SCAQMD METHOD 314-91

QUANTITATION OF PHOTOCHEMICALLY REACTIVE COMPOUNDS

1. Principle

1.1 Identification of components in a sample is performed by Gas Chromatography/Mass Spectrometry (GC/MS). The sample is then separated into its components by a gas-liquid partition column of a gas chromatograph equipped with a thermal conductivity detector. Either packed or capillary columns may be used. Response factors are used in the quantitation when the identity of the compound is known and the standard is available. For compounds in a given class, for which the standard is not available, another compound from that class may be used as a standard for quantitation purposes.

2. Apparatus

2.1 Gas Chromatograph (GC), equipped with a thermal conductivity detector that has the following performance characteristics

2.1.1 The system should be capable of quantitating at least 0.1 volume percent of any compound of interest.

2.1.2 The chromatograph should be equipped to allow for both capillary and packed columns.

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

2.3 Recommended Columns

2.3.1 DB^{R}-WAX 30 m x 0.53 mm 1.0 u film thickness

2.3.2 DB^{R}-1 30 m x 0.53 mm 5.0 u film thickness

2.3.3 DB^{R}-624 30 m x 0.53 mm 3.0 u film thickness

2.3.4 TCEP^{R} (10%) 10' x 1/8"

2.3.5 SP^{R}-2100 20'x1/8"

2.4 Microliter syringes or autosampler may be used for sample introduction.

3. Reagents/Materials

3.1 Helium, Carrier Gas, 99.5%

3.2 Standards of 98% purity or better

3.3 Vials, glass, 15 mL, Screw-top

3.4 Vial Septa, Teflon^{R}-coated, to fit vial

3.5 Graduated cylinder, Class A, one liter

3.6 Pipets, Class A, 15 mL

3.7 Volumetric Flasks, Class A

3.8 Micro-syringe, 10 uL capacity

3.9 Vials, autosampler

3.10 Crimper, to fit autosampler vials

4. Analytical Procedure

4.1 Sample Storage

4.1.1 Due to the volatility of these materials, samples and standard blends are stored at a temperature of 60^{o}F or less. Transfers of samples and standards from the container to vials should be made only when the liquid in the container is at 60^{o}F or less.

4.2 Preparation of Sample

4.2.1 Carefully mix sample by inverting several times. Do not mix the sample by shaking the containers.

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

4.2.3 If sample requires clean-up, follow SCAQMD Method 302 (Distillation of Solvents from Paints, Coatings and Inks) before proceeding to Section 4.3.

4.3 Initial identification of components

4.3.1 Analyze and identify each component by GC/MS (See Appendix A).

4.4 Preparation of GC

4.4.1 Install appropriate column and insure that the system has no leaks.

4.4.3 Turn on the detector and allow the system to equilibrate, as indicated by a stable recorder baseline.

4.4.2 Adjust operating conditions to optimize resolution of components for quantitation and establish the run time needed to elute all the components of the sample.

4.4.4 See Appendix B for recommended conditions using a GC/TCD instrument with a DB^{R}-1 column (30 m X 0.53 mm, 5.0 u film thickness).

4.5 Identification of components by GC/TCD

4.5.1 Inject an aliquot of the sample to obtain a chromatogram of the sample. The aliquot injected should yield a chromatogram that shows optimum peak separation.

4.5.2 Inject standard(s) of components identified in 4.3.1 to determine the retention time(s).

4.5.3 Use these retention times to verify the identity of each component obtained in Section 4.3.1.

4.5.4 If the peak identity is doubtful, spike the sample with the standard(s) to establish the correct identity.

4.5.5 If peaks resulting from 4.5.1 and 4.5.3 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.

4.5.6 Determine the area percents associated with the identified peaks verified in 4.5.3 to establish the relative proportions of each component.

4.6 Preparation of Standard

4.6.1 Identify a solvent that does not interfere with the identification of the components of the sample which can be used for the preparation of the standard solution.

4.6.2 Prepare a standard solution containing all identified components in the proportions obtained in 4.5.6.

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

4.6.4 Fill the volumetric flask to the volume using the solvent identified in 4.6.1.

4.6.5 If a non-interfering solvent cannot be identified, select two components identified in 4.5.3 which have non-overlapping peaks. Using one of the selected compounds as a solvent, prepare a standard as in 4.6.3, 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.

4.7 Quantitation of Components

4.7.1 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).

4.7.2 Set up the blank(s), standard(s), and sample(s) on the autosampler in the following manner.

4.7.2.1 Two vials blank(s), two vials standard(s), two vials sample(s), 1 vial blank, and 1 vial standard 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)

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

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

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

4.7.5 If either 4.7.3 or 4.7.4 are outside of the $\pm$5% range, the analysis must be repeated correcting the problems which cause these ranges to be exceeded.

4.8 Calibration and Quality Assurance

4.8.1 Within each class of compounds (example: aliphatics, aromatics, oxygenates, etc.) a 3- or 5- point calibration should be performed to establish the linear working range. The maximum concentration for any standard preparation should be established from information obtained from 4.5.5.

4.8.2 Compound(s) not positively identified by GC/MS will also require spiking of the suspected compound(s) to identify them.

4.8.3 Spikes of any compound(s) with questionable retention times are also required.

4.8.4 Replicates are made of all samples to demonstrate uniformity of the samples and to improve the reliability of the data obtained.

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 in the sample
A(std) = peak area of component i in the standard
V(std) = volume percent of component i in the standard

5.2 Report the volume percent of each component.

Appendix A

IDENTIFICATION OF PHOTOCHEMICALLY REACTIVE SPECIES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Apparatus

1.1 Gas Chromatography/Mass Spectrometer HP 5995A

1.2 RTE-A Data station

1.3 Column

1.3.1 Packed 10% TCEP^{R} 10' X 1/8"

1.4 Sample introduction - microliter syringe

2. Reagents/Materials

2.1 Helium, carrier gas, 99.5%

2.2 Air, compressed

3. Analytical Procedure

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

3.2 GC/MS Parameters

	Temp, ^{o}C
Injector	200
Source	250
Analyzer	180
Transfer line	180

Injection volume: 0.2 uL
Column flow: 20 mL/min

3.3 Oven temperatures
Hold at 75^{o}C for 3.5 min
Ramp 10^{o}C/min to 150^{o}C
Hold at 150^{o}C for 5 min
Ramp 20^{o}C/min to 165^{o}C
Hold at 165^{o}C for 5 min

3.4 Oven temperature program may be varied to maximize resolution.

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

Appendix B

Conditions for Analysis by GC/TCD

Column: Megabore capillary DB^{R}-1, 30 m X 0.53 mm 5.0 um film thickness

Carrier Flowrate

Column:	5 mL/min
Reference:	10 mL/min
Make-up:	15 mL/min (Aux gas)

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 should be varied to optimize resolution for the sample under investigation.

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Solvents or distillates of unknown composition are tested for photochemically reactive constituents by Gas Chromatography/Mass Spectrometry. The solvents or distillates are then analyzed by Gas Chromatography/Thermal Conductivity Detection for percent volume composition of photochemically reactive components (as defined in Rule 102 of the SCAQMD Rules and Regulations).

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