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Guidance for Total Organics

Final Report

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Abstract

This document provides guidance to those wishing to determine the total organics content of source samples. Writers of air quality permit applications for waste combustion units require total organics data for their assessments. This document identifies specific techniques to determine the total organics sampled from stationary sources. It describes the measurement of total organics from stack emissions and related field sampling efforts, combining the organics from three specific boiling point/vapor pressure classes: light hydrocarbons and volatile organics (boiling points <100°C), semivolatile organics (boiling points 100°C to 300°C), and non-volatile organics (boiling points >300°C). It describes methods for measuring and reporting the individual parameters. The document seeks to avoid the confusion about organics measurement and eliminate the misleading and non-descriptive titles often given to different facets of organics analysis. It also provides information about combining the component parts of the organics analysis results into a helpful description of the data. Knowing the amount of previously uncharacterized organic material enables more accurate risk assessment estimates to be made. Discussions of the specific methods and operating procedures are found in the appendices and references.

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Acronyms and Abbreviations

AREAL - Atmospheric Research and Exposure Assessment Laboratory, RTP

AEERL - Air and Energy Engineering Research Laboratory, RTP

CH_4 - Methane

C_7 - Heptane

C_{17} - Heptadecane

Draft Method 0040 - "Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags"

Draft Method 3542 - "Extraction of Semivolatile Analytes Collected Using Modified Method 5 (Method 0010) Train"

EPA - Environmental Protection Agency

FID - Flame ionization detector

Field GC - Field gas chromatography, light organics collected in Tedlar® bags and analyzed in the field by GC/FID

GC - Gas chromatograph

GRAV - Gravimetric mass, nonvolatile organics with boiling point > 300°C

heptane - Straight chain hydrocarbon, saturated, 7 carbon atoms

heptadecane - Straight chain hydrocarbon, saturated, 17 carbon atoms

Level 1 - IERL (AEERL) Procedures Manual: Level 1 Environmental Assessment

m - Meter

Method 8270 - "SW-846, Method 8270, Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique"

Acronyms and Abbreviations, Continued

Method 0010 - "SW-846, Method 0010, Modified Method 5 Sampling Train"

mL - Milliliter

µg - Microgram

µL - Microliter

m^3 - Cubic meter

MS - Mass spectrometry

purge and trap - Analytical technique where the water sample is introduced to the instrument by gas purging, trapping of the gas, and desorption from the trap

QC - Quality control

RCRA - Resource Conservation and Recovery Act

Recoverable organics - Those organic compounds capable of being collected in a specific sampling train (Method 0010, Draft Method 0040) and subsequently analyzed.

RTP - Research Triangle Park, North Carolina

semivolatile - Compound class between the volatile and non volatile compounds, generally defined by boiling point between 100°C and 300°C.

SW-846 - Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Manual, 3rd Edition.

Tedlar® - Trade name for sampling bag material used in direct collection of air samples

total organics - Combination of Field GC, TCO, and GRAV mass

TCO - Total chromatographable organics

volatiles - Volatile organic compounds with boiling points < 100°C

Section 1

Introduction/Background

The characterization of stationary source emissions requires screening and analysis procedures that identify components of several compound classes. The need to characterize emissions containing multiple organic compounds continues to increase. Revisions to the guidance for conducting risk assessments at Resource Conservation and Recovery Act (RCRA) hazardous waste combustion units have recently included the requirement that total organic carbon analysis be conducted.[1,2] The portion of organic emissions that have not been specifically identified and quantified by other methods must be measured. By knowing the amounts of previously uncharacterized organic material, more accurate risk assessment estimates can be made. Writers of air quality permit applications for waste combustion units require total organics data for their assessments. This document identifies specific techniques to determine the total organics sampled from stationary sources.

This document describes the measurement of total organics from stack emissions and related field sampling efforts, combining the organics from three specific boiling point/vapor pressure classes: light hydrocarbons and volatile organics, semivolatile organics, and nonvolatile organic compounds. The total organics measurements are not merely a mass measurement of carbon, soot, or particulate content alone. Total organics in this case combines the low boiling point organic compounds (Field GC and Purge & Trap GC) with the organic compounds with boiling points greater than heptane (TCO and GRAV) collected with a Method 0010 sampling train. The combination of the three fractions and techniques gives the analyst specific identified organic compound classes and provides the means to analyze the components of each boiling point class. The sampling and analytical information necessary to characterize the full boiling point range of organic material encountered in source emissions is provided in this document.

Field gas chromatography (Field GC) with flame ionization detection (FID) of an integrated Tedlar® bag sample is recommended for organics of boiling points less than 100°C. Total chromatographable organic (TCO) analysis is recommended for compounds boiling between 100°C and 300°C. Finally, gravimetric (GRAV) techniques are appropriate for compounds boiling at 300°C or higher. The total organics are the sum of volatile organic compounds (VOC), TCO, and GRAV. The summary of these three techniques is shown in Figure 1.

Total organic carbon in this document refers to the volatile organics (boiling point < 100°C) from a field GC and purge and trap GC measurement combined with organics of boiling point > 100°C collected in a Method 0010 sampling train. The combination of two sampling and three analytical techniques gives the investigator the approximate mass of all identified and unidentified "recoverable" organic material. The mass of organic material that remains after correction for the identified organic compounds found using RCRA SW-846 methods is the residual organic carbon and this quantity is used to estimate risk from unidentified organic emissions. A description of the measurement techniques is found in the following pages. Detailed discussions of methods and operating procedures are found in the references and appendices of this document.

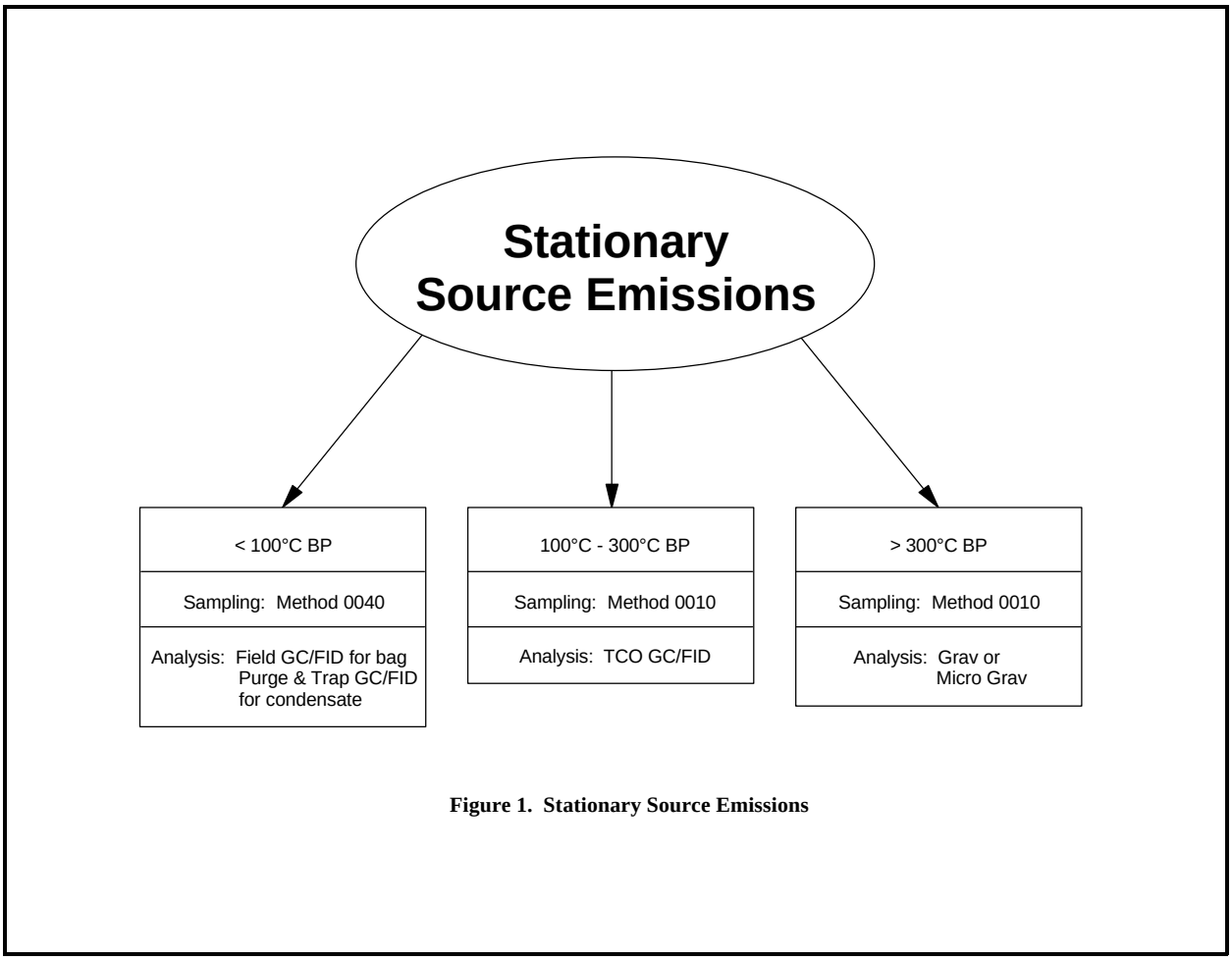

Figure 1. Stationary Source Emissions

Section 2

Method for Total Organics Measurement

The method for total organics measurement incorporates three distinct sets of analyses, described in the following sections:

- First, the light organics are collected and measured by a technique known as Field GC using bag sampling according to Draft Method 0040. Emphasis is made on the identification of methane, because methane may appear in significant quantities in stack sampling efforts and correct identification may be vital to subsequent analysis of risk assessment of the stationary source. In addition, the light organics collected in the condensate trap of Draft Method 0040 are analyzed by Purge and Trap GC/FID.

- Second, Method 0010 samples are collected and the extracts of the train components are analyzed. The 100°C to 300°C organic compounds, TCO, are determined by GC/FID of the dichloromethane extracts of the pooled components of the sampling train. C_7 and C_{17} are used as marker compounds because their boiling points are 98°C and 302°C, respectively.

- Finally, the 300°C and higher boiling organics, non-volatile organics, are determined by a gravimetric procedure known as GRAV from the same pooled dichloromethane extract of the train components as the TCO procedure.

The data from these three analytical determinations are collected and added to obtain a total organics value for the sample of choice, as shown in Table 1. The value provides a benchmark of total organic content for specific identification of individual compounds, necessary for emission and/or risk assessment calculations. The total value is then comparable from site to site or application to application, and the end-user or researcher can more easily compare total organics data from various sources.

The three analysis components allow the reviewer of the data to keep track of the total organics in a material balance manner. The individual boiling point ranges allow identification of

organic compounds by defined classes and assist in the estimate of completeness of characterization. This identification of known vs. unidentified organics is of benefit in subsequent risk assessment calculations.

Table 1. Total Organics Components

Component	Method		Units	Boiling Point Range	Vapor Pressure
	Sampling	Analysis			
Field GC, volatile organics	0040	GC/FID and Purge & Trap GC/FID	$\mu g/m^3$	< 100°C	> 40 mm at 22.3°C (> heptane)
TCO, semivolatile organics	0010	GC/FID	$\mu g/m^3$	100° C < BP < 300°C	1 mm Hg at 115°C > VP > 40 mm at 22.3°C
GRAV, non-volatile organics	0010	gravimetric	$\mu g/m^3$	> 300°C	< 1 mm Hg at 115°C (< heptadecane)
Total Organics = (Field GC + Purge and trap GC) + TCO + GRAV in units of $\mu g/m^3$					

Section 3

Field Gas Chromatography (Field GC) Method and Purge and Trap GC Method

The field GC portion of total organics is determined by field analysis of a bag sample by GC with a flame ionization detector (FID). This procedure is described in this document as Appendix A and in EPA Draft Method 0040 (Appendix E). The identified range of organics for field GC is defined by boiling point range, in this case < 100° C. The analysis procedures are normally performed in the field to minimize sample (compound) loss due to storage and shipping. Additionally, the condensate collected as a part of the bag sampling is analyzed for low boiling organics by purge and trap GC/FID. The condensate fraction is normally transferred to a vial with no headspace and shipped to the laboratory for analysis.

Bag Sampling/Analysis

Compounds with boiling points below 100°C are sampled into Tedlar® bags and require on site gas chromatographic analysis of the collected sample. The operating procedure for this methodology is included in this document as Appendix A and Draft Method 0040. The range of applicable compounds is very large: methane has a boiling point of -160°C, and hexane boils at 69°C. The reporting range for the methodology extends to 100°C. If a packed column is used to perform all of the gas chromatographic analysis, a very judicious selection of phase and analytical conditions must be made in order to achieve chromatographic resolution for methane at the same time as the total analysis time is limited to no more than 15-20 minutes. Some investigators prefer the use of two gas chromatographs, one with an appropriate column and conditions for C_1 - C_4 and the second with an appropriate column and conditions for the C_4 - C_6 range. A capillary column is required to perform the analysis over the entire volatility range with adequate resolution. A capillary column with a length of 60 m may be required to provide adequate

resolution for the C_2-hydrocarbon isomers. The gas chromatographic analysis will primarily be separating compounds on the basis of boiling points, but the separation will also be influenced by the polarity of the compounds in some cases. Numerous chromatographic conditions such as column temperature, ramp for temperature programming, duration of an isothermal hold, and temperature of any transfer line will all have to be optimized for the best chromatographic results. A flame ionization detector is required to perform the analysis.

The gas chromatograph must be calibrated for quantitative analysis with a normal hydrocarbon curve. The curve is prepared using certified cylinders containing the n-alkanes from C_1 through C_6. A multipoint calibration of at least three points (in duplicate) is required. Calibration for methane (CH_4) must be performed carefully so that the quantity of methane can be determined accurately. Methane is often found in significant quantities when incinerator stacks are sampled, and it is essential to be able to identify the compound correctly and provide an accurate quantitative measurement when calculations of risk or regulatory significance are being performed. The certified C_1 - C_6 standard gas mixture is used to calibrate the field gas chromatograph and a point approximately in the middle of the calibration range should be analyzed at least once per day as a calibration check. The multipoint calibration is achieved either through the use of multiple cylinders at different concentrations or by the use of sample loops of varying sizes.

After full calibration, sample analysis is initiated when the sample container (the Tedlar® bag) is connected to the sampling valve and the sample gas is drawn through the valve and sample loop. When the valve is sufficiently purged, the valve is actuated and the contents of the loop are injected into the chromatograph. Simultaneously with the injection of the sample, the temperature programmer and integrator/data system data acquisition are started. Chromatograms and integrator/data system output are collected. Retention times and responses must agree to within 5 percent relative standard deviation with the calibration curve. Uniform FID response for varying compound classes is assumed in this methodology. The resulting quantitative results therefore tend to be biased low for compounds which are not n-alkanes. In many, if not most, cases the species present are not identical to those used for calibration of the on-site chromatograph; an

exact correspondence between standard peaks and the peaks observed in the sample chromatogram will not be achieved.

Purge and Trap Sampling/Analysis

Compounds with boiling points below 100°C are sampled by Draft Method 0040 into the condensate ahead of the Tedlar® bag. The operating procedure for this methodology is included in this document as Appendix B. This condensate requires purge and trap gas chromatographic analysis of the collected water sample. A gas chromatograph with an appropriate column and conditions for the C_5 - C_7 range is required. A capillary column with a length of 60 m may be required to provide adequate resolution for smaller organic and hydrocarbon isomers. A flame ionization detector is required to perform this analysis.

The purge and trap GC must be calibrated for quantitative analysis with a normal hydrocarbon curve. The curve is prepared using liquid alkane standards containing the n-alkanes from C_5 through C_7. A multipoint calibration of at least three points (in duplicate) is required. The alkane mixture is used to calibrate the GC and a point approximately in the middle of the calibration range should be analyzed at least once per day as a calibration check. The multipoint calibration is achieved through the use of serial dilutions of the primary stock standard mixture in methanol solution.

After full calibration, sample analysis is initiated when an aliquot of the water sample in the VOA vial is transferred to the purge flask. The purge gas is actuated, purging the vapor with an inert gas to the sorbent trap (VOCOL®, VOCARB®, or equivalent). When the sample is sufficiently purged from the vessel into the trap, the valve is actuated and the trap contents are desorbed by rapid heating onto the head of the GC column with the FID detector. The temperature programmer and integrator/data system data acquisition are started. Chromatograms and integrator/data system output are collected. Uniform FID response for varying compound classes is assumed in this methodology. Compounds found with retention times prior to the C_4 retention time are quantified with an appropriate response factor and the value reported as C_4 with the other organic results.

Section 4

Source Sampling and Sample Extract Preparation for TCO and GRAV

In order to obtain the sample required for TCO and GRAV analysis, the field sample must be collected in the appropriate manner. The sample is collected using the Semivolatile Organic Sampling Train, Method 0010, included in this document as Appendix F. This sampling method, also known as the Modified Method 5 Sampling Train, generates a set of sampling train components which must be carefully handled in order to preserve the compounds of interest.

The sampling train is disassembled and "broken-down" according to the specifications of Draft Method 3542, "Extraction of Semivolatile Analytes Collected Using Modified Method 5 (Method 0010) Train (Appendix G). There are, however, several exceptions to the method as written which must be observed in order to obtain valid data for total organics determinations. They are listed below:

- The component parts of the sampling train are normally collected in three parts: 1) particulate matter filter and front half rinse, 2) condensate and condensate rinse, and 3) XAD-2® and back half rinse. These components are combined into a single pooled extract for the purposes of total organics measurements. As in Method 3542, the three parts may be taken to final volumes of 5 mL each, but the three extracts are then combined and taken to a final pooled volume of no less than 5 mL. **Note**: At no time should any of the extracts (parts or pooled) be reduced to volumes less than 3 mL, or loss of semivolatile compounds may occur.

- Since the extracts for total organics determinations are analyzed by GC/FID and gravimetric techniques, none of the surrogates, isotopically-labeled standards, or internal standards associated with GC/MS analysis (Method 8270) should be added to the extractors or sample extracts. After the sampling train is disassembled, the components are rinsed and extracted normally, but without the addition of surrogate compounds.

- The final pooled extract sample volume is recorded and an aliquot is used for the TCO GC/FID, while duplicate aliquots are used in the GRAV measurements.

Section 5

Total Chromatographic Organic (TCO) Method

The TCO Method has been described in detail in the Level 1 Procedures Manual[3] and revised as an interim EPA/AEERL operating procedure (Appendix C). The identified range of organic compounds is defined by boiling point range, in this case 100-300°C. Compounds with boiling points between 100°C and 300°C are analyzed by GC with an FID detector after collection using a Method 0010 sampling train. The TCO procedure is carried out by analysis of a dichloromethane extract (a combination of the extracts from the three major components of the sampling train). The analysis is generally performed in the laboratory after extraction and compositing of the extracts of the individual components of the Method 0010 sampling train.

TCO Method

The TCO Method, in its current form, is a capillary GC/FID method quantifying chromatographable material in the 100°C to 300°C boiling point range. An aliquot of the Method 0010 dichloromethane extract is injected onto a capillary GC column with an FID detector, and the peak areas are summed over the retention time window that encompasses the TCO boiling point range. The entire analysis window is established by injecting *n*-heptane (C_7) and *n*-heptadecane (C_{17}) as the reference peaks between which the TCO integration will occur. As described in the method, heptane and heptadecane are used as retention time reference peaks for boiling point.

The TCO value is determined from the calibration standard curve, generated with hydrocarbon standards which fall within the TCO range, specifically decane (C_{10}), dodecane (C_{12}), and tetradecane (C_{14}). An integrator or GC data system is used to record the data points as they

are obtained from the injections of calibration standards and samples. The organics identified in the prescribed boiling point range are quantified and summed (totalled) to obtain the TCO portion of the total organics number. Reporting units are generally in terms of µg per sample, which is then converted to $\mu g/m^3$, based on the sampling volume.

Analysis may be performed using a capillary (preferred) or packed column GC. A non-polar or slightly polar column is used to provide adequate resolution and analysis in a total run time of approximately 45 minutes. A 15 to 30 m non-polar wide bore column (0.32 mm) has been found to be effective for TCO analysis. As a capillary or packed column procedure, the GC/FID is operated in a manner consistent with the manufacturer's recommendations for gas flow, temperature zones, and injection volume. Analysis is performed most easily using a GC with a liquid autosampler, so that calibrations and sample injections can be performed in a consistent and automated fashion. The GC used for TCO analysis is calibrated using specific hydrocarbon standards. A multipoint calibration of at least three different concentrations in duplicate is required for this procedure. After calibration has been performed, a daily quality control (QC) check sample is run to verify that the GC is performing correctly. The QC check sample is run with a standard in the middle of the working range of the GC calibration standards.

While it is understood that the compounds in this volatility and boiling point range might include compounds that are not hydrocarbons, the FID detector is seen as a good all-purpose detector for the quantification of the sample extracts.

Section 6

Gravimetric (GRAV) Method

The third component of the total organics measurement process is called gravimetric mass (GRAV). The GRAV Method has also been described in detail in the Level 1 Procedures Manual[3] and also revised as an interim EPA/AEERL operating procedure (Appendix D). The GRAV procedure is carried out by analysis of an aliquot of the same dichloromethane extract from the Method 0010 sampling train as was used for TCO determinations. GRAV is a gravimetric mass measurement of the nonvolatile (boiling point >300°C) organics found in the extract of the sampling train, which was established for the Level 1 procedures by an exhaustive study of hydrocarbon evaporative properties. The range of organics is defined by boiling point, in this case greater than 300°C. The analysis is generally performed in the laboratory after extraction and compositing of the extracts of the individual components of the Method 0010 sampling train.

GRAV Method

The GRAV Method, in its current form, quantifies nonvolatile organic material with a boiling point greater than 300°C. A carefully measured aliquot of the Method 0010 dichloromethane extract is placed in a precleaned aluminum weighing pan and allowed to dry in air at room temperature, then come to complete dryness in a room temperature desiccator, while exposure to dust and contaminants are minimized. The residue in the pan is weighed accurately, and the mass is recorded to determine the GRAV value. For this procedure, the three individual dichloromethane extracts from Method 0010 are pooled and reduced to a final volume of 5.0 mL. A volume of 1 mL of the pooled extract is used for the GRAV determinations, which are performed in duplicate. Other final extract and GRAV aliquot volumes may be used, but the sample extraction and concentration procedures of Method 3542 (Appendix G) should be

followed closely to avoid loss of more volatile organics. The GRAV organics in the greater than 300°C range are measured on an analytical balance and recorded for the GRAV portion of the total organics number. This value, in µg, is converted to units of µg per sample, which is then divided by sample volume to obtain $\mu g/m^3$. This sum is added to the previously determined TCO and field GC values to find the total organics value, in units of micrograms per m^3.

Section 7

References

1. Revised Draft of Risk Assessment Implementation Guidance for Hazardous Waste Combustion Facilities. Memorandum from Michael H. Shapiro, Office of Solid Waste. U. S. Environmental Protection Agency, May 5, 1994.

2. Johnson, Larry D., M. Rodney Midgett, Ruby H. James, Michael M. Thomason, and M. Lisa Manier. Screening Approach for Principal Organic Hazardous Constituents and Products of Incomplete Combustion. Journal of Air & Waste Management Association. Vol. 39, No. 5, May 1989.

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Appendix A

Recommended Operating Procedure for Field Gas Chromatography

(From SW-846, Method 8240 and Method 18 - 40 CFR Part 60, Appendix A)

RECOMMENDED OPERATING PROCEDURE FOR FIELD GAS CHROMATOGRAPHY

A.1.0 INTRODUCTION

Field analyses are performed for samples that are subject to significant degradation if analysis is delayed even for the amount of time required to ship samples to a laboratory, or in situations where performing analysis in the field is preferable to handling and shipping samples such as Tedlar® bags. In determining Total Organics, field gas chromatography is performed to determine compounds in the C_1 - C_7 hydrocarbon range. This range encompasses alkanes, alkenes, cyclic compounds, and functionalized organic compounds. For example, methane, chloromethane, formaldehyde, and methanol are all C_1 compounds. The methodology is applicable to C_1 - C_7 hydrocarbons, organic compounds boiling in the range -160°C to 100°C. When performing field gas chromatographic analysis, species eluting in the specified boiling point range are quantified as n-alkanes. The sensitivity of the flame ionization detector varies from compound to compound, but n-alkanes as a class have a higher flame ionization response than other classes of compounds such as oxygenated or halogenated hydrocarbons. Therefore, using n-alkanes as calibrants and assuming equivalent responses for all other compounds in the appropriate boiling point range tends to bias results low. That is, if an alkane standard and a non-alkane peak have equivalent system responses, the non-alkane peak is assigned a quantitative value equivalent to the alkane. The non-alkane peak, however, has a poorer response to the flame ionization detector than the alkane. The amount of non-alkane required to produce the same response as an alkane may be several times higher than the amount of alkane, so the reported value shows a low bias.

A.2.0 SCOPE AND APPLICATION

This procedure defines the field gas chromatographic analysis of gaseous stationary source emissions sampled into a Tedlar® bag for C_1 - C_7 hydrocarbons, a chromatographic elution range defining organic compounds boiling in the range of -160°C to 100°C.

A.3.0 SUMMARY OF METHOD

A gas sample contained in a Tedlar® bag is analyzed in the field by gas chromatography/flame ionization detection (GC/FID). The instrument is set up in the field with column and conditions appropriate for the analysis of C_1 - C_7 n-alkanes. Retention times are determined and calibration is performed with a certified gaseous standard of C_1 - C_7 alkanes in air or nitrogen. Compounds of interest are identified by retention times or retention time ranges and quantitative analysis is performed.

A.4.0 SAMPLE HANDLING AND PRESERVATION

Samples for this analysis are contained in Tedlar® bags. These samples should be analyzed as soon after acquisition as possible, preferably within two hours. Exposure to extremes of light and temperature should be avoided.

A.5.0 APPARATUS AND REAGENTS

A.5.1 Gas Chromatograph

The gas chromatograph to be used for this analysis must be capable of being moved into the field, with a flame ionization detector, temperature-controlled sample loops of varying sizes with a valve assembly, temperature-programmable oven, and an appropriate chromatographic column to obtain the resolution desired for the analysis.

A.5.2 Recorder/Integrator/Data System

A recorder is required. Appropriate parameters are 1 inch/min chart speed, 1 mV full scale, 1 sec full scale response time. An integrator is required. The function of both the recorder and integrator may be superseded by a data system, if available. Parameters which should be specified and recorded in the instrument log include noise suppression, up-slope sensitivity, down-

slope sensitivity, baseline reset delay, area threshold, front shoulder control, rear shoulder control, and data sampling frequency.

A.5.3 Columns

For the C_1 -C_4 hydrocarbons, a packed stainless steel SP-1000® column (6 ft x 1/8 inch outer diameter), or equivalent which can be calibrated over the specified hydrocarbon range is required. Some possible equivalent columns include PLOT® or TCEP® columns. If a PLOT column is used, this column could be used for the C_5 to C_7 hydrocarbon range as well. An alternative is to use a second gas chromatograph with a generic nonpolar packed or capillary column for the C_5 to C_7 range and a flame ionization detector.

A.5.4 Gas Standard

A certified n-alkane gas standard of C_1 - C_7 n-alkanes in air or nitrogen is required. The concentrations of the alkanes in the certified standard may range from 5 - 100 ppm. A multipoint calibration curve at different concentrations may be obtained by using sample loops of different sizes or multiple gas cylinders at different concentrations.

A.5.5 Cylinder Gases

Helium carrier gas, hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column is required. Fuel (hydrogen), as recommended by the manufacturer for operation of the flame ionization detector, and zero air, hydrocarbon free air for operation of the flame ionization detector, are required.

A.5.6 Regulators

Appropriate regulators are required for all gas cylinders for both support gases and for certified gaseous standards.

A.5.7 Teflon® Tubing

Diameter and length determined by requirements for connection of gas cylinder regulators and the gas chromatograph.

A.6.0 GAS CHROMATOGRAPH SETUP AND CHECK

The gas chromatograph must be completely calibrated at each new test site in the field. Whenever the gas chromatograph is set up, the following parameters must be verified for correct operation:

1) All support gas supplies must be at the proper pressure.

2) Verify that the carrier gas flow to the analytical column is correct (for a packed column, the gas flow rate should be 30 ± 2 mL/min; for a capillary column, flow rate will depend upon the column diameter and should be adjusted according to the manufacturer's specifications for the column). Flow rate is checked at the analytical column outlet after disconnection from the detector. The instrument must be at ambient temperature.

3) Verify that the hydrogen flow is appropriate for the operation of the flame ionization detector. The flow rate is checked at the control panel on the gas chromatograph.

4) Verify that the air flow is appropriate for the operation of the flame ionization detector. The air flow rate is checked at the gas control panel on the gas chromatograph.

5) Verify that the electrometer is functioning properly. The electrometer must be balanced and the bucking controls set as required.

6) Verify that recorder/integrator/data system are functioning properly.

A.7.0 CALIBRATION

To determine the temperature ranges for reporting the results of GC analyses for the C_1 - C_7 compounds, the gas chromatograph is given a normal boiling point - retention time calibration. The n-alkanes, their boiling points, and the data reporting ranges are shown below.

Compound	Boiling Point, °C	Reporting Range, °C	Report As
methane	-161	-160 to -100	C_1
ethane	-88	-100 to -50	C_2
propane	-42	-50 to 0	C_3
butane	0	0 to 30	C_4
pentane	36	30 to 60	C_5
hexane	69	60 to 90	C_6
heptane	98	90 to 98	C_7

To perform a multipoint calibration, connect the C_1 - C_7 certified standard gas cylinder to the sampling valve, and allow the gas to flow through the valve at a constant, low, and reproducible flow rate of 20 mL/min measured at the sample valve outlet using a bubble flowmeter. When the sample valve has purged (approximately 5 min), allow the sample loop pressure to equilibrate to atmospheric pressure and actuate the valve and inject the contents of the sample loop into the gas chromatograph. Simultaneously, start the integrator and/or data system and the temperature programmer, if used. Obtain chromatograms and integrator/data system output. Retention times and responses shall agree to within 5% relative standard deviation. Repeat the standard injection until two consecutive injections give area counts within 5 percent of their mean value. The average value multiplied by the attenuation factor is then the calibration area value for the concentration.

The multipoint calibration must encompass at least three concentration levels, with each point analyzed at least in duplicate (a minimum of six calibration data points for each n-alkane). The different concentrations are achieved either by analysis of standards from cylinders at three different concentrations or by use of sample loops of different sizes with one certified gaseous standard. Prepare a plot of the concentration versus the calibration area values, perform a regression analysis, and draw the least squares line.

A.8.0 DAILY CALIBRATION CHECK

The C_1 - C_7 certified standard gas mixture will be injected and analyzed at the start of each day, at a concentration at approximately the midpoint of the calibration curve. Retention times and responses for each component should agree with the initial calibration data to within ± 10 percent. If the daily calibration check meets this specification, the full calibration need not be repeated.

A.9.0 ANALYSIS OF SAMPLES

If any doubt exists concerning the relationship between the stationary source sample GC peaks and the GC peaks obtained from calibration, a small amount of the calibration gas should be spiked with the sample in order to verify retention times.

To perform the analysis of gaseous samples, the chromatograph, recorder, integrator/data system must be set up according to the manufacturer's manuals and calibrated. Operating parameters should be confirmed. The operating parameters are to be listed on each chromatogram, and each recorder chart should be labeled. The sample bag should be connected to the gas sample valve, the sample loop purged with the sample, and the contents of the loop should be injected. The integrator/data system and recorder should be started simultaneously with injection.

If any doubt exists concerning the relationship between the stationary source sample GC peaks and the peaks obtained from analysis of the calibration standard, a small aliquot of the calibration gas should be spiked with the sample in order to verify retention times.

A.10.0 CALCULATIONS FOR C_1 - C_7 HYDROCARBONS

The calibration curve for the n-alkanes is constructed in the following manner:

1) For each alkane, the average retention time and relative standard deviation are calculated.

2) Plot boiling point of each alkane versus the average retention times (in seconds).

3) Draw the curve, manually or by computer.

4) On the curve, locate and record the retention times corresponding to the reporting ranges: -160°C to -100°C, -100°C to -50°C, -50°C to 0°C, 0°C - 30°C, 30°C to 60°C, 60°C to 90°C, and 90°C to 98°C.

5) Calculate average area response and relative standard deviations for the propane calibration standard.

6) Plot response (µV/sec) as ordinate versus concentration of the standard in mg/m^3 injected as abscissa. Draw in the curve. Perform least squares linear regression and obtain the slope (µV/sec * m^3/mg).

7) In each retention time range of the sample, sum up the peak areas.

8) Convert peak areas (µV / sec) to mg/m^3 by dividing by the proper response (slope factor).

9) Record the total concentration of material in each retention time range.

Appendix B

Recommended Operating Procedure for Purge and Trap Gas Chromatography With FID Detection

(From SW-846 Method 8240 and Draft Method 0040)

RECOMMENDED OPERATING PROCEDURE FOR PURGE AND TRAP GAS CHROMATOGRAPHY WITH FID DETECTION

B.1.0 INTRODUCTION

As a complement to the Field Gas Chromatography analysis of total organics, the condenser component of the Draft Method 0040 sampling train is analyzed using purge and trap techniques and an FID detector. In determining total organics, purge and trap gas chromatography is performed to determine compounds in the C_1 - C_7 hydrocarbon range. This range encompasses alkanes, alkenes, cyclic compounds, and functionalized organic compounds. For example, methane, chloromethane, formaldehyde, and methanol are all C_1 compounds. The methodology is applicable to C_1 - C_7 hydrocarbons, organic compounds boiling in the range -160°C to 100°C. In performing purge and trap gas chromatographic analysis, species eluting in the specified boiling point range are quantified as n-alkanes. The sensitivity of the flame ionization detector varies from compound to compound, but n-alkanes as a class have a higher flame ionization response than other classes of compounds such as oxygenated or halogenated hydrocarbons.

B.2.0 SCOPE AND APPLICATION

The field gas chromatographic analysis encompasses gaseous stationary source emissions sampled into a Tedlar® bag in the sampling train. Analysis is performed for the organic compounds boiling in the range of -160°C to 100°C. In Draft Method 0040, the condenser, the condensate trap and the sample line from trap to the Tedlar® bag are carefully rinsed and the combined water sample is transferred to a graduated cylinder. After carefully measuring the sample volume, the water sample is transferred to a 20 mL or 40 mL amber glass VOA vial with a Teflon® septum screw cap with zero void volume. VOA vials under zero headspace conditions may be stored on ice or in a refrigerated container until analysis. This procedure defines the gas chromatographic analysis of gaseous stationary source emissions sampled into the condensate component of a Draft Method 0040 train.

B.3.0 SUMMARY OF METHOD

The volatile compounds are introduced into the gas chromatograph (GC) by the purge and trap method. The components are separated via the GC and detected using a flame ionization detector (FID), which is used to provide quantitative information.

An inert gas is bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. The sorbent columns of choice are a VOCOL® or VOCARB 3000® design, or equivalent. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a GC column. The GC column is heated via a temperature program to elute the components, which are detected with an FID detector.

A volatile organic sample contained in a VOA vial is analyzed in the laboratory by gas chromatography/flame ionization detection (GC/FID). The instrument is set up with column and conditions appropriate for the analysis of C_4 - C_7 n-alkanes. Retention times are determined and calibration is performed with a liquid standard of C_5 - C_7 alkanes. Compounds of interest are identified by retention times or retention time ranges and quantitative analysis is performed.

B.4.0 SAMPLE HANDLING AND PRESERVATION

Samples for this analysis are transferred from the condenser vessel to VOA vials. These samples should be analyzed as soon after acquisition as possible, preferably within two weeks of collection. Samples are refrigerated without headspace in the vials until analysis. Exposure to extremes of light and temperature should be avoided.

B.5.0 APPARATUS AND REAGENTS

Apparatus and reagents needed to perform the purge and trap analysis techniques are summarized in the following paragraphs. Glassware, vials, laboratory refrigerators, compressed gas storage, and items customarily found in an analytical laboratory are assumed to be readily available.

B.5.1 **Purge and trap device**

The purge and trap device consists of three major components: a purge chamber for the water, a trap, and a desorber capable of rapidly heating the trap. The purge chamber should be designed to accept 5 mL samples of water with a water column of at least 3 cm. The purge gas must pass through the water column as finely divided bubbles, normally obtained by passing the gas through a medium porosity glass frit. The packing material for the trap should be a commercially available sorbent material (or combination of materials) capable of trapping and releasing low boiling (volatile) organic compounds. VOCOL® or VOCARB 3000® (Carbopack B and Carboxen® in series) sorbent packing materials, or an equivalent sorbent, are acceptable for the traps, providing they adequately trap and desorb the organic components of interest. The desorber should be capable of rapidly heating the trap to a temperature of at least 180°C for desorption.

B.5.2 **Reagent water**

Reagent water for this analysis is defined as water in which interferents are not observed at the method detection limit (MDL) of the parameters of interest. Purified water (carbon filtration or deionized distilled water) may be used. Alternatively, water may be boiled and subjected to a bubbled stream of inert gas, then sealed until used.

B.5.3 Gas Chromatograph Setup

For the C_1 -C_4 hydrocarbons, a packed stainless steel SP-1000® column (6 ft x 1/8 inch outer diameter), or equivalent which can be calibrated over the specified boiling point range is required. Some possible equivalent columns include PLOT® or TCEP® columns. If a PLOT column is used, this column could be used for the C_5 to C_7 hydrocarbon range as well. An alternative is to use a second gas chromatograph with a generic nonpolar packed or capillary column for the C_5 to C_7 range and a flame ionization detector.

The gas chromatograph must be completely calibrated for use. Whenever the gas chromatograph is set up, the following parameters must be verified for correct operation:

1) All support gas supplies must be at the proper pressure.

2) Verify that the carrier gas flow to the analytical column is correct (for a packed column, the gas flow rate should be 30 ± 2 mL/min; for a capillary column, flow rate will depend upon the column diameter and should be adjusted according to the manufacturer's specifications for the column). Flow rate is checked at the analytical column outlet after disconnection from the detector. The instrument must be at ambient temperature.

3) Verify that the hydrogen flow is appropriate for the operation of the flame ionization detector. The flow rate is checked at the control panel on the gas chromatograph.

4) Verify that the air flow is appropriate for the operation of the flame ionization detector. The air flow rate is checked at the gas control panel on the gas chromatograph.

5) Verify that the electrometer is functioning properly. The electrometer must be balanced and the bucking controls set as required.

6) Verify that recorder/integrator/data system are functioning properly.

B.5.4 Regulators

Appropriate regulators are required for all gas cylinders for detector and carrier gases.

B.5.5 Liquid Standard

A set of n-alkane liquid standards of C_5 - C_7 n-alkanes is required. The concentrations of the alkanes in the standard may range over several orders of magnitude within the working range of the GC/FID. A multipoint calibration curve at different concentrations may be obtained by using multiple dilutions of a stock standard solution.

Calibration standards should be prepared from secondary dilution of stock standards. The solutions should be prepared in methanol, with one of the concentrations at a level near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples (not exceeding the working range of the GC/FID system). Each standard should contain the straight chain hydrocarbons C_5 to C_7. The lower boiling organic compounds (C_1 to C_3) are not expected to be found in the condensate solutions collected in a Draft Method 0040 sampling train. If compounds are found with retention times prior to the C_4 retention time, an appropriate response factor will be used to determine the concentration of those components and their value reported as C_4 (butane) with the other organic results.

B.5.6 Cylinder Gases

Helium carrier gas, hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column. Fuel (hydrogen), as recommended by the manufacturer for operation of the flame ionization detector, and zero air, hydrocarbon free air for operation of the flame ionization detector, are required.

B.5.7 Recorder/Integrator/Data System

A recorder is required. Appropriate parameters are 1 inch/min chart speed, 1 mV full scale, 1 sec full scale response time. An integrator is required. The function of both the recorder and integrator may be superseded by a data system, if available. Parameters which should be specified and recorded in the instrument log include noise suppression, up-slope sensitivity, down-slope sensitivity, baseline reset delay, area threshold, front shoulder control, rear shoulder control, and data sampling frequency.

B.6.0 CALIBRATION

To determine the temperature ranges for reporting the results of GC analyses for the C_5 - C_7 compounds, the gas chromatograph is given a normal boiling point - retention time calibration. The n-alkanes, their boiling points, and the data reporting ranges are shown below.

Compound	Boiling Point, °C	Reporting Range, °C	Report As
methane	-161	-160 to -100	C_1
ethane	-88	-100 to -50	C_2
propane	-42	-50 to 0	C_3
butane	0	0 to 30	C_4
pentane	36	30 to 60	C_5
hexane	69	60 to 90	C_6
heptane	98	90 to 100	C_7

To perform a multipoint calibration for purge and trap analysis, the most practical method is to prepare liquid standards in methanol of the C_5 through C_7 alkanes by dilution of a primary stock. A set of dilutions is prepared, covering the working range of the instrument and the solutions are spiked directly into clean reagent water in VOA vials. The purge and trap system is activated to purge the standard from the purge vessel into the trap. After trapping is complete, the desorber is activated (heated) and simultaneously the integrator and/or data system and the

temperature programmer are started. Obtain chromatograms and integrator/data system output. Retention times and responses shall agree to within 5% relative standard deviation. Repeat the standard injection until two consecutive injections give area counts within 5 percent of their mean value. The average value multiplied by the attenuation factor is then the calibration area value for the concentration.

The multipoint calibration must encompass at least three concentration levels, with each point analyzed at least in duplicate (a minimum of six calibration data points for each n-alkane). The different concentrations are achieved by analysis of standards at three different concentrations of liquid standards of the C_5 through C_7 alkanes. Prepare a plot of the concentration versus the calibration area values, perform a regression analysis, and draw the least squares line.

B.7.0 DAILY CALIBRATION CHECK

A C_5 - C_7 standard mixture will be injected (purge and trap) and analyzed at the start of each day, at a concentration at approximately the midpoint of the calibration curve. Retention times and responses for each component should agree with the initial calibration data to within ± 10 percent. If the daily calibration check meets this specification, the full calibration need not be repeated.

B.8.0 ANALYSIS OF SAMPLES

If any doubt exists concerning the relationship between the stationary source sample GC peaks and the GC peaks obtained from calibration, a small amount of the calibration standard should be spiked with the sample in order to verify retention times.

To perform the analysis of condensate water samples, the chromatograph, recorder, integrator/data system must be set up according to the manufacturer's manuals and calibrated. Operating parameters should be confirmed. The operating parameters are to be listed on each chromatogram, and each recorder chart should be labeled. The sample vial should be correctly

labeled and transferred to the purge vessel. After purging and trapping, the organics are desorbed onto the head of the GC column ("injection"). The integrator/data system and recorder should be started simultaneously with injection.

B.10.0 CALCULATIONS FOR C_5 - C_7 HYDROCARBONS

The calibration curve for the n-alkanes is constructed in the following manner:

1) For the alkanes C_5 through C_7, the average retention time and relative standard deviation are calculated.

2) Plot boiling point of each alkane versus the average retention times (in seconds).

3) Draw the curve, manually or by computer.

4) On the curve, locate and record the retention times corresponding to the reporting ranges: 0°C - 30°C, 30°C to 60°C, 60°C to 90°C, and 90°C to 100°C .

5) Calculate average area response and relative standard deviations for the hexane calibration standard.

6) Plot response (µV/sec) as ordinate versus concentration of the standard in mg/m^3 injected as abscissa. Draw in the curve. Perform least squares linear regression and obtain the slope (µV/sec * m^3/mg).

7) In each retention time range of the sample, sum up the peak areas.

8) Convert peak areas (µV / sec) to mg/m^3 by dividing by the proper response (slope factor).

9) Record the total concentration of material in each retention time range.

Appendix C

Recommended Operating Procedure for Total Chromatographable Organics (TCO) Analysis

(This document was originally prepared for the EPA/AEERL Laboratory in RTP, NC and developed and reviewed by the QA Program of AEERL, under the direction of Judith S. Ford, QA Manager of EPA/AEERL)

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Disclaimer

This recommended operating procedure has been prepared for the sole use of the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

Acknowledgements

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SECTION C.1

INTRODUCTION

C.1.1 Scope

This method provides semi-quantitative data for organic compounds with boiling points between 100 and 300°C. Samples that might include organic compounds in this volatility range are organic liquids, solid sample extracts, aqueous extracts, extracts from Source Assessment Sampling System (SASS) and Modified Method 5 (MM5) train sorbent modules, and liquid chromatography (LC) fractions obtained from those samples. This method is based on separating the components of a gas or liquid mixture in a gas chromatography (GC) column and measuring the separated components with a suitable detector.

This upper end of applicability is limited by column overloading and detector saturation. Typical range is 1 to 20 mg/mL. The operating range can be extended by dilution of samples with solvent (e.g., dichloromethane). The sensitivity limit shall be determined by the minimum detectable concentration of standards.

C.1.2 Limitations

Recommended operating procedures (ROPs) describe non-routine or experimental research operations where some judgment in application may be warranted. ROPs may not be applicable to activities conducted by other research groups and should not be used in place of standard operating procedures. Use of ROPs must be accompanied by an understanding of their purpose and scope. Questions should be directed to AEERL or to project personnel listed in the Acknowledgments.

C.1.3 Definitions

- **Accuracy** - The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random and systematic error or bias components which are due to sampling and analytical operations; a data quality indicator.

- **Calibrate** - To determine, by measurement or comparison with another standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of calibration standards should bracket the range of planned measurements.

- **Calibration Standard** - A substance or reference material used to calibrate the instrument.

- **Method Blank** - A clean sample processed simultaneously with samples containing an analyte of interest through all steps of the analytical procedure.

- **Precision** - The degree of variation among individual measurements of the same property, usually obtained under similar conditions; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

- **Quality Control (QC) Sample** - A sample prepared from substances or materials of known composition and quantity. It is used to assess the performance of a measurement method or portions thereof. It is intended primarily for routine intralaboratory use in controlling precision and bias in the method. It should be prepared from, or be traceable to, a standard other than the calibration standard.

- **Reagent Blank** - A sample of reagent(s), without the target analyte, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine their contribution to error in the observed value.

SECTION C.2

STARTUP

C.2.1 Personnel Requirements

This ROP is written for individuals with a BS/BA degree in chemistry and at least two years experience in gas chromatography, or equivalent.

C.2.2 Facilities Requirements

This procedure requires a standard analytical chemistry laboratory with counter space, secured areas for compressed gas storage, and electricity to operate the equipment. Flasks, beakers, tubing, etc., customarily found in such a laboratory are also needed and assumed to be readily available. GC tools (e.g., wrenches, screwdrivers, and spare parts, etc.) also need to be available in the laboratory.

C.2.3 Safety Requirements

Routine safety precautions required in any analytical chemistry laboratory are applicable here. These include such measures as no smoking while in the laboratory; wearing safety glasses, lab coats, and gloves when handling samples; and handling organic solvents in a fume hood, etc. Compressed gases considered to be fuels (e.g., hydrogen) must be stored on a pad outside the confines of the laboratory. A safety shower, eye wash, first aid kit, and fire extinguisher must be readily available inside the laboratory.

C.2.4 Apparatus

C.2.4.1 Equipment Needed

- **Gas chromatography:** With packed column and/or capillary column capabilities, oven temperature controller, and flame ionization detector (FID) (e.g., Perkin Elmer Sigma 115 or Hewlett Packard 5890).
- **Autosampler (optional):** Capable of handling methylene chloride extracts and appropriate wash vials.
- **Autosampler vials (optional):** Clear glass with Teflon® faced crimp caps, typically 100 µL or 1 mL size.
- **Crimping tool (optional):** Used to secure caps on autosampler vials.

C.2.4.2 Reagents And Materials

- **Methylene chloride:** Burdick and Jackson or equivalent grade.
- **Syringe:** 5 µL or 10 µL, gas tight, for hand injections. Otherwise, 3 µL or 10 µL syringes are used for autosampler injections.
- **Pasteur pipettes:** Disposable, used for sample transfer.
- **Pipette bulbs:** 1 mL, amber.
- **Squeeze bottle:** Teflon®, 250 mL or equivalent, used for methylene chloride rinse of vials.

C.2.4.3 Maintenance

- **Glassware:** Clean all glassware used in the total chromatographable organics (TCO) analysis by the method described in Reference 1.
- **Gas Chromatograph:** Change the GC inlet septum daily; follow this with a column bakeout at 250°C for 20 minutes or, until the detector response is stable and all evidence of contamination is gone (no peaks), or run an injection of clean solvent to verify column contamination is eliminated. Repeat this procedure during the run if evidence of septum failure appears (e.g., increasing peak elution time with each run, or major loss of sensitivity).

C.2.4.4 Theory Of FID Detector

Flame ionization detectors operate by burning organic compounds in the detector's flame. The burning process oxidizes the carbon atoms, producing electrons and positive ions. An anode and cathode on either side of the flame collect the charged particles, and the resulting current is proportional to the concentration of oxidized carbon in the sample. Instrument electronics convert the detector current to a voltage, which changes linearly with changes in analyte concentration.

C.2.5 Interferences

The analytical system shall be demonstrated to be free from internal contaminants on a daily basis by running a bakeout or a QC sample. A reagent blank must be run for each new batch of reagents used to determine that reagents are contaminant-free. This is verified by an instrument response less than the detection limit.

If duplicate runs of a sample show increasing concentration greater than 15% or if cross-contamination is suspected (e.g., high-level sample followed by a low-level sample), a reagent blank shall be run to verify no contamination in the system. If contamination is evident, the column shall be baked out at approximately 250°C for twenty minutes or until the detector is stable, and the blank check repeated.

SECTION C.3

OPERATION

C.3.1 Summary of Method

TCO analysis quantifies chromatographable material with boiling points in the range of 100° to 300°C. This analysis is applied to all samples that might contain compounds in this volatility and boiling point range.

For TCO analysis, a 0.9 to 3 L portion of the extract is analyzed by gas chromatography using a flame ionization detector (FID). Column conditions are described in this document in tabular form in Table 3-1. The peak areas are converted to concentration values using quantitative calibration standards.

For more information, consult Lentzen et al., IERL Procedures Manual: Level 1 (Reference 1).

C.3.2 Samples/Sampling Procedures

Samples for TCO analysis arrive or are prepared as methylene chloride (or occasionally as methanol) extracts of environmental samples, filters, resins, or ambient sampling components. An aliquot of the extract is transferred to a TCO vial and loaded into the autosampler as required.

All samples will be stored in a refrigerator at or below 4°C to retard analyte degradation. Samples will be analyzed as soon as possible after sample receipt and preparation to avoid loss of sample due to volatilization and degradation.

TABLE C-1

INSTRUMENTAL OPERATING CONDITIONS FOR GAS CHROMATOGRAPHY

Column	Fused Silica Capillary Column (15 meters, wide bore, typically DB-1, DB-5, or equivalent)	Packed Column (Methyl Silicone oil or equivalent, 1/8 in. x 6 ft. steel)
Temperature Program	40°C for 3 min, 8°C/min increase to 250°C and hold for total run time of 45 min	50°C for 5 min, 20°C/ min increase to 250°C, then hold
Injector	300°C	300°C
Detector	F.I.D. at 300°C	F.I.D. at 300°C
Carrier Gas	Helium, 1-3 mL/min	Helium, 30 mL/min
Split Injector (optional)	10/1 split ratio	Not Applicable
Injector Volume	Not to exceed 3 L (Typically 1 L)	1-5 L
Solvent	Dichloromethane (pesticide grade, distilled in glass or equivalent)	Dichloromethane (pesticide grade, distilled in glass or equivalent)

C.3.3 Operation

Note: All glassware coming in contact with a sample shall be cleaned by Level 1 procedures (Ref. 1). Briefly, this entails sequential cleaning with soapy water, deionized water, 50:50 (V/V) nitric acid/sulfuric acid, deionized water, methyl alcohol, and methylene chloride, followed by oven drying.

Those steps that are only applicable to automatic injection are shown with an asterisk (*).

- Start up by the manufacturer's suggested method.

* • Replace septum on auto-sampler and column.

* • Ensure injection needle is in line with injection port. The autosampler needle should be manually "injected" through the injection port to verify alignment.

- Bakeout GC at 200°C for 20 minutes until FID response is stable and all evidence of column contamination is gone (no peaks), or run an injection of clean solvent as the first injection of the day to verify that column contamination is eliminated.

* • Load auto-sampler tray with samples.

* • Check the autosampler flush by placing the autosampler in manual mode and flushing a vial of clean solvent through the needle assembly.

* • Set auto-sampler to inject approximately 1 L of samples. Capillary column can be damaged if too great a volume is injected.

- Run a QC standard using the specified conditions to verify that the system is operating properly. Check the TCO window (C_7 to C_{17}) to ensure the range has not changed. (Retention times may change with column aging.) The TCO window for calculations should be adjusted as required.

- Flush needle with solvent (dichloromethane) between injections.
- Run samples and collect data.
- Analyze data according to the method described in Section 3.4.
- After all analyses are complete, bakeout the column at 200°C for 20 minutes, or run clean solvent as a "sample."
- Shut down instrument by method suggested by manufacturer.

C.3.4 Analysis

The peak area (FID response/ L) is summed over the TCO range window and corresponding TCO value (mg/mL) is determined from the calibration curve. In the event that the TCO value is outside the linear working range, the sample shall be concentrated or diluted, depending on the requirements, and reanalyzed. If there is not enough sample to concentrate, the values are reported as found, and an appropriate qualifying statement is included in the analytical report.

It is important that the observed values of the total integrated area for samples be corrected by subtracting an appropriate solvent blank, prepared in the same manner as the samples.

SECTION C.4

TROUBLESHOOTING

C.4.1 Calibration

Quantitative calibration of the TCO procedure is accomplished by the use of mixtures of known concentration of the normal hydrocarbons decane, dodecane, and tetradecane. Retention time limits correspond to the TCO range of boiling points and are defined by the peak maxima for n-heptane (C_7, B.P. 98°C) and n-heptadecane (C_{17}, B.P. 303°C). Therefore, integration of detector response should begin at the retention time of C_7 and terminate at the retention time of C_{17}. The C_7 and C_{17} peaks are not included in this integration. By this procedure, the integrated area will cover material in the boiling range of approximately 100°C to 300°C. Calibrate the GC with dilutions of a stock solution, generating a response/concentration curve. The calibration curve must be 1 and must have a correlation coefficient greater than 0.97 to be acceptable. The preparation and dilution of the stock solution is described below:

- Weigh approximately 100 L aliquots of each (heptane, decane, dodecane, tetradecane, and heptadecane, C_7, C_{10}, C_{12}, C_{14}, C_{17}) (99% + pure) into a 10 mL volumetric flask or septum-sealed vial. Weigh each hydrocarbon successively into the vial starting from least volatile to most volatile.

- Dilute the vial contents up to approximately 3 mL with dichloromethane.

- Transfer this quantitatively to a clean, 10 mL amber volumetric flask and add dichloromethane up to the 10 mL mark. This stock solution will have approximately 22 mg (C_7 to C_{12})/mL and

15 mg(C_{14} to C_{17})/mL. Several (at least three) dilutions of the stock solution are made to cover the linear working range.

C.4.2 Method Precision and Accuracy

Duplicate results by the same operator will be rejected if they differ by more than 15%. The result of a quality control sample, run daily, will be considered deficient if it differs by more than 15% from the preparation value. If this value falls outside the accepted range, the system must be evaluated for the probable cause, and a second standard run or a new calibration performed over the range of interest.

SECTION C.5

DATA REDUCTION

C.5.1 Calculations

The peak area (FID response/ L) is summed over the TCO window and a corresponding TCO value (mg/mL) is determined from the calibration curve.

- Construct the calibration line by fitting a linear regression equation to the results of the analysis of the calibration standard solution. The concentration of the standards must fall within the linear working range of the instrument and bracket the concentration of the sample. Use the C_{10} to C_{14} standards for calibration.

  Standard Calibration Equation:

  $$R_i = (M)\, C_i + (B) \qquad (1)$$

  Where R_i = FID Response (total C_{10} to C_{14} Peaks),
  C_i = Concentration mg/L (total of C_{10} to C_{14} standards),
  M = Slope of line, and
  B = Intercept of line.

- Calculate the TCO value for the sample (C_u, measured value) and blank (C_B, blank value) by summing the FID response over the TCO retention time span and calculating the concentration from the calibration equation.

  It is important that the observed values of the total integrated area for samples be corrected by subtracting an appropriate solvent blank prepared in the same manner as the samples. The sample is corrected for the blank:

  $$C_u \text{ corrected} = C_u \text{ measured} - C_B \qquad (2)$$

C.5.2 Data Reporting

The results of each TCO analysis should be reported as one number (in milligrams), corresponding to the quantity of material in the 100°C to 300°C boiling range in the original sample collected. If more information is available (e.g., cubic meters of gas sampled), the mg/sample value can then be easily converted to the required reporting units.

SECTION C.6

QUALITY ASSURANCE/QUALITY CONTROL

C.6.1 QC Checks

If evidence of septum failure appears (e.g., increasing peak elution time with each run or major loss of sensitivity), perform a column bakeout at 250°C for twenty minutes or until the FID response is stable and all evidence of contamination is gone (no peaks), or run an injection of clean solvent to verify that column contamination is eliminated.

C.6.2 QC Controls

Run a reagent sample for each new batch of reagent or lot of solvent used. If the analysis fails to show organic contaminants to be below detection limits under identical instrument operating conditions as used for samples, then the reagent shall be distilled in glass and retested, or the reagent batch will be unacceptable for TCO analyses.

Prepare a QC sample that is approximately mid-way in the linear working range. Run this QC sample daily to verify the performance of the GC. Determine the TCO value using the calibration curve and its value plotted compared to the theoretical value. If two runs of the QC sample differ by more than 15% of the actual value, prepare a new QC sample and repeat the test. If the new sample fails the test, determine if there is a loose column connection, septum, or altered split flow. After correction, run a new QC sample. If the new sample fails the test, re-calibrate the instrument and/or perform a column change if needed.

SECTION C.7

REFERENCES

1. Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition). EPA 600/7-78/201, NTIS No. PB 293-795, pp. 140-142, October 1978.

Appendix D

Recommended Operating Procedure for Gravimetric (GRAV) Analysis of Organic Extracts

(This document was originally prepared for the EPA/AEERL Laboratory in RTP, NC and developed and reviewed by the QA Program of AEERL, under the direction of Judith S. Ford, QA Manager of EPA/AEERL)

Disclaimer

This recommended operating procedure has been prepared for the sole use of the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

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D.1.0 PROCEDURAL ELEMENTS

D.1.1 Scope and Application

Organic compounds with boiling points of 300°C and higher, after extraction with methylene chloride, evaporation of the solvent, and drying to constant weight, can be determined quantitatively by the gravimetric analysis described in the procedure.[1] This method is applicable to organic liquids, solid sample extracts, aqueous extracts, and extracts from the Source Assessment Sampling System (SASS) or Modified Method 5 train sorbent module. This analysis should be performed after enough of the sample extract has been concentrated to weigh accurately.[2] The suggested solvent is methylene chloride because of its good extraction properties and high volatility. Other solvents may give different results (e.g., methyl alcohol may extract polar compounds which would not be extracted with methylene chloride). All samples being dried to constant weight should be stored in a desiccator.

The range of applicability is limited by the sensitivity of the balance and the organic content of the sample. The balance must be accurate to ± 0.01 mg. If a sample of five milliliters is used for the analysis, then a sensitivity of 0.1 mg/5 mL or 0.002 mg/mL of sample can be achieved. This sensitivity can be improved by further concentration of more sample.

D.1.2 Definitions

- Method Blank: Provides a check on contamination resulting from sample preparation and measurement activities. Typically run in the laboratory after receipt of samples from the field by preparing a material known not to contain the target parameter. Addresses all chemicals and reagents used in a method.
- Reagent Blank: Provides information on contamination due to specific chemical reagents used during sample preparation, plus any background from the measurement system.

- Audit Sample: Has known "true values," but is flagged for the laboratory as a "performance evaluation (PE) sample." Provides information on performance, but this information must be tempered with the understanding that the sample may be given extra attention by the analyst. An internal PE sample is created by the in-house analytical laboratory, while an external PE sample is created outside of the analytical laboratory.

D.1.3 Interferences

Results may be biased due to contamination of the solvent, glassware, or both. A method blank (control) shall be run in duplicate for each lot of solvent and/or set of samples to provide a control check on the purity of the solvent and the glassware cleaning procedure. The method blank, consisting of a solvent sample from the same lot as that used to prepare samples, shall be prepared and concentrated in an identical manner.

Two reagent blanks shall be analyzed each day samples are run to ensure results which are not biased due to solvent contamination. The reagent blank shall be a solvent sample from the same lot used to prepare the samples and shall not be concentrated prior to analysis. To minimize error in weight due to moisture condensation, the pans containing the sample must appear visually dry before being placed in a desiccator in preparation for drying to constant weight.

D.1.4 Apparatus

(1) Analytical Balance: Capable of weighing 0.01 mg with an accuracy of ± 0.005 mg.

(2) Desiccating Cabinet: Seal-tight gasketed with gum rubber. (Desiccators which use silicone sealant shall not be used because of possible contamination of the sample. Silicone grease may interfere with subsequent analysis.)

(3) Oven: Capable of operation to 175°C.

(4) Fume Hood: Standard laboratory.

(5) Dust Cover, Plexiglass®, or equivalent: To protect samples drying in hood.

D.1.5 Reagents and Materials

(1) Disposable Aluminum Weighing Pans: Approximately 2" in diameter, 1/2" deep; crimped sides; weighing approximately 1.0 grams.

(2) Tweezers.

(3) Aluminum Foil

(4) Pipets: 1 to 5 mL (Class A Volumetric).

(5) Glass Beakers: 50 to 400 mL.

(6) Wash Bottles: Teflon® or equivalent.

(7) Deionized Water.

(8) Nitric Acid/Sulfuric Acid, 50:50 (V/V): Prepared from reagent-grade acids.

(9) Methylene Chloride: Burdick and Jackson or equivalent grade.

(10) Methyl Alcohol: Burdick and Jackson or equivalent grade.

(11) Drierite® and/or Silica Gel: New Drierite® or silica gel may be used as received. Used Drierite® or silica gel may be reactivated by drying it in an oven for at least two hours at 175°C.

D.1.6 Sample Handling

All apparatus that contacts either the concentrated or evaporated residue samples shall be glass, Teflon®, aluminum, or stainless steel. Evaporation of samples shall be carried out in an area free of airborne dust and organic vapors that could contaminate the samples.

Ordinarily, all glassware coming in contact with a sample, in either dilute or concentrated form, must be cleaned by complete Level 1 procedures.[2] Briefly, this cleaning procedure entails

sequential cleaning with soapy water, deionized water, 50:50 (V/V) nitric acid:sulfuric acid, deionized water, methyl alcohol, and methylene chloride, followed by oven drying. The use of deionized water for cleaning glassware is critical when inorganic substances are being analyzed or heavy metal contaminants are present in high concentration in tap water.

This ROP, however, covers only the analysis of organic constituents. Tap water can be substituted for deionized water in glassware cleaning whenever the organic concentration exceeds 1 mg/sample as measured by this ROP. Experience has shown that tap water adds no measurable amount of organic contaminants to the method or reagent blanks under these conditions.

D.1.7 Sampling/Analysis Procedures

(1) Label aluminum sample pans on the underside using a ballpoint pen or other sharp object. Handle dishes only with clean tweezers.

(2) Clean the weighing pans by first rinsing them with deionized water, then dipping them successively into three beakers of methyl alcohol, methylene chloride, and, finally, methyl alcohol again.

(3) Dry the cleaned weighing pans to constant weight on a shelf lined with clean aluminum foil in an oven heated to at least 105°C. Cool the plans in a desiccator for a minimum of 4 to 8 hours or overnight.

(4) Weigh pans to constant weight to an accuracy of ± 0.01 mg, recording the pan tare weight.

(5) By pipet, transfer a 1.0 mL aliquot of the sample to the aluminum sample pan or use 1/10 of the concentrated sample. Aliquot size must never exceed 5 mL to avoid loss of sample through capillary action.

(6) Place the sample pan on a clean piece of aluminum foil in a clean fume hood. Shield the pan from dust with a Plexiglas® or other cover positioned to allow for adequate air circulation. Evaporate sample to visual dryness at room temperature. Solvent evaporation usually takes about 30 minutes.

(7) Place sample pan in desiccator over Drierite® and/or silica gel for at least 8 hours.

(8) Weigh sample pan at approximately 4-hour intervals until three successive values differ by no more than ± 0.03 mg. If the residue weight is less than 0.1 mg, concentrate more sample in the same sample pan. If there is insufficient sample remaining for this purpose, report the initial value obtained, along with an explanation.

D.1.8 Calculations

The gravimetric range organics (GRAV) is calculated in units of mg/sample as follows:

$$\text{GRAV} = \frac{(\text{Sample Weight}_{mg} + \text{Pan Weight}_{mg}) - (\text{Pan Tare Weight}_{mg})}{\text{Aliquot Volume}_{mL} / \text{Total Concentration Sample Volume}_{mL}}$$

The calculated GRAV weight is corrected for the method blank:

Corrected GRAV mass = Measured GRAV mass – Method Blank mass

D.1.9 Data Reporting

The results of the analysis are averaged and reported in units of mg organics/original sample.

D.1.10 Precision

Duplicate analyses shall be run by the same analyst and shall be rejected if results differ by more than 20% from the average. If insufficient material is present to rerun the sample, both values will be reported with a qualifying statement.

D.1.11 Accuracy

Dry sample weight should be at least 1 mg per analysis whenever possible. Accuracy of the analysis is ± 20% of actual value. A proficiency test should be performed by each analyst as described in Section 2.0.

D.2.0 QUALITY CONTROL ELEMENTS

- All operators should demonstrate proficiency with Gravimetric Analysis of Organic Extracts (GRAV) prior to sample analysis. In the proficiency testing, include a GRAV analysis of a reagent blank, a method blank, and an audit sample. The method or reagent blank shall be less than 5 mg/mL of sample. Results of the audit sample shall be within the precision and accuracy specifications outlined in this ROP.

- Two types of audit samples are used. The first contains 100 mg of eicosane [$CH_3(CH_2)_{18}CH_3$] in 250 mL of methylene chloride. Concentrate this solution to 10 mL in a manner identical to that used for sample preparation prior to GRAV analysis. The second type of audit sample can be either prepared in-house or received from an independent laboratory. An external audit sample must contain organic compounds with chain lengths of more than 18 carbons (and boiling points above 300°C) in sufficient concentration to be determined accurately. Perform the GRAV analysis in duplicate as described in Section 1.7 of this procedure.

- Determine the GRAV value of duplicate method blanks for each new lot of solvent and/or set of samples. Run a method blank any time contamination is suspected. Prepare the blank using the same lot of reagent and the same concentration procedure as that used to prepare the samples. The solvent sample shall be a volume equivalent to that used for sample preparation. If the blank GRAV value is unusually high (i.e., 5 mg/mL of sample), find the cause of the contamination and repeat the method blank GRAV analysis.

- Analyze two reagent blanks for GRAV each day samples are run to ensure the results are not biased due to solvent contamination. The reagent blank shall consist of an aliquot of the solvent used to prepare the samples. If both reagent blank GRAV values are high (i.e., 2 mg/mL of sample), find the cause of the contamination and reanalyze samples and reagent blanks.

- Analyze all samples in duplicate. Samples are analyzed by the same analyst and must agree to within 20% of the average. In the event this condition is not met, repeat the analyses.

  NOTE: If the conditions require the sample to be reanalyzed (e.g., high blank values or poor precision) and insufficient sample remains, then report the value obtained by the initial analysis and include a qualifying statement.

The following section (D.3.0, MicroGRAV) is a supplement to the original GRAV SOP, dated 9/86.[3]

D.3.0 MICROGRAV

The microGRAV technique allows the analyst to use a lighter gravimetric weigh pan and a smaller aliquot of sample extract to perform the extract weighings. All of the procedures used in traditional GRAV analysis are used with the following exceptions:

D.3.1 Reagents and Materials

(1) Weigh pans: Disposable weigh pans are constructed using heavy duty aluminum foil and a molding jig similar to the one shown in Figure D-1. The jig may be constructed of any inert material (nylon, plastic, Teflon®), providing it conforms to the general shape of the figure and the internal surfaces have generally rounded edges for ease of molding. The foil is cut into 2 inch circles or squares of foil, molded into shape by hand pressing, and the excess foil is cut away from the outer edges of the pan with a sharp knife or scissors. This produces pans weighing approximately 0.25 grams each, replacing the commercial 1 gram weigh pans.

(2) Pipets: Positive displacement pipets, fixed volume 250 µL or adjustable volume 100-250 µL are recommended (Rainin Pipetman® or equivalent with a Teflon® plunger internal to the pipet). Disposable tips are used as received from the manufacturer, one per sample extract.

D.3.2 Sampling/Analysis Procedures

(1) Label aluminum foil pans by marking on the underside using a dull pencil or toothpick. Use caution to avoid piercing through the pan.

(2) There is no need to clean the pans with solvent as long as they are kept from contact with excess dust or moisture. Experience has shown that the homemade pans are quite free of organic contamination indicated by the analysis of many solvent and dust blanks.

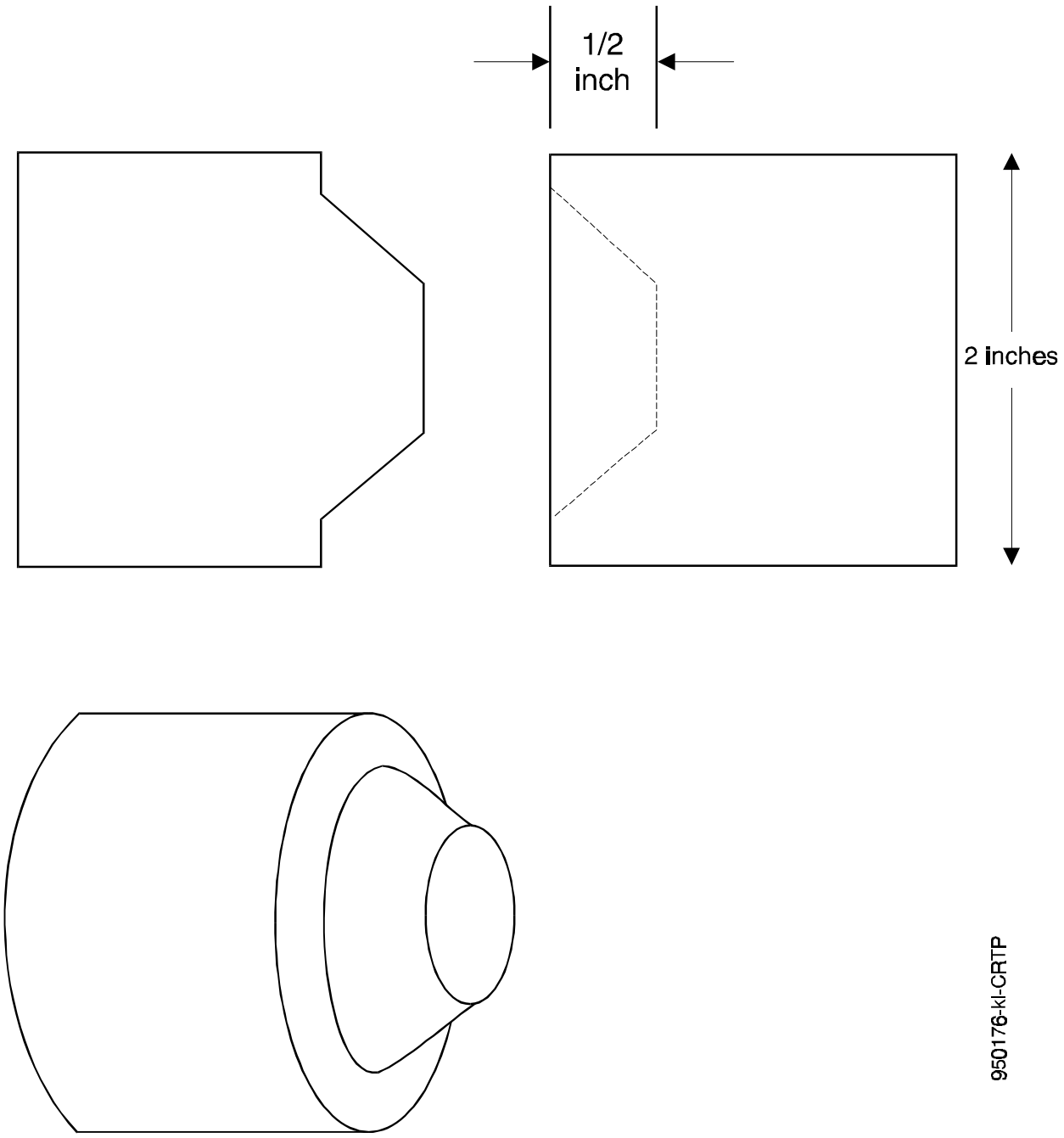

Figure D-1. Molding Jig for Construction of MicroGRAV Pans

(3) The pans are ready to use after molding and desiccating prior to tare weighing. No preheating or drying with an oven is necessary.

(4) Using a positive displacement disposable pipet, transfer a 0.250 mL aliquot of sample to the microGRAV pan. If necessary for a specialized application requiring larger aliquots, repeated transfers of 0.250 mL can be added to an individual pan, allowing the extract to air dry in the fume hood between transfers.

(5) All other procedures of microGRAV analysis are identical to the traditional GRAV techniques: carefully handle the pans with tweezers, air dry to visual dryness in a protective fume hood prior to desiccating, weigh the sample with a manual or digital microbalance, perform mass calculations, etc.

D.4.0 REFERENCES

1. Harris, J.C. et al. Laboratory Evaluation Level 1 Organic Analysis Procedure. EPA-600/S7-82-048, NTIS PB 82-239, pp. 30-36, March 1982.

2. Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. IERL Procedures Manual: Level 1 Environmental Assessment (Second Edition). EPA-600/7-78-201, NTIS PB 293-795, pp. 26-142, October 1978.

3. Assisting in the preparation of this supplement, dated 9/91 were Robert F. Martz and David F. Natschke of Acurex Environmental Corporation, Research Triangle Park, NC, under EPA contract 68-02-4701 in support of the multi-laboratory Boise and Roanoke Integrated Air Cancer Program. James Dorsey and Raymond Steiber of EPA were the technical directive managers for the EPA contract with Acurex Environmental. Judith S. Ford was the EPA QA Manager of record for the AEERL contract.

Appendix E

EPA Method 0040
Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar Bags

This method was proposed as part of the Third Update to the SW-846 Methods Manual in July of 1995. At the time of this writing (5/15/97), promulgation of the final version of the method is expected within weeks. Please contact MICE at 703-821-4690 (or e-mail to mice@lan828.ehsg.saic.com) for the most recent version of Method 0040.

Appendix F

EPA Method 0010

Modified Method 5 Sampling Train

This method was promulgated as part of the 3rd Edition of the SW-846 Methods Manual, for which the complete citation is:

> *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Manual, 3rd ed.* Document No. 955-001-000001. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC, November 1986.

The full document is available from U. S. Government Printing Office, telephone 202-783-3238, or on CD-ROM from National Technical Information Center at 703-487-4650 (or at http://www.ntis.gov).

For individual methods, or information about the methods, call MICE at 703 821-4690 (or e-mail to mice@lan828.ehsg.saic.com).

Appendix G

EPA Method 3542

Preparation of Modified Method 5 (SW-846, Method 0010)
Train Components for Analysis by SW-846 Method 8270

This method was proposed as part of the Third Update to the SW-846 Methods Manual in July of 1995. At the time of this writing (5/15/97), promulgation of the final version of the method is expected within weeks. Please contact MICE at 703-821-4690 (or e-mail to mice@lan828.ehsg.saic.com) for the most recent version of Method 3542.