

Evaluation of Total Organic Emissions Analysis Methods



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By

Raymond G. Merrill Eastern Research Group, Inc. 1600 Perimeter Park Drive Morrisville, NC 27560

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Project Officer: Jeffrey V. Ryan National Risk Management Research Laboratory Air Pollution Prevention and Control Division Air Pollution Technology Branch U.S. Environmental Protection Agency Research Triangle Park, NC 27711

> U.S. Environmental Protection Agency Office of Research and Development Washingtion, DC 20460

Abstract

The rationale and supporting experimental data for revising EPA's 1996 *Guidance for Total Organics* are summarized in this document, which reports both the results of research and the investigation of improvements to the Total Organic Emissions (TOE) guidance used by EPA to measure recoverable organic material from stationary source emission samples in support of the Office of Solid Waste Risk Burn requirements. This document describes the purpose, experimental design, and results from several related investigations into the performance of specific techniques to determine TOE. Results include analysis of recoverable organic material from three specific boiling point/vapor pressure classes: light hydrocarbons and volatile organics, semivolatile organics, and nonvolatile organics, and nonvolatile organic compounds. Improved procedures for analysis of volatile organics, semivolatile organics, and nonvolatile organics, and nonvolatile organics in TOE analysis procedures is discussed, and the effect of improvements to these measurement procedures is reported. The experimental results in this report support the sampling and analytical guidance necessary to characterize the full range of recoverable organic material encountered in source emissions.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Acting Director National Risk Management Research Laboratory

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Acronyms and Abbreviations

Term	Definition		
AEERL	EPA's former Air and Energy Engineering Research Laboratory		
BP	boiling point		
C ₇	<i>n</i> -heptane (straight chain hydrocarbon, saturated, 7 carbon atoms)		
C ₁₀	<i>n</i> -decane		
C ₁₂	<i>n</i> -dodecane		
C ₁₄	<i>n</i> -tetradecane		
C ₁₇	<i>n</i> -heptadecane (straight chain hydrocarbon, saturated, 17 carbon atoms)		
CH_4	methane		
DSCM	dry standard cubic meter		
EPA	U.S. Environmental Protection Agency		
FGC	field gas chromatography		
FID	flame ionization detector		
GC	gas chromatograph or gas chromatography		
GMW	gram molecular weight		
GRAV	gravimetric mass		
IDL	instrument detection limit		
Level 1	AEERL Procedures Manual: Level 1 Environmental Assessment		
MDL	minimum detection limit		
MS	mass spectrometry		
NERL	EPA's National Exposure Research Laboratory		
nonvolatile	compound class generally defined by boiling point above 300 °C		
ORD	EPA's Office of Research and Development		
ppmv	parts per million by volume		
OSW	EPA's Office of Solid Waste		
QC	quality control		
RCRA	Resource Conservation and Recovery Act		
ROP	recommended operating procedure		
RTP	Research Triangle Park		
SCOT	surface coated open tubular chromatographic column		
SVOCs	semivolatile organic compounds		
ТСО	total chromatographable organic compounds		
Tedlar	trade name for sampling bag material used in direct collection of air samples		
TOE	total organic emissions (combination of FGC, TCO, and GRAV mass)		
VOCs	volatile organic compounds		

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Section 1 Introduction

The EPA's Office of Solid Waste (OSW) has developed guidance¹ for conducting stack emissions tests in association with requirements for the permitting of hazardous waste combustion facilities. The guidance for conducting a risk burn requires a comprehensive characterization of organic and inorganic emissions, including the determination of total organic emissions (TOE). Stand alone guidance for determining TOE was previously released in 1996.² The TOE determination represents a gross measurement of the total volatile, semivolatile, and nonvolatile organic compounds emitted. The TOE are used to derive an organic mass balance to qualify the completeness and uncertainty of the associated risk assessment.

Peer and public reviews of OSW's Risk Burn Guidance for Hazardous Waste Combustion Facilities were critical of the TOE methodology, particularly with respect to the total chromatographable organic compound (TCO) and gravimetric mass (GRAV) measurement procedures used to characterize the semivolatile and nonvolatile organic fractions respectively. Significant concern was raised regarding the potential for high bias in the GRAV determination due to the presence of inorganic compounds in the TOE sample. Combined with the GRAV method's lack of measurement sensitivity relative to the nonvolatile, organic analyte-specific measurement methods, the GRAV portion may dominate the overall TOE measurement, resulting in a poor quantitative characterization of the identified compounds.

As a result of these comments and concerns, a series of experiments were conducted to investigate identified measurement issues and achieve procedural improvements in order to ultimately revise and update the TOE methodology. This document describes the purpose, experimental design and results from several related investigations into the performance of specific techniques to determine TOE.

The procedures described in this report measure and report TOE mass. These procedures are performed to permit comparison of the portion of organic emissions that have been characterized by "target analyte specific" methods to the total organic emissions from source sampling.

TOE procedures allow the total volatile and extractable organic mass from stationary source emissions to be quantified. The total recoverable organic mass reported as TOE is the result of combining data from three fractions of organic compounds: volatile organic compounds (VOCs), TCO for semivolatile organic compounds, and GRAV measurements for nonvolatile organic material. These three fractions are defined as follows:

- VOCs include organic compounds with boiling points less than 100 °C. These compounds are measured by two analytical techniques. Gas samples collected by EPA SW-846 Method 0040³ or equivalent are analyzed using a field gas chromatography (FGC). Volatile organic materials captured in the condensate of the EPA SW-846 Method 0040 train are analyzed using purge and trap gas chromatography/flame ionization detection (GC/FID);
- Semivolatile organic compounds (SVOCs) include organic material with boiling points between 100 and 300 °C. SVOCs are measured by TCO analysis performed by an

analytical laboratory using GC/FID and sample extract(s) from an EPA SW-846 Method 0010^4 sampling train; and

• Nonvolatile organic compounds (GRAV) with boiling point greater than 300 °C are measured as the residual mass of sample extract(s) from a Method 0010 sampling train.

The combination of two sampling and four analytical techniques gives the investigator the gross mass of all recoverable organic material. The total organic emissions are the sum of VOCs, TCO, and GRAV. A summary of these three techniques is shown in Figure 1.



Figure 1. Stationary Source Emissions Sampling and Analysis Techniques.

Section 2 Conclusions and Recommendations

Conclusions

Results of the research performed on synthetic and authentic environmental samples focused on issues ranging from the availability of calibration standards for field GC analysis to determining the cause for inorganic interference with the nonvolatile organic analysis.

Volatile organic compounds (BP<100 °C) present in samples collected in Tedlar bags according to the procedures in EPA SW-846 Method 0040³ require analysis in the field by GC/FID (FGC). The recovery of gaseous standard material containing methane, ethane, propane, n-butane, n-pentane, n-hexane, and n-heptane was confirmed. Polymer-based packed columns such as Alltech Haysep Q 80/100 mesh and surface coated open tubular (SCOT) gas chromatography columns such as J&W GS-Q or equivalent were found to provide adequate resolution and sensitivity for this analysis. The minimum detection limit (MDL) of FGC is limited by the amount of sample that can be introduced through the sample loop. The MDL that can be achieved by FGC is in the range of 0.6 ppm (1500 μ g/m³). For stationary source samples with volatile organic material present at or below 1 ppm, the FGC method is not sensitive enough to provide a reliable basis for volatile TOE unless samples are concentrated using alternative techniques. Where FGC shows results less than 1 ppm, independent laboratory analysis of the bag samples for methane should be performed followed by cryogenic preconcentration and analysis of C_2 - C_7 organic compounds. For volatile compounds collected in bags, uniform FID response for all compound classes is assumed in this methodology.

Determination of SVOC mass in samples collected by

EPA SW-846 Method 0010⁴ requires extraction and concentration of the various train components as described in EPA SW-846 Method 3542⁵ and subsequent analysis by GC/FID. Field samples collected in this way require additional preparation to remove polar volatile solvents (methanol or acetone), inorganic interferents, and water prior to concentration. Experimental results demonstrate that the performing the separatory funnel extraction of the XAD-2 and particulate filter Soxhlet extracts followed by 0.45 µm filtering was adequate to remove the field recovery solvents, inorganic interferents, and water. The separatory funnel extraction of the Soxhlet extracts represents a minor operational modification to the Method 3542 sample preparation approach but offers significant improvement in analytical results. Experimental results also showed that XAD-2 porous polymer resin used to collect SVOCs can be cleaned with an extraction procedure using water, methylene chloride, and methanol.

Nonvolatile organic material analysis is also performed for the Method 0010 train components. The same sample extract used to determine SVOCs is used to determine nonvolatile organic materials. Evaporation of a known volume of the Method 0010 organic extract has resulted in variable and artificially high results because of improper sample preparation and inorganic interferents retained during sample preparation. The experimental results from GRAV analysis of synthetic and authentic combustion particulate sample extracts showed that the separatory funnel extraction of the XAD-2 and particulate filter Soxhlet extracts followed by 0.45 µm filtering was adequate to remove more than 90% of the potential inorganic interferences to gravimetric determination of nonvolatile organic material in Method 0010 samples. Methanol solvent wash and methylene chloride extraction of solid particulate from municipal waste combustion fly ash and a cement kiln dust showed the presence of dissolved inorganic materials. The separatory funnel extraction of these Soxhlet extracts followed by 0.45 µm filtering was adequate to reduce the level of inorganic interference below detection limit for the GRAV measurement. As a result, the modifications to Method 3542 to include the separatory funnel extraction of the XAD-2 and particulate filter Soxhlet extracts followed by 0.45 µm filtering specifically for TCO and GRAV analysis will be included in the revised TOE guidance. Additional experimental results indicated the need for precautions to monitor and minimize airborne dust depositing in GRAV samples. GRAV mass of particulate extracts was so low in the two cases studied that deposition of room air dust could make a significant contribution to the total mass of GRAV samples. GRAV analysis samples must be covered using procedures described in the method so that airborne dust is minimized as an interference. Finally, GRAV analysis results indicated a need to perform analysis in duplicate and report the average result to achieve the required accuracy.

Recommendations

FGC procedures should be modified to require calibration with a gaseous hydrocarbon standard containing methane, ethane, *n*-propane, *n*-butane, *n*-pentane, *n*-hexane, and *n*-heptane. Concentrations of individual hydrocarbons and the total hydrocarbon balance should be calculated in units of μ g/m³. Total volatile organic material measured from Method 0040 bag samples at concentrations less than 1500 μ g/m³ are likely to be below detection limits, and samples should be concentrated for accurate comparison to speciated volatile compound analysis of the same stationary source emissions.

Packed column analysis should be performed with a minimum of 1 mL gaseous injection. SCOT column analysis should be performed at an injection volume that provides the optimum peak shape without split-

ting the methane elution profile (peak).

XAD-2 must be cleaned within 2 weeks of use or reevaluated for blank content requirements for TCO and GRAV. Preparation of XAD-2 requires cleaning to the minimum standards reported here which includes washing with water, extraction with methanol, and extraction with methylene chloride, described elsewhere in this report.

For TCO and GRAV analysis, Method 0010 samples must follow the modified Method 3542 preparation procedures. Method 3542 does not remove all of the potential inorganic interference in methylene chloride extracts of the mixture of inorganic salts studied in this evaluation. Following soxhelt extraction, the XAD-2 and particulate filter methylene chloride extracts should be extracted at least twice with adequate volumes of both high and low pH water followed by 0.45 μ m filtering to ensure complete removal of potential inorganic interferences in source samples. Either glass wool or cellulose fiber filters may be used in the final drying step prior to concentration of the extract.

The entire analysis window for TCO is established by injecting *n*-heptane (C_7) and *n*-heptadecane (C_{17}) as the retention time reference peaks between which the TCO integration will occur. The retention time window for TCO is established during calibration. The TCO range is defined by all peaks falling after C_7 (*n*-heptane) and before C_{17} (*n*-heptadecane). Integration of the detector response must begin after the C_7 returns to within 10% of baseline, and terminate when the beginning (front) of C_{17} is more than 10% of baseline.

GRAV analysis must be performed on a balance of at least 5 place accuracy (10 μ g detection limit). GRAV analysis must be performed in duplicate and reported as the average of the two measurements. Samples must be protected from deposition of room air dust to achieve the quality control (QC) limits shown in this report.

Section 3 Methods and Materials

Total Volatile Organic Emissions

Compounds with boiling points below 100 °C are sampled into Tedlar bags using EPA SW-846 Method 0040 sampling procedures and analyzed in the field by GC/FID. The GC/FID recommended operating procedure (ROP) for this method is found in *Guidance for Total Organics*.² The range of applicable compounds for total VOC determination includes methane, with a boiling point of -160 °C, to *n*-heptane, with a boiling point of 98 °C. The nominal reporting range for the methodology extends to 100 °C. Methane, ethane, and propane can be separated and reported individually. The FGC results are reported as a total.

Analysis Recommendations and QC Requirements

Calibration standards can be ordered at several concentrations or prepared by dilution of a certified

stock standard in Tedlar bags or pressurized cylinders. A dilution of a certified $C_1 - C_7$ standard gas mixture should also be prepared as a daily quality control calibration check sample. This QC sample should be prepared at a concentration approximately in the middle of the calibration range and should be analyzed at least once per day during stationary source field sampling. QC requirements for field GC analysis of volatile compounds are shown in Table 1.

A custom certified calibration gas standard purchased commercially that contained methane, ethane, *n*-propane, *n*-butane, *n*-pentane, *n*-hexane, and *n*heptane at approximately 100 ppm each in nitrogen was used for all work on FGC work reported here. The concentration of each hydrocarbon and of the total mixture was calculated in micrograms per cubic meter as described later in this section. The stock standard contained compounds shown in Table 2.

Table 1. Field GC Analysis Recommendations and QC Requirements.

Instrumental Parameter	Recommended Value
Injection Temperature	Ambient
Detector Temperature	220 °C
Initial Column Temperature	100 °C
Column Oven Temperature Program	100 °C to 190 °C at 15 °C/min
Final Column Oven Hold Parameters	Hold at 190 °C for 12 min
Packed Chromatographic Column Capable of $C_1 - C_7$ Normal Hydrocarbon Separation	HaysepQ 80/100 mesh, 2 m by 3.18 mm by 2.16 mm ID stainless steel (or equivalent) (Alltech)
SCOT Chromatographic Column Capable of $C_1 - C_7$ Normal Hydrocarbon Separation.	GS-Q, 30M by 0.53 mm ID fused silica J&W Scientific (or equivalent)
	continued

Analysis Recommendations

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Table 1. (concluded)

Quality Indicator	Performance Requirements
Peak Resolution	$R = 1.25^2$
Calibration Materials	Certified gas cylinder(s) containing methane, ethane, propane, butane, pentane, hexane, and heptane
Calibration Curve	 Three concentrations that bracket the sample analysis range. Correlation coefficient of 0.995 or greater Single calibration measurements should agree within 20% of the average calibration curve or a mean response factor.
Sensitivity	5 µg/dry standard cubic meter (DSCM)
Precision	$\pm 15\%$ relative standard deviation on replicate analysis.
Bias	±10% relative standard deviation on daily QC analyses. Fresh QC check samples are prepared if analysis fails QC check requirements. If subsequent analysis results also fail QC requirements, instrument is recalibrated.
Completeness	100% of the aliquots are reanalyzed if analysis calibra- tion check results do not meet quality specifications.
Retention Time	$\pm 5\%$ relative standard deviation from mean retention time for each calibration compound.

QC Requirements

Table 2. Calibration Standard Specifications.

Compound	Concentration (ppm)	Concentration (µg/m ³)
Methane	103	67,700
Ethane	105	129,000
<i>n</i> -Propane	104	188,000
<i>n</i> -Butane	105	250,000
<i>n</i> -Pentane	101	299,000
<i>n</i> -Hexane	101	357,000
<i>n</i> -Heptane	101	415,000
Total	720	1,706,000

The concentration of each hydrocarbon in parts per million was converted to micrograms per cubic meter using

$$C_{\mu g/m^3} = C_{ppm} \frac{GMW}{24.414} \times 1000$$
 (1)

where:

 $C_{\mu g/m^3}$ = concentration of each hydrocarbon expressed in micrograms per cubic

meter;

- C_{ppm} = concentration of each hydrocarbon expressed in parts per million;
- GMW = gram molecular weight of each hydrocarbon.

The following steps were applied to each component of the multi-component standard:

- 1. Determine the concentration of each component of the standard in parts per million.
- 2. Using the equation above, convert the concentration of each component to micrograms per cubic meter.
- 3. Sum the concentrations of each of the components in micrograms per cubic meter to obtain a total concentration, which can then be related to the sum of the chromatographic peak areas at each concentration level.

To determine total mass of the hydrocarbons for the calibration curve, the concentrations of each of the hydrocarbons (in micrograms per cubic meter) are summed, and total concentration (sum of the concentration of each component of the standard) is plotted vs. area counts. Calibration values for individual hydrocarbons and the sum of the entire group were determined using linear regression and average response calculations.

A Varian Model 3400 gas chromatograph equipped with a HaysepQ 80/100 mesh, packed chromatographic column measuring 2 m by 3.18 mm by 2.16 mm ID stainless steel and a FID was configured to perform VOC analysis. Gas was introduced into the injection port of the gas chromatograph using a 1 mL stainless steel gas sampling loop. A SCOT column coated with Porapak QS was also evaluated for FGC analysis. An example of column(s), conditions, and QC requirements is shown in Table 1. The chromatographic column(s) used in the field GC must be capable of resolving the $C_1 - C_7$ hydrocarbons at baseline level. A multipoint calibration consisting of at least three points (analyzed in triplicate) at different concentrations was prepared.

Sample Analysis

After calibration of the field GC, sample analysis begins when the sample container (the Tedlar bag) is connected to the sampling valve and the sample gas is drawn through the valve and into the GC sample loop or a gas-tight syringe. The sample is injected into the chromatograph. The temperature program and integrator/data system data acquisition are started simultaneously with the injection of the sample. Chromatograms and integrator/data system output are collected.

The sample is analyzed twice (i.e., duplicate injections) and integrated from a retention time of zero to the end of the C_7 peak. The total concentration in micrograms per cubic meter is calculated from the summed integrated area of the standard peaks from zero through the end of C_7 to yield the value for the gaseous portion of the TOE analysis for each injection.

The simple arithmetic mean of the duplicate injections is reported as the bag portion of the FGC results.

XAD-2 Cleaning Methods

XAD-2 is a macroreticulate porous polymer made from styrene (vinylbenzene) and divinylbenzene. The emulsion block copolymerization process used to form cross-links in the resin gives the resin a pore structure and chemical stability ideally suited for sampling and recovery of SVOCs from the Method 0010 sampling train. The polymer synthesis process also exposes the raw resin to high concentrations of naphthalene, styrene (vinylbenzene), divinylbenzene and low molecular weight byproducts of these reagents and the polymerization reaction. If these components are not removed during XAD-2 cleaning, they will be extracted as part of the sample preparation procedures and will provide a positive bias to the TCO results. It is essential that XAD-2 be clean and free from contaminants that could contribute a positive bias to the TCO and GRAV determination.

Preparation of XAD-2 within 2 weeks of sampling or experimental work provides sufficient time for the cleaning and drying process and avoids extended storage, which may result in contamination and elevated levels of extractable material in blanks. The cleaning method described below has proven to be a cost-effective and high quality procedure for preparing XAD-2.

The procedure for cleaning XAD-2 is derived from the Procedures Manual: Level 1 Environmental Assessment (Second Edition)⁶ developed by the U.S. EPA. The original methodology has been improved to provide a reproducible method for preparing sorbent material sufficiently clean for low level organic compound capture and analysis. The complete cleaning cycle requires approximately 5 working days to finish. Typical background or blank total organic concentrations (TCO) from XAD-2 prepared by this procedure are on the order of $1 \mu g$ per gram of sorbent medium. Typical GRAV background after cleaning by this procedure is on the order of $6 \mu g$ per gram of sorbent medium. The cleaning procedure used to obtain these results includes the following steps:

- Resin is obtained from the manufacturer, supplier or recycled from prior use. Resin cleaned by a secondary vendor should be treated like recycled resin. Recycled and recleaned resin usually contains less organic contamination and is preferred over raw material straight from the manufacturer. Naphthalene is the most common contaminant in sorbent that has not been properly cleaned.
- The resin is soaked and washed several times

with deionized water if new from the manufacturer. Resin "fines" float to the surface of the water wash and are removed by skimming the surface with a fine screen or dipping the fines out with a glass beaker before the next cleaning step.

- The water-washed or recycled resin is loaded directly into the extractor for solvent cleaning. The entire cleaning procedure is done "wet" with final drying taking place only at the end of the process.
- Distillation type extractors, each capable of • holding 900 g of resin, are typically used to extract the resin with sequential extractions of methanol, methylene chloride, and methylene chloride again. An extraction apparatus following the design in Appendix B of the Procedures Manual: Level 1 Environmental Assessment (Second Edition)⁶ and shown in Figure 2 is efficient and effective for XAD-2 cleaning. Solvent sufficient to completely fill the extraction chamber and at least 30% of the solvent reservoir is required for the extraction. Fresh solvent is used for each step of the extraction. Solvent is drained between steps, and the extractor is pre-rinsed with the solvent to be used in the next step.
- After the final extraction, the methylene chloride is drained and the extractor body is removed to a hood where the resin is dried. Drying is accomplished by a gentle stream of nitrogen. The nitrogen is delivered from the gas output of a liquid nitrogen tank through a heat exchanger to the sorbent to remove methylene chloride residue from the final extraction step. Residual methylene chloride is reduced to 1000 µg/g of resin.
- The dried resin is transferred to a clean, dry glass jar with a Teflon or equivalent lined screw cap lid. For blank QC purposes, a portion of the dried sorbent equal to a typical field sample (usually 40 g) is extracted, prepared and analyzed by the method used for field samples.
- If the analysis of the clean XAD-2 meets method acceptance criteria, it is labeled with



Figure 2. Schematic of Solid Sorbent Extractor.

a laboratory identification number and stored at room temperature in a clean, solvent-free cabinet for use in sampling. The clean resin is stable and can be stored for 2 to 3 weeks. Longer storage times are possible if the material is refrigerated, but a blank sample must be checked before material stored for longer than 3 weeks is used for field sampling.

Method 0010 Sample Recovery and Preparation

Stationary source samples for application of this analysis method are taken by SW- 846 Method 0010⁴ and prepared by SW-846 Method 3542⁵ (as modified for TCO and GRAV analysis). A flow chart for preparation of SW-846 Method 0010 samples using modified SW-846 Method 3542 is shown in Figure 3. The Method 0010 sampling train generates three sample fractions from various train components that must be carefully recovered and prepared to ensure results that meet the quality requirements for TCO and GRAV analysis. Solvents used to rinse sampling train glassware may dissolve inorganic material and

water. The inorganic material is carried through the sample preparation process with the water and polar solvents and remains in the concentrated extracts unless steps are taken to remove the water and polar solvents. The interferents must be removed during the sample extraction and preparation steps before the organic extract is concentrated for final analysis. Several minor modifications were made to Method 3542 to ensure that water soluble (polar) solvents and inorganic material are removed from the samples prior to TOE analysis. At the end of the preparation procedures, extracts may be combined and concentrated to a final volume of 5 mL, producing one extract per Method 0010 sampling train for the TOE analysis. Alternatively, each of the three sample extracts may be analyzed for TOE separately.

Total Chromatographable Organics

TCO analysis is used to measure the total organic mass of compounds boiling between 100 and 300 °C. The TCO Method is described in detail in *Guidance for Total Organic*.² The TCO procedure consists of analysis of the combined concentrated probe wash,



Figure 3. Modified Method 3452 Sample Preparation Scheme for Method 0010 Components Analyzed for TCO and GRAV.

filter, XAD-2, and impinger extracts from the three major components of the sampling train. The analysis is generally performed in the laboratory after extraction, compositing, filtration, and concentration of the extracts of the individual components of the Method 0010 sampling train.

Capillary chromatography is used to obtain the best possible resolution of chromatographic peaks. For stationary source emission gas samples, an aliquot of the Method 0010 methylene chloride 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 and *n*-heptadecane as the retention time reference peaks between which the TCO integration will occur. The retention time window for TCO is established during calibration. The TCO range is defined by all peaks falling after C_7 and before C₁₇. Integration of the detector response begins after the C_7 peak returns to within 10% of baseline and terminates when the beginning (front) of the C_{17} peak is more than 10% of baseline.

The TCO calibration standard curve is generated with hydrocarbon standards that fall within the TCO range, specifically *n*-decane (C_{10}), *n*-dodecane (C_{12}), and *n*-tetradecane (C_{14}). Calibration is performed using a solution of standards prepared from neat liquid standards of the individual hydrocarbons in methylene chloride. The quantitative calibration standards should be prepared to cover the concentration range expected in the source samples. A multipoint calibration of at least three points (in triplicate) is generated in units of micrograms per milliliter. The calibration curve for TCO is calculated using linear regression statistics. The total detector response for the TCO range reported as one number is used in the linear regression calculation. The C7 and C17 detector response is not included for the calibration point determination. After calibration has been performed, a daily QC check sample is run to verify that the GC is performing correctly. The QC check sample consists of a standard in the middle of the working range of the GC calibration standards.

Nonvolatile (GRAV) Organics

The third component of the total organics measurement process is called gravimetric mass (GRAV). The GRAV method has also been described in detail in *Guidance for Total Organics*.² Extractable organic materials with nominal boiling points of 300 °C and higher are determined by this procedure. Samples extracted from sampling media using methylene chloride and dried to constant weight are determined quantitatively by this procedure. GRAV analysis measures organic compounds with vapor pressures less than or equal to *n*-heptadecane (C₁₇). The range of organics is defined by boiling point, in this case greater than 300 °C.

For stationary source emission gas samples, the GRAV procedure is carried out on an aliquot of the same Method 0010 methylene chloride extract used for TCO determinations. GRAV analysis is performed using samples prepared using the modified SW-846 Method 3542 procedures to remove both inorganic interferents and water from the sampling train recovery process. The analysis is generally performed in the laboratory after extraction, compositing, filtering, and concentrating the extracts of the individual components of the Method 0010 sampling train.

The GRAV method quantifies organic material with a boiling point greater than 300 °C. A carefully measured aliquot of the Method 0010 methylene chloride extract is placed in a cleaned, dry, preweighed aluminum weighing pan. The solvent is allowed to evaporate in a fume hood at room temperature. Exposure to dust and contaminants is minimized by covering the samples with an aluminum tent or placing them under some form of clean cover. The GRAV samples are then dried completely to constant weight in a room temperature desiccator. The residue in the pan is weighed accurately, and the mass is recorded as the GRAV value. For this procedure, a portion of the pooled extracts from the Method 0010 sampling train used for TCO are also used for GRAV. A volume of 1 mL of the pooled extract is used for each of the GRAV determinations. Duplicate GRAV analyses are performed, and the results are averaged.

GRAV organics with BP greater than 300 °C are measured on an analytical balance capable of weighing accurately to ± 0.005 mg (5 µg). The GRAV value, in micrograms, is converted to units of

micrograms per sample by multiplying the average pan results for the sample by the ratio of total extract volume to GRAV aliquot volume. Final GRAV results are reported in micrograms per cubic meter by dividing micrograms per sample by the Method 0010 sample volume (expressed as cubic meters).

Section 4 Experimental Procedures

Measurement of Volatile Organic Emissions

The Volatile Organic Emissions portion of the Total Organic Emissions measurement is determined in two parts:

- First, a field GC analysis of the gaseous portion of the Method 0040³ sample is conducted using sample collected in a Tedlar bag. The range of organic material identified by field GC is defined by the boiling point range less than 100 °C. The procedure is normally performed in the field to minimize sample (compound) loss due to storage and shipping.
- Second, the aqueous portion of the sample (condensate from the Method 0040 sampling train) is analyzed in the laboratory using purge and trap GC with a FID. This aqueous portion, which is actually the condensate from Method 0040 sample, is normally transferred to a vial with no headspace for shipment to the laboratory.

Field GC analysis is limited by a detection limit of 1 - 10 parts per million by volume (ppmv), equivalent to $2000 - 20,000 \ \mu g/m^3$. Identification of methane, ethane, and propane is possible although specific compound identification is not required for the TOE determination. These compounds may be present in significant quantities in stack samples, and correct identification and quantification will more accurately characterize the organic emissions.

Once both portions have been quantified, they are added together to yield the volatile organic emissions contribution to the TOE.

Evaluation Experiments

A series of laboratory experiments was completed to determine the quality parameters and detection limits for the FGC method. The goal of the FGC evaluation experiments was to confirm that calibration standards that include *n*-heptane could be prepared and analyzed using the FGC analytical procedure. A second goal of the FGC evaluation was determination of detection limits for samples collected in Tedlar bags. Previous FGC experiments were performed with nhexane as the latest-eluting compound in the calibration gas. Prior to these evaluation experiments, the volatile organic material in the boiling point range between n-hexane and n-heptane was erroneously not included in the FGC results. (Note that the TCO determination begins after elution of the C₇ peak, whereas the FGC determination includes the C_7 peak).

The experimental work included evaluation of a commercially prepared standard containing normal hydrocarbons from methane to *n*-heptane and a detection limit study for the method.

Experiments were performed to:

- Confirm that *n*-heptane could be included in the calibration mixture;
- Determine the response factor for individual calibration compounds and the average response factor for the C₁ C₇ calibration mixture; and
- Evaluate both a polymer based packed gas chromatographic column and a SCOT column for FGC analysis.

FGC Calibration Performance

The stock standard was diluted into reusable 1.5-L

high pressure aluminum cylinders. The concentrations of all hydrocarbons in calibration standards were 74,500 μ g/m³ (31 ppm); 117,000 μ g/m³ (51 ppm); 337,000 μ g/m³ (148 ppm); 845,000 μ g/m³ (371 ppm); and 1,706,000 μ g/m³ (720 ppm). The FGC was calibrated by injecting each of these calibration samples into the gas chromatograph three times. A linear regression was performed on the resulting peak area versus concentration data. Calibration response factors in units of area per concen-

tration were determined from the linear regression statistics of the calibration sample analysis results. Gas chromatographic conditions used to generate calibration response factors and detection limits are shown in Table 3. Response factors for individual hydrocarbons and the total VOC response factor are shown in Table 4. An example packed column chromatogram showing peak shape, resolution, and retention times is presented in Figure 4.

Table 3. FGC Chromatographic Conditions.

FGC Instrument Parameter	Instrument Set Point
Injector Temperature	Ambient
Initial Column Temperature	100 °C
Column Oven Temperature Program	100 °C to 190 °C at 15 °C/min
Final Column Oven Hold Parameters	Hold at 190 °C for 12 min
Column Carrier Gas Flow	Approximately 30 mL/min
FID Detector Temperature	220 °C

Table 4. Calibration Response Factors.

Compound	Response Factor ^a	Linear Regression Correlation Coefficient (r ²)
Methane	5.0575	0.9987
Ethane	5.611	0.99995
Propane	5.6159	0.99995
<i>n</i> -Butane	5.7466	0.99996
<i>n</i> -Pentane	5.6923	0.99993
<i>n</i> -Hexane	5.749	0.99993
<i>n</i> -Heptane	5.6889	0.99998
Average	5.6783	0.99957

^a Varian GC/FID Model 3400



Figure 4. Packed Column FGC Calibration Chromatogram.

Other choices of polymer-based column packing may give satisfactory results but should be evaluated before use. Most polymer-based columns capable of separating methane, ethane, and propane suffer from breakdown and bleed at the temperatures needed to elute *n*-heptane.

Instrument Detection Limit Study

The lowest calibration standard concentration (i.e., 74,500 μ g/m³, or 31 ppm) was used to determine an approximate instrument detection limit for this method under the operating conditions described in Table 3. The detection limit for individual compounds C_1 through C_7 was calculated using the approach in EPA 40 CFR 136, Appendix B. Results of the instrument detection limit (IDL) for individual components and for the sum of the compounds in the calibration standard are shown in Table 5. The approximate instrument detection limit was determined for each of the calibration components and for the sum of the components because the detection limit will vary depending on the composition of the sample. The lowest calibration point was not within 2 to 5 times the estimated detection limit as specified by 40 CFR Part 136, Appendix B. Precision for fixed loop injections was very high resulting in a minimum detection limit range (on a per compound basis) of 100 to 200 μ g/m³. FGC instrument detection limits can be as high as 1400 μ g/m³ (0.6 ppm) for the sum of the calibration standard components due to the chromatographic data system imprecision integrating the broad peaks for C₆ and C₇ hydrocarbons.

Table 5. FGC Detection Limits.

Compound	IDL (µg/m ³)	Std. Deviation
Methane	106	33.8
Ethane	106	33.9
<i>n</i> -Propane	167	53.4
<i>n</i> -Butane	219	69.8
<i>n</i> -Pentane	270	86.1
<i>n</i> -Hexane	460	147
<i>n</i> -Heptane	1112	353
Total	1440	459

Procedures to Evaluate XAD-2 Preparation and Blanking

Prior to sampling, the sampling train and sampling media must be prepared, cleaned and blanked. Although some forms of "precleaned" resin are commercially available, all XAD-2 used for TCO and GRAV analysis must be analyzed before use to ensure the extractable background of semivolatile and nonvolatile organic materials meets the appropriate quality requirements. Many unexpectedly high TCO and GRAV field sample results originate from poor preparation and cleaning of sampling train or XAD-2 sampling media. The experimental procedures provided in this section demonstrate that XAD-2 can be cleaned to meet quality control requirements for TCO and GRAV analysis.

Experiments were performed to evaluate the ability to clean XAD-2 to acceptable levels for use as a solid sorbent for TOE measurements and to establish the quality control requirements for properly cleaned XAD-2 sampling media. The cleaning requirements, including acceptable blank levels for TCO and GRAV determination, are included in this section. Untreated XAD-2 is available from the manufacturer, Supelco, Inc.; precleaned XAD-2 is available from various commercial vendors. All XAD-2 used for TCO and GRAV analysis, recleaned just prior to use or not, must be checked for TCO and GRAV blank levels. The quality control check for XAD-2 cleanliness requires extracting a portion of the sorbent approximately equal to the quantity that will be used to collect samples (typically 20 to 40 g). If TCO and GRAV blank levels do not meet the method quality control requirements, the XAD-2 should be recleaned. XAD-2 should be prepared within 2 weeks of the sampling episode and can be stored at room temperature in a clean glass bottle closed by a Teflon lined cap. Refrigerated storage is acceptable and may retard increases in blank contamination.

In the experimental work described here, TCO analysis was performed on portions of XAD-2 sorbent media cleaned according to the procedures described in Section 3. XAD-2 sorbent was then checked for residual TCO and GRAV. Two lots of

approximately 1000 g of XAD-2 were cleaned. One lot of XAD-2 was untreated (raw) resin directly from the manufacturer. A second lot was prepared using recycled XAD-2 that had been cleaned and stored dry in a clean glass jar with Teflon lined screw cap for over 6 months. Each lot of XAD-2 was extracted and dried as it would be for a source sampling episode.

Two (2) 40-g portions of XAD-2 from each lot were extracted with pesticide grade methylene chloride in a Soxhlet extractor to determine the residual TCO and GRAV in the cleaned resin. TCO and GRAV were determined for both lots of XAD-2. Blank aliquots were concentrated using a 3-ball Snyder column. Final concentrates were never taken below 3.0 mL. Final sample volume used for TCO and GRAV analysis was 5 mL. The TCO and GRAV analysis results from these two lots of XAD-2 are shown in Table 6.

Table 6. XAD-2 Blank Results.

	ТСО	GRAV
LotDescription	(µg/g)	(µg/g)
New XAD-2	0.975	5.94
New XAD-2 (Duplicate)	NA ^a	5.62
Used XAD-2	0.985	6.56
Used XAD-2 (Duplicate)	NA	NA

 $^{a}NA = not available.$

A second issue associated with residual organic material in clean XAD-2 involves the effect of preparing XAD-2 extracts using EPA SW-846 Method 3542⁵ separatory funnel extraction procedures. The question investigated was whether preparing methylene chloride extracts using Method 3542 increases, decreases, or has no effect on the background organic material in the clean resin. Therefore, two sets of XAD-2 blank extracts were prepared. The first set was extracted with methylene chloride and dried by filtration through anhydrous sodium sulfate. The second set of extracts was processed through SW-846 Method 3542 separatory funnel extraction procedures. The results of these experiments are shown in Table 7. The practical detection limit for GRAV is 6.6 µg/gram XAD-2 based on a balance

Table 7. XAD-2 GRAV Blanks.

Sample Description	mg/mL ^a	mg GRAV/ 40 g XAD-2	µg GRAV/ gm XAD-2	Average μg GRAV/ gm XAD-2
Recycled XAD, Rep 1 without Method 3542 preparation	0.090	0.45	11.	6.6
Recycled XAD, Rep 2 without Method 3542 preparation	0.015	0.08	2.0	0.0
New XAD, Rep1 without Method 3542 preparation	0.025	0.12	3.0	5.0
New XAD, Rep2 without Method 3542 preparation	0.070	0.35	8.8	5.9
Recycled XAD, after Method 3542 Preparation Rep 1	0.045	0.22	5.5	
Recycled XAD, after Method 3542 Preparation, Rep 2	0.005	0.02	0.5	2.4
Recycled XAD, after Method 3542 Preparation, Rep 3	0.010	0.05	1.2	
New XAD, after Method 3542 Preparation, Rep 1	0.015	0.08	2.0	
New XAD, after Method 3542 Preparation, Rep 2	0.025	0.12	3.0	2.7
New XAD, after Method 3542 Preparation, Rep 3	0.025	0.12	3.0	

^a milligrams GRAV per milliliter extract. Extracts were taken to a final volume of 5 mL; 1-mL aliquot used to perform GRAV determination.

sensitivity of 10 μ g. Results in Table 7 have been reported using 0.01 mg as the lower limit of weight for a 10 μ balance. Using Method 3542 provides an added step that reduces the blank GRAV component of the XAD-2 sorbent material and is more representative of the blank contribution to SW-846 Method 0010 samples prepared using SW-846 Method 3542.

Procedures for Evaluating the Artifacts and Interferences with GRAV Analysis

Artifacts and interferences in GRAV measurements have been reported by several investigators,⁷ production of GRAV artifacts from inorganic carryover during sample preparation is one of the most commonly reported concerns. Common interferents include

- Fine particles, which may be collected during sampling of stationary source emissions or may be due to XAD-2 fragments;
- Methanol, collected during sampling or a residual of the solvents used in the field to rinse the sampling train components;
- Water, used in the sampling train or collected during sampling because of the moisture content of the stationary source; and

• Inorganic salts collected during sampling.

These materials must be removed from sample extracts prior to sample concentration and TCO and GRAV analysis. Improper filtering of the sample extracts can result in GRAV analyses biased high. Inadequate removal of methanol and/or water results in loss of TCO material. Inadequate removal of methanol and/or water also causes a positive bias in GRAV results due to carryover of inorganic salts. Inorganic salts can also be extracted from filter samples by methylene chloride. Inorganic salts must be removed from the sampling train extracts prior to concentration to avoid a positive bias in GRAV.

Methanol and water must also be removed from the organic extracts of the Method 0010 samples prior to any concentration step so that the only solvent present during evaporative concentration is methylene chloride (BP 49 °C). The presence of water and/or methanol in the final extract will result in a higher boiling solvent during the sample concentration step. This higher boiling mixture will cause a loss of semivolatile organic material in the TCO boiling point range.

Experiments were designed to investigate these issues as well as to determine if modifications to EPA SW-846 Method 3542 would mitigate the commonly reported interferences to the TCO and GRAV analyses.

Authentic fly ash samples from a municipal waste incinerator and from a cement kiln were used to represent a typical field sample. Environmental fly ash and cement kiln dust were extracted both individually and in a 50:50 mixture. Mixtures of 10 inorganic salts as shown in Table 8 were also prepared by weighing equal portions of each salt into a high density linear polyethylene container and mixing together thoroughly. Experimental work was performed using recovery solvents specified in EPA SW-846 Method 0010 and extraction solvents specified in EPA Method 3542. The solid fly ash and synthetic inorganic mixture were extracted separately with several solvents typical of source sample recovery to determine whether inorganic interference occurred in standard sample preparation procedures and whether separatory funnel extraction followed by 0.45 µm filtering mitigated those interferences.

Table 8. Inorganic Salts Mixture Used for GRAVInterferents Analysis.

Aluminum Chloride Calcium Chloride Calcium Chloride Dihydrate Calcium Sulfate Hemihydrate Calcium Sulfate Dihydrate Calcium Sulfate Dihydrate Ferric Chloride Iron(II) Sulfate Heptahydrate Lead (II) Chloride Potassium Chloride Potassium Sulfate Sodium Nitrate Zinc Chloride Zinc Sulfate

Fine Particulate Filtration Evaluation

Cement kiln dust was extracted with methylene chloride for 16 hours in a Soxhlet extractor. Two

procedures were performed on the sample extract. First, the sample was filtered through 1 g of anhydrous sodium sulfate supported by a glass wool plug as specified in EPA Method 3542. The resulting liquid filtrate was concentrated to 5 mL and analyzed for nonvolatile mass using the GRAV technique. In a second procedure the glass wool plug was replaced by a cellulose filter that was folded and placed into the glass filtration funnel. One gram of anhydrous sodium sulfate was added to the filter paper in the funnel, and the sample extract was filtered through this apparatus. The results of glass wool plug versus cellulose filter filtration, shown in Table 9, indicate there is no difference between the two approaches to remove fine particulate from methylene chloride particulate extracts.

Table 9. Filtration Simulation, Glass Wool versusCellulose Filtration.

Sample Description ^a	Glass Wool µg/gram par- ticulate	Cellulose Filter µg/gram par- ticulate	
Sample 1	120	120	
Sample 2	185	210	

^a Cement kiln dust methylene chloride extract

Filter Extract Inorganic Interference Evaluation

Methylene chloride was used to extract particulate material and a mixture of inorganic salts to test whether samples prepared using SW-846 Method 0010 contained materials that interfere with the GRAV methodology. Potential interferents include the presence of dissolved solids or fine particulates. The purpose of extracting real and synthetic particulate material was to determine whether inorganic salts could be extracted with methylene chloride and produce an interference or artifact in the GRAV analysis procedure.

The inorganic salt mixture was extracted in a Soxhlet extractor using 100% methylene chloride for 16 hours. The mixture of inorganic salts was extracted in

duplicate. Methylene chloride extraction was followed by drying with anhydrous sodium sulfate, filtration through cellulose filter media, and Kuderna Danish concentration to 5 mL. Replicate GRAV analysis was performed on each 5-mL extract. The results of these analyses are shown in Table 10, where GRAV results as high as 1900 μ g/gram of salt mixture are observed. A separate set of extracts of the inorganic salt mixture was also prepared. Water was added to this second set of methylene chloride extracts and extracted using the separatory funnel liquid/liquid extraction procedures described in SW-846 Method 3542. These extracts were prepared following Method 3542, dried by filtration through anhydrous sodium sulfate, filtered using a 0.45 µm Teflon syringe filter, and concentrated to 5 mL. Treatment of these samples using the EPA Method 3542 separatory funnel liquid/liquid extraction and 0.45 µm filtering resulted in a significant decrease of the inorganic interferences. The results of the salt mixture extraction and Method 3542 preparation are shown in Table 10. Results from the extraction of the salt mixture show that interference with the GRAV analysis is possible if inorganic salts are present in source emission samples and that separatory funnel liquid/liquid extraction and 0.45 µm filtering removes most of the dissolved inorganic interference.

Table 10. Filter Extraction Simulation, Methylene Chloride Extracts.

Sample Description	GRAV in Extract μg/gm solid	GRAV in Ex- tract after Method-3542 Cleanup
Salts Mixture	1962	309
Salts Soxhlet Duplicate	1650	368
Cement Kiln Dust	110	175
Cement Kiln Dust, Duplicate	215	220
Municipal Waste Fly Ash (Extract 1)	190	200

A similar treatment of fly ash and cement kiln dust (Table 10) indicates that organic GRAV material is present on the real fly ash and is not affected by the separatory funnel liquid/liquid extraction and 0.45 μ m filtering cleanup.

Probe Wash Inorganic Interference Evaluation

To evaluate the potential inorganic interference from Method 0010 probe washes, the mixture of inorganic salts was added to a solution of methylene chloride saturated with methanol. The mixture contained 20% methanol in methylene chloride. Five (5) grams of salt mixture were added to the methanol/methylene chloride solvent, thoroughly mixed and allowed to stand for 30 minutes. The same treatment was performed on a mixture of cement kiln dust (2.5 g) and municipal waste combustor fly ash (2.5 g).

Soluble salts and organic material were recovered by filtering the supernatant liquid from these extracts. GRAV analysis was performed on the soluble fraction. The results are shown in Table 11. Samples were further processed using SW-846 Method 3542 separatory funnel liquid/liquid extraction and 0.45 µm filtering. The results of the GRAV analysis of the Method 3542 preparations are also shown in Table 11. The GRAV results from methanol/methylene chloride extracts of cement kiln dust and municipal waste combustor fly ash were approximately 50 times higher in mass than the comparable methylene chloride sample extracts. Greater than 90% of the potential interference was removed by processing the samples with the separatory funnel liquid/liquid extraction and 0.45 µm filtering.

Table 11. Probe Rinse Simulation, Meth-
anol/Methylene Chloride Extracts.

Sample Description	GRAV in Extract µg/gm solid	GRAV in Ex- tract after Method 3542 Cleanup
Mixed Salts	584,400	2016
50/50 Mixed MWC Ash/Cement Kiln Dust	10,900	100

Section 5 Quality Control Procedures

QC results for TOE measurements are summarized in this section.

QC for Volatile Organic Analysis by FGC

QC for FGC analysis is performed during calibration and daily QC check sample analysis. QA/QC requirements for FGC method evaluation are shown in Table 12.

XAD-2 QA/QC

Analytical interferences or contaminants appear in the resin after storage. These contaminants may cause the cleaned resin to fail the QC requirements for the method used in sample analysis. Contaminants originate from both external contamination or oxidation and from internal "bleeding" of entrained chemicals from very small or inaccessible pores in the resin. Subsequent recleaning and reuse reduces the internal contributions to blank during storage. Consequently, cleaned XAD-2 has a usable shelf life of 1 month after cleaning unless the sorbent is refrigerated.

Contaminant levels may also increase if XAD-2 is exposed to high concentrations of oxidizing agents such as ozone or oxides of nitrogen during sampling. In an oxidizing environment, oxidation or decomposition products of XAD-2 such as naphthalene, benzoic acid, benzaldehyde, aromatic esters, carboxylic acids, and aldehydes will be observed. Sufficiently high levels of NO_x (mole percent levels) can cause destruction of the resin itself.

Cleaned XAD-2 resin was checked for blank contamination by extracting a quantity of resin equivalent to the amount to be used during sampling (typically 40 g). The resin was prepared and analyzed using the

Quality Indicator	Requirements
Peak Resolution (R)	$R = 1.25^2$.
Calibration Materials	Certified gas cylinder(s) containing methane, ethane, propane, butane, pentane, hexane, and heptane.
Calibration Curve	Three concentrations that bracket the sample analysis range. Correlation coefficient of 0.995. Single calibration measurements should agree within 20% of the average calibration curve or a mean response factor.
Sensitivity	1500 μg/dry standard cubic meter (DSCM).
Precision	$\pm 15\%$ relative standard deviation on replicate analysis.
Bias	$\pm 10\%$ relative standard deviation on daily QC analyses. Fresh QC check samples are prepared if analysis fails QC check requirements. If subsequent analysis results also fail QC requirements, instrument is recalibrated.

Table 12. Field GC Analysis QC Requirements.

same volumes of solvent and preparation procedures that are used for field samples following the procedures in EPA SW-846 Method 3542 for Method 0010 samples. Extracts were analyzed for TCO and GRAV and must meet the QC criteria in Table 13 in order for the XAD-2 to be acceptable for sampling. If the extracted resin fails to meet the acceptance criteria, the resin should be recleaned by sequential Soxhlet extractions (once each) with methanol and methylene chloride. A sample of resin failing after a recleaning should be discarded, and no further attempts made to clean that batch.

Table 13. QC Guidelines for XAD-2 ResinPreparation.

Analysis	Maximum Blank (per gram of Resin)	XAD-2 (used in this evaluation)
ТСО	1 μg/g resin	0.98 µg/g resin
GRAV	10 µg/g resin	5.9 to 6.4 μ/g

QC for Total Chromatographable Organics

Quality control for TCO analysis by GC/FID is performed during calibration and daily QC check

sample analysis. QA/QC requirements and performance experienced during TCO method evaluation are shown in Table 14. All QA/QC for TCO analysis is performed external to field sample analysis.

QC Requirements for GRAV

The predominant interferences for GRAV are incomplete cleaning of XAD-2, airborne dust deposited during weighing procedures, and inadequate control of environmental conditions in weighing facilities. Blank weighing pans without solvent or sample were carried through the evaporation and drying process as a quality control check for each set of samples. Sample weights were not corrected for blank weighing pan mass gain. Solvent blank samples consisting of concentrated reagent solvent should be analyzed in duplicate for each batch of samples. GRAV results were not corrected for solvent blanks. Therefore, the GRAV results represent a worst case for possible blank contamination.

The QC requirements for GRAV include calibration of the analytical balance, use of Class A volumetric glassware, duplicate analysis of each sample, and weighing samples to constant weight $\pm 10 \mu g$. QC requirements for GRAV analysis of volatile compounds are shown in Table 15. Performance targets

	Table 14. (QC Requirements	for Total	Chromatographable	Organics.
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Quality Indicator	Requirements
Compound Resolution	separation (α) = 1.25.
Calibration Curve	Three concentrations that bracket the sample analysis range. Correlation coefficient of 0.995. No single calibration point deviation more than 20% from the average calibration curve.
Sensitivity	5 μg/mL in solution.
Precision	$\pm 15\%$ relative standard deviation on replicate analysis.
Bias	$\pm 10\%$ relative standard deviation on daily QC analyses. Fresh QC check samples are prepared if analysis fails QC check requirements. If subsequent analysis results also fail QC requirements, instrument is recalibrated.
Completeness	100% of the aliquots are reanalyzed if analysis calibration check results do not meet quality specifications.
Retention Time	$\pm 5\%$ relative standard deviation from the mean retention time for each compound.

Quality Indicator	Requirements
Analytical Balance Sensitivity	$\pm 0.01 \text{ mg} (\pm 10 \mu\text{g}).$
Analytical Balance Calibration	Annually by NIST Traceable Standards.
Analytical Balance Calibration Checks	Daily during analysis periods using NIST Class S weights.
Precision	$\pm 15\%$ relative standard deviation on replicate analysis or $\pm 15 \ \mu g$, whichever is greater.
Bias	$\pm 5\%$ relative standard deviation on daily QC check. If bias criteria are failed, analytical balance is recalibrated.
Completeness	100%; aliquots are reanalyzed if analysis calibration check results do not meet quality specifications.
Blank GRAV Pan	<50 µg
Reagent Blank	<60 µg

Table 15.	QC Requirements	for GRAV Analys	is of Volatile	Compounds.
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have been established from experimental laboratory data.⁶

Inorganic salts and contamination of samples by microfragments of XAD-2 and other fine particulate matter can cause artifacts or interference in GRAV analyses if the procedures described in this guidance document are not followed. The use of Method 3542 with the additional procedures described in Section 4 to prepare samples collected from Method 0010 air samples reduces the contamination. Either filtration with prerinsed cellulose filter media (Whatman #1 filter media or equivalent) and drying with sodium sulfate or filtration through anhydrous sodium sulfate supported by a glass wool plug followed by 0.45 μ m filtering is effective at removing fine particle artifacts that interfere with GRAV analysis.

The following steps are crucial to quality control for GRAV analysis:

• Use high quality reagents for performing procedures (extractions, rinses, etc.) "Ultra-

pure" reagents are recommended.

- Assure that all glassware and field and laboratory equipment have been cleaned thoroughly with high quality reagents. Cover the weighing pan containing GRAV analysis aliquot for drying by building a tent with aluminum foil, shiny side out.
- Allow solvent in GRAV pans to evaporate to dryness before placing GRAV pans in a desiccator for final drying to constant weight.
- Run control pans: dry pan blank (dust blank) and solvent blank. Blank weighing pans without solvent or sample should be carried through the evaporation and drying process as a quality control check for each set of samples. Solvent blank samples consisting of concentrated reagent solvent should be analyzed in duplicate for each batch of samples. Sample weights should be corrected for blank weighing pan mass gain using the dust blank.
- Check balance calibration prior to each weighing.

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The EPA Project Officer is Jeffrey V. Ryan, Mail Drop E ryan.jeff@epa.gov	E305-01, phone (919) 541-1437	, e-mail	
summarized in this document, which reports both the results of research and the investigation of improvements to the Total Organic Emissions (TOE) guidance used by EPA to measure recoverable organic material from stationary source emission samples in support of the Office of Solid Waste Risk Burn requirements. This document describes the purpose, experimental design, and results from several related investigations into the performance of specific techniques to determine TOE. Results include analysis of recoverable organic material from three specific boiling point/vapor pressure classes: light hydrocarbons and volatile organics, semivolatile organics, and nonvolatile organic compounds. Improved procedures for analysis of volatile organics, semivolatile organics, and nonvolatile organic compounds are described. The experimental approach used to address weaknesses in TOE analysis procedures is discussed, and the effect of improvements to these measurement procedures is reported. The experimental results in this report support the sampling and analytical guidance necessary to characterize the full range of recoverable organic material encountered in source emissions.			
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