procedures currently in use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable results (i.e. documentation of method performance within each laboratory situation is required). Types of documentation required are described elsewhere in this method.

1.3 Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80° - 200°C. However, not all compounds falling into this category can be determined. Table 1 gives a listing of compounds for which the method has been used. Other compounds may yield satisfactory results but validation by the individual user is required.

2. Applicable Documents

2.1 ASTM Standards:

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis.

E355 Recommended Practice for Gas Chromatography Terms and Relationships.

2.3 Other documents:

Existing procedures (1-3).
U.S. EPA Technical Assistance Document (4).

3. Summary of Protocol

3.1 Ambient air is drawn through a cartridge containing ~1-2 grams of Tenax and certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

3.2 For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge onto a cold trap and subsequently onto the front of the GC column which is held at low temperature (e.g. - 70°C). The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophistacated detectors (e.g. electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

3.3 Due to the complexity of ambient air samples only high resolution (i.e. capillary) GC techniques are considered to be acceptable in this protocol.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc. Many of these compounds are toxic; hence knowledge of the levels of

such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Conventional air monitoring methods (e.g. for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1-5% of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system fulfills this need for enhanced sensitivity.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(6). All abbreviations and symbols are defined with this document at the point of use.

6. INTERFERENCES

6.1 Only compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the Tenax cartridge with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - should be capable of subambient temperature programming. Unit mass resolution or better up to 800 amu. Capable of scanning 30-440 amu region every 0.5-1 second. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Unit - Designed to accommodate Tenax cartridges in use. See Figure 2a or b.

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the Tenax cartridge. (See Figure 3a or b.)

7.4 Vacuum oven - connected to water aspirator vacuum supply.

7.5 Stopwatch

7.6 Pyrex disks - for drying Tenax.

7.7 Glass jar - Capped with Teflon-lined screw cap. For storage of purified Tenax.

7.8 Powder funnel - for delivery of Tenax into cartridges.

7.9 Culture tubes - to hold individual glass Tenax cartridges.

7.10 Friction top can (paint can) - to hold clean Tenax cartridges.

7.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

7.12 Thermometer - to record ambient temperature.

7.13 Barometer (optional).

7.14 Dilution bottle - Two-liter with septum cap for standards preparation.

7.15 Teflon stirbar - 1 inch long.

7.16 Gas-tight glass syringes with stainless steel needles - 10-500 µl for standard injection onto GC/MS system.

7.17 Liquid microliter syringes - 5.50 µL for injecting neat liquid standards into dilution bottle.

7.18 Oven - 60 $\pm$ 5°C for equilibrating dilution flasks.

7.19 Magnetic stirrer.

7.20 Heating mantel.

7.21 Variac

7.22 Soxhlet extraction apparatus and glass thimbles - for purifying Tenax.

7.23 Infrared lamp - for drying Tenax.

7.24 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.25 Psychrometer - to determine ambient relative humidity. (optional).

8. Reagents and Materials

8.1 Empty Tenax cartridges - glass or stainless steel (See Figure 1a or b).
8.2 Tenax 60/80 mesh (2,6-diphenylphenylene oxide polymer).
8.3 Glasswool - silanized.
8.4 Acetone - Pesticide quality or equivalent.
8.5 Methanol - Pesticide quality, or equivalent.
8.6 Pentane - Pesticide quality or equivalent.
8.7 Helium - Ultra pure, compressed gas. (99.9999%)
8.8 Nitrogen - Ultra pure, compressed gas. (99.9999%)
8.9 Liquid nitrogen.
8.10 Polyester gloves - for handling glass Tenax cartridges.
8.11 Glass Fiber Filter - one inch diameter, to fit in filter holder. (optional)
8.12 Perfluorotributylamine (FC-43).
8.13 Chemical Standards - Neat compounds of interest. Highest purity available.
8.14 Granular activated charcoal - for preventing contamination of Tenax cartridges during storage.

9. Cartridge Construction and Preparation

9.1 Cartridge Design

9.1.1 Several cartridge designs have been reported in the literature (1-3). The most common (1) is shown in Figure 1a. This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the <u>outside</u> portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption porcess.

Clean polyester gloves must be worn at all times when handling such cartridges and exposure of the open cartridge to ambient air must be minimized.

9.1.2 A second common type of design (3) is shown in Figure 1b. While this design uses a metal (stainless steel) construction, it eliminates the need to avoid direct contact with the exterior surface since only the interior of the cartridge is purged.

9.1.3 The thermal desorption module and sampling system must be selected to be compatible with the particular cartridge design chosen. Typical module designs are shown in Figures 2a and b. These designs are suitable for the cartridge designs shown in Figures 1a and 1b, respectively.

9.2 Tenax Purification

9.2.1 Prior to use the Tenax resin is subjected to a series of solvent extraction and thermal treatment steps. The operation should be conducted in an area where levels of volatile organic compounds (other than the extraction solvents used) are minimized.

9.2.2 All glassware used in Tenax purification as well as cartridge materials should be thoroughly cleaned by water rinsing followed by an acetone rinse and dried in an oven at 250°C.

9.2.3 Bulk Tenax is placed in a glass extraction thimble and held in place with a plug of clean glasswool. The resin is then placed in the soxhlet extraction apparatus and extracted sequentially with methanol and then pentane for 16-24 hours (each solvent) at approximately 6 cycles/hour. Glasswool for cartidge preparation should be cleaned in the same manner as Tenax.

9.2.4 The extracted Tenax is immediately placed in an open glass dish and heated under an infrared lamp for two

9.3.4 After the four hour heating period the cartridges are allowed to cool. Cartridges of the type shown in Figure 1a are immediately placed (without cooling) in clean culture tubes having Teflon-lined screw caps with a glasswool cushion at both the top and the bottom. Each tube should be shaken to ensure that the cartridge is held firmly in place. Cartridges of the type shown in Figure 1b are allowed to cool to room temperature under inert gas purge and are then closed with stainless steel plugs.

9.3.5 The cartridges are labeled and placed in a tightly sealed metal can (e.g. paint can or similar friction top container). For cartridges of the type shown in Figure 1a the culture tube, not the cartridge, is labeled.

9.3.6 Cartridges should be used for sampling within 2 weeks after preparation and analyzed within two weeks after sampling. If possible the cartridges should be stored at -20°C in a clean freezer (i.e. no solvent extracts or other sources of volatile organics contained in the freezer).

10. Sampling

10.1 Flow rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per gram of adsorbent) which must not be exceeded. Since the retention volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety to ensure good collection efficiency. Some considerations and guidance in this regard are provided in a recent report (5). Approximate breakthrough volumes at 38°C (100°F) in liters/gram of Tenax are provided in Table 1. These retention volume data are supplied only as rough guidance and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions.

hours in a hood. Care must be exercised to avoid over heating of the Tenax by the infrared lamp. The Tenax is then placed in a vacuum oven (evacuated using a water aspirator) without heating for one hour. An inert gas (helium or nitrogen) purge of 2-3 ml/minute is used to aid in the removal of solvent vapors. The oven temperature is then increased to 110°C, maintaining inert gas flow and held for one hour. The oven temperature control is then shut off and the oven is allowed to cool to room temperature. Prior to opening the oven, the oven is slightly pressurized with nitrogen to prevent contamination with ambient air. The Tenax is removed from the oven and sieved through a 40/60 mesh sieve (acetone rinsed and oven dried) into a clean glass vessel. If the Tenax is not to be used immediately for cartridge preparation it should be stored in a clean glass jar having a Teflon-lined screw cap and placed in a desiccator.

9.3 Cartridge Preparation and Pretreatment

9.3.1 All cartridge materials are pre-cleaned as described in Section 9.2.2. If the glass cartridge design shown in Figure 1a is employed all handling should be conducted wearing polyester gloves.

9.3.2 The cartridge is packed by placing a 0.5-1cm glass-wool plug in the base of the cartridge and then filling the cartridge to within approximately 1 cm of the top. A 0.5-1cm glasswool plug is placed in the top of the cartridge.

9.3.3 The cartridges are then thermally conditioned by heating for four hours at 270°C under an inert gas (helium) purge (100 - 200 ml/min).

where

B is the calculated linear flow velocity in centimeters per minute.

r is the internal radius of the cartridge in centimeters.

If B is greater than 500 centimeters per minute either the total sample volume (V_{MAX}) should be reduced or the sample flow rate (Q_{MAX}) should be reduced by increasing the collection time. If B is less than 50 centimeters per minute the sampling rate (Q_{MAX}) should be increased by reducing the sampling time. The total sample value (V_{MAX}) cannot be increased due to component breakthrough.

10.1.4 The flow rate calculated as described above defines the maximum flow rate allowed. In general, one should collect additional samples in parallel, for the same time period but at lower flow rates. This practice yields a measure of quality control and is further discussed in the literature (5). In general, flow rates 2 to 4 fold lower than the maximum flow rate should be employed for the parallel samples. In all cases a constant flow rate should be achieved for each cartridge since accurate integration of the analyte concentration requires that the flow be constant over the sampling period.

0.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow velocities (e.g. less than 100 milliliters/minute). Figure 3a illustrates a sampling system utilizing mass flow controllers. This system readily allows for collection of parallel samples. Figures 3b shows a commercially available system based on needle valve flow controllers.

10.1.2 To calculate the maximum total volume of air which can be sampled use the following equation:

$$V_{MAX} = \frac{V_b \times W}{1.5}$$

where

V_{MAX} is the calculated maximum total volume in liters.

V_b is the breakthrough volume for the least retained compound of interest (Table 1) in liters per gram of Tenax.

W is the weight of Tenax in the cartridge, in grams.

1.5 is a dimensionless safety factor to allow for variability in atmospheric conditions. This factor is appropriate for temperatures in the range of 25-30°C. If higher temperatures are encountered the factor should be increased (i.e. maximum total volume decreased).

10.1.3 To calculate maximum flow rate use the following equation:

$$Q_{MAX} = \frac{V_{MAX}}{t} \times 1000$$

where

Q_{MAX} is the calculated maximum flow rate in milliliters per minute.

t is the desired sampling time in minutes. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained.

10.1.4 The maximum flow rate Q_{MAX} should yield a linear flow velocity of 50-500 cm/minute. Calculate the linear velocity corresponding to the maximum flow rate using the following equation:

$$B = \frac{Q_{MAX}}{\pi r^2}$$

pressure, relative humidity, dry gas meter reading (if applicable) flow rate, rotameter reading (if applicable), cartridge number and dry gas meter serial number.

10.2.6 Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than four hours.
At the end of the sampling period record the parameters listed in 10.2.5 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10% the cartridge should be marked as suspect.

10.2.7 Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment to the laboratory for analysis. Store cartridges at reduced temperature (e.g. - 20°C) before analys if possible to maximize storage stability.

10.2.8 Calculate and record the average sample rate for each cartridge according to the following equa ion

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

where

Q_A = Average flow rate in ml/minute.

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

N = Number of points averaged.

10.2.9 Calculate and record the total volumetric flow fo each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}{1000}$$

10.2.2 Prior to sample collection insure that the sampling flow rate has been calibrated over a range including the rate to be used for sampling, with a "dummy" Tenax cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter. The flow calibration device is connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D3686 describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. If the sampling interval exceeds four hours the flow rate should be checked at an intermediate point during sampling as well. In general, a rotameter should be included, as showed in Figure 3b, to allow observation of the sampling flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process. If glass cartridges (Figure 1a) are employed they must be handled only with polyester gloves and should not contact any other surfaces.

10.2.5 A particulate filter and holder are placed on the inlet to the cartridges and the exit end of the cartridge is connected to the sampling apparatus. In many sampling situations the use of a filter is not necessary if only the total concentration of a component is desired. Glass cartridges of the type shown in Figure 1a are connected using teflon ferrules and Swagelok (stainless steel or teflon) fittings. Start the pump and record the following parameters on an appropriate data sheet (Figure 4): data, sampling location, time, ambient temperature, barometric

where

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

T_2 = Stop time.

T_1 = Start time.

T = Sampling time = $T_2 - T_1$, minutes

10.2.10 The total volume (V_s) at standard conditions, 25°C and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where

P_A = Average barometric pressure, mmHg

t_A = Average ambient temperature, °C.

11. GC/MS Analysis

11.1 Instrument Set-up

11.1.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.1.2 A block diagram of the typical GC/MS system required for analysis of Tenax cartridges is depicted in Figure 5. The operation of such devices is described in 11.2.4. The thermal desorption module must be designed to accommodate the particular cartridge configuration. Exposure of the sample to metal surfaces should be minimized and only stainless steel, or nickel metal surfaces should be employed.

The volume of tubing and fittings leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.1.3 The GC column inlet should be capable of being cooled to -70°C and subsequently increased rapidly to approximately 30°C. This can be most readily accomplished using a GC equipped with subambient cooling capability (liquid nitrogen) although other approaches such as manually cooling the inlet of the column in liquid nitrogen may be acceptable.

11.1.4 The specific GC column and temperature program employed will be dependent on the specific compounds of interest. Appropriate conditions are described in the literature (1-3). In general a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from 30°C to 200°C at 8°/minute will be suitable. Fused silica bonded phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line.

11.1.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.1.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 5. Helium purge flows (through the cartridge) and carrier flow are set at approximately 10 ml/minute and 1-2 ml/minute respectively. If applicable, the injector sweep flow is set at 2-4 ml/minute.

11.1.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.1.8 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5×10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1 Tuning and mass standarization of the MS system is performed according to manufacturer's instructions and relevant information from the user prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g. lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria.

However, these alternate values must be repeatable on a day-to-day basis.

11.2.2 After the mass standarization and tuning process as been completed and the appropriate values ntered into the data system the user should hen calibrate the entire system by introducing nown quantities of the standard components f interest into the system. Three alternate rocedures may be employed for the calibration rocess including 1) direct syringe injection f dilute vapor phase standards, prepared n a dilution bottle, onto the GC column, 2) njection of dilute vapor phase standards nto a carrier gas stream directed through the enax cartridge, and 3) introduction of permeation r diffusion tube standards onto a Tenax cartridge. he standards preparation procedures for each f these approaches are described in Section 3. The following paragraphs describe the instrument calibration process for each of these approaches.

11.2.3 If the instrument is to be calibrated by direct injection of a gaseous standard, a standard is prepared in a dilution bottle as described in Section 13.1. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 ml) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe.

The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g. 30°C). The temperature program is started at a consistent time (e.g. four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted acquisiton is terminated and the data is processed as described in Section 11.2.5. The standard injection process is repeated using different standard volumes as desired.

11.2.4 If the system is to be calibrated by analysis of spiked Tenax cartridges a set of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored as described in Section 9.3. If glass cartridges (Figure 1a) are employed care must be taken to avoid direct contact, as described earlier. The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C. The inlet valve is placed in the desorb mode and the standard cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The cartridge is purged for 10 minutes and then the inlet valve is placed in the inject mode and the liquid nitrogen source removed from the collection trap. The GC column is maintained at -70°C for two minutes and subsequent steps are as described in 11.2.3. After the process is complete the cartridge is removed from the desorption module and stored for subsequent use as described in Section 9.3.

11.2.5 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.3 Sample Analysis

11.3.1 The sample analysis process is identical to that described in Section 11.2.4 for the analysis of standard Tenax cartridges.

11.3.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reverse-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general quantities of component greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. One standard concentration, near the midpoint of the analytical range of interest, should be chosen for injection every day to determine day-to-day response reproducibility.

12.1.3 If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area

X = quantity of component, nanograms

A,B, and C are coefficients in the equation

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A$$

where

Y_A is the area of the analyte characteristic ion for the sample cartridge.

X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.

A,B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_S}$$

where

C_A is the calculated concentration of analyte in nanograms per liter.

V_S and X_A are as previously defined in Section 10.2.10 and 12.2.1, respectively.

13. Standard Preparation

13.1 Direct Injection

13.1.1 This process involves preparation of a dilution bottle containing the desired concentrations of compounds of interest for direct injection onto the GC/MS system.

13.1.6 The bottle is placed in a 60°C oven for at least 30 minutes prior to removal of a vapor phase standard.

13.1.7 To withdraw a standard for GC/MS injection the bottle is removed from the oven and stirred for 10-15 seconds. A suitable gas-tight microber syring warmed to 60°C, is inserted through the septum cap and pumped three times slowly. The appropriate volume of sample (approximately 25% larger than the desired injection volume) is drawn into the syringe and the volume is adjusted to the exact value desired and then immediately injected over a 5-10 seconds period onto the GC/MS system as described in Section 11.2.3.

13.2 Preparation of Spiked Cartridges by Vapor Phase Injection

13.2.1 This process involves preparation of a dilution bottle containing the desired concentrations of the compound(s) of interest as described in 13.1 and injecting the desired volume of vapor into a flowing inert gas stream directed through a clean Tenax cartridge.

13.2.2 A helium purge system is assembled wherein the helium flow 20-30 mL/minute is passed through a stainless steel Tee fitted with a septum injector. The clean Tenax cartridge is connected downstream of the tee using appropriate Swagelok fittings. Once the cartridge is placed in the flowing gas stream the appropriate volume vapor standard, in the dilution bottle, is injected through the septum as described in 13.1.6. The syringe is flushed several times by alternately filling the syringe with carrier gas and displacing the contents into the flow stream, without removing the syringe from the septum. Carrier flow is maintain through the cartridge for approximately 5 minutes after injection.

13.1.2 Fifteen three-millimeter diameter glass beads and a one-inch Teflon stirbar are placed in a clean two-liter glass septum capped bottle and the exact volume is determined by weighing the bottle before and after filling with deionized water. The bottle is then rinsed with acetone and dried at 200°C.

13.1.3 The amount of each standard to be injected into the vessel is calculated from the desired injection quantity and volume using the following equation:

$$W_T = \frac{W_I}{V_I} \times V_B$$

where

W_T is the total quantity of analyte to be injected into the bottle in milligrams

W_I is the desired weight of analyte to be injected onto the GC/MS system or spiked cartridge in nanograms

V_I is the desired GC/MS or cartridge injection volume (should not exceed 500) in microliters.

V_B is total volume of dilution bottle determined in 13.1.1, in liters.

13.1.4 The volume of the neat standard to be injected into the dilution bottle is determined using the following equation:

$$V_T = \frac{W_T}{d}$$

where

V_T is the total volume of neat liquid to be injected in microliters.

d is the density of the neat standard in grams per milliliter.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609(6). Note that a method of accuracy maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean Tenax cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked cartridges are then stored or immediatel analyzed as in Section 11.2.4.

14. Performance Criteria and Quality Assurance

This section summarizes quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Opreating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory:

1) assembly, calibration, and operation of the sampling system,
2) preparation, handling and storage of Tenax cartridges,
3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and
4) all aspects of data recording and processing.

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

14.2 Tenax Cartridge Preparation

14.2.1 Each batch of Tenax cartridges prepared (as described in Section 9) should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates as described in Section 10.1. If agreement between parallel samples is not generally within $\pm$ 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set

of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass calibration have been discussed in Section 11.2 and Table 2. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GC/MS as

described in Section 11.4. The perfluorotoluene (or other reference compound) peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The assymmetry factor (See Figure 6) should be between 0.8 and 2.0. The assymmetry factor for any polar or reactive compounds should be determined using the process described above. If peaks are observed that exceed the peak width or assymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7). Such schemes cannot be conducted by placing the substances onto Tenax because many of the compounds (e.g. acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax.

14.4.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.1 or 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required.

In general the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g. perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than $\pm$ 2 standard deviations from the mean (calculated

excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

REFERENCES

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

5. Walling, J. F., Berkley, R. E., Swanson, D. H., and Toth, F. J. "Sampling Air for Gaseous Organic Chemical-Applications to Tenax", EPA-600/7-54-82-059, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1982.

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

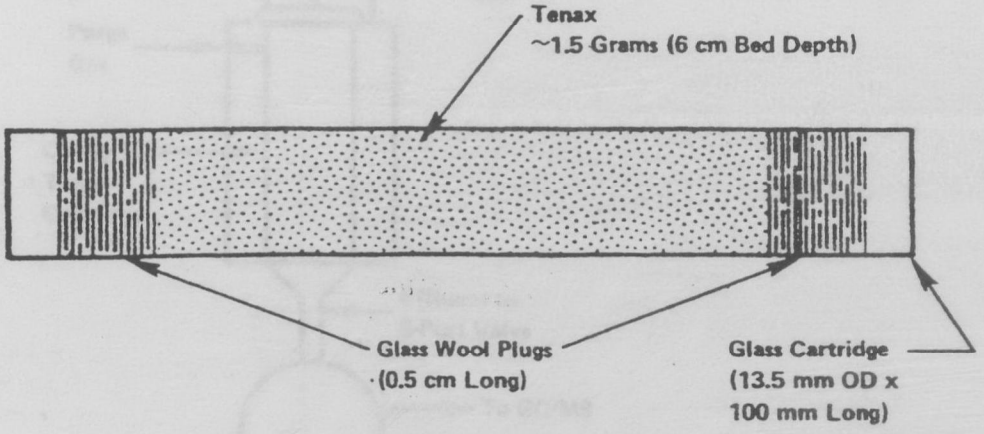
7. Grob, K., Jr., Grob, G., and Grob, K., "Comprehensive Standardized Quality Test for Glass Capillary Columns", J. Chromatog., 156, 1-20, 1978.

TABLE 1. RETENTION VOLUME ESTIMATES FOR COMPOUNDS ON TENAX

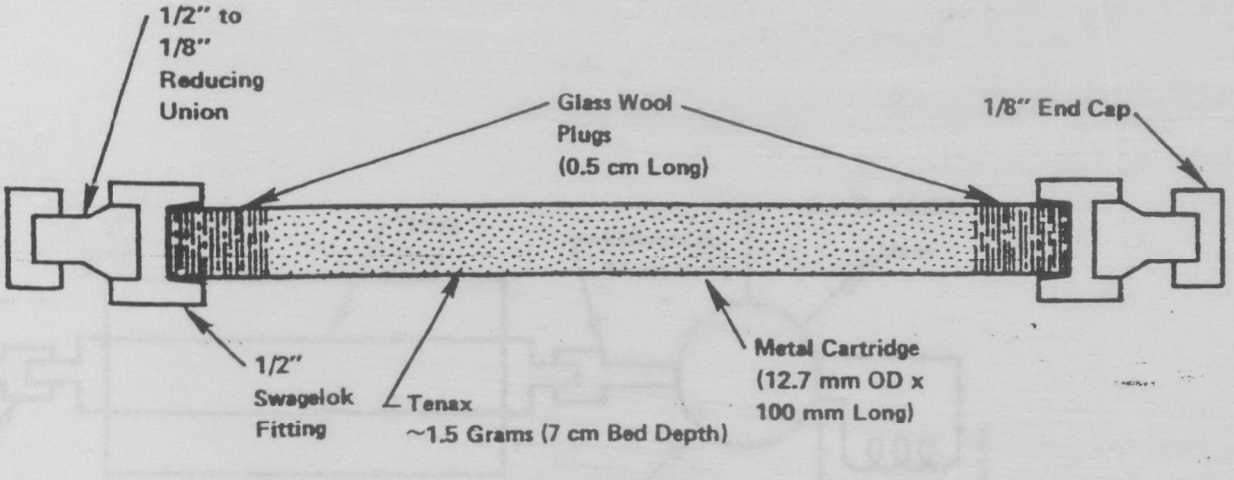
COMPOUND	ESTIMATED RETENTION VOLUME AT 100°F (38°C)-LITERS/GRAM
Benzene	19
Toluene	97
Ethyl Benzene	200
Xylene(s)	~ 200
Cumene	440
n-Heptane	20
1-Heptene	40
Chloroform	8
Carbon Tetrachloride	8
1,2-Dichloroethane	10
1,1,1-Trichloroethane	6
Tetrachloroethylene	80
Trichloroethylene	20
1,2-Dichloropropane	30
1,3-Dichloropropane	90
Chlorobenzene	150
Bromoform	100
Ethylene Dibromide	60
Bromobenzene	300

TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% RELATIVE ABUNDANCE
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

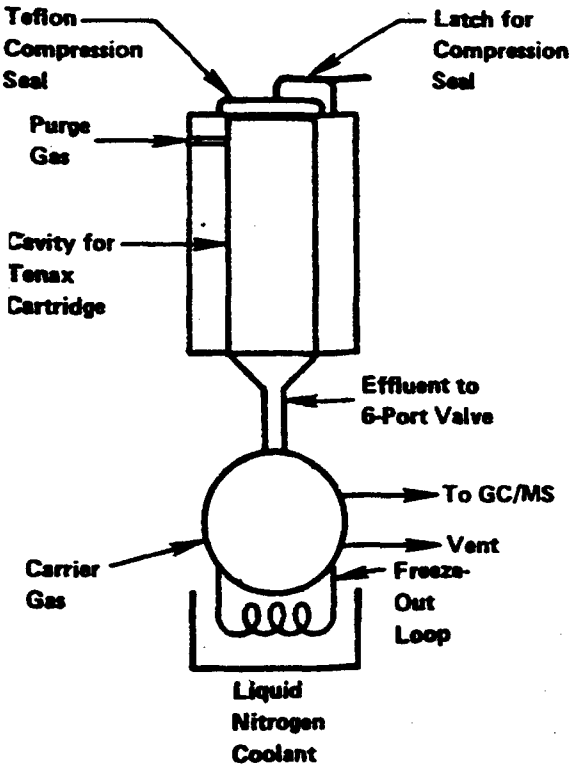


(a) Glass Cartridge

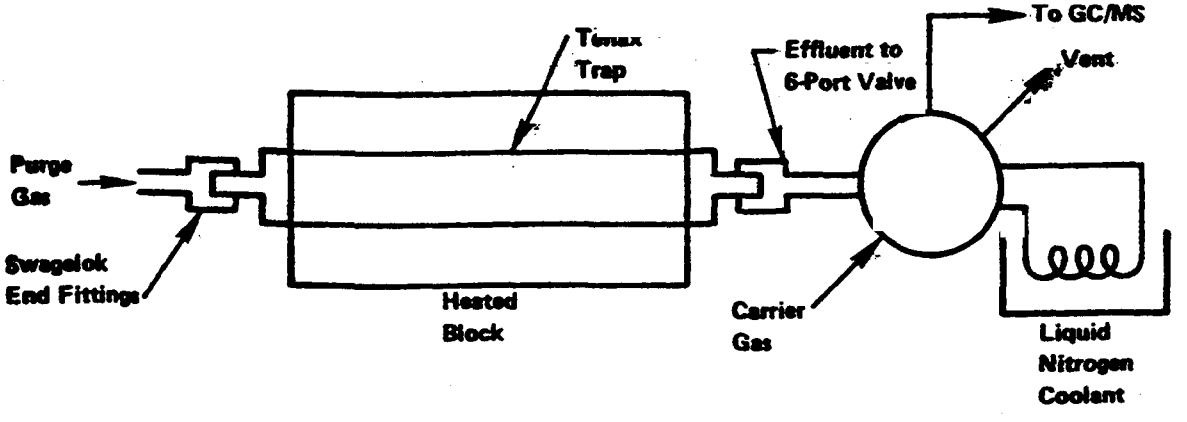


(b) Metal Cartridge

FIGURE 1. TENAX CARTRIDGE DESIGNS

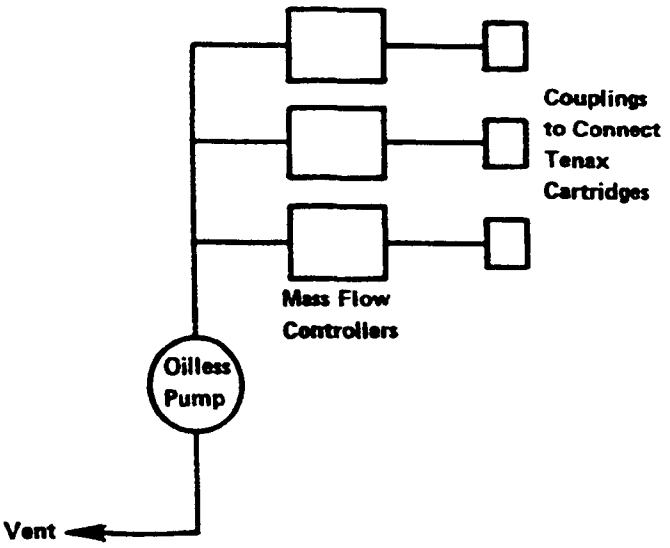


(a) Glass Cartridges (Compression Fit)

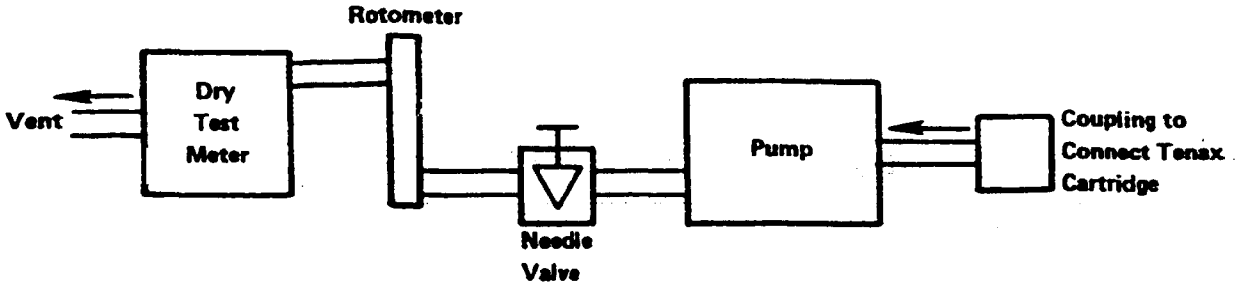


(b) Metal Cartridges (Swagelok Fittings)

FIGURE 2. TENAX CARTRIDGE DESORPTION MODULES



(a) Mass Flow Control



(b) Needle Valve Control

FIGURE 3. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

OJECT:_____ DATE(S) SAMPLED:_____

TE:_____ TIME PERIOD SAMPLED:_____

ICATION:_____ OPERATOR:_____

ISTRUMENT MODEL NO:_____ CALIBRATED BY:_____

MP SERIAL NO:_____

MPLING DATA

Sample Number:_____

Start Time: _____ Stop Time: _____

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

Total Volume Data**

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

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

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

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

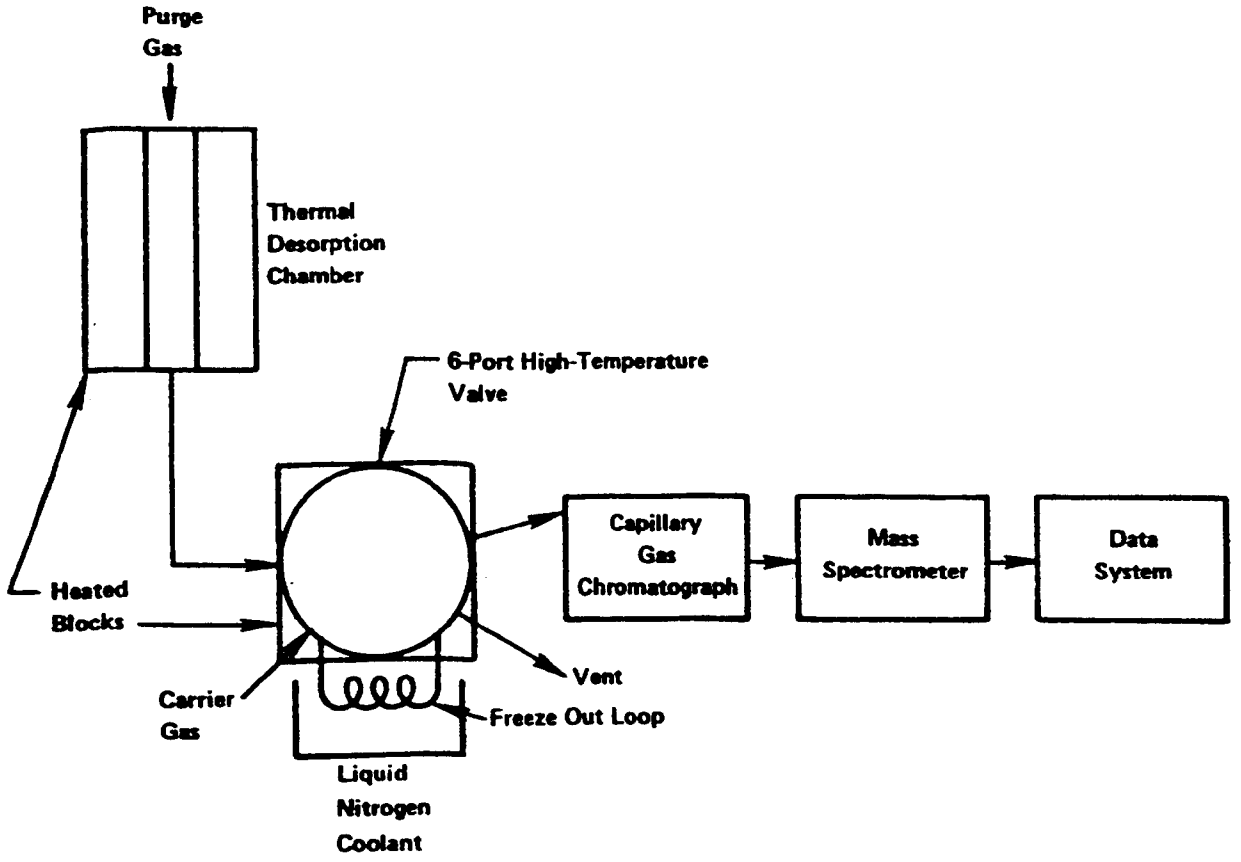
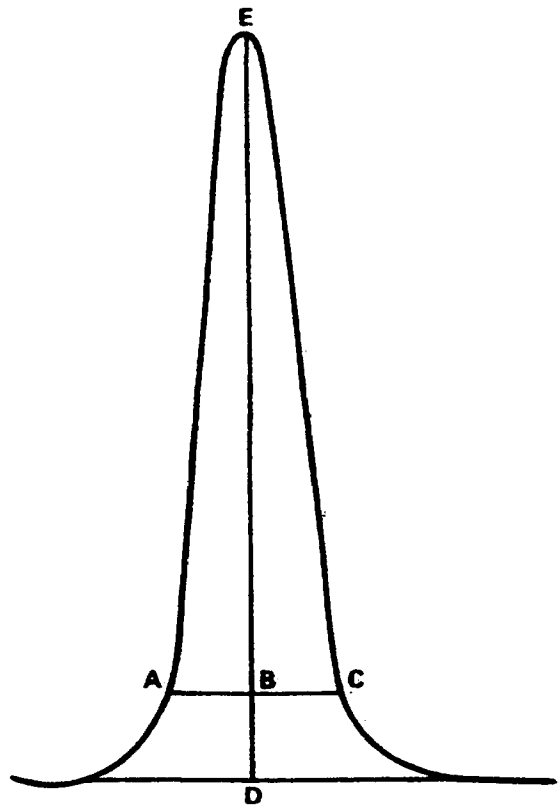


FIGURE 5. BLOCK DIAGRAM OF ANALYTICAL SYSTEM



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

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: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 6. PEAK ASYMMETRY CALCULATION

APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT—REVISION 1.11

Definition

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 analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representa samples of a given matrix.

3. (a) If the MDL is to be determined in agent (blank) water, prepare a laborat standard (analyte in reagent water) at a centration which is at least equal to or the same concentration range as the e mated method detection limit. (Recomm between 1 and 5 times the estimated meth detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in other sample matrix, analyze the sample the measured level of the analyte is in recommended range of one to five times estimated detection limit, proceed to Step

If the measured level of analyte is le than the estimated detection limit, add known amount of analyte to bring the lev of analyte between one and five times the e timated detection limit.

If the measured level of analyte is great than five times the estimated detectio limit, there are two options.

(1) Obtain another sample with a low level of analyte in the same matrix if pos sible.

(2) The sample may be used as is for deter mining the method detection limit if th analyte level does not exceed 10 times th MDL of the analyte in reagent water. Th variance of the analytical method changes a the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each

through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1S}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} X_i\right)^2}{n}\right] \quad S = \left(S^2\right)^{\frac{1}{2}}$$

where:

X_i; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha\ =\ 0.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha\ =\ .99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 1.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 1. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681\ (S_{pooled})$$

where 2.681 is equal to $t_{(12,\ 1-\alpha\ =\ .99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL

UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\ .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title ald the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iter-

ated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

APPENDIX C TO PART 136—INDUCTIVELY COUPLED PLASMA—ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES METHOD 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

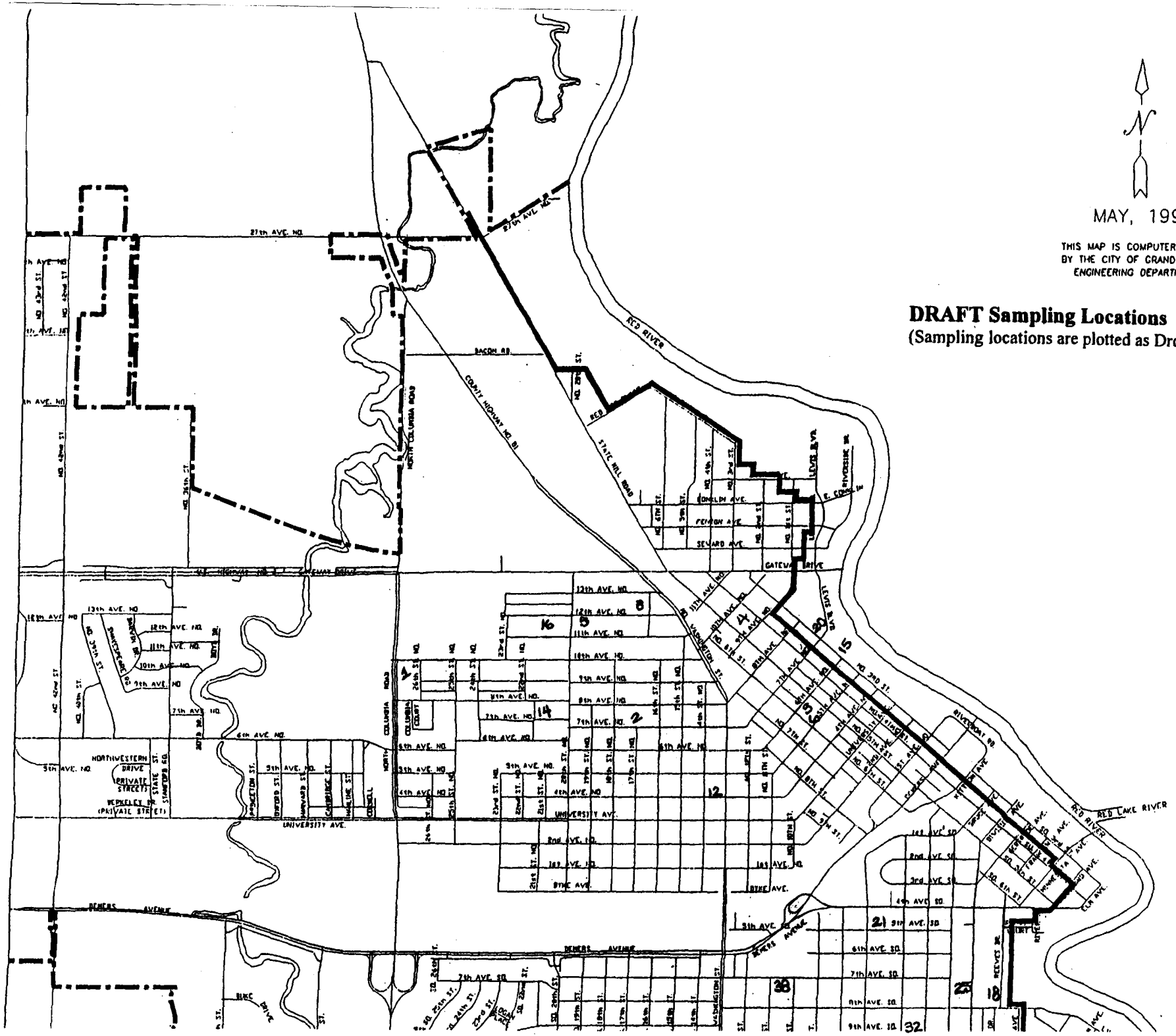
3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

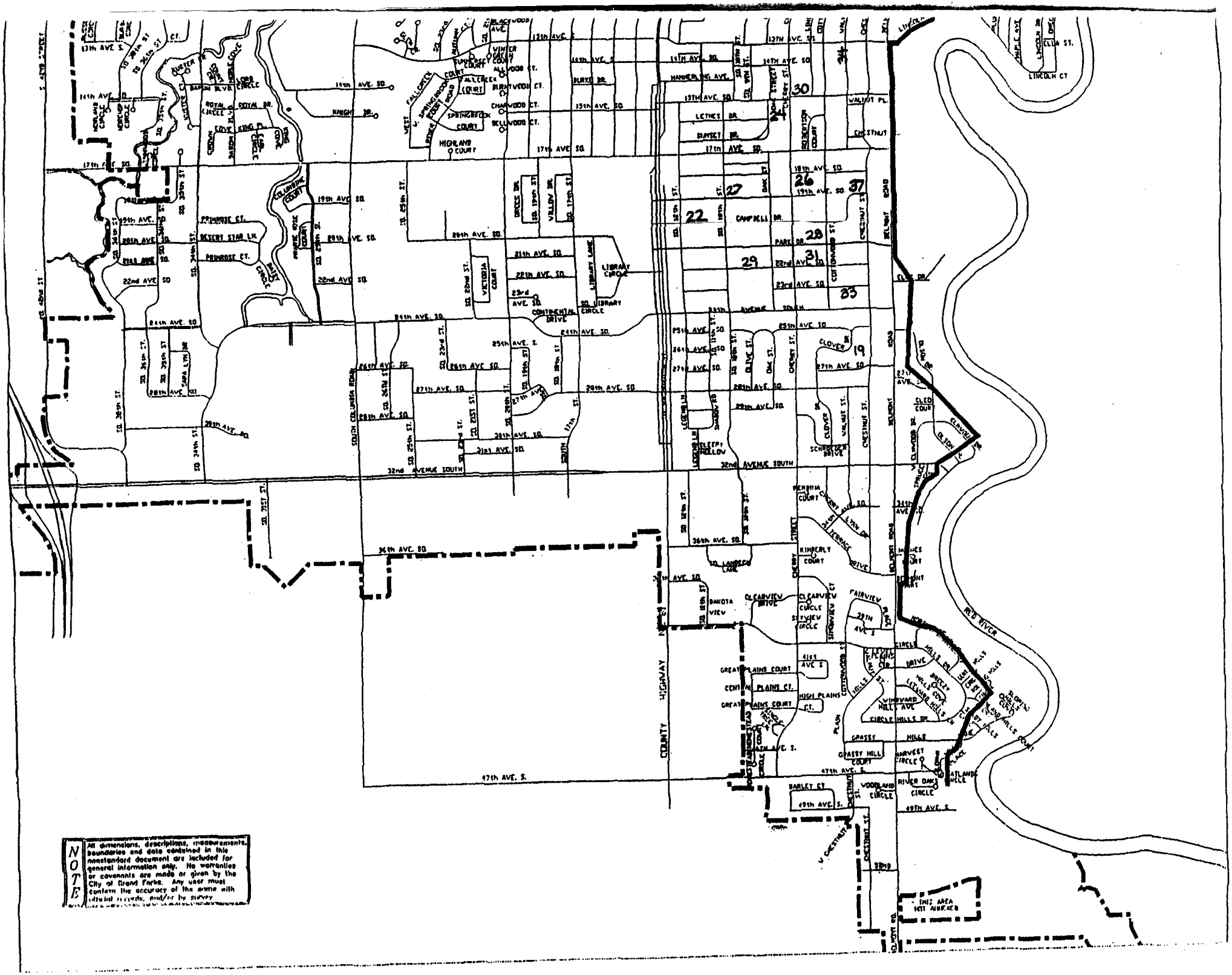
3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 *Interference check sample*—A solution containing both interfering and analyte elemelts of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)

3.9 *Quality control sample*—A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

Appendix E7: Map of Sampling Areas


MAY, 1997
THIS MAP IS COMPUTER DRAWN
BY THE CITY OF GRAND FORKS
ENGINEERING DEPARTMENT
DRAFT Sampling Locations
(Sampling locations are plotted as Drop number on Table
RED RIVER
COUNTY HIGHWAY NO 81
STATE MILL ROAD
BACON RD
DONLIN AVE.
FERGUS AVE.
SEWARD AVE.
GATEWAY DRIVE
LEVEE BVD
RIVERSIDE DR.
DEMERS AVENUE
UNIVERSITY AVE.
NORTH COLUMBIA ROAD
COLUMBIA COURT
NORTHWESTERN DRIVE (PRIVATE STREET)
BERKELEY DR. (PRIVATE STREET)
STANFORD RD
WASHINGTON ST.
RIVERSIDE RD.
RED LAKE RIVER
BIKE DRIVE
BIKE AVE.


NOTE
All dimensions, descriptions, measurements, boundaries and data contained in this nonstandard document are included for general information only. No warranties or covenants are made or given by the City of Grand Forks. Any user must confirm the accuracy of the same with official records, and/or by survey
32nd AVENUE SOUTH
47th AVE. S.
COUNTY HIGHWAY
RED RIVER
DEMERS AVE.
GRAND FORKS
THIS AREA NOT ANNEXED