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ANALYSIS OF VOLATILE ORGANIC COMPOUNDS FROM CHARCOAL BADGES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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1.0 SCOPE AND APPLICATION

1.1 This is a general purpose method that provides for the determination of volatile organic hydrocarbons (VOCs) in air samples by gas chromatography/mass spectrometry (GC/MS).

1.2 Analytes appropriate to this analysis are shown in Table 1.

2.0 SUMMARY OF THE METHOD

This method is for the analysis of VOCs in air by GC/MS in the selected ion monitoring mode (SIM). Charcoal badge samplers are extracted with a suitable solvent (acetone/carbon disulfide; 2.1 v/v) containing internal standards and then the sample extract is injected into a GC/MS having a fused silica capillary column. The compounds are identified by retention time and at least two representative mass fragment ions as compared to standards. One ion, a primary ion, is used for the quantitation of a given compound. The secondary ion is utilized as a confirmation ion for a given compound. Quantitation is carried out by the method of internal standards by utilizing the areas of the primary ion and internal standard to determine relative response factors for each specific analyte of interest.

Method Reference

Pellizzari, E., L. C. Michael, and S. Cooper. "Performance and Validation of VOC Collection and Analysis Using OVM 3500 Charcoal Badges", manuscript in preparation.

3.0 INTERFERENCES

3.1 During analysis, major contaminant sources are reagents and sample collection materials. Analysis of field and method blanks provide information about the presence of contaminants.

3.2 Carry over contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations

of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed.

3.3 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by method blanks as described in Section 8.2.

4.0 SAFETY

4.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references of laboratory safety are available for the information of the analyst.

4.2. Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

5.0 EQUIPMENT

5.1 Laboratory Equipment

- 5.1.1 All glassware must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with water, distilled water, or solvents, air-drying, and heating (where appropriate) in an oven.
- 5.1.2 Volumetric flasks, various sizes.
- 5.1.3 Micro syringes, various sizes.
- 5.1.4 Vials. Various sizes of amber vials with Teflon-lined screw or crimpseal caps.

5.1.5 Analytical balance. Capable of weighing 0.0001 g accurately.

5.2 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

5.2.1 The GC must be capable of temperature programming and be equipped for splitless/split injection. The injection tube liner should be quartz and about 3 mm in diameter. The injection system must not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition.

5.2.2 The GC may be equipped with an autosampler capable of handling the sample vials and injecting the samples in a specific run sequence. Both the sample injection size and the number of syringe rinses should be controllable by the operator.

5.2.3 The GC/MS interface should allow the capillary column or transfer line exit to be placed within a few mm of the ion source. Other interfaces, for example the open split interface, are acceptable as long as the system has adequate sensitivity.

5.2.4 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 45 to 450 amu or selected ion monitoring with a complete scan cycle time (including scan overhead) of 1.5 sec or less. (Scan cycle time = Total MS data acquisition time in sec divided by number of scans in the chromatogram.) The spectrometer must produce a mass spectrum that meets all criteria for the tune of perfluorotributylamine (FC-43) as described in RTI/ACS-SOP-184-002.

5.2.5 A data system is required to acquire, store, reduce, and output mass spectral data. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as defined in Section 10.1.5 (or construction of a first or second order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of

analytes using either the calibration curve or the equation in Section 13. Optionally, data may be transferred from the instrument to another computer to carry out calculations after identifications and integrations are complete.

6.0 REAGENTS AND STANDARDS

6.1 Helium Carrier Gas

6.2 Solvents

Methylene chloride, carbon disulfide, toluene and acetone (pesticide grade or equivalent).

6.3 Stock Standard Solutions

Individual solutions of analytes, surrogates, and internal standards are prepared from certified solutions or from pure (neat) materials. The solutions are prepared in a suitable solvent (i.e., acetone/carbon disulfide; 2.1 v/v). The stock solutions are stored in vials with Teflon lined caps at -10EC or sealed in clean glass ampules for storage.

6.4 Primary Dilution Standard

The stock standards are used to prepare a primary dilution standard solution that contains multiple analytes. Aliquots of each of the stock standard solutions are combined to produce the primary dilution standard in which the concentration of the analytes is at least equal to the concentration of the highest calibration solution. Store the primary dilution standard solution in a vial sealed with a Teflon lined cap at 4EC or less.

6.5 Internal Standard Solution

The stock internal standard solutions are used to prepare a primary dilution standard containing the internal standards. The solution is prepared at a level which facilitates the delivery of an appropriate amount of internal standards to the final sample extracts with a small (i.e., 5-50 µL) volume. The solution is also used in the preparation of the calibration solutions.

6.6 Calibration Solutions

A series of calibration solutions are prepared to span the expected range of analyte concentrations found in the sample extracts. Typically five concentration levels are prepared and analyzed in duplicate. The calibration should cover the nominal range from 0.075 to 250 Fg/mL of each target analyte. The specific analytes contained in the calibration solutions may be prepared at different concentration levels which reflect the ratios found in typical environmental extracts. Each calibration solution contains equal amounts of the selected internal standards. Table 2 lists the suggested calibration levels, target analytes, and internal standards for the calibration curve standards. Octafluorotoluene (PFT) will be used as the internal standard for quantitation. The solutions are stored in vials with Teflon caps at 4EC. Aliquots of the solutions are transferred to amber autosampler vials and sealed with Teflon lined septa for analysis by GC/MS.

7.0 SAMPLE STORAGE

All sample extracts are stored in a freezer at -10EC.

8.0 QUALITY CONTROL

8.1 Field Blanks

Processing of field blanks will be performed by extracting unexposed charcoal badges. The results of these analyses will help define contamination resulting from field sampling and transport activities and lot to lot variations. Field blanks are unspiked cartridges taken to the field and treated exactly as field samples.

8.2 Method Blanks

Laboratory processing of method blanks will be performed along with each batch of samples extracted as a means of assessing the contamination resulting from the sample extraction and cleanup procedures. Method blanks are simply extraction solvent processed and analyzed with field samples.

8.3 Field Controls

Field controls, containing known quantities of target analytes, will be processed for each sample type. The results of these analyses will be a means of assessing the overall recovery of the target analytes from the charcoal badge. The recovery of the target analytes will be monitored. Field controls are spiked then taken to the field, returned, and stored along with field samples.

The chosen levels of each analyte loaded onto charcoal badges will yield a nominal level of 500 pg/FL in the final extract.

8.4 Laboratory Controls

Laboratory controls will be processed and analyzed prior to processing field controls. Laboratory controls are used to demonstrate acceptable method performance prior to extracting field samples. Laboratory controls will contain all target analytes, and undergo all extraction and procedures which the samples are subjected to. The recovery of the target analytes will be monitored.

The chosen levels of each analyte loaded onto charcoal badges will be identical to field controls.

8.5 Method Controls

Method controls will be processed and analyzed with each extraction batch to evaluate recovery of target VOCs during sample manipulation and analyses. Method controls are extracting solvent spiked with all target VOCs then processed and analyzed with field samples.

The chosen levels of each analyte in the extraction solvent will be at a nominal level of 500 pg/FL.

9.0 SAMPLE EXTRACTION

Samples received from the field or retrieved from storage are first inspected for (a) the closure cap being firmly snapped to the monitor body and (b) the closure cap plugs being firmly sealed in the cap parts. [NOTE: If these conditions are violated, the sample may be compromised.]

The center port of the cap is opened and 1.5 mL of acetone/carbon disulfide [2:1 v/v] desorption solvent which contains the three internal standards (Table 2, 5 ng/FL each) is injected. The rim part may be open to allow venting. Both ports are resealed. With occasional gentle agitation the monitor is let stand for 1/2 hour.

Both ports are carefully opened. The decanting spout is inserted into the rim port and the liquid is carefully transferred into a sampler vial used with the automatic sampler of the GC/MS system. The vial is immediately sealed, and is ready for analysis.

Recoveries of analytes from charcoal badges exposed to atmospheres containing known levels and processed by this procedure followed by GC/MS analysis has been shown to be 70-110% (Table 3). Precision of duplicate 144 hr samples from six participants ranged from 0-28% RSD across all analytes and samples (avg. RSD – 10%).

10.0 CALIBRATION AND STANDARDIZATION

Demonstration and documentation of acceptable initial calibration are required before any samples are analyzed and are required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required at the beginning of each 8 hour period during which analyses are performed. Additional periodic calibration checks are good laboratory practice.

10.1 Initial Calibration

10.1.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Section 10.1.2.

10.1.2 Configure the GC/MS system as described in Table 4.

10.1.3 Inject a 1 µL aliquot of a medium concentration calibration solution (5 Fg/mL nominal concentration) and acquire and store data from the selected ions with a total cycle time (including scan overhead time) of 1.5 sec or less. Cycle time should be adjusted to measure at least five or more spectra during the elution of each GC peak.

10.1.4 If medium standard demonstrates acceptable chromatographic performance, as described in Section 13.1.4, inject a 1 µL aliquot of each of the other calibration solutions using the same GC/MS conditions.

10.1.5 Calculate a response factor (RF) for each analyte for calibration solution using the octafluorotoluene (PFT) internal standard. Table 5 contains quantitation ions for all selected compounds and internal standard. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent. RF is calculated as:

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where:

A_x = integrated abundance of the quantitation ion of the analyte.

A_{is} = integrated abundance of the quantitation ion internal standard.

Q_x = quantity of analyte injected in concentration units.

Q_{is} = quantity of internal standard injected in concentration units.

For each analyte and surrogate, calculate the mean (M) RF from the analysis of the multipoint calibration solutions. Calculate the standard deviation (SD) and the percent relative standard deviation (%RSD) for each mean: %RSD = 100 (SD/M). If the RSD of any analyte mean RF exceeds 25%, either analyze additional aliquots of appropriate calibration solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance.

10.1.6 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available software to generate a linear or second order regression calibration curve. Acceptable calibration curves must have correlation coefficients (r) values $ 0.99.

10.2 Continuing Calibration Check

Verify the MS tune and initial calibration at the beginning of each 8 hr work shift during which analyses are performed using the following procedure.

10.2.1 Inject a 1 µL aliquot of a medium concentration calibration solution (5 Fg/mL) and analyze with the same conditions used during the initial calibration.

10.2.2 Demonstrate acceptable chromatographic performance.

10.2.3 Determine that the absolute areas of the quantitation ions of the internal standards and surrogate(s) have not decreased by more than 25% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Section 10.3.5 and recalibration.

10.2.4 Calculate the RF for each analyte from the data measured in the continuing calibration check. The RF for each analyte is in control if its primary ion RF is within ± 25% of the mean value of the same level standard measured in the initial calibration. Record the performance of the RF for each analyte and surrogate on a control chart. Acceptable performance for the analytical system is met if:

- All primary target analytes, (see Table 1), are in-control.
- No more than two (2) secondary target analytes are out-of-control.

If these conditions are not achieved, remedial action must be taken, which may include recalibration.

10.2.5 Remedial Actions

Possible remedial actions include major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require recalibration.

10.2.5.1 Check and adjust GC and/or MS operating conditions; check MS resolution, and calibrate the mass scale.

10.2.5.2 Clean or replace the splitless injection liner, silanize a new injection liner.

10.2.5.3 Flush the GC column with solvent according to the manufacturer's instructions.

10.2.5.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action may cause a change in retention times, requiring recalibration of retention windows.

10.2.5.5 Prepare fresh calibration solutions, and repeat the initial calibration step.

10.2.5.6 Clean the MS ion source and rods (if a quadrupole).

10.2.5.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.2.5.8 Replace the MS electron multiplier, or any other faulty components.

11.0 PROCEDURE

11.1 Analyze a 1-2 µL aliquot of each sample with the GC/MS system under the same conditions used for the initial and continuing calibrations (Section 10.2.2). The samples are analyzed in sets which consist of calibration check standards, method controls and blanks, a NIST reference check, and eight (8) sample extracts. The order of analysis is:

Continuing calibration check standard
Method control
Method blank
NIST reference standard
Sample extracts
Continuing calibration check standard

11.2 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to tentatively identify peaks in retention time windows of interest.

11.3 Identification of analytes - identify a sample component by its retention time and extracted ion profiles. The GC retention time of the sample components should be within 10 sec of the time observed for that same compound when a continuing calibration solution was analyzed. Manually check the peak integration to verify that the extracted ion profile was properly integrated and the most accurate peak area was obtained.

12.0 METHOD PERFORMANCE

Method detection limits (MDLs) are based upon the lowest calibration concentration used for the sample analysis.

13.0 DATA MANAGEMENT

13.1 Calculations

Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if *unique* ions with adequate intensities are available for quantitation.

13.1.1 Calculate analyte and surrogate concentrations using the following equations:

$$C_x = \frac{(A_x)(Q_{is})}{(A_{is})(RF)}$$

where:

C_x = concentration of analyte or surrogate in ng/sample in the sample extract.

A_x = integrated abundance of the quantitation ion of the analyte in the sample.

A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.

Q_{is} = total quantity (in nanograms) of internal standard added to the sample.

RF = mean response factor of analyte from the initial calibration.

13.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from first or second order regression curves.

13.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty).

13.1.4 Chromatographic performance will be evaluated at the beginning of analysis. The retention characteristics of target analytes, resolution of target analytes, and chromatographic peak shapes of target analytes will be used to evaluate chromatographic performance. In addition, the instrument operator will visually monitor analyte resolution for standards daily. Resolution (R) will be measured using a pair of closely eluting analytes (methyl chloroform and benzene) by

$$R = \frac{2 \times (\Delta RT)}{(W_1 + W_2)}$$

where:

ΔRT is the difference in retention (benzo[a]pyrene and benzo[e]pyrene), W_1, and W_2 are peak widths measured at 10% above the baseline for each compound.

Resolution must be $\geq$1.0.

13.2 Data Management

13.2.1 Sample Management

A series of unique sample codes will be used for sample identification. These sample codes will be placed on all samples and associated documents. A sample protocol record will be used to document sample preparation. Custody records for the sample are completed in the same record (Figure 1). Detailed information regarding sample extraction will be recorded in RTI

Laboratory Notebooks. Samples batched for extraction and submitted to the GC/MS lab for analysis will be tracked using a batch sample submission form (Figure 2). This form will assist in tracking samples and will include important processing information such as amounts of internal standards added.

13.2.2 Sample Custody

Sample custody procedures will be used to track samples and sub-samples generated during this work assignment. Custody documents will be utilized for all sample preparation and analysis activities. The analyst is responsible for sample custody. Sample chain-of-custody and batch records are kept in the laboratory until the data has been electronically transferred to the database manager. Upon complete review of the data once it is merged into the database, the chain-of-custody and batch records will be returned to the field supervisor.

13.2.3 Electronic Datafile Management

Electronic datafiles containing the sample results as ng/sample will be created for each individual sample. These files will be incorporated into a project database where calculations to determine the actual concentration in air will be performed (RTI/ACS-AP-209-400). The laboratory manager is responsible for reviewing the data prior to its transfer as electronic data files to the database manager. This review will be for completeness of the dataset to insure that all samples, blanks and QC samples have been included in the electronic datafile.

TABLE 1. TARGET VOC ANALYTES

Primary Analytes	Secondary Analytes
Benzene	Methylchloroform
Chloroform	Methylene Chloride
Perchloroethylene	Styrene
Trichloroethylene	Toluene
	o-Xylene
	m,p-Xylenes
	p-Dichlorobenzene

TABLE 2. NOMINAL CALIBRATION SOLUTIONS

	Concentration of Analytes in (Fg/mL) Levels				
Compound	0.1X	0.3X	5X	50X	250X
Benzene	0.075	0.30	5.0	50	250
Chloroform	0.075	0.30	5.0	50	250
Perchloroethylene	0.075	0.30	5.0	50	250
Trichloroethylene	0.075	0.30	5.0	50	250
Methylchloroform	0.075	0.30	5.0	50	250
Methylene Chloride	0.075	0.30	5.0	50	250
Styrene	0.075	0.30	5.0	50	250
Toluene	0.075	0.30	5.0	50	250
o-Xylene	0.075	0.30	5.0	50	250
m,p-Xylene	0.075	0.30	5.0	50	250
p-dichlorobenzene	0.075	0.30	5.0	50	250
Internal Standards					
Octafluorotoluene (PFT)	5.0	5.0	5.0	5.0	5.0
Hexafluorobenzene (PFB)	5.0	5.0	5.0	5.0	5.0
Bromopentafluorobenzene (BFB)	5.0	5.0	5.0	5.0	5.0

TABLE 3. PERCENT RECOVERIES OF VOCs FROM CHARCOAL BADGE

Chemical	Low[a]	Medium	High
Chloroform	81±4.2	80±2.8	86±1.4
1,1,1-Trichloroethane	80±2.1	80±2.1	86±2.8
Benzene	78±4.9	71±2.8	78±3.5
Trichloroethylene	74±2.8	72±2.1	79±5.7
Toluene	95±5.7	81±4.2	88±4.9
p-Xylene	84±3.5	82±2.1	92±4.9

[a] Low = 0.9 - 3 Fg total spiked onto badge from atmosphere.
Medium = 6.4 - 20 Fg total spiked onto badge from atmosphere.
High = 12.8 - 41 Fg total spiked onto badge from atmosphere.

TABLE 4. OPERATING PARAMETERS FOR THE CAPILLARY GC/MS SYSTEM

Parameter	Setting
GAS CHROMATOGRAPH	
Instrument	Hewlett-Packard 5890
Column	60m x 0.32 mm DB-5 fused silica capillary column
Temperature Program	0EC (3 min) to 150EC @ 4EC/min
Carrier Gas Flow Rate	1.0 mL/min
Capillary Injector	1 min splitless
Injector Temperature	200EC
MASS SPECTROMETER	
Instrument	Hewlett Packard, Model 5988A
Ionization Mode	Electron Ionization
	Selected Ion Monitoring
Emission Current	0.3 mA
Source Temperature	200EC
Electron Multiplier	2000 volts[a]

[a] Typical value

TABLE 5. ANALYTE SIM IONS

Compound	Primary	Secondary
Benzene	78	74
Chloroform	83	85
Perchloroethylene	166	94
Trichloroethylene	130	95
Methylchloroform	61	97
Methylene chloride	84	86
Styrene	104	78
Toluene	91	92
m/p-Xylene	91	106
o-Xylene	91	106
p-Dichlorobenzene	146	148

RESEARCH TRIANGLE INSTITUTE
SAMPLE PROTOCOL AND CUSTODY RECORD
PROJECT NO.-XXXXXXXXX

SAMPLE CODE: _____

INITIALS	I.D. NO.	DATE	TIME	OPERATION PERFORMED

Research Triangle Institute
Post Office Box 12194
Research Triangle Park, NC 27709

Figure 1. Example sample information and custody record.

ACS MASS SPECTROMETRY SAMPLE SUBMISSION FORM

PROJECT SAMPLE SET OF _____

PLEASE LIST SAMPLE CODES OF SAMPLES SUBMITTED ON / / . Page 1 of __

SURROGATES	CONCENTRATION LEVELS	INTERNAL STDS	CONCENTRATION LEVELS	COMMENTS
TARGET ANALYTES				

Figure 2. Example sample batch submission form.