# 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 AND PROHIBITED COMPOUNDS BY GC MS FID

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|---|---|
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**Revision history page**

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|---|---|
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## Revision changes from previous version

## List of abbreviations:

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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. This method may also be used to develop speciation information for SCAQMD Program or Rule development or for 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). It may also be used 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. This method is not to be used for 2-component coatings or Ultraviolet/Electron Beam (UV/EB)-cured coatings but 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".

This method has been developed to achieve a reportable limit of 5 g/L. However, method sensitivity and certainty depend on the number of identified individual VOCs in any sample. A large number of small analyte peaks in a sample can decrease the sensitivity of the method, and a large number of unidentified 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. Peaks are then quantified by FID using the same or similar compound as a calibration standard.

However, petroleum distillate-based samples may demonstrate a complex hydrocarbon profile with few or no fully resolved peaks; these samples must be quantified using the FID area summation slices and n-hydrocarbon (nHC) standards.

Peak integration is ended just before methyl palmitate (MeP) elutes.

If required by Clean Air Solvent (CAS), Clean Air Choices Cleaner (CACC), or other District Rules, Protocols, or purposes, identified compounds are screened against Volatile Organic

Hazardous Air Pollutant (VOHAP) compounds, Maximum Incremental Reactivity (MIR) compounds, Global Warming (GW) compounds, Ozone Depleting Compounds (ODC) or other specified lists.

A list of commonly analyzed compounds, as well as their Relative Response Factors (RRFs), may be found 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 Contamination from solvents and standards

Contamination from solvents and standards should not be counted as VOC. After checking for co-elution (Section 4.2), exclude solvent peaks and contaminants from the final VOC summation of the sample. Always use the reagent blank (RB) (Section 7.2) analysis and Continuing Spike Verification (CSV) (Section 7.3) analysis that is closest to the sample being analyzed as a guide for which peaks to exclude.

4.2 Co-elution

There is a chance that the solvent, surrogate standards, internal standard, or associated impurities will co-elute with sample compounds. By comparing CSV and sample analysis area counts (as above), a significant difference between CSV analysis area counts (which contain all potentially co-eluting compounds) and sample analysis area counts may indicate where peaks are co-eluting. Suspect peaks may also be examined by mass spectrometry. Samples may be screened in the solvent that is not used for analysis in order to determine the extent of any co-elution. Ethylene glycol, commonly found in paints and coatings, may co-elute with the internal standard, EGDE. These compounds may be separated by slowing the carrier gas flow rate during instrument optimization (Section 10.1).

Samples requiring VOHAP analysis cannot be diluted in methanol since methanol is a common VOHAP.

Samples containing petroleum-distillates often also contain co-solvents or surfactants such as dipropylene glycol ethers which elute within the retention time range of hydrocarbon peaks. 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.

4.3 Early eluting nonvolatiles

Early eluting nonvolatile (EENV) compounds elute prior to the quantitation endpoint marker, methyl palmitate (MeP), but are less volatile than MeP. Glycerin is an example of an EENV, and is measured as a nonvolatile by EPA Method 24. EENVs are approved for integration exclusion by a regulatory body such as SCAQMD after evaluation of compelling evidence. It is not incumbent on SCAQMD to seek out non-conforming compounds.

4.4 Inlet breakdown and contamination

Some samples or compounds have been determined to decompose in the injection port at elevated temperatures. 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 spikes, and siliconates may leave a residue in the injection port. This is indicated when subsequent CSV or sample injections containing DIIBA result in analyses that fail to meet quality control (QC) requirements. Some samples contain a compound which reacts with DIIBA in methanol to form a residue which has been tentatively identified as hydrazine sulfate. This is indicated when the DIIBA surrogate standard fails to meet QC requirements for the sample.

Cleaners with very high or very low pH may leave a residue in the injection port. This is indicated when subsequent CSV or sample injections containing DIIBA result in analyses that fail to meet QC requirements. Some samples and standards may be hygroscopic and protected from excessive water absorption.

4.5 Poor mixing/non-homogeneity

All samples must be thoroughly mixed and remain homogenous throughout subsampling and preparation. Non-homogenous samples or preparations may produce nonrepresentative results. See Section 11 for the sample preparation procedure.

4.6 Carryover

Analysis of samples containing highly retained compounds can lead to carryover between runs. Reagent blanks between injections of samples as seen in Section 11.6 is necessary to prevent the need for re-analysis. Attention should be paid to the relative percent difference (RPD) of total VOC in duplicate injections to identify and correct for carryover.

## 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. Other manufacturers' equipment than the ones mentioned in this method should work so long as the equipment is equivalent.

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 DB-624®, 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) 50 cm in length
Agilent Gas Clean Filter System or equivalent
Chemstation data system
Clean 10, 25, 50 mL Volumetric flasks, Class A
1 mL Volumetric pipets, Class A
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 will also require reagents for every compound detected above 1 g/L "as triglyme". All standards should be gravimetrically prepared on a calibrated balance with sequential addition of each compound. Final concentrations of each standard should factor in the purities of individual lot numbers. Always use ACS grade chemicals or equivalent.

7.1 Required Pure Compounds

| Compound, abbreviation | CAS # |
|---|---|
| 4-bromofluorobenzene, BFB | 460-00-4 |
| Methanol, MeOH | 67-56-1 |
| Tetrahydrofuran, THF | 109-99-9 |
| Triethylene glycol dimethyl ether, triglyme | 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 |
| p-Toluenesulfonic acid monohydrate, pTSA | 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 |
| 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)

| 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) and Method Blank (MB)

| 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, triglyme | 112-49-2 | 1 |
| Heptane, nC7 | 142-82-8 | 1 |

7.4 Instrument Optimization Mix (IOM)

| 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, triglyme | 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 Target Compound Mix (TCM)

A list of compounds required for the TCM may be generated from knowledge of sample formulation, previous analysis, or by sample pre-screening. The TCM is a compilation of all identified compounds seen in the samples that comprise the analytical sequence (up to a maximum of 8 compounds) that exceed a concentration of 3 g/L.

| 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 | 3 |

7.6 Calibration Compounds

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 1 g/L.

| Compound | CAS # | Concentration (g/L) |
|---|---|---|
| Solvent (THF or MeOH) | NA | NA |
| Ethylene glycol diethyl ether, EGDE | 629-14-1 | 5 |
| Compounds > 2 g/L "as triglyme" seen in samples | NA | 15 |

7.7 Triglyme Standard (1 g/L)

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

## 8.0 Sample Collection, Preservation and Storage

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

Spiked samples should be used immediately, as spiking causes matrix disruptions that change sample consistency and make handling difficult or impossible. Spiked samples should be used no later than 30 minutes after spiking, and only if there is no discernable change from the initial preparation.

Diluted samples should be sealed using a stopper and parafilm wax immediately after preparation if they are to be stored overnight. Diluted samples should not be used more than 24 hours after dilution due to the potential for solvent loss. Dilutions should only be re-used if there is no discernable change from previous conditions.

## 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. The laboratory is required to maintain performance records that define the quality of the data thus generated.

***The following describe the limits for quality control injections which are required as part of calibration and analytical sequences.***

9.1 Internal Standard Limits

EGDE is the internal standard added to reagent blanks, calibration solutions, TCMs, CSVs, and samples. EGDE recoveries are acceptable if they fall between 90-110% of the prepared concentration for all laboratory solutions except samples, and between 50-150% for samples, provided surrogate standards or CSV recoveries are acceptable and the instrument is still able to meet sensitivity requirements.

For laboratory solutions, high or low internal standard recoveries may indicate faulty syringe mechanics such as plugged syringes, or faulty sample split mechanics such as a plugged flow controller filter. For samples, low internal standard recoveries may indicate partial injection of thick samples, and high internal standard values are usually found in samples with high solids content due to the filtration of those solids prior to GC injection. The source of any unacceptable internal standard recovery must be investigated and corrected before proceeding with the analysis.

Analysts should be aware that internal standard recoveries near the 50% 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 the injection volume and a large sample aliquot was originally used for dilution.

9.2 Reagent Blank Limits

Reagent blanks should be injected, at minimum, prior to every sample injection and following the final sample injection in a sequence to demonstrate system cleanliness. Special attention should be paid to any contaminants which may co-elute with compounds in the CSV standard. 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. See Section 7.2 for a description of the reagent blank standard and Section 10.5 for its preparation.

9.3 CSV Limits

Bracket every calibration and analysis sequence with CSV standards. These should be prepared daily. Recoveries are acceptable if they fall between 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 can be linked to any number of instrument issues, but are most often the result of leaky fittings at the detectors or contamination in the inlet liner from prior sample injections. See Section 7.3 for a description of the CSV standard and Section 10.5 for its preparation.

9.4 IOM Limits

Inject the IOM at the beginning of every calibration and analysis sequence. Record the area counts of each n-hydrocarbon (nHC) peak. Normalize each nHC by dividing the area counts by the weight that was added to the standard. Use the normalized area counts of nC10 as the base value for comparison. The % Difference (%D) between nC10 normalized area counts and subsequent nHC normalized area counts must be 15% or better.

$$\%D = \frac{normalized\ area\ count\ of\ nHC\ compound - \ normalized\ area\ count\ of\ nC10}{normalized\ area\ count\ of\ nC10} \times 100$$

The IOM must also pass EPA TO-15 criteria for BFB as listed in Section 10.2. Additionally, chromatographic resolution must be 90% or better for the EG, EGDE, and PG peaks. Note and record the methyl palmitate retention time. Methyl palmitate is the first peak not to be integrated. See Section 7.4 for a description of the IOM, Section 10.5 for its preparation steps, and Section 10.2 for more detailed information regarding instrument tuning, optimization, and tuning requirements.

9.5 TCM Standard

A TCM standard contains all compounds above 1 g/L which are found in the samples of an analysis sequence. Bracket every analysis sequence with TCM injections. Recoveries for each compound in the standard must fall within 90-110%. Failing TCM 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. See Section 7.5 for a description of the TCM standard and Section 11.4 for its preparation.

9.6 Surrogate Standard Limits

Surrogate standards are added to each sample prior to dilution. Recoveries are acceptable if they fall between 85-115% of the prepared concentration. 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 suspect sample, and in the ensuing CSV and sample recoveries. In that case, change the injection port liner and inject the other samples separately with their own bracketing CSVs; inject the suspect sample separately with its own bracketing CSV.

Recoveries exceeding 115% tend to fail due to co-eluting compounds. It is prudent to re-spike the sample without the co-eluting surrogate standard and compare the area counts in the retention time of interest in these cases. Recoveries below 85% indicate incomplete VOC extraction and the sample should be diluted in an alternative solvent.

9.7 Triglyme Standard (1 g/L)

Bracket every pre-screening sequence with a 1 g/L triglyme standard. Prepare the triglyme standard fresh every sequence. Recoveries are acceptable if they fall between 90-110% of the

prepared concentration. The Triglyme standard is used to ensure that the pre-screening instrument is quantifying each peak consistent with the analysis instruments. See Section 7.7 for a description of the CSV standard and Section 10.5 for preparation steps.

***Other quality control***

9.8 Total Unidentified Components

In order to limit uncertainty, the total concentration of compounds using the triglyme "default calibration standard" RRF should not exceed 5 g/L.

The above notwithstanding, 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 required calibrations for 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.

9.9 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, the co-elution of VOC peaks with the main solvent peak, a fault in the Karl Fischer analysis, the presence of exempt compounds or EENVs which have not been appropriately subtracted from the equation, or a misidentified peak or erroneous RRF. While agreement between M24/ M304-91 and M313 is not mandatory, a difference of more than 3% should initiate a review for errors which could produce the discrepancy, including re-analysis of water content and screening for hidden VOC peaks using an alternate solvent.

9.10 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

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 11.5 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 |
| 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 °C |
| Init. Hold Time | 2 - 5 min |
| 1st Ramp Rate | 4 - 8 degrees per minute |
| 1st Ramp Temp | 75 °C |
| 1st Hold Time | 0 - 4 min |
| 2nd Ramp Rate | 10.0 degrees per minute |
| 2nd Ramp Temp | 225 °C |
| 2nd Hold Time | 6.0 min |
| 3rd Ramp Rate | 25.0 degrees per minute |
| 3rd Ramp Temp | 255 °C |
| 3rd Hold Time | 4 – 10 min |
| Total Run Time | 35 - 50 min |

| FID Detector Parameters: | |
|---|---|
| Detector Heater | 240-255 °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 °C |
| MS Source | 230 °C |
| MS Quad | 150 °C |
| MS Scan Start Time | 0.0 min |
| MS Scan Range | 5-505 amu |

This method is configured for a post-column split to the MS and FID. Install a capillary column splitter and use a length of fused-silica tubing to connect the splitter to each detector. Use 0.32 mm ID tubing for the FID and 0.1 mm tubing for the MS.

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

It is recommended that analyte resolution be optimized first, followed by analyte discrimination and analyte sensitivity. Prepare a IOM (Sections 7.4, 9.4) for the following process; it will take a series of IOM injections with different instrument parameters to determine optimal conditions.

Analysis of the IOM 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 5 g/L must be at least 90% resolved
(2) The %D of weight-normalized area counts for each hydrocarbon must be within ±15% to the weight-normalized area counts for nC10
(3) The 0.1 g/L triglyme peak must have a method detection limit (MDL) at 99% confidence limit of 0.01 g/L or lower
(4) BFB must pass the EPA TO-15 tuning criteria for a 0.1 g/L prep (Section 10.2)

Use the following oven temperature ramp profile as a starting point when optimizing analyte resolution:

| **Oven** | **°C/Min** | **Next °C** | **Hold Time (min)** | **Run Time (min)** |
|---|---|---|---|---|
| Initial | NA | 35 | 5 | 5 |
| Ramp 1 | 1 | 50 | 5 | 25 |
| Ramp 2 | 10 | 255 | 7 | 52.5 |

Adjust the GC oven temperature ramp profile and carrier gas flow rate such that you get the optimum resolution among the components in the IOM. Maximize the resolution of the critical analytes EG, EGDE, and PG. In general, better resolution is often obtained at lower flow rates and THF may require a longer splitless hold time. Do not be too concerned if these analytes are not yet fully resolved.

After optimizing analyte resolution, proceed to minimizing analyte discrimination and optimizing analyte sensitivity. Wide-bore, large volume, double-gooseneck inlet liners containing deactivated glass wool have been helpful in minimizing discrimination. The instrument's discrimination profile is assessed by analysis of the n-hydrocarbon (nHC) peaks in the IOM. Normalize the area counts of each nHC with the weight (g) of the nHC added to the IOM. Use the normalized value for each nHC and generate a %D from the normalized nC10

value for each compound as shown in Section 9.4. The discrimination profile is within tolerance if no compound's %D exceeds 15%.

If the initial parameters fail the specified tolerance, run an instrument sequence comprised entirely of IOMs and alter the following instrument parameters slightly, one at a time, with each injection:

(1) hold the inlet split vent closed and open the vent purge at a different time (0.0 to 0.5 minutes after injection)
(2) adjust the inlet vent purge flow rate (40 to 60 mL/min)
(3) change the injection amount (0.2 to 1 µL) and injection speed, dwell time, plunger draw speed and other syringe/injector mechanics.

Through repeated injections, discrimination trends will become apparent and can be utilized for quick optimization.

To determine detection sensitivity, assess the 0.1 g/L triglyme peak in the IOM analysis. Refer to EPA Pt. 136, App B to determine the method detection limit (MDL) of triglyme in the standard. If necessary, increase or decrease the injected volume to get the desired detection sensitivity or to avoid sample overload. Pay close attention to resolution of EG, EGDE, and PG while adjusting the detection sensitivity. Note that any adjustment in injection volume may necessitate a re-optimization of the resolution, discrimination profile, and detection sensitivity. Detection sensitivity must be robust enough that it should not be significantly compromised by slight fluctuations in the amount of sample introduced into the column. It should, however, not be so high that the common VOCs EG and PG are overloaded and co-elute with the EGDE internal standard.

After conditions are optimized, run the IOM 7 times with the final chosen GC conditions to check for consistency. If all injections are consistent and pass the optimization criteria, proceed to Section 10.2. If injections are inconsistent, check the integrity of the syringe and check for leaks in the system. To improve precision, use a syringe that has a volume capacity closest to the actual dispensed sample volume.

10.2 Mass Spectrometer Tuning
Two tuning conditions must be met to ensure that the tune profile is sensitive enough for accurate identifications during sample analysis.

Tune the instrument using perfluorotributylamine (PFTBA) following the manufacturer's procedures. When 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 meet PFTBA criteria, then check the system for air leaks by looking at the amount of air present during the PFTBA optimization run. 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 the mass spectrometer cannot be tuned using PFTBA, troubleshoot the instrument following the manufacturer's procedures. The source should be removed and cleaned according to the manufacturer's instructions if the instrument tune still fails to meet the requirements.

After a successful PFTBA tune, the instrument must also demonstrate a successful 4-bromofluorobenzene (BFB) tune. Check the BFB tune by injecting the IOM in the appropriate solvent at the start 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/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, previous analysis, or by sample pre-screening.

When pre-screening samples, calculate individual peak concentrations using a triglyme default standard to establish which compounds require calibration. Compounds greater than 2 g/L "as triglyme" require an exact compound match, except in the case of hydrocarbon mixtures (see below). Compounds between 1-2 g/L "as triglyme" may be calibrated with the same compound or a substitute standard, provided that the functional groups are identical and the number of carbons is ± 1. Compounds less than 1 g/L are quantified “as triglyme”. Compounds less than 0.1 g/L are not quantified.

Petroleum distillate-based samples may demonstrate a complex hydrocarbon profile with few or no fully resolved peaks; these samples must be quantified using the FID area summation slices and n-hydrocarbon standards.

Appendix 3 lists compounds which are commonly seen in paints and coatings and provides a recommendation for optimized calibration mixes. It is recommended that no more than 8 compounds be calibrated at once due to time and co-elution constraints.

It is beneficial to calibrate as many compounds as possible prior to sample analysis, as discovery of uncalibrated compounds in a sample will slow analysis throughput.

10.4 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 some amines such as N,N-Dimethylethylenediamine and Monoethanolamine, all compounds calibrated to date are linear up to at least 20 g/L on FID.

Demonstrate system linearity by successfully calibrating the 4 surrogate standard spike compounds used in the CSV (Section 7.2) with a multi-level calibration. All other compounds can be calibrated using a single point.

Single point calibrations require only the preparation of 1 standard mix (15 g/L) injected in duplicate. Linearity of single point calibrations is verified with the preparation of a 3 g/L check standard which is run at the end of the calibration sequence.

The table below summarizes a single 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 |
| 0 | 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 Solutions Preparation

Laboratory solutions are:
Reagent Blank
IOM
CSV (if triglyme, IPA, DIIBA and nC7 are already calibrated)

Laboratory solutions are to be prepared in the following way.

**NOTE:** Some standards, 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 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 solvent 3 times, then rinse it again with the compound to be added. Using Section 7 as a guide for each QC standard and Section 10.4 as a guide for calibration levels, add the volume of compound necessary to create the required concentration. Record the mass 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 standard 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 and correct the concentrations for compound purity.

CSV standards should be included in both analytical and calibration sequences after 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 1 month in a -5 °C freezer in a capped, glass vial. All other standards must be prepared on the same day that either a calibration is prepared or samples are spiked and analyzed.

10.6 Calibration Sequence
Replace the inlet liner prior to every analysis or calibration sequence to remove the potential for contamination.

Use the following sequence for multi-level calibration:

Reagent Blank (RB)
BFB, Discrimination, and Methyl Palmitate (IOM)
CSV (if previously calibrated)
RB
0.1 g/L Calibration Standard
RB
0.1 g/L Calibration Standard (duplicate)
RB
1 g/L Calibration Standard
RB
1 g/L Calibration Standard (duplicate)
RB
10 g/L Calibration Standard
RB
10 g/L Calibration Standard (duplicate)
RB
15 g/L Calibration Standard
RB
15 g/L Calibration Standard (duplicate)
RB
CSV (if previously calibrated)
RB
*Secondary standard (3 g/L)
*RB

*Only required for single point calibration sequences

10.8 Calculating multi-level 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 levels (8)

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

$RRF =$ 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 concentrations. The allowable error for each point from the prepared concentration is 5% of the prepared value or 0.05 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 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 that exhibit a lower RRF than triglyme 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 no less than once per year, or 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 column.

## 11.0 Procedure

11.1 Pre-Screening vs. Sample Analysis
All compounds with a concentration greater than 2 g/L in a sample require calibration in the same solvent used for sample analysis. Pre-screening is a tool to determine whether any compounds in a sample surpass the calibration threshold. Pre-screening is not required if all compounds in a sample are known and currently calibrated.

Pre-screening may be performed on the same instrument used for analysis of samples, or on a dedicated pre-screening instrument. Calibrate triglyme (single point, forced through zero) at 15 g/L on any instrument used for pre-screening. Linearity of the calibration should be checked by preparing and analyzing a 1 g/L triglyme standard as described in Section 7.7. Calculate the %D of the secondary standard from the theoretical concentration.

11.2 Pre-Screening Procedure

11.2.1 Pre-Screening Laboratory Solutions Preparation
Do not include surrogate standards in the sample preparation, as their presence can mask VOC peaks contained in the sample. Prepare reagent blank, 1 g/L Triglyme, and IOMs as detailed in Section 10.5.

11.2.2 Pre-Screening Sample Dilution
Prior to sample pre-screening, ensure that the sample has been analyzed for density, water content and nonvolatile content using SCAQMD Method 304-91.

Note whether ASTM D5095 has been requested. 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.

Determine the appropriate dilution solvent using Section 11.5 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 no less than 2.5 grams of sample and re-weigh the flask. 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 150 uL of EGDE internal standard and reweigh. If ASTM D5095 has been requested, add approximately 20 mg of p-

toluenesulfonic acid (pTSA) monohydrate to the flask. Fill to the mark, cap, and mix well. The sample should be sonicated for at least 1 minute to ensure appropriate mixing, but should not be sonicated longer than 30 minutes. Samples should never be heated during sonication, and attention should be paid that the volume in the volumetric flask does not change during the process. Samples requiring ASTM D5095 must react for at least one hour at room temperature prior to transfer to an autosampler vial. Cloudy samples sometimes clear if allowed to stand overnight.

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

11.2.3 Instrument Sequence Preparation for Pre-Screening
Install a new inlet liner prior to each pre-screening sequence due to the potential for contamination from previous analyses. Fill autosampler vials with each sample and standard to be analyzed, cap, and place in autosampler tray. Inject each vial using the following sequence as a guide:

Reagent Blank (RB)
BFB, Discrimination and Methyl Palmitate standard (IOM)
1 g/L Triglyme Standard
RB
Sample 1
RB
Sample 1 (duplicate)
RB
Sample 2
RB
Sample 2 (duplicate)
Etc.

End sequence with:
1 g/L Triglyme Standard
RB

Samples should always be injected in duplicate with a reagent blank in between injections; reagent blanks ensure that potential carryover will not affect the results. The syringe wash solvent must be the same solvent that was used in the dilution of the sample. 1 g/L Triglyme

recoveries which do not fall within the allowable QC range of 90-110%, BFB evaluations that do not meet passing criteria, and failing discrimination profiles indicate instrument malfunction. Do not continue with pre-screening until the instrument is brought back under control. See Section 12.1 for pre-screening data analysis.

11.3 Sample Analysis

Begin sample analysis only if all sample peaks greater than 2 g/L are calibrated on the instrument. A list of compounds requiring calibration can be generated from formulation data, previous analysis, or sample pre-screening.

11.3.1 Sample Analysis Laboratory Solutions Preparations

Prepare reagent blank, CSV, and IOM, and TCM standards as detailed in Section 10.5. The TCM standard contains all compounds (to a maximum of 8) detected above 1 g/L in pre-screening for all samples in the analytical sequence.

11.3.2 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.

Note whether ASTM D5095 has been requested. 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 (triglyme, 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 260 uL of DIIBA, and reweigh the vial to the nearest 0.1 mg. Add approximately 250 uL of triglyme, and reweigh the vial to the nearest 0.1 mg. Add approximately 350 uL of nC7, and reweigh the vial to the nearest 0.1 mg. Add approximately 310 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 spiked and and nC7 and DIIBA should again be excluded. The minimum required surrogate standard spike for any sample is triglyme.

11.3.3 Sample Analysis Dilution

Determine the appropriate dilution solvent using Section 11.5 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 no less than 2.5 grams of surrogate-spiked sample and re-weigh the flask. Add 150 uL EGDE internal standard and reweigh. If ASTM D5095 has been requested, add approximately 20 mg of p-toluenesulfonic acid (pTSA) monohydrate to the flask. Fill to the mark, cap, and mix well. The sample should be sonicated for at least 1 minute to ensure appropriate mixing, but should not be sonicated longer than 30 minutes. Samples should never be heated during sonication, and attention should be paid that the volume in the volumetric flask does not change during the process. Cloudy samples sometimes clear if allowed to stand overnight. For ASTM D5095 samples, allow the sample to react for at least one hour prior to analysis.

Observe the diluted sample for uniformity. Samples which gel, form large clumps or develop two liquid layers must be re-prepared using whichever 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.

11.3.4 Instrument Sequence Preparation for Analysis

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, and place in autosampler tray.

Inject each QC standard and sample using the following sequence as a guide:

RB
IOM
CSV
TCM
RB
Sample 1
RB
Sample 1 (duplicate)
RB
Sample 2
RB
Sample 2 (duplicate)
Etc.

End sequence with:
CSV
TCM
RB

Samples should always be injected in duplicate with a reagent blank in between injections; reagent blanks ensure that potential carryover will not affect the results. 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 four sample analyses be included in each analytical sequence due to the potential for solvent loss and settling.

CSV and TCM recoveries which do not fall within the allowable QC range of 90-110%, BFB evaluations that do not meet passing criteria, and failing discrimination profiles 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. See Section 12.6 for data analysis of samples.

11.4 Solvent Choice for Pre-Screening and Analysis Dilutions
Both THF and methanol have been used successfully to dissolve samples for sample analysis and pre-screening. Methanol is less toxic and has fewer contaminant peaks, but should not be used for paint samples which are labeled as "acrylic" (often contain methanol), CAS, CACC samples (methanol is a VOHAP analyte), samples which require pTSA, and samples which are known to contain high 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 triglyme must be calibrated in whichever solvent is used for pre-screening.

## 12.0 Data Analysis and Calculations

12.1 Pre-Screening Data Analysis
Examine all peaks for proper integration. Examine the sample chromatogram to determine whether the sample exhibits a petroleum-distillate profile.

Using the immediately previous RB FID area counts and retention times as a reference, ignore sample FID area counts which are attributable to dilution solvent, the internal standard,

associated contaminants, column bleed, or carryover. If a sample peak and RB peak elute at the same retention time, classify the peak as originating from the sample if the area counts of the sample peak are larger than the RB area counts by a factor of 2 or more. The total concentration of contaminants seen during sample processing should not differ from the total concentration of contaminants seen in the RB by more than 0.5 g/L.

Report FID data in a format which shows the area counts and retention time for each peak. Calculate each peak "as triglyme". If any peaks are observed over the pre-screening threshold of 0.08 % or 0.8 g/L, identify those peaks with the MS.

Calculate sample VOC concentrations as follows:

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

$$RRF_{triglyme} = \frac{area\ counts\ triglyme\ std}{area\ counts\ internal\ std} \times \frac{g/L\ internal\ std}{g/L\ triglyme\ std}$$

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

Calculate the concentrations of each peak using the triglyme RRF.

Flag all sample peaks greater than 2 g/L "as triglyme" as “exact std”, except in the case of hydrocarbon mixtures (see Section 12.5). Ensure that the sample analysis instrument is calibrated for all compounds flagged as “exact std”, as these peaks require an exact compound match during sample analysis. Flag all sample hydrocarbon peaks above 0.8 g/L and all other sample peaks between 0.8-2 g/L as “subst std” prior to sample analysis. The threshold of identification for pre-screening is lower than that of sample analysis so as to ensure that all “borderline” peaks of interest will be accounted for.

Examine sample concentrations for any peaks which exceed the instrument’s linear range for triglyme. If any sample peak concentrations exceed the linear range, this should be noted so that the sample can be diluted appropriately for analysis.

12.2 Peak Identifications

To the extent possible, identify each peak which has been flagged as requiring an “exact std” or “subst std”. Samples may be very complex and contain hundreds of peaks. Analysts must use mass spectrometry to examine peaks to determine whether the peak concentrations which rise above the thresholds for pre-screening (0.8 g/L "as triglyme") and sample analysis (1.0 g/L "as triglyme") have been properly identified.

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.

Peak 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".

12.3 Sample Data Analysis

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

Using the immediately previous RB and CSV FID area counts and retention times as a reference, ignore sample FID area counts which are attributable to dilution solvent, the internal standard, associated contaminants, column bleed, or carryover. If a sample peak and RB or CSV peak elute at the same retention time, classify the peak as originating from the sample if the area counts of the sample peak are larger than the RB or CSV area counts by a factor of 2 or more. The total concentration of contaminants seen during sample processing should not differ from the total concentration of contaminants seen in the RB or CSV by more than 1.0 g/L.

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. The final concentration of identified peaks will be calculated using each calibrated peak's RRF, or a valid substitute RRF if the concentration as triglyme is greater than 1.0 g/L and less than 2.0 g/L.

Calculate sample VOC concentrations as follows:

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

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

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

Calculate the concentrations using the compound-specific RRF or an appropriate substitute RRF. Ignore peaks calculated to be less than 0.1 g/L as triglyme. Peaks that elute at the same retention time as methyl palmitate are the first peaks to be ignored for VOC summation. Sum the remaining VOC concentrations of all compounds and report as g/L (material). 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:

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

$$VOC_{g/L}(coating) = \frac{VOC_{\%wt} \times 10}{\left(\frac{100}{D} - \frac{W_{\%wt}}{0.997}\right)}$$

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

For CAS and CACC Protocols, samples which contain prohibited compounds in excess of the quantification 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 reanalyzed 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 required calibrations for 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

Samples with a strong petroleum distillate character can mask “heteroatom-containing” co-solvents or surfactants such as dipropylene glycol ethers in the densest portion of the chromatograms. Misidentifying these peaks may under-report VOC content significantly because hydrocarbon and glycol ether RRFs are very different; thus, all peaks should be identified or characterized, if possible. If peaks are identified as specific hydrocarbons or exhibit alkane characteristics, quantify them as follows: The straight chain (normal) isomer is assumed to be the last-eluting hydrocarbon in a homologous series. Therefore, use the straight-chain hydrocarbon as the calibration standard for itself and for all hydrocarbon peaks which elute before it, excluding the previous n-hydrocarbon peak. For example a nC15 peak will be used to quantify all peaks just after nC14 through nC15. Peaks with retention time greater than or equal to pentadecane will be labeled as pentadecane.

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
TCM 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 trilgyme”
Annotations about the sample analysis

## 13.0 Method Performance

## 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

## Appendix 1: Glossary

**CAS # -** Chemical Abstracts Service registry number assigned as unique numerical identifiers 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 at 1 g/L each dissolved in either methanol or tetrahydrofuran: isopropanol (IPA), heptane (nC7), triglyme, and diisobutyl adipate (DIIBA). This solution is analyzed before and after a sample set to assess the quality of the instrument control during a batch (sequence) analysis. 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, EGDE, and PG are common critical analytes. EG and PG are typical VOCs found in coatings in relatively large amounts.

**Detected peaks (as injected) -** Peaks 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 screened with the RRF of triglyme. A MDL of 0.01 g/L or better, “as injected”, is confirmed by using seven replicate injections of a 0.1 g/L triglyme 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 triglyme .

**Sample discrimination -** During sample injection, the analytes in a sample may unevenly split inside the inlet. This uneven split must be avoided to ensure that a representative mass 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.

**Substitute standard -** A compound considered as an acceptable replacement standard used to calibrate and quantify an otherwise known compound. It must have similar structure; be within 1 carbon atom, and have the same functional groups as the target compound.

**Surrogate standards -** Four compounds (IPA, triglyme, DIIBA, nC7) spiked neat and mixed uniformly into a sample. These are used to monitor the extraction efficiency of an aliquot of the aforementioned spiked sample into the extraction solvent of choice. The surrogates should have a target concentration of 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; 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, etc., creating 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) | 1.36 |
| 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 | 0.73 |
| Ethylene glycol butyl ether, EGBE | 111-76-2 | 1.11 |
| Diethyleneglycol butyl ether, DEGBE | 112-34-5 | 0.99 |
| Dipropylene glycol monomethyl ether, DPGME, occurs as four isomers, | 34590-94-8 (mixture)<br>13429-07-7<br>20324-32-7<br>13588-28-8<br>55956-21-3 | 1.15 |
| Dipropylene glycol, DPG occurs as three isomers | 25265-71-8 (mixture) | 1.34 |
| 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 | 1.64 |
| n-Methylpyrrolidinone, NMP | 872-50-4 | 0.98 |
| 2,2,4-Trimethyl-1,3-pentanediol, TMPD | 144-19-4 | 1.37 |
| 1-(2-Butoxyethoxy)-ethanol,DEGBE | 54446-78-5 | 0.89 |
| 1-Butanol | 71-36-3 | 1.32 |
| p-Xylene | 106-42-3 | 2.15 |
| 3-Iodo-2-propynyl n-butyl carbamate | 55406-53-6 | 0.56 |
| 2-Methyl-1-propanol | 78-83-1 | 1.44 |
| Butyl acrylate | 141-32-2 | 0.86 |
| 1-Phenoxypropan-2-ol | 770-35-4 | 1.28 |
| 2,3-Dimethylpyrazine | 5910-89-4 | 1.31 |
| Tetraethylene glycol | 112-60-7 | 0.47 |
| Pentaethylene glycol | 4792-15-8 | 0.5 |
| Cyclohexanone | 108-94-1 | 1.19 |
| Methyl acetate | 79-20-9 | 0.62 |
| Decane | 124-18-5 | 2.01 |
| 1,2,3-Trimethylbenzene | 526-73-8 | 2.09 |
| Tripropylene glycol mono methyl ether, TPGME<br>TPGME is a mixture of isomers | 25498-49-1<br>and 20324-33-8 | 0.93 |

| Compound | CAS # | RRF |
|---|---|---|
| Ethyl benzene | 100-41-4 | 2.14 |
| Nonane | 111-84-2 | 2.01 |
| Undecane | 1120-21-4 | 2.07 |
| Dodecane | 112-40-3 | 2.08 |
| Triethylamine | 121-44-8 | 1.57 |
| Propylene glycol butyl ether | 5131-66-8 | 1.16 |
| Methyl methacrylate | 80-62-6 | 1.02 |
| Toluene | 108-88-3 | 2.56 |
| 1-Dodecanol | 112-53-8 | 1.78 |
| Diethylene glycol ethyl ether | 111-90-0 | 0.8 |

## Appendix 3: Recommended Calibration Mixes

| Mix #1 | Mix #2 | Mix #3 | Mix #4 |
|---|---|---|---|
| 2-Methyl-1-propanol | 1-Butanol | Toluene | Methyl acetate |
| PG | p-Xylene | Ethyl Benzene | Triethylamine |
| EGBE | TPGME | Nonane | Ethylene glycol |
| DPGME | 1,2,3-Trimethylbenzene | Decane | Cyclohexanone |
| NMP | 1-Dodecanol | Undecane | Tetraethylene glycol |
| DEGBE | DPG | Dodecane | Pentaethylene glycol |
| 1-Phenoxy-propan-2-ol | 2,2,4-TMPD | 3-Iodo-2-propynyl n-butylcarbamate | |
| | Propylene glycol butyl ether | | |

## Appendix 4: QC Summary

| Standard | Hold Time | Run | Requirement |
|---|---|---|---|
| Reagent Blank | same day | before and after each sample injection | Area count at surrogate standard retention times<br>< 1% of total area of surrogate standard spikes |
| CSV Standard | same day | before and after each batch of samples | Surrogate standard recoveries between 90 - 110%<br>EGDE recovery between 90 - 110% |
| TCM Standard | same day | before and after each batch of samples | Calibration check recoveries between 90 - 110%<br>EGDE recovery between 90 - 110% |
| IOM Standard | 1 month | at the start of each sequence | Acceptable BFB recovery as per EPA TO-15<br>%D ± 15% for nC6-nC15 (compare to nC10)<br>Triglyme recovery between 90 - 110% |
| Spiked surrogate standards | same day | in each sample | Recoveries between 85-115%<br>EGDE recovery between 50- 150% |