SCAQMD METHOD 308-91

QUANTITATION OF COMPOUNDS BY GAS CHROMATOGRAPHY

1. Principle

1.1 Samples of unknown composition are qualitatively analyzed by Gas Chromatography/Mass Spectroscopy (GC/MS). The identified sample constituents are then analyzed by Gas Chromatography with Thermal Conductivity Detection (GC/TCD) and/or by Gas Chromatography with Flame Ionization Detection (GC/FID). The volume percent of each component is obtained using the external standard method. These volume percentages are converted to the mole fraction values for the calculation of vapor pressure.

1.2 Multiple component solvents can be analyzed using a blend of standards. Response factors are used in the quantitation of known compounds for which standards are available. For compounds in a given class, for which no standard is available, similar compounds in the class may be used as a standard for quantitation purposes.

2. Apparatus

2.1 Gas Chromatograph

2.1.1 Detector Types: Thermal Conductivity and/or Flame Ionization

2.1.2 The chromatograph should be capable of using both capillary and packed columns.

2.1.3 The system should be capable of quantitating 0.1 volume percent of any compound of interest.

2.2 Integrator, capable of being programmed to present data in area percent

2.3 Recommended Columns

2.3.1 Non-polar phase columns:

2.3.1.1 DB^{R}-1 Megabore 30 m X 0.53 mm, 5.0 u film thickness (See Appendix B, Table 1 for run conditions)

2.3.1.2 SP^{R}-2100, packed 20' X 1.8" 80/100 mesh (See Appendix B, Table 2 for run conditions)

2.3.1.3 Ultra^{R}-1, capillary 25 m X 0.22 mm, 0.33 u film thickness

2.3.2 Porous-polymer columns:

2.3.2.1 Porapak^{R} R or Porapak^{R} Q, 4' X 1/8" 80/100 mesh (See Appendix C, Table 1 for run conditions)

2.3.2.2 Heyesep Q^{R}, Alltech Associates, 6' X 1/8" (See Appendix C, Table 2 for run conditions)

2.3.2.3 Precolumn: 6" X 1/8" packed with same material as column

2.4 Sample Introduction: Microliter syringes and/or autosampler may be used.

3. Reagents and Materials

3.1 Air, compressed, hydrocarbon free

3.2 Helium, carrier gas, minimum purity of 99.5%

3.3 Hydrogen, minimum purity of 99.5%

3.4 Nitrogen, minimum purity of 99.5%

3.5 Standards, reagent grade, minimum purity of 99%

3.6 Toluene, minimum purity of 99%

3.7 Micro syringe, 10 uL capacity

3.8 Volumetric flasks, Class A

3.9 Volumetric pipettes, Class A

3.10 Graduated cylinder, Class A, one liter

3.11 Vials, glass, 15 mL screw top

3.12 Septum, Teflon^{R} coated

3.13 Vials and caps for autosampler

3.14 Crimpers, to fit autosampler vials

4. Analytical procedure

4.1 Sample Storage

4.1.1 Due to the volatility of these materials, the samples must be refrigerated at 60^{o}F or less but not below each sample's freezing point. Transfer of all samples and standard preparations from their containers to the vials should be performed at these reduced temperatures.

4.2 Sample Preparation

4.2.1 Samples received in 1-quart containers.

4.2.1.1 Carefully mix sample by inverting the sample container several times; do not mix the sample by shaking the container.

4.2.2 For homogeneous samples

4.2.2.1 Immediately pipette out enough sample to completely fill a 15 mL vial, cap with a Teflon^{R}-coated septum and proceed to Section 4.3.

4.2.3 For nonhomogeneous samples

4.2.3.1 Transfer sample from 1-quart can to 1 liter graduated cylinder and stopper.

4.2.3.2 Allow sample to attain room temperature.

4.2.3.3 Record volume of each layer to the nearest mL.

4.2.3.4 Transfer a portion of each layer into appropriate vials such that there is no headspace present.

4.3 Initial identification of components

4.3.1 Analyze and identify each component by GC/MS (See Appendix A) to determine the appropriate column, parameters and standards required for the GC quantitation.

4.4 Preparation of GC

4.4.1 Install the desired column and set at the operating conditions to those listed in the Appendices B or C.

4.4.2 Check the system for leaks.

4.4.3 After confirming no leaks, turn on the detector and allow the system to equilibrate, as indicated by a stable recorder baseline.

4.4.4 Set-Up Gases

4.4.4.1 The TCD requires 100 psi Helium as the carrier, detector make-up, and reference gas.

4.4.4.2 The FID requires 15 psi hydrogen gas, 40 psi air, and carrier gas.

4.4.4.3 Column head pressure is set to 10 psi to produce a column flow of 5 mL/min.

4.5 Separation of Components

4.5.1 For gasoline-type samples use an appropriate column from the recommended non-polar columns in 2.3.1. (See Appendix B)

4.5.2 For samples containing water, oxygenates, amines and compounds containing reactive hydroxyl groups use the recommended porous-polymer column in 2.3.2. (See Appendix C).

4.5.3 Establish an injection volume (typically 1 uL) which yields optimum peak separation. Inject the sample on the instrument and establish a chromatogram.

4.6 Identification of components

4.6.1 Inject standards(s) of components identified in 4.3.1 to obtain the retention time(s).

4.6.2 Using the information obtained from 4.5.3 and 4.6.1 verify the identity of each component in the sample.

4.6.3 Determine the area percents associated with the identified peaks from 4.5.3 and which have been verified in 4.6.2.

4.6.4 If peaks resulting from 4.6.1 and 4.6.2 are not within their linear range, inject the appropriate volume of sample and standard such that the resulting peaks are within the linear quantification range.

4.7 Preparation of Standards

4.7.1 Identify a compound (solvent) which can be used for the preparation of the standard solution. Toluene can be used as the solvent for most oxygenated component samples. Alternatively, any compound that does not interfere with the sample components may be used.

4.7.2 Prepare a standard solution containing all identified components (except water) in the proportions obtained in 4.6.3.

4.7.3 Using a 100 mL volumetric flask, add the known components successively (starting with the least volatile) to the flask using appropriate volumetric pipettes until all identified components have been added. Adjust the volume percents to the nearest whole milliliter or the most appropriate pipette available.

4.7.4 Fill the volumetric flask to volume using the solvent identified in 4.7.1.

4.7.5 If a non-interfering solvent could not be identified in 4.7.1, select two components identified in 4.6.2 which have non-overlapping peaks. Using one of the selected compounds as a solvent, prepare a standard as in 4.7.3, omitting those compounds which would co-elute with the solvent. Repeat with the other selected solvent compound for previously omitted compounds. The components of both standards will provide a standard for each component in the sample.

4.8 Analysis of Samples and Standards for Quantitation of Components

4.8.1 Transfer the standard(s) and sample(s) into autosampler vials and crimp closed. Include the solvent(s) used in the preparation of the standard(s) as a blank(s).

4.8.2 Set up the blank(s), standard(s), and sample(s) on the auto sampler in the following manner:

4.8.2.1 Two vials blank(s), two vials standard(s), two vials sample(s), 1 vial blank(s), and 1 vial standard(s) each using two injections per vial. (Two vials are used for each prepared standard at the beginning of the run requiring the double listing of the standard. Two vials are also prepared for each sample for a total of four injections).

4.8.2.2 Analyze no more than two samples (8 injections) between standards.

4.8.3 Peak areas of each set of duplicate runs (4 injections total) must be within $\pm$5% relative standard deviation for the samples.

4.8.4 The average peak area of all standard runs must be within $\pm$5% relative standard deviation.

4.8.5 If either 4.8.3 or 4.8.4 are outside the $\pm$5% range, the analysis must be repeated correcting the problems which caused these ranges to be exceeded.

4.9 Quality Assurance

4.9.1 Within each class of compounds (example: aliphatics, aromatics, oxygenates, etc.) a 5-point calibration should be performed to establish the linear working range.

4.9.2 Compound(s) in the sample not positively identified by GC/MS or which have questionable retention times will require spiking of the sample with the suspected compound(s).

4.9.3 Samples are analyzed in replicate to demonstrate the repeatability of the analysis.

5. Calculations

5.1 Calculate the volume percent of each component as follows:

$$V(i) = \frac{A(i)}{A(std)} \times V(std)$$

where,

V(i) = volume percent of component i

A(i) = peak area of component i

A(std) = peak area of standard for component i

V(std) = volume percent of standard for component i

5.1.1 For homogeneous samples report the volume percent of each component.

5.1.2 For non-homogeneous samples calculate the volume percent of each component as follows:

$$V(a) = V(i) \times \frac{L}{T}$$

Where:

V(a) = Volume percent in original sample

V(i) = Volume percent analyzed (See 5.1)

L = Volume of the layer in which the compound is located, mL (Sec. 4.2.3.3)

T = Total volume of the sample, mL.

APPENDIX A

IDENTIFICATION OF COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

1. Apparatus

1.1 GC/MS

1.1.1 RTE-A Data System

1.1.2 Hewlett Packard 5995

1.1.2.1 Membrane Separator

1.1.2.2 Jet Separator

1.1.3 Hewlett Packard 5890/5970

1.1.3.1 2 Valco Valves (four port)

1.1.3.2 SGE Splitter h/p# 0101-0595

1.2 GC Columns

1.2.1 J & W DB-624 30 m x 0.53 mm id x 5.0 um

1.2.2 J & W DB-Wax 30 m x 0.53 mm id x 3.0 um

1.2.3 J & W DB-1 30 m x 0.53 mm id x 3.0 um

1.2.4 J & W DB-5 30 m x 0.53 mm id x 5.0 um

1.2.5 J & W DB-17 30 m x 0.53 mm id x 1.0 um

1.3 Miscellaneous Lab Equipment

1.3.1 Microliter Syringes

1.3.1.1 Hamilton 1801N 10 uL gastight syringe

1.3.1.2 Hamilton 1810N 100 uL gastight syringe

1.3.1.3 Hamilton 1001N 1000 uL gastight syringe

1.3.2 Septa 11mm dia.

1.3.3 Injector Inserts HP# 5080-8732

1.3.4 Ferrules

1.3.4.1 Graphite/Vespel for MS interface

1.3.4.2 Graphite for HP injectors & detectors

2. Reagents/Materials

2.1 Gases

2.1.1 Air, compressed (for HP 5995)

2.1.1.1 25 psi for GC oven door

2.1.1.2 95 psi for GC/MS valve

2.1.2 Helium (99.999% , UHP or Carrier Grade)

2.1.3 Liquid Nitrogen (for sub-ambient cooling)

2.1.4 Cooling Water and Circulator (hp 5995 only)

2.2 Tuning Compounds

2.2.1 Perfluorotributylamine (PFTBA)

2.2.2 Bromofluorobenzene (BFB)

2.2.3 Decafluorotriphenylphosphine (DFTPP)

3. Analytical Procedure

3.1 Samples should be in a vial with a Teflon^{R} coated septum.

3.2 Set-up for the Hewlett Packard 5890/5970 GC/MS and 5995 GC/MS

3.2.1 Running parameters using the HP 5890/5970 GC/MS appear in Table 1 of Appendix A.

3.2.2 Using the SGE split capillary interface on the HP 5890/5970 adjust the parameters (3.2.1) as desired.

3.2.3 Running parameters using the HP 5995 GC/MS appear in Table 2 of Appendix A.

3.2.4 Using either the jet or membrane separator on the HP 5995 GC/MS adjust the parameters as desired.

3.3 Tuning of the GC/MS

3.3.1 Using perfluorotributylamine (PFTBA) run the autotune program to optimize the MS running parameters. This will also establish if the instrument is functioning properly.

3.3.2 Using either decafluorotriphenylphosphine (DFTPP) or bromofluorobenzene (BFB) as a reference compound, manually adjust the MS parameters as necessary for selective tuning.

3.4 Sample Analysis

3.4.1 Thick samples (adhesives, paints, or sludges) may require distillation prior to analysis.

3.4.2 Inject 1 uL of the liquid sample. Use parameters selected in Table 1, Appendix A.

4. Identification

4.1 Identify each component in the sample using any of the following methods for confirmation.

4.1.1 Library search encompassing probability base matching on mass spectrum obtained.

4.1.2 Matching fragmentation patterns using EPA/NIH Mass Spectral Data Base.

4.1.3 Retention time and fragmentation pattern comparison with known standards.

5. Reporting

5.1 Printout each identified peak, its spectrum and spectra of possible matches.

5.2 Analyze standards to verify identification by matching retention time and spectra.

5.3 Quantitate components using suitable GC method. GC parameters are found in Appendix B and C.

APPENDIX A
Table 1

Conditions for using HP 5890/5970 GC/MS

Tuning File Name:	MT2149 (same as in MTUNE)
Data File Name:	>b1234 (sequential)
Sample Name (Include injection volume):	[Type in information]
Misc.:	liq inj B DB-624, eM2149 th20 50/200c 5-350amu
Method File Name:	ME6245
Cartridge:	D1
Review Input:	N
Scanning Method:	L
Column Type:	C
Injection Mode:	N
Ionization Technique:	E
Sample Introduction:	G

Method File Name ME6245 specifies the following parameters:

Temperature Zones

Injection Port:	250^{o}C
Interface Oven:	280^{o}C

GC/DIP Parameters

Initial Temperature:	50^{o}C
Time:	5.0 min.
Rate:	15.0^{o}/min.
Temp 2:	200^{o}C
Time 2:	5.0 min.
Run Time:	20.0 min.
Splitless Time:	0.0 min.
Scan Start Time:	0.0 min.

Scan Parameters

Mass Range:	5 to 350 amu
Multiplier Voltage:	2149 V
Number of A/D Samples:	2^3=8
GC Peak Threshold:	5,000
Threshold:	20
Display Ions:	as desired

This method is also suitable for the DB-Wax , DB-1, DB-5, and DB-17 columns. Change the Misc. information to match the column used.

APPENDIX A
Table 2

Conditions for Analysis Using the HP 5995 GC/MS

Tuning File Name:	MT7002 (same as in MTUNE)
Data File Name:	>C1234 (sequential)
Sample Name (Include injection volume):	[Type in information]
Misc.:	liq inj DB-624, eM2000 th20 50/200c 5-350amu
Method File Name:	ME5995
Cartridge:	D2
Review Input:	N
Scanning Method:	L
Column Type:	C
Injection Mode:	Y
Ionization Technique:	E
Sample Introduction:	G

Method File Name ME5995 specifies the following parameters:

Temperature Zones

Injection Port:	250°C
Transfer Line:	280°C
Ion Source:	280°C
Analyzer:	280°C
FID:	0°C

GC/DIP Parameters

Initial Temperature:	50°C
Time:	5.0 min.
Rate:	15.0°/min.
Temp 2:	200°C
Time 2:	5.0 min.
Run Time:	20.0 min.
Splitless Time	0.5 min.
Scan Start Time:	0.0 min.

Scan Parameters

Mass Range:	5 to 350 amu
Multiplier Voltage:	2007 V
Number of A/D Samples:	2^3=8
GC Peak Threshold:	5,000
Threshold:	20
Display Ions:	as desired

This method will also be suitable for the DB-Wax , DB-1, DB-5, and DB-17 columns. Change the Misc. information to match the column used.

Appendix B
Table 1

Conditions for Analysis by GC/TCD

Column: Megabore capillary DB^{R}-1, 25 m X 0.53 mm 5.0 um film thickness

Flowrates

Column:	5 mL/min
Reference:	10 mL/min
Make-up:	15 mL/min

Run Conditions

Injection Port:	200^{O}C
Detector:	200^{O}C
Injection Volume:	0.5 ul

Temperature Program:

Hold at 35^{O}C for 1 min
Ramp 5^{O}C/min to 140^{O}C
Ramp 10^{O}C/min to 200^{O}C
Hold at 200^{O}C for 10 min

Compounds will be separated in decreasing order of volatility.

Above conditions may be varied to optimize resolution.

Appendix B
Table 2

Conditions for Analysis by GC/FID

Column: SP^{R} 2100, 20' X 1/8"

Flowrates

Hydrogen: 25 mL/min
Air: 250 mL/min
Carrier Flow for packed column: >15 mL/min (15-30 mL range normally)

Run Conditions

Injection Port:	240^{o}C
Detector:	240^{o}C
Injection Volume:	0.2 to 0.5 ul

Temperature Program:

Hold at 40^{o}C for 1.5 min
Ramp 15^{o}C/min to 150^{o}C
Ramp 25^{o}C/min to 180^{o}C
Hold at 180^{o}C for 5 min

Above conditions may be varied to optimize resolution.

A capillary column may be used with a variation in GC conditions.

Appendix C
Table 1

Conditions for Analysis by GC/TCD

Column: Porapak^{R} R or Porapak^{R} Q, 4' X 1/8" 80/100 mesh

Precolumn: 6" X 1/8" packed with same material as column

Flowrate (Helium)

Column:	30 mL/min
Reference:	45 mL/min

Run Conditions

Injection Port:	200^{o}C
Detector:	200^{o}C
Injection Volume:	0.5 to 3.0 ul

Temperature Program:

Hold at 90^{o}C for 1 min
Ramp 10^{o}C/min to 160^{o}C
Hold at 160^{o}C for 2 min

Elution order: H_2O, MeOH, EtOH.....

Above conditions may be varied to optimized resolution

Appendix C
Table 2

Conditions for Analysis by GC/FID

Column: Heyesep Q^{R}, Alltech Associates, 6' X 1/8"

Precolumn: 6" X 1/8" packed with same material as column

Flowrates

Hydrogen:	25 mL/min
Air:	250 mL/min
Carrier (Nitrogen):	30 mL/min

Run Conditions

Injection Port:	240^{o}C
Detector:	240^{o}C
Injection Volume:	0.2 ul

Temperature Program:

Hold at 80^{o}C for 1.5 min
Ramp 15^{o}C/min to 140^{o}C
Ramp 30^{o}C/min to 240^{o}C
Hold at 240^{o}C for 10 min

Above conditions may be varied to optimized resolution

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

APPLIED SCIENCE & TECHNOLOGY DIVISION

LABORATORY SERVICES BRANCH

SCAQMD METHOD 308-91

QUANTITATION OF COMPOUNDS BY GAS CHROMATOGRAPHY

Approved June 1, 1991
Revised February 1993

SCAQMD METHOD 308-91

QUANTITATION OF COMPOUNDS BY GAS CHROMATOGRAPHY

This method is used to obtain information needed for the calculation of vapor pressure of samples for which the true vapor pressure can not be obtained from the Reid Vapor Pressure (RVP). It may be used to identify or quantify the components of various organic materials. This method is applicable to the analysis of samples regulated by rules in Regulation IV and Regulation XI.

CONTENTS