SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

SCIENCE & TECHNOLOGY ADVANCEMENT

MONITORING & ANALYSIS

LABORATORY SERVICES & SOURCE TEST ENGINEERING

Method 313 Determination of Volatile Organic Compounds (VOC) by Gas Chromatography/ Mass Spectrometry/ Flame Ionization Detection (GC/MS/FID)

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT
preparations, reviews and approvals page

VOC ANALYSIS BY GC MS FID

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Revision history page

VOC ANALYSIS BY GC MS FID

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List of abbreviations:

SCAQMD	South Coast Air Quality Management District
VOC	Volatile Organic Compound
CACC	Clean Air Choices Certification
CAS	Clean Air Solvent
SIP	State Implementation Plan
EPA M24	Environmental Protection Agency Method 24
ASTM 5095	American Society of Testing and Materials Method 5095 "Determination of the Nonvolatile Content in Silanes, Siloxanes and Silane-Siloxane Blends used in Masonry Water-Repellent Treatments"
UV/EB	Ultraviolet/Electron Beam
VOHAP	Volatile Organic Hazardous Air Pollutant
MeOH	Methanol
THF	Tetrahydrofuran
GC	Gas Chromatograph
MS	Mass Spectrometer
FID	Flame Ionization Detector
RRF	Relative Response Factor
HC	Hydrocarbon
nC6 – nC15	Hexane - Pentadecane
MIR	Minimum Incremental Reactivity
GWC	Global Warming Compound
ODC	Ozone Depleting Compound
RB	Reagent Blank
SOP	Standard Operating Procedure
PPE	Personal Protective Equipment
BFB	4-Bromoflurobenzene
TRIG	Triglyme
IPA	Isopropyl Alcohol
EGDE	Ethylene Glycol Diethyl Ether
DIIBA	Diisobutyl Adipate
MeP	Methyl Palmitate
EG	Ethylene Glycol
PG	Propylene Glycol
p-tSAM	p-Toluenesulfonic Acid Monohydrate
%D	% Difference
RPD	Relative Percent Difference
PBM	Probability Base Matching
NIST	National Institute of Standards and Technology
AMDIS	Automated Mass spectral Deconvolution and Identification System
PFTBA	Perfluorotributylamine

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1.0 Scope and Application

This method is for Volatile Organic Compound (VOC) analysis of materials regulated under South Coast Air Quality Management District (SCAQMD) State Implementation Plan (SIP) Rules and SCAQMD voluntary certification programs, such as Clean Air Solvents (CAS) and Clean Air Choices Cleaners (CACC). SCAQMD Rules or Protocols may also require this method. M313 may be used to develop speciation information for SCAQMD Program or Rule Development or special studies.

Method 313 applies to materials such as paints, coatings, solvents, and other liquid/dispersed-solid materials containing less than 150 g/L VOC material as measured by SCAQMD Method 304-91 or Environmental Protection Agency Reference Method 24 (EPA M24). Method 313 may be used for samples requiring ASTM D5095 "Determination of the Nonvolatile Content in Silanes, Siloxanes and Silane-Siloxane Blends used in Masonry Water-Repellent Treatments" and for materials which do not reach a stable weight by EPA M24 with a demonstrated additional weight loss of greater than 0.2% absolute or 3% relative difference (whichever is greater) after one additional hour of oven heating even if over 150 g/L VOC material. This method is not to be used for 2-component coatings, Ultraviolet/Electron Beam (UV/EB)-cured coatings, or other coatings which require specialized curing conditions. Samples requiring Volatile Organic Hazardous Air Pollutant (VOHAP) analysis cannot be diluted in methanol since methanol is a common VOHAP, unless methanol is demonstrated not to be in the sample.

This method has been developed to achieve a reportable limit of 5 g/L; however, method sensitivity and analytical certainty depend on the number of individual VOCs in the analyzed sample. A large number of small analyte peaks in a sample can decrease the sensitivity of the method, and a large number of unidentified analyte peaks in a sample will result in lower certainty.

The method must be performed by staff which is fully-trained and well-experienced in gas chromatographic analysis and mass spectrometric interpretation.

2.0 Summary of Method

Samples are spiked with surrogate standards and diluted with internal standard in either methanol (MeOH) or tetrahydrofuran (THF) solvent, then injected into a Gas Chromatograph (GC) equipped with a Mass Spectrometer (MS) and Flame Ionization Detector (FID). Eluted samples are split post-column to the MS and FID. Individual peaks are identified by MS, and their respective concentrations are estimated using their FID area counts and the Relative Response Factor (RRF) of triglyme (TRIG) calculated from the FID.

The estimated concentration of each peak is then used to determine whether each compound must be quantified using a matching standard RRF, or may be estimated from the RRF of a similar compound or from the default TRIG RRF. VOC Material and VOC Coating values are

then calculated from the summed concentrations of all peaks that elute prior to Methyl Palmitate (MeP).

Petroleum distillate-based samples may demonstrate a complex hydrocarbon profile with few or no fully resolved peaks; these samples must be quantified using the summed area counts of FID time slices and the RRF of appropriate hydrocarbon (HC) standards.

Identified compounds are screened against VOHAP compounds, Maximum Incremental Reactivity (MIR) compounds, Global Warming Compounds (GWC), Ozone Depleting Compounds (ODC) or other specified lists when required by CAS, CACC, or other District Rules, Protocols, or purposes.

A list of commonly analyzed compounds and their corresponding RRFs are presented in Appendix 2.

3.0 Definitions of Method

See Appendix 1 for the definition of method-specific terms.

4.0 Interferences

Analysts must remain alert to the presence of novel compounds, unpredictable solvent interactions, and the following interferences:

4.1 Co-elution

Surrogate spike compounds are added to samples in order to examine the extraction efficiency of the dilution solvent. These compounds and the solvent selected for dilution may co-elute with compounds found in the sample chromatogram. Following instructions provided in Section 10, optimize the instrument in such a way as to reduce potential co-elution between spikes, solvent, and compounds commonly seen during analysis.

Not all sample peaks may separate chromatographically. Identify the overlapping constituents and determine which area counts belong to which compound and assign the appropriate calibration factors to each component. Attempt analysis with a different solvent if the interference makes or identification or area count apportionment too difficult.

4.2 Contamination

Contaminants in the samples that originate from the dilution solvent and extraction markers should not be quantified as VOC during sample processing. Use the RB and CSV injections nearest to the sample in the sequence to determine which peaks in the sample injection are contaminants derived from the solvent and/or the surrogate spikes.

4.3 Inlet breakdown and contamination
Compounds which are determined to elute prior to MeP only due to inlet fragmentation may be excluded from quantitation. Reducing inlet temperature for specific samples may alleviate this problem.

Materials labeled as “sanitizers” or “disinfectants” may contain benzalkonium chloride (quaternary ammonium compounds, commercially labeled as “quat”) which fractures in the injection port. In addition to product labeling, the presence of these compounds is indicated by multiple peaks of chloro-, benzene-, and amine-derived fragments.

Concrete sealers labeled as “non-VOC” may contain siliconates. These samples typically do not accept any extraction marker spikes, and may leave a residue in the injection port. Ensuing DIIBA-containing injections often fail to meet quality control requirements after these sample types, and these samples should be analyzed at the end of a sequence when possible.

Cleaners with very high or very low pH may leave a residue in the injection port. This contamination should be suspected when subsequent CSV or sample injections containing DIIBA result in analyses that fail to meet QC requirements and these samples should be analyzed at the end of a sequence when possible.

Some samples contain a compound which reacts with DIIBA in methanol to form a residue which has been tentatively identified as hydrazine sulfate. Some samples also have been seen to convert DIIBA to dimethyl adipate when the sample is dissolved in methanol.

4.4 Hygroscopicity
Some compounds may be hygroscopic and must be protected from excessive water absorption as this will dilute the compound and reduce its response. Examples of hygroscopic compounds include TRIG, glycerol, and N-methylpyrrolidone.

4.5 Poor mixing/non-homogeneity
All samples must be thoroughly mixed and must remain homogenous throughout subsampling and preparation. Non-homogenous samples or preparations may produce non-representative results. See Section 11 for the sample preparation procedure.

4.6 Carryover
Analysis of samples containing highly retained compounds can lead to carryover between injections. Inject reagent blanks between sample injections as described in Section 11.6 to limit carryover. Evaluate the Relative Percent Difference (RPD) of total VOC in replicate injections to identify carryover, and re-inject the affected samples once the carryover in the system has been eliminated.

5.0 Safety

This method does not purport to address all safety concerns. This method requires the use of compressed gases and hazardous solvents such as THF, which may require specific Standard Operating Procedures (SOPs). Solvent handling must be conducted in a fume hood using appropriate Personal Protective Equipment (PPE). In all cases, follow required safety procedures.

6.0 Equipment and Supplies

Mention of a manufacturer does not constitute endorsement or recommendation for use. Equivalent equipment from any manufacturer is suitable for use.

Agilent 6890Plus to 7890A GC with split-vent injection port
Agilent 5973 to 5775C Mass spectrometer
Agilent 6890 Enhanced to 7693 Autosampler
Inlet liner, split/splitless FocusLiner with taper; Supelco Product Number 2879925-U
Column G43 phase with maximum temperature exceeding 300° C, 30m X 0.32 mm, 1.8 um film
Chromatographic post-column splitter with zero dead volume unions
Capillary tubing, 0.32 mm id (from post-column splitter to FID) 80 cm in length
Capillary tubing, 0.10 mm id (from post-column splitter to MS) minimum of 50 cm in length; can be adjusted longer depending on instrument needs and discrimination profile
Agilent Gas Clean Filter System or equivalent
Chemstation processing and instrument operation software, or equivalent
Clean 10, 25, 50 mL Class A Volumetric Flasks
1 mL Class A Volumetric pipets
Analytical balance (0.1 mg sensitivity)
Vials, 1.8 mL, screw cap with Teflon® faced septa
Gas-tight syringe, 10 µL with needle
Gas-tight syringe, 50 µL with needle
Gas-tight syringe, 250 µl with needle
Gas-tight syringe, 500 µl with needle
Gas-tight syringe, 5 mL with needle
Vials, 60 mL, screw cap with Teflon face
Acrodisc Syringe filters (25 mm diameter, 1 µm glass fiber membrane)
Glass mixing beads

6.1 Compressed Gases

Gas	CAS #
Helium carrier gas	7440-59-7
Hydrogen FID fuel gas	1333-74-0
Air FID oxidant gas	132259-10-0
Nitrogen FID make-up gas	7727-37-9

7.0 Pure Compounds and Laboratory Solutions

The compounds listed in Section 7.1 are required for instrument optimization and initial calibration. This method requires reagents for every compound detected above 3 g/L "as triglyme". Prepare all standards gravimetrically on a calibrated balance via sequential addition. The final concentration of each prepared standard should factor in the stated purities of each compound. Use the purity value from a Certificate of Analyses if it has been provided by the vendor.

7.1 Required Pure Compounds

Compound, abbreviation	CAS #
4-bromofluorobenzene, BFB	460-00-4
Methanol, MeOH	67-56-1
Tetrahydrofuran, THF (preferably inhibited with BHT)	109-99-9
Triethylene glycol dimethyl ether, TRIG	112-49-2
Isopropyl alcohol, IPA	67-63-0
Ethylene glycol diethyl ether, EGDE	629-14-1
Diisobutyl adipate, DIIBA	141-04-8
Methyl palmitate (Methyl hexadecanoate), MeP	112-39-0
Ethylene glycol, EG	107-21-1
Propylene glycol, PG	57-55-6
p-Toluenesulfonic acid monohydrate, pTSAM	104-14-4
Hexane, nC6	110-54-3
Heptane, nC7	142-82-8
Octane, nC8	111-65-9
Nonane, nC9	1118-84-2
Decane, nC10	124-18-5
Undecane, nC11	1120-21-4
Dodecane, nC12	112-40-3
Tridecane. nC13	629-50-5
Tetradecane, C14	629-59-4
Pentadecane, nC15	629-62-9
Other organic compounds as needed for specific calibrations	NA

Note: All chemicals must be ACS grade or equivalent.

The following are descriptions only. For quality control requirements, please see Section 9.0. For preparation instructions, please see Section 10.5.

7.2 Reagent Blank (RB)
This mix is used to demonstrate system cleanliness.

Compound	CAS #	Concentration (g/L)
Solvent (THF or MeOH)	NA	NA
Ethylene glycol diethyl ether, EGDE	629-14-1	5

7.3 Continuing Spike Verification (CSV)
This mix of compounds is used to establish that the calibrations of the extraction marker compounds have not drifted.

Compound	CAS #	Concentration (g/L)
Solvent (THF or MeOH)	NA	NA
Ethylene glycol diethyl ether, EGDE	629-14-1	5
Isopropyl alcohol, IPA	67-63-0	1
Diisobutyl adipate, DIIBA	141-04-8	1
Triethylene glycol dimethyl ether, TRIG	112-49-2	1
Heptane, nC7	142-82-8	1

7.4 Instrument Optimization Mix (IOM)
This mix of compounds is used to test and optimize injection representativeness, peak resolution, instrument sensitivity, mass spectrometer tuning, and endpoint.

Compound(s)	CAS #	Concentration (g/L)
Solvent (THF or MeOH)	NA	NA
n-Hydrocarbons (nC6-nC15)	NA	3 (each)
Ethylene glycol diethyl ether, EGDE	629-14-1	5
Triethylene glycol dimethyl ether, TRIG	112-49-2	0.1
Ethylene glycol, EG	107-21-1	3
Propylene glycol, PG	57-55-6	3
p-Bromofluorobenzene, BFB	460-00-4	0.1
Methyl palmitate, MeP	112-39-0	3

7.5 Continuing Calibration Verification (CCV) Mix

This mix is a compilation of the highest concentration compounds in exceedance of 1 g/L "as triglyme" identified across an analytical sequence. Starting with the highest concentration compound from each sample in the sequence and the five subsequent lower concentration compounds seen across the sequence. A list of compounds required for the CCV may be generated from knowledge of sample formulation, previous analysis, or by sample screening the sample prior to quantitation and should not exceed a total of 8 compounds.

Compound	CAS #	Concentration (g/L)
Solvent (THF or MeOH)	NA	NA
Ethylene glycol diethyl ether, EGDE	629-14-1	5
Compounds > 1 g/L "as triglyme" seen in samples	NA	1

7.6 Calibration Standards

A list of compounds required for instrument calibration may be generated from knowledge of sample formulation, previous analysis, or by sample pre-screening to determine which compounds are seen above 3 g/L "as triglyme".

Compound	CAS #	Concentration (g/L)
Solvent (THF or MeOH)	NA	NA
Ethylene glycol diethyl ether, EGDE	629-14-1	5
Compounds > 1 g/L "as triglyme" seen in samples	NA	15, 10, 5, 1, or 0.1

8.0 Sample Collection, Preservation and Storage

Samples submitted for compliance determination must be accompanied by approved versions of Analysis Request/Chain of Custody form and should be stored in a secure, temperature controlled location. Samples will be stored at room temperature in tightly closed containers unless stated otherwise in accompanying analysis requests.

Dilute samples within 30 minutes of spiking each sample. Spiking may cause matrix disruptions and change sample consistency, making sample handling difficult or impossible.

Seal diluted samples using a stopper and parafilm wax immediately following preparation if they are to be stored overnight. Do not use diluted samples after 24 hours after due to potential solvent loss. Dilutions should only be used within 24 hours if there is less than a 1% change in total sample mass. Store the other lab solutions under the same conditions as the samples to demonstrate that no bias has been introduced during sample storage.

9.0 Quality Control

The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of the following laboratory solutions as a continuing check on performance. Laboratories performing this analysis are required to maintain performance records which detail the quality of the generated data.

The following describe the limits for quality control injections which are required as part of calibration and analytical sequences. A summary of allowable QC recoveries is provided in Appendix 4.

9.1 Internal Standard Limits

EGDE is the internal standard added to reagent blanks, calibration solutions, CCVs, CSVs, and samples. EGDE recoveries are acceptable if they fall within 85-115% of the prepared concentration for all laboratory solutions, and within 50-150% for samples, provided surrogate standards or CSV recoveries are acceptable and the instrument is able to meet sensitivity requirements. The source of any unacceptable internal standard recovery must be investigated and corrected before proceeding with the analysis. One common acceptable reason for changed EGDE is the purchase of a syringes from a different manufacturer.

High or low internal standard recoveries for low viscosity solutions may indicate faulty syringe mechanics, such as plugged syringes or faulty sample split mechanics such as a plugged flow controller filter. Low internal standard recoveries may indicate partial injection for thick solutions.

High sample internal standard recoveries may be due to the filtration of solids prior to GC injection for high-solids solutions or the co-elution of 2-amino-2-methyl-1-propanol CAS 124-68-5) with EGDE.

Analysts should be aware that internal standard recoveries near the 50% recovery limit can imply meaningful changes to the instrument sensitivity, rendering the current LOD less than required for analysis. Analysts may re-prepare dilutions with the minimum allowable weight of sample (2.5 g) if high viscosity is limiting syringe performance.

9.2 Reagent Blank Limits

See Section 7.2 for a description of the reagent blank standard and Section 10.5 for its preparation. Reagent blanks must be injected prior to every sample injection and following the final sample injection in a sequence to demonstrate system cleanliness. Follow the sequence in Section 11.6 for an example of how RB interlacing should be performed. Special attention should be paid to any contaminants which may co-elute with compounds in the CSV. The area counts for any contaminant peak should not exceed 5% of the area counts of any CSV standard with which it co-elutes. Reagent blank contamination and carryover should be investigated in the case of reagent blank QC failure.

9.3 CSV Limits
See Section 7.3 for a description of the CSV standard and Section 10.5 for its preparation. Bracket every calibration and analysis sequence with replicate CSV injections. The CSV standard should be prepared at the same time as the samples. Recoveries are acceptable if they fall within 90-110% of the prepared concentration. Failing CSVs indicate a general instrument drift, and analysis should be stopped until corrective action can be taken to restore the instrument to expected performance. CSV failures are most often the result of leaky fittings at the detectors or contamination in the inlet liner from prior sample injections. Section 11.6 provides an example sequence demonstrating how to bracket with CSVs.

9.4 IOM Limits
See Section 7.4 for a description of the IOM, Section 10.5 for its preparation steps, and Section 10.1 for more detailed information regarding instrument tuning and optimization. Inject the IOM at the beginning and end of every calibration and analysis sequence as described in Section 11.6.

9.4.1 Representativeness
Test the representativeness of the system by looking for excessive discrimination against any molecular weight in the nC6 through nC15 region

The %D between nC10 normalized area counts and each individual nHC normalized area count must be within ± 15%. (See appendix for calculation.)

9.4.2 MS Tuning
The IOM must pass EPA TO-15 ionization criteria for BFB as listed in Section 10.2.

9.4.3 Resolution
Chromatographic resolution must be 90% or better for the EG, EGDE, and PG peaks.

9.4.4 Endpoint
Note and record the methyl palmitate retention time for each IOM injection. Methyl palmitate is the first peak that is not integrated during sample analysis. The retention time drift between IOM injections should not exceed 0.1 minutes.

9.4.5 Sensitivity
Recoveries of the 0.1 g/L TRIG peak in the IOM should be within 0.02 g/L

9.5 CCV Standard
See Section 7.5 for a description of the CCV standard and Section 11.4 for its preparation.
A CCV standard contains compounds above 1 g/L which are found in the samples of an analysis sequence. The highest concentration compound in each sample must be selected for the CCV, followed by compounds in decreasing concentration, to a maximum of eight compounds per

CCV. Bracket every analysis sequence with CCV injections as shown in Section 11.6. Recoveries for each compound in the standard must fall within 85-115%. Failing CCV QC indicates calibration drift for the compounds in the mixture. QC failures are most often the result of leaky fittings at the detectors or contamination in the inlet liner from prior sample injections.

9.6 Surrogate Standard Limits

Surrogate standards are added to each sample prior to dilution to evaluate the extraction efficiency of the solvent used for dilution. See Section 11.4 for a description of the sample spiking process. Recoveries are acceptable if they fall within 85-115% of the prepared concentration.

Recoveries exceeding 115% often fail due to co-elution with compounds in the sample. When this occurs, re-spike the sample and do not include the co-eluting surrogate standard. Compare the area counts in the retention time of interest between the sample injections and calculate the corrected spike recovery amount. Recoveries below 85% indicate incomplete VOC extraction, in which case the sample should be diluted in an alternative solvent.

Some sample matrixes do not accept certain spikes. Samples with greater than 80% water will not accept the nC7 spike, in which case the nC7 spike may be eliminated. nC7 and DIIBA may form an oily layer on the top of some samples, in which case both spikes should be eliminated for cause. Some spikes may cause some samples to gel, making mixing and subsequent injection impossible. Record observations when spikes interfere with the sample matrix and eliminate them in subsequent preparations.

Certain samples react with DIIBA in the presence of either THF or methanol, especially when using p-toluenesulfonic acid for samples requiring ASTM D5095. These reactions can activate the inlet liner for several injections and may be identified by the sudden and continued suppression of DIIBA in the sample, along with the ensuing CSV and sample recoveries. When this occurs, change the injection port liner and inject the other samples separately with their own bracketing CSVs, then inject the suspect sample separately with its own bracketing CSV.

Other quality control

9.7 Total Unidentified Components

All sample peaks are first calculated “as triglyme” to determine the appropriate quantitation technique for each peak. The default treatment for sample peaks below 1 g/L as triglyme is to classify those peaks as “unidentified” and continue calculating them “as triglyme”; however, the total concentration of unidentified peaks should constitute no more than 5 g/L material or 10% of the final VOC Material result, whichever is larger.

If the total concentration of unidentified components produces an unacceptably large value, continue to identify and quantify smaller peaks until the total “as triglyme” value becomes

acceptable. If the "as triglyme" values cannot be brought to acceptable levels- for example, the sample contains many unidentifiable peaks- flag the result.

9.8 Percent Water Comparisons
Comparisons can be made between the water % weight values determined experimentally from EPA M24 and water values calculated from M313 determinations with the following formula:

$$W_{\%wt} = 100 - NV_{\%wt} - Exempts_{\%wt} - VOC_{\%wt}$$

A difference of greater than 3% between calculated and derived values can signal sample misidentification, co-elution of VOC peaks with the main solvent peak, a fault in the Karl Fischer analysis, the presence of exempt compounds which have not been subtracted correctly, a misidentified peak, an erroneous RRF, or the presence of semi-volatile compounds. While agreement between M24/ M304-91 and M313 is not mandatory, a difference of more than 3% should initiate a review of the discrepancy, including re-analysis of water content and screening for co-eluting VOC peaks using an alternate solvent.

9.9 QC Requirement Summary
See Appendix 4.

10.0 Calibration and Standardization

If the instrument has not been previously configured for M313 analysis, begin with Section 10.1; otherwise, skip to Section 10.2 to evaluate the quality of the MS tune.

10.1 Instrument Parameters and Setup
Set up the GC/MS/FID in liquid analysis mode with a 10 µL autosampler syringe and the appropriate wash solvent (see section 11.2 for guidance). A wide variety of instrument parameters have been used successfully, but the following parameters should be used as a starting point for instrument configuration.

Injector Parameters:

Injector Type	Split/Splitless using Splitless Mode
Injector Temp	255 °C or lower
Injector Pressure	8-14 psi
Total Flow Rate	60-75 mL/min
Purge Flow Rate to Split Vent	>35 mL/min @ 0.1 – 0.5 min
Gas Saver On	20 mL/min after 2 min
Injection volume	1 µL

Column Parameters:

Flow Mode	Constant Flow

Column Flow Rate	1.5 - 4 mL/min
Total Run Time	35 - 50 min

GC Oven Temperature Ramp:

Initial Temp	35 ^{o}C or higher
Init. Hold Time	2 - 5 min
1st Ramp Rate	4 - 8 degrees per minute
1st Ramp Temp	75 ^{o}C
1st Hold Time	0 - 4 min
2nd Ramp Rate	10.0 degrees per minute
2nd Ramp Temp	225 ^{o}C
2nd Hold Time	6.0 min
3rd Ramp Rate	25.0 degrees per minute
3rd Ramp Temp	255 ^{o}C
3rd Hold Time	4 – 10 min
Total Run Time	35 - 50 min

FID Detector Parameters:

Detector Heater	240-255 ^{o}C
Hydrogen Flow Rate	40 mL/min
Air Flow Rate	450 mL/min
Makeup Flow Rate	45 mL/min

MSD Parameters:

MS Transfer Line	280 ^{o}C
MS Source	230 ^{o}C
MS Quad	150 ^{o}C
MS Scan Start Time	0.0 min
MS Scan Range	18-505 amu

An equitable distribution of compounds to the FID, regardless of each compound's molecular weight, is required for this method to quantify "unknown" sample peaks lower in concentration than 1 g/L. The distribution of molecular weights is colloquially referred to as a "discrimination profile". An evenly distributed discrimination profile is essential to reliably quantify VOC components throughout the entire retention time span of the chromatogram

The method described in this document utilizes a splitless injection mode. Splitless-mode is recommended over split-mode due to its greater likelihood to generate acceptable discrimination profiles. An instrument running on split-mode may produce better chromatography, but its discrimination profile may also suffer due to fluctuations in the inlet flow dynamics caused by insufficient equilibration time. In splitless-mode, the low and high molecular mass components

have time to equilibrate, and this hold time is easily adjustable to achieve good discrimination. Injecting in splitless mode will also provide greater sensitivity towards compounds present in very low concentrations since more sample will be delivered to the column.

The method described in this document is also configured for a post-column split to the MS and FID. This practice is not required to perform this method, but does cut down on column costs. In this configuration, the analytical column is connected to a T-splitter where two different transfer lines allow the sample to distribute to both MS and FID. Use 80 cm of 0.32 mm ID tubing to the FID and at least 50 cm of 0.1 mm tubing to the MS. Using 0.1 mm transfer line to the MS is essential to obtain an acceptable discrimination profile. The small ID tubing serves as a critical orifice, thus preventing the vacuum at the MS detector from favoring the low mass hydrocarbons. It should be emphasized that the FID is used to quantify the compounds in the samples being analyzed. Thus it is important to configure the post-split appropriately to allow evenly distributed and well resolved chromatograms in the FID channel.

Turn the MS “off” whenever the solvent (MeOH or THF) peak emerges, and turn it back on just before the peak reaches baseline.

Prepare an IOM standard (Sections 7.4, 9.4) to test the suitability of the instrument for analysis. The IOM results must meet the following minimum criteria for the instrument to be considered fit for use:

(1) EG at 3 g/L, EGDE at 5g/L, and PG at 3 g/L must be at least 90% resolved from each other
(2) The %D of mass-normalized area counts for each hydrocarbon must be within ±15% to the mass-normalized area counts for nC10 (see Section 9.4)
(3) Triglyme requires a method detection limit (MDL) at 99% confidence limit of 0.02 g/L or lower. This is verified in the IOM by a 0.1 g/L triglyme recovery between 80-120%
(4) BFB must pass the EPA TO-15 tuning criteria for a 0.1 g/L prep (Section 10.2)

It may be the case that the initial instrument parameters meet all IOM QC requirements. In the event that the instrument parameters require modification, it is recommended that analyte resolution be optimized first, followed by analyte discrimination, and lastly the analyte sensitivity.

10.2 Mass spectrometer Tuning
Ensure that the instrument is free of leaks by evaluating the amount of air present during an air and water check or a PFTBA tuning attempt. Air peak ions should meet the following criteria:

m/z	Ion Type	Ion Abundance Requirement
18	ion of water	< 1% of 69 amu of PFTBA
28	ion of nitrogen	< 1% of 69 amu of PFTBA

32	ion of oxygen	< 1% of 69 amu of PFTBA

If a leak is present in the system, tighten any loose fittings and perform air and water checks until air peak ion criteria is met, then tune the instrument using perfluorotributylamine (PFTBA) following the manufacturer's instruction. Once tuned, the instrument should meet the following criteria:

m/z	Ion Abundance	Reference Ion
69	Base Peak (100%)	NA
219	30 - 60%	of 69 amu
502	1 - 10%	of 69 amu

If the mass spectrometer cannot be tuned using PFTBA, troubleshoot the instrument following the manufacturer's recommended steps. The source should be removed and cleaned according to the manufacturer's instructions if the instrument tune still fails to meet the requirements.

Following a successful PFTBA tune, the instrument must demonstrate appropriate ionization of 4-bromofluorobenzene (BFB). Check the BFB ionization by injecting an IOM made up in the solvent to be used for analysis.

The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

The BFB ionization should be evaluated in the IOM at the beginning and end of every sequence (calibration or analysis), every week when not used daily, after cleaning the source, and after re-tuning PFTBA. Stop any instrument sequence that is running and go through the complete PFTBA and BFB re-tuning procedure if the instrument fails to meet the following BFB requirements:

m/z	Ion Abundance	Reference Ion
50	8 - 40%	of 95 amu
75	30 - 66%	of 95 amu
95	Base peak	NA
96	5 - 9%	of 95 amu
173	< 2%	of 174 amu
174	50 – 120%	of 95 amu
175	4 - 9%	of 174 amu
176	93 - 101%	of 174 amu
177	5 - 9%	of 176 amu

10.3 Calibration List

A list of compounds required for instrument calibration may be generated from knowledge of sample formulation or prior analysis. The instrument must be calibrated for compounds identified in a sample which have a concentration greater than 1 g/L. When screening samples, calculate individual peak concentrations using a TRIG default standard to establish which compounds require calibration. Compounds greater than 3 g/L "as triglyme" require an exact compound match, except in the case of hydrocarbon mixtures (see Section 10.4). Compounds with a concentration between 1 and 3 g/L "as triglyme" may be calibrated with the identified compound or a substitute standard, provided that the functional groups are identical and the number of carbons is ± 1. Peaks less than 1 g/L are quantified “as triglyme” unless their calibration is required in order to meet the limit for total unidentified compounds (see Section 9.8). Peaks less than 0.1 g/L are not quantified.

It is recommended that no more than 8 compounds be calibrated at once due to time and co-elution concerns.

10.4 Calibrations for Petroleum Distillate-Based Samples

Samples of this type may demonstrate a complex hydrocarbon profile with few or no fully resolved peaks; these samples must be quantified using the FID area summation slices regardless of the concentration of each peak; thus, analysis of these sample types requires that the appropriate substitute compounds be calibrated. Adhere to the following rules to ensure that appropriate compounds are calibrated for these sample types:

(1) Substituted alkanes and cycloalkanes should be quantified using the RRF of the n-alkane which elutes closest to and following the compound of interest. For instance, 2-methyl decane elutes prior to undecane and would be quantified using undecane’s RRF.
(2) Substituted aromatics should be quantified using the RRF of a substituted aromatic compound that matches the number of carbon substitutions for the compound of interest. For example, mesitylene and propyl benzene share the same number of carbons and same degree of saturation; as such, each compound can be used as a substitute for the other this example.

10.5 Calibration Levels

The concentration of individual components in a sample rarely exceeds 15 g/L when samples are diluted according to the method; thus, the maximum required calibration is usually no more than 15 g/L. The SCAQMD laboratory has found that with the exception of amines such as N,N-dimethylethylenediamine and monoethanolamine, compounds calibrated on an FID are linear up to at least 15 g/L when forced through zero.

Single point calibrations can be used for most compounds once system linearity has been demonstrated by successfully calibrating the 4 surrogate standard spike compounds used in the

CSV (Section 7.2) with a multi-level calibration and replicate injections at each level. The RRF of the 4 surrogate standards are considered linear when they all demonstrate correlation coefficients of at least 0.999 and once residual concentrations are calculated for each level and determined to be within 0.02 g/L or 10%; whichever is larger, at each level.

Single point calibrations require the preparation of 1 standard mix (15 g/L) injected in replicate. Linearity of single point calibrations is verified with replicate injections of a 0.1 g/L check standard containing the calibrated compounds. Linearity is verified with a percent recovery between 80 – 120% for each compound in the 0.1 g/L check mix.

The table below summarizes a single level calibration preparation forced through zero. It is acceptable that standard levels at and below 1 g/L be prepared via serial dilutions.

Calibration Level (g/L)	**Compound (g)**	**EGDE (g)**	**Quantity Sufficient (QS) to volume (ml)**
15	0.375	0.13	25
0.1	0.01	0.52	100
0	0	.13	25

The table below summarizes the multi-level calibration preparation forced through zero.

Calibration Level (g/L)	Compound (g)	EGDE (g)	Quantity Sufficient (QS) to volume (ml)
15	0.375	0.13	25
10	0.25	0.13	25
1	0.025	0.13	25
0.1	0.01	0.52	100
0	0	0.13	25

10.5 Laboratory Solution Preparation For Calibrations

The required laboratory solutions for calibration are:
Reagent Blank
IOM
CSV (if TRIG, IPA, DIIBA and nC7 are already calibrated)

NOTE: Some compounds, especially glycol ethers and polyols, are hygroscopic and may become diluted with absorbed water from frequent opening. Do not use compounds if they are past their expiry.

Prepare laboratory solutions in the following way:

Prepare QC and calibration standards in separate Class A volumetric flasks. Place each flask on a balance and add approximately 10 mL of the solvent used for sample analysis. Record the exact weight to the nearest 0.1 mg. Rinse a clean gas-tight syringe with the solvent used for analysis 3 times, then rinse it 3 additional times with the compound to be added. Use Section 7 as a guide for the preparation of each QC standard and Section 10.4 as a guide for each calibration level. Add the volume of compound necessary to create the required concentration for each standard or level. Record the weight of the added compound to the nearest 0.1 mg. Do this for each compound to be added to the mixture. Do not mix the flask until the solution has been brought to volume. QS the solution once the last compound has been added to the volumetric flask, mix, then weigh to the nearest 0.1 mg. Calculate the concentrations of each compound in the mixture, taking care to correct the concentrations for each compound's stated purity.

CSV standards should be included in sequences following the calibration of the 4 compounds in the CSV. IOM solutions prepared in methanol will require extended mixing; alternatively, analysts may reduce the concentration of each hydrocarbon to 2 g/L. IOMs may be prepared ahead of time and stored for up to 2 months in a freezer in a capped, glass vial. All other standards must be prepared immediately before or immediately after the calibration is prepared.

10.6 Calibration Sequence

Replace the inlet liner prior to every analysis or calibration sequence to eliminate the potential for contamination from a previous set of injections.

Use the following sequence as a template for calibrations:

RB
IOM
CSV (if previously calibrated)
RB
CSV (replicate, if previously calibrated)
RB
0.1 g/L Calibration Standard
RB
0.1 g/L Calibration Standard (replicate)
RB
1 g/L Calibration Standard*
RB*
1 g/L Calibration Standard (replicate)*
RB*
10 g/L Calibration Standard*
RB*
10 g/L Calibration Standard (replicate)*
RB*
15 g/L Calibration Standard
RB
15 g/L Calibration Standard (replicate)
RB
CSV (if previously calibrated)
RB
CSV (replicate, if previously calibrated)
RB
IOM
RB

*Not required for single point calibrations

10.8 Calculating RRFs

Determine each compound's RRF using the following equations:

$$X_i = \frac{Conc.\ of\ \ STD\ (g/L)}{Conc.\ of\ internal\ STD\ (g/L)} \qquad Y_i = \frac{Area\ counts\ STD}{Area\ counts\ internal\ STD}$$

$$X_{ave} = \frac{\sum X_i}{n} \qquad Y_{ave} = \frac{\sum Y_i}{n}$$

$n =$ number of calibration injections

$$RRF = \frac{\sum(X_i - X_{ave})(Y_i - Y_{ave})}{\sum(X_i - X_{ave})^2} \qquad r^2 = \frac{\sum[(X_i - X_{ave})(Y_i - Y_{ave})]^2}{\sum(X_i - X_{ave})^2\,(Y_i - Y_{ave})^2}$$

$RRF =$ Relative Response Factor $\quad r^2 =$ correlation coefficient

Calculate the error of each point on the calibration curve by applying the area counts of each point to the determined RRF as in the calculations above to calculate "residual" concentrations. The allowable error for each residual is 10% of the prepared value or 0.02 g/L; whichever is larger.

In the event of a non-linear curve, reduce the applicable calibration range to the portion of the curve which meets requirements.

Note that some compounds such as 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (Texanol™) and dipropylene glycol dimethyl ether exist as more than one isomer. When calibrating these compounds, sum the area of all isomer peaks before further calculation.

Collect RRF, retention-time, and mass spectral libraries of prohibited and quantified compounds as they are calibrated. If a compound's RRF has been determined in a previous calibration or on a different instrument, it is prudent to compare current and historical RRFs. A difference of more than 15% from the average of previously obtained RRFs requires review of sample preparation and instrument conditions.

10.10 Instrument Sensitivity (MDL)

Compounds which exhibit a lower RRF than TRIG must have their MDL determined at the time of their calibration. Refer to EPA Pt. 136, App B to determine the MDL of each compound.

10.11 Calibration Frequency

Update calibrations after any repairs or method modifications which result in a demonstrated change in instrument sensitivity. The instrument does not require recalibration after changes to the liner or minor changes to the column. It is important to ensure that the instrument is still under control after any changes by analyzing an IOM and CSV mix and verifying their quality.

11.0 Analysis Procedure

11.1 Sample Analysis

Begin sample analysis only if all compounds in the sample in exceedance of 3 g/L are calibrated, and all compounds between 1 and 3 g/L are calibrated with an exact or appropriate substitute compound. A list of compounds requiring calibration can be generated from formulation data, previous analysis, or sample pre-screening.

11.2 Solvent Choice for Sample Dilutions

Both THF and methanol have been used successfully to dissolve samples for sample analysis and sample screening. Methanol is less toxic and has fewer contaminant peaks, but should not be used for paint samples which are labeled as "acrylic" (they often contain methanol), CAS, CACC samples (methanol is a VOHAP analyte), samples which require pTSAM, and samples which are known to contain a high number of molecular-weight hydrocarbons (C12 or greater).

Some samples may only be successfully dissolved or extracted in one solvent. When samples are diluted for analysis, pay close attention to resulting homogeneity. Large clumps, gels, layering, etc. may inhibit VOC extraction and require a different solvent. This method has been extensively tested only with THF and methanol as the solvents; do not use water or acetone as solvents. The solvent used for compound calibration and sample analysis must be consistent, and TRIG must be calibrated in any solvent that is used for sample screening.

11.3 Sample Analysis Laboratory Solutions Preparations

Prepare reagent blank, CSV, and IOM, and CCV standards in the same manner as described in Section 10.5. See section 7.5 for details on how to determine which compounds to include in the CCV standard.

11.4 Sample Surrogate Spiking

Prior to sample spiking, ensure that the sample has been analyzed for density, water content and nonvolatile content using SCAQMD Method 304-91 or EPA Method 24.

Vigorously shake the sample container either by hand or mechanical shaker for several minutes. The sample should be homogeneous before proceeding. Drag a stirring tool across the bottom of the container to ensure that no solids have settled in the sample.

Dissolution and VOC extraction is verified by spiking samples with surrogate standards (TRIG, nC7, IPA and DIIBA) prior to dilution. Begin surrogate spiking by weighing a 40-mL vial to the nearest 0.1 mg. Add approximately 30 grams of sample to the vial, and reweigh. If a sample will not remain homogenous during this step, allow the sample to separate, measure the volume of each layer, and prepare each layer separately. Add approximately 317 uL of DIIBA, and reweigh the vial to the nearest 0.1 mg. Add approximately 317 uL of TRIG, and reweigh the vial

to the nearest 0.1 mg. Add approximately 443 uL of nC7, and reweigh the vial to the nearest 0.1 mg. Add approximately 382 uL of IPA, then reweigh the vial to the nearest 0.1 mg and add four to six glass mixing beads to the sample mixture. Cap and vigorously shake by hand until the spiked sample is completely mixed.

Inspect the sample. Some resins swell and solidify with the addition of nC7 and/or DIIBA; if this occurs, re-spike a fresh sample aliquot, but exclude nC7. If the re-spiked sample also demonstrates a matrix incompatibility, re-spike again but exclude both nC7 and DIIBA. Sample layering can occur in high water (> 80%) samples. In these cases, the sample must be freshly re-spiked and nC7 and DIIBA should again be excluded. The minimum required surrogate standard spike for any sample is TRIG.

11.5 Sample Analysis Dilution

Determine the appropriate dilution solvent using Section 11.2 as a guide. Fill a clean 25 mL volumetric flask approximately one-third full with the solvent of choice. Weigh the volumetric flask to the nearest 0.1 mg. Add between 2.5 grams to 3.5 grams of surrogate-spiked sample and re-weigh the flask. Add 150 uL EGDE internal standard and re-weigh. If ASTM D5095 has been requested, add approximately 20 mg of p-toluenesulfonic acid monohydrate (pTSAM) to the flask. Fill to the mark, cap, and mix well. The sample should be sonicated for 5 minutes to ensure appropriate mixing, but should be sonicated for 30 minutes if the sample contains glycerol. Samples should never be heated during sonication, and attention should be paid that the volume in the volumetric flask does not change during sonication. Cloudy samples sometimes clear if allowed to stand overnight. Allow the sample to react for at least one hour prior to analysis for samples requiring ASTM D5095.

Observe the diluted sample for uniformity. Samples which gel, form large clumps or develop two liquid layers must be re-prepared using whichever dilution solvent was not used in the original preparation. Allow solids to settle, then transfer the liquid portion of the dilution to an autosampler vial, minimizing headspace. Samples with a high concentration of solids may be filtered through an Acrodisc filter to extend the lifetime of the GC’s capillary column.

11.6 Analysis Sequence

A new inlet liner should be installed prior to each analysis due to the potential for contamination from previous analyses. Fill autosampler vials with each sample or standard to be analyzed, cap them, and place in autosampler tray. Inject each QC standard or sample using the following sequence as a guide:

RB
IOM
CSV
CSV
CCV

RB
CCV
RB
Sample 1
RB
Sample 1 (replicate)
RB
Sample 2
RB
Sample 2 (replicate)
RB
Sample 3
RB
Sample 3 (replicate)
RB
CCV
RB
CCV
RB
CSV
CSV
IOM
RB

RBs in between and immediately following CCV injections can be removed if there is no chance of carryover between their injections. Samples should always be injected in replicate with a RB in between injections, as reagent blanks reduce the potential for carryover into the second injection of the sample. The syringe wash solvent must be the same solvent that was used in the dilution of the sample. It is recommended that no more than three sample analyses be included in each analytical sequence due to the potential for solvent loss and settling of solids.

CSV and CCV recoveries which do not fall within the allowable QC range of 85-115%, BFB evaluations that do not meet passing criteria, and failing discrimination % differences indicate instrument drift and/or malfunction. Do not continue with sample analysis until the instrument is brought back under control. Internal standards and surrogate standard spikes which are high or low may indicate sample partitioning, poor extraction, or the presence of co-eluting compounds.

12.0 Data Analysis and Calculations

12.1 Peak Identifications
Samples may be very complex and contain hundreds of peaks. Analysts must use mass spectrometry to examine peaks. Analyte identification should only be performed by experienced

GC-MS operators. If components are present which cannot be positively identified by matching to known spectra, the analysts should utilize spectrum background subtraction capabilities made available in the system's chromatography software to improve spectrum signal and increase confidence in identifications. When no identifications can be made using the default library matching algorithm, usually Probability Base Matching (PBM), the analyst may use the National Institute of Standards and Technology (NIST) library matching algorithm, or the analyst may use deconvolution tools such as the Automated Mass spectral Deconvolution and Identification System (AMDIS) combined with PBM algorithm and/or the NIST library matching algorithm.

12.2 Sample Data Analysis

Examine all peaks for proper integration. Examine the sample chromatogram to determine whether the sample exhibits a petroleum-distillate profile.

Use the FID area counts and retention times from the RB and CSV which immediately precede the sample as a guide for which peaks to ignore; do not quantify any peaks that are attributable to column bleed, carryover, the dilution solvent, the internal standard, surrogate spikes, or their associated contaminants. Ethylene glycol, commonly found in paints and coatings, is of particular interest due to its potential to co-elute with the internal standard. Many co-eluting compounds may be separated by adjusting the carrier gas flow rate or modifying the oven temperature ramp profile. Follow the instrument optimization guide in Section 10.1 for further details. Samples may be screened in a solvent that is not to be used for analysis in order to examine potential co-elution with the solvent peak. If a sample peak and an RB or CSV peak elute at the same retention time, classify the peak as sample if the area counts of the sample peak are larger than the RB or CSV area counts by a factor of at least 2x.

Report FID data in a format which shows the area counts and retention time for each peak. Calculate the concentration of each peak "as triglyme" using FID area counts. If any peaks are observed over the quantification threshold of 0.1 % or 1 g/L, identify those peaks with the MS list their identities alongside the area counts and retention time. The final concentration of identified peaks will be calculated using each calibrated peak's RRF, or a valid substitute RRF if the concentration as TRIG is greater than 1 g/L and less than 3 g/L.

Peaks may be generically characterized (e.g. C9 hydrocarbon isomer) when an exact match cannot be determined. If the analyst cannot come up a reasonable analyte identification or generic characterization using all the tools available, the analyte should be flagged as "UNKNOWN" and the concentration should be calculated and reported "as triglyme".

Calculate sample VOC concentrations as follows:

$$VOC_{g/L} = \frac{area\ counts\ compound}{area\ counts\ internal\ std} \times \frac{\text{g/L internal std}}{RRF} \times \frac{volume\ (ml)}{sample\ weight\ (g)} \times D$$

$$RRF \quad = \frac{area\ counts\ std}{area\ counts\ internal\ std} \times \frac{g/L\ internal\ std}{g/L\ std}$$

$$volume\ (ml) = \ volume\ of\ dilution\ volumetric\ flask\ (mL)$$
$$D = \ density\ of\ sample\ (g/mL)$$

Calculate the final concentration of each compound in the sample by using the compound-specific RRF or an appropriate substitute RRF. Ignore peaks calculated to be less than 0.1 g/L as TRIG and any exempt compounds. Peaks that elute at the same retention time as methyl palmitate are the first peaks to be ignored for VOC quantitation. Ignore any peaks that elute at or after MeP's retention time. Sum the VOC concentrations of all sample compounds and report the sum as g/L (material), but do not include the surrogate spikes and internal standard in the total. For paints and coatings, calculate the Solids lb/gal and VOC g/L (coating) using weight percent nonvolatiles (NV) and density in grams per milliliter (D) measured by Method 304-91 as follows:

$$VOC_{\%wt} = \frac{VOC_{g/L}material}{(D * 10)} \qquad W_{\%wt} = 100 - NV_{\%wt} - VOC_{\%wt}$$

$$VOC_{g/L}(coating) = \frac{VOC_{\%wt} \times 1000}{\left(\frac{100}{D} - \frac{W_{\%wt}}{0.997}\right)}$$

$$Solids_{lb/gal} = \frac{NV_{\%wt}}{100} \times \frac{D}{454} \times 3785$$

The precision of this method has been estimated at 5 g/L material. It may be used to estimate the error in the final VOC g/L (coating) value first by adding the estimated error to the final VOC g/L (material) and calculating the VOC g/L (coating), then subtracting the estimated error and performing the same calculations. See the following equations:

To estimate the minimum VOC coating value for an analysis, $VOC_{g/L}(coating)_{min}$:

$$VOC_{g/L}(coating)_{min} = \frac{\left(VOC_{\%wt} - \left[\frac{5}{D * 10}\right]\right) \times 1000}{\left(\frac{100}{D} - \frac{W_{\%wt}}{0.997}\right)}$$

To estimate the maximum VOC coating value for an analysis, $VOC_{g/L}(coating)_{max}$:

$$VOC_{g/L}(coating)_{max} = \frac{\left(VOC_{\%wt} + \left[\frac{5}{D * 10}\right]\right) \times 1000}{\left(\frac{100}{D} - \frac{W_{\%wt}}{0.997}\right)}$$

Samples submitted for CAS or CACC analysis which contain prohibited compounds in excess of the quantitation threshold (1 g/L) are rejected before further calculation.

Peak concentrations must be examined to determine whether they fall within linear instrument range. Peaks found to exceed the instrument's calibrated range for that compound can be re-prepared and re-analyzed using a smaller sample size if a large aliquot was originally used; otherwise, the instrument's calibrated range must be expanded. All peaks should also be examined for proper integration and analysts should be aware that GC software occasionally combines two peaks into one, erroneously exceeding the 1 g/L threshold for identification used in this method.

Peaks which have been quantified "as triglyme" should constitute no more than 5 g/L material or 10% of the final VOC result, whichever is larger. If the above procedure produces an unacceptably large number of peaks quantified "as triglyme", continue to identify and apply appropriate RRFs to each successively smaller peak until the total "as triglyme" value becomes acceptable. If the "as triglyme" values cannot be brought to acceptable levels- for example, the sample contains many unidentifiable peaks- flag the result.

12.4 Petroleum Distillate Based Samples

In this profile, assume that peaks are hydrocarbons unless otherwise demonstrated. However, samples containing petroleum-distillates often contain co-solvents or surfactants such as dipropylene glycol ethers which elute within the retention time range of hydrocarbon peaks. Therefore it is important to examine the chromatogram for surfactants because hydrocarbon and glycol ether RRFs are very different, and misidentifying these peaks may under-report VOC content significantly

12.5 Sample Analysis Reporting
On the summary page, report the sample
VOC in g/L (material)
VOC g/L (coating)
Solids lb/gallon

On the detailed page, report
CCV and CSV recoveries
Surrogate standard recoveries
Weight percent solids (from SCAQMD Method 304-91/ EPA Method 24)
Sample density in g/mL (from SCAQMD Method 304-91/ EPA Method 24)
Weight percent water, measured (EPA Method 24)
Weight percent water, calculated (SCAQMD Method 313)
Total g/L (material) of compounds reported “as triglyme”
Annotations about the sample analysis

13.0 Method Performance

This section is currently reserved

14.0 Pollution Prevention

No specific pollution prevention steps have been identified.

15.0 Waste Management

Follow the laboratory guidelines for handling and disposal of waste generated from using this method.

16.0 References

17.0 Tables, Diagrams, Flowcharts and Validation Data

This section is currently reserved

Appendix 1: Glossary

CAS # - Chemical Abstracts Service registry number assigned as a unique numerical identifier to every chemical described in open scientific literature.

Clean Air Solvents (CAS) - An SCAQMD voluntary certification program.

Co-elute - When a compound elutes at the same retention time as that of another compound.

Continuing Spike Verification (CSV) standard - A mix of four compounds prepared at 1 g/L each: isopropanol (IPA), heptane (nC7), TRIG, and diisobutyl adipate (DIIBA). This standard is prepared in either methanol or tetrahydrofuran. This solution is analyzed before and after a sample set to assess the quality of the instrument control during an analysis or calibration sequence. This solution is also used to discount from samples any contaminants that are introduced into a sample when the same four compounds are used as surrogate standards in the sample preparation.

Coalescing solvent (co-solvent) - A VOC compound which remains after water evaporates whose function is to soften paint particles and cause them to fuse into a continuous film.

Critical analytes - Analytes that elute close to one another. They may co-elute in a GC analysis depending on their concentrations in a sample. EG and PG are typical VOCs found in coatings in relatively large amounts and are common critical analytes due to their potential co-elution with EGDE.

Detected peak (as injected) – A peak seen on the chromatogram from the final diluted solution that is injected into the GC. The concentrations determined by quantifying these peaks would still need to be corrected for any dilution made throughout the sample preparation process in order to get the original value in the neat sample.

EPA M24 - An analysis for VOC using gravimetric measurement of sample nonvolatiles and density, a titrimetric or gravimetric measurement of water, and a gas chromatographic measurement of exempt compounds. VOC is assumed to be the remainder, once nonvolatiles, water, and exempt compounds are subtracted.

Injection - The emplacement of a small sample aliquot into a GC injection port for subsequent analysis.

Method detection limit (MDL) - A method-defined limit of detection set at 0.1 g/L material VOC in the neat sample. The method must at least be able to quantify individual VOCs at and

above 0.1 g/L material with the RRF of TRIG. An MDL of 0.01 g/L or better, "as injected", is confirmed by using seven replicate injections of a 0.1 g/L TRIG standard, calculating the standard deviation (SD) of the area counts, multiplying the SD by the student's t value for 99% confidence level (3.14), and calculating that value as g/L.

Novel compounds - Compounds seen in the chromatogram which are not typically part of a coating formulation. The analyst needs to flag these compounds as something that may "require further investigation" as to its origin. These may be decomposition products, contamination, "dirty" liner reaction products, extraction solvent-sample reaction products, etc.

Percent difference (%D) - The difference of one value *(V)* to a reference value *(Vr)* expressed as a percentage of the reference value *(Vr): %D = ((V-Vr)/Vr)*100*

QS to volume - "Quantity sufficient to volume" means "add enough solvent to bring the total volume to..." For example, "QS to 25 ml" means "add the volume necessary to make the total volume 25 ml."

Reagent blank (RB) - A solution consisting of the sample extraction solvent of choice and EGDE internal standard. This solution is analyzed prior to diluted samples to identify and subtract contaminants inherent in the extraction solvent and in the internal standard from the VOCs found in the diluted, spiked sample aliquots.

Relative percent difference (RPD) - A measure of precision, calculated by:
$RPD = [X_1 - X_2]/X_{ave} \times 100\%$
where, e.g:
X_1 = VOC content determined in first injection
X_2 = VOC content determined in duplicate injection
X_{ave} = average VOC amount determined = $((X_1 + X_2) / 2)$

Relative Response Factor (RRF) - The normalized peak area response (to its amount, g/L) of a VOC standard relative to the normalized value of the internal standard (EGDE)

"as triglyme" - Quantitation of detected VOC peaks using the default calibration standard RRF of TRIG .

Sample discrimination - During sample injection, the analytes in a sample may split unevenly at the inlet. This uneven split must be avoided to ensure that a representative weight of each sample analyte is delivered onto the column. When all lab instruments have similar discrimination profiles, this ensures comparable RRFs from instrument to instrument. This is important in assessing instrument stability, standard resolution, and/or standard purity.

Minimizing discrimination also ensures that a default RRF can be universally applied to unidentified VOCs across an entire chromatogram.

Sample pre-screening - Refers to the analysis of a neat sample only diluted in the solvent of choice with the internal standard. This is done to determine if there are any VOCs in the sample that may co-elute with the spikes and its contaminants that are introduced into the neat sample in a regular analysis. This process may also be used to determine if any compounds in the sample must be calibrated for quantitation.

Substitute standard - A compound considered as an acceptable replacement standard used to calibrate and quantify an otherwise known compound. It must have the same functional groups and must differ from the target compound by only 1 carbon atom.

Surrogate standards - Four compounds (IPA, TRIG, DIIBA, nC7) spiked neat and mixed uniformly into a sample. These are used to monitor the extraction efficiency of the solvent (methanol of THF) on the spiked sample. The surrogate standards should have a concentration of nominally 1 g/L in the final sample dilution.

Syringe/Injector mechanics - Mechanical aspects of the syringe and injector function parameters like plunger draw speed, injection speed, plunger dispense speed, and dwell time. Optimum recommended settings to improve precision include a slow syringe plunger draw speed, a fast syringe inject speed, and a fast syringe plunger dispense speed. There should also be enough syringe post-injection dwell time for the plunger to completely dispense the sample into the inlet before the syringe is drawn out and back to home position by the autosampler turret. Syringe injection mechanics affect analyte discrimination, and any adjustment in these settings may necessitate a re-optimization of the other parameters.

Multi-component coatings - See SCAQMD Rule 1113 for a definition of multi-component coatings.

Unpredictable solvent interactions - Phenomenon where the extraction solvent of choice reacts with the sample matrix resulting in sample clumping, sample hardening, or the creation of an inefficient extraction environment for VOC analytes.

VOC Coating - The VOC of coating is the same as the term “regulatory VOC”, which is equivalent to the term "VOC, less water and exempts". It is the amount of VOC in a sample volume, from which the volume of water and exempt volumes have been mathematically subtracted from the fully formulated sample.

VOC Material - The VOC of material is the same as the term "actual VOC ", which is equivalent to the term "VOC, including water and exempts". It is the amount of VOC in a volume of fully formulated sample.

Volatile Organic Compounds (VOC) - See SCAQMD Rule 102 for the definition of VOC.

Appendix 2: Commonly seen compounds and Relative Response Factors (RRF)

Compound	CAS #	RRF
2,2,4-trimethylpentane-1,3-diol monoisobutyrate, Texanol™, TX, a mixture of two isomers	25265-77-4 (mixture)	1.4
Texanol™ A, propanoic acid 2-methyl- 1- (2-hydroxy- 1-methylethyl)-2,2-dimethylpropyl ester	74367-33-2	
Texanol™ B, propanoic acid 2-methyl-, 3-hydroxy- 2,4,4-trimethyl-pentyl ester	74367-34-3	
Ethylene glycol, EG	107-21-1	0.5
Propylene glycol, PG	57-55-6	0.7
Ethylene glycol butyl ether, EGBE	111-76-2	1.1
Diethyleneglycol butyl ether, DEGBE	112-34-5	1.0
Dipropylene glycol monomethyl ether, DPGME, occurs as four identifiable isomers	34590-94-8 (mixture) 13429-07-7 20324-32-7 13588-28-8 55956-21-3	1.2
Dipropylene glycol, DPG occurs as three identifiable isomers	25265-71-8 (mixture)	1.3
2,2'-Oxybis-1-propanol	110-98-5	
2,2’-Oxybis-2-propanol	108-61-2	
2-(2-Hydroxypropoxy)-1-propanol	106-62-7	
2,4,7,9-tetramethyl-5-decyn-4,7-diol, TMDD	126-86-3	1.6
n-Methylpyrrolidinone, NMP	872-50-4	1.0
2,2,4-Trimethyl-1,3-pentanediol, TMPD	144-19-4	1.4
1-(2-Butoxyethoxy)-ethanol,DEGBE	54446-78-5	0.9
1-Butanol	71-36-3	1.3
p-Xylene	106-42-3	2.1
3-Iodo-2-propynyl n-butyl carbamate	55406-53-6	0.6
2-Methyl-1-propanol	78-83-1	1.4
Butyl acrylate	141-32-2	0.9
1-Phenoxypropan-2-ol	770-35-4	1.3
2,3-Dimethylpyrazine	5910-89-4	1.3
Tetraethylene glycol	112-60-7	0.5
Pentaethylene glycol	4792-15-8	0.5
Cyclohexanone	108-94-1	1.2
Methyl acetate	79-20-9	0.6
Decane	124-18-5	2.0
1,2,3-Trimethylbenzene	526-73-8	2.1
Tripropylene glycol mono methyl ether, TPGME	25498-49-1	0.9
TPGME is a mixture of isomers	and 20324-33-8	

Compound	CAS #	RRF
Ethyl benzene	100-41-4	2.1
Nonane	111-84-2	2.0
Undecane	1120-21-4	2.1
Dodecane	112-40-3	2.1
Triethylamine	121-44-8	1.6
Propylene glycol butyl ether	5131-66-8	1.2
Methyl methacrylate	80-62-6	1.0
Toluene	108-88-3	2.6
1-Dodecanol	112-53-8	1.8
Diethylene glycol ethyl ether	111-90-0	0.8

Appendix 3: QC Summary

Standard	Hold Time	Run	Requirement
Reagent Blank	two days	before and after each sample injection	Area count at surrogate standard retention times < 1% of total area of surrogate standard spikes
CSV Standard	two days	before and after each batch of samples	Surrogate standard recoveries within 85 - 115% EGDE recovery within 85 - 115%
CCV Standard	two days	before and after each batch of samples	Calibration check recoveries within 85 - 115% EGDE recovery within 85 - 115%
IOM Standard	2 months	at the start of each sequence	Acceptable BFB recovery as per EPA TO-15 %D ± 15% for nC6-nC15 (compare to nC10) TRIG recovery within ± 0.02 g/L.
Spiked surrogate standards	two days	in each sample	Recoveries within 85 - 115% EGDE recovery within 50 -150%

Appendix 4: IOM % Difference Calculation Example

IOM Compound	Retention Time (min)	Mass (g)	% Purity	Purity Adjusted Mass (g)	Area Counts	Area/P.A. Mass	%D from C10
Hexane	8.83	0.0966	99.0	0.0956	2492674954	26064735910	105.5
Heptane	12.18	0.0985	99.0	0.0975	2454428253	25169750838	101.9
Octane	16.51	0.0993	99.0	0.0983	2465421237	25078796393	101.5
Nonane	19.19	0.1092	99.3	0.1084	2634660258	24297004471	98.4
Decane	21.41	0.1078	99.0	0.1067	2636157632	24701164071	100.0
Undecane	23.26	0.1111	99.0	0.1100	2666157609	24240220468	98.1
Dodecane	24.89	0.1127	99.0	0.1116	2729565353	24464389709	99.0
Tridecane	26.37	0.1135	99.0	0.1124	2739759287	24382675095	98.7
Tetradecane	27.75	0.1164	99.0	0.1152	2830475046	24562420129	99.4
Pentadecane	29.03	0.1162	99.0	0.1150	2822626975	24536474687	99.3