California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

MLD SOP SAS07

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF EXEMPT AND NON-EXEMPT COMPOUNDS GENERALLY FOUND IN CONSUMER PRODUCTS BY GAS CHROMATOGRAPHY-FID

August 28, 2012 Revision 1.9

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9-06-12
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DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1 INTRODUCTION

In the analysis of volatile organic compounds (VOCs) in consumer products, the percent total volatile content is determined by MLD SOP SAS01. From this total is subtracted that portion of volatile material not classified as VOC, e.g. water and ammonium. Several compounds have been identified as less reactive and therefore exempt from the VOC definition and are subtracted from the total volatile content. To characterize the volatile content present in a consumer product, this procedure analyzes a series of compounds both exempt and non-exempt commonly found.

Appendix A describes the determination of the exempt compounds: ethanol (AP/DO only), acetone, methyl acetate and perchloroethylene. Additional analytes are methanol, isopropanol, n-propanol, isobutanol, and limonene.

Appendix B describes the determination of the exempt compounds: dichloromethane and 1,1,1-trichloroethane. Additional analytes are ethyl acetate, toluene, ethyl benzene, the xylenes, and pinene.

Appendix C describes the determination of the exempt compounds: hexamethyldisiloxane, hexamethylcyclotrisiloxane, octamethyltrisiloxane, octamethylcyclotetrasiloxane, decamethyltetrasiloxane, decamethylcyclopentasiloxane, and benzyl alcohol.

Appendix D describes the determination of the exempt compound p-chlorobenzotrifluoride. Additional analytes are methyl ethyl ketone, propylene glycol methyl ether acetate (PM acetate), and 2-butoxyethanol.

Appendix E describes the determination of the exempt compounds: ethylene glycol, propylene glycol, 2-(2-ethoxyethoxy) ethanol (Carbitol), 2-(2-butoxyethoxy)ethanol (Butyl Carbitol), propylene carbonate and dipropylene glycol.

> **NOTE**: *The analyses performed under this appendix requires a different analytical column for the detection of the targeted glycols.*

Appendix F describes the determination of the exempt compound hexylene glycol.

2 SUMMARY OF METHOD

The samples of consumer products are prepared as 1:10 wt. / volume dilutions in 1-methoxy-2-propanol (MPA). After thorough mixing, the solution may require filtering to remove insoluble material. If under special circumstances another solvent is required, then the standards, control, checks and trip sample are to be made with the same solvent and analyzed with those samples.

The diluted sample is then analyzed on a gas chromatograph equipped with a

flame ionization detector. The data is reported as weight fraction of analyte in the product.

3 INTERFERENCES AND LIMITATIONS

With the increase in the number of compounds being identified, overlap of the retention times may start to occur. The increase in the number of compounds is the basis for grouping several analyses of specific functional groups. Care must be taken to make certain of the identity of the compounds, if possible through headspace gas chromatography/mass spectrometry analysis.

4 INSTRUMENTATION AND EQUIPMENT

4.1 Gas Chromatograph (GC) configured with a Flame Ionization Detector (FID), configured by appendix configuration:

4.1.1 For Appendices A,B,C,D,F:

GC System: Agilent 7890
GC Column: J & W DB-624, 30 m x 0.32 mm I.D. with 1.8 µm film.
GC Parameters are as follows:

<u>Oven Conditions</u>

Initial temperature:	40 °C
Initial time: 6.0 min	
Rate:	10 °C/min
Final temperature:	200 °C
Final time: 1.0 min	
Run time: 23.0 min	
Oven equilibration:	0.3 min
Injector temperature:	250 °C
Detector temperature:	250 °C
Carrier gas (He):	8.9 psi (31 cm/sec)
DET B FID: ON	
Split Ratio: 76.6 mL/min	

4.1.2 For Appendix E:

GC System: Agilent 6850
GC Column: Restek Rtx-Stabliwax, 30 m, 0.53 mm, 1µ film thickness.
GC Parameters are as follows:

<u>Oven Conditions</u>

Initial temperature:	80 °C

Initial time:	2.0 min	
Rate:	6°C/min	
Final temperature:		200 °C
Final time:	1.0 min	
Run time:	20.17 min	
Oven equilibration:		0.3 min
Injector temperature:		220°C
Detector temperature:		250°C
Carrier gas (He):		5.0 psi (6 cm/sec)
DET B FID:	ON	
Split Flow:	70.9 mL/min	

4.2 Volumetric Flasks:

4.2.1 10 mL and 500 mL.

4.3 Pipettors:

4.3.1 Rainin, electronic: 250 µL, 1.0 mL, 2.5 mL, and 10 mL, with tips.

4.3.2 Biohit, manual: 4.0 mL, with tips.

4.4 Vials:

4.4.1 5 mL, 16mL & 20 mL with PTFE-lined cap, for standards.

4.4.2 8 mL with PTFE-lined cap, for dilutions.

4.4.3 2 mL with caps, for GC analysis.

4.5 Analytical Balance, Sartorious MC1 or Mettler XP 205:

4.5.1 capacity of 100 g x 0.00001 g (readability).

4.6 Vortex Mixer, Vortex Genie 2, variable speed

4.7 Homogenizer, IKA T8.01 S1 .

5 **REAGENTS**

5.1 1-Methoxy-2-propanol (MPA), 98%.

5.2 Analytes, spectrophotometric grade - see specific appendix for listing.

5.3 Stock Standards: The 80 mg/mL stock standard is prepared gravimetrically. Analytes are specified in each of the appendices. All standards are prepared as 40 g of analyte in 500 mL volumetric flask, to volume with MPA.

5.4 Control/Check Stock Solution: A control/check stock solution is prepared using a specified analyte in MPA, for each of the appendices covered in this SOP. Control/checks are prepared as 25% of the targeted analyte. All are prepared as 25 g targeted analyte in 100 mL volumetric and brought to volume with MPA.

5.5 Trip Sample Stock Solution (Appendix A analysis only): A trip sample stock solution is prepared by weighing 300 g of water and 50 g each of sodium chloride, acetone, methanol, and ethanol into a 500 mL volumetric flask and bringing to volume with MPA.

5.6 Helium, grade 5.

5.7 Air, compressed, ultra high purity.

5.8 Hydrogen Generator: Whatman, model 75-32 or equivalent, 20 – 25 psi output.

6 PROCEDURE

6.1 Instrument Preparation:

6.1.1 Verify helium and air cylinder pressures are above 500 psi.

6.1.2 Check that the water level in the hydrogen generator is above the refill line.

6.1.3 Load appropriate method to be used. The FID will ignite automatically.

6.2 Analysis Preparation:

6.2.1 Solvent Blank: Prepare solvent blank by filling a GC vial with the same MPA used to make the dilutions in steps 6.2.2 – 6.2.4. Cap the vial.

6.2.2 Calibration Standards: Prepare the five calibration standards in 10 mL volumetric flasks as follows:

Concentration	Volume of Stock Standard
1.0 mg/mL	0.125 mL
10 mg/mL	1.25
20 mg/mL	2.50
40 mg/mL	5.0
80 mg/mL	----

Bring to volume with MPA, mix thoroughly and place in dilution vials.

6.2.3 Transfer an aliquot of each standard into a GC vial and cap.

6.2.4 Control/Check: Prepare the control/check by diluting 1.0 mL of the control/check stock standard to 10 mL with MPA. The control is analyzed after the calibration. The check is run after every ten samples and at the end of the run.

6.2.5 Trip Sample (Appendix A analysis only): Prepare the trip sample by diluting 1.0 mL of the trip stock standard to 10 mL with MPA. The trip sample is run after the control.

6.2.6 Sample: A 1.0 mL aliquot of the consumer product sample is weighed into a 10 mL volumetric flask. After the weight is recorded, the aliquot is diluted to 10 mL with MPA. (Samples may require filtering/settling.)

6.2.7 Transfer an aliquot of each control/check, trip and sample into appropriately labeled GC vials and cap.

6.3 Sample Analysis:

6.3.1 Place vials in the autosampler in the following order: MPA blank, calibration standards, MPA blank, control/check, trip sample, and diluted samples. The MPA blank followed by the check standard is run every tenth sample and at the end of the run. Additional blanks between standards and samples maybe used if carryover is suspected.

6.3.2 Perform Sample Analysis: See appropriate appendices based on analytes of interest. Calculate the value for each analyte found by dividing the amount from the report (mg/mL) by the sample dilution weight (see Section 8).

7 QUALITY CONTROL

7.1 An MPA solvent blank must be analyzed for each batch of samples. The analyte concentration in the blank must be less than 0.1% wt/volume. An MPA blank is run before the control and each check to prevent carry over from the previous sample. If interference or an analyte of interest is identified during a blank, the corresponding value is subtracted from the value of an actual compound of interest for a sample, once confirmed. Should the interference or analyte of interest be seen in all of the blanks, the average of the values is subtracted. This is known as “blank subtraction”.

7.2 The correlation coefficient for compounds present in the calibration must be greater than 0.98. If the calibration fails, the sequence is stopped and corrective action is implemented. Corrective action may include replacing the inlet liner, reanalyzing the calibration curve or making up a new dilution of the calibration curve and then reanalyzing.

7.3 A control sample is run after the calibration. The control must fall within the established control limits. If the control is not within the control limits, it may be necessary to recalibrate and rerun the sequence.

7.4 A check sample is run after every ten samples and at the end of the run. The check must fall within the established control limits. If one of the checks is out of the control limits, re-run the check and any samples that follow until the next check.

7.5 The trip sample contains 60% water, 10% ethanol, 10% methanol, 10% acetone and 10% sodium chloride. The recovery for the trip sample should be within the error of the method (± 3%).

7.6 LIMS assigns at least one duplicate sample for every sample set. Duplicate analysis should not have an absolute difference greater than ±3%.

7.7 Each limit of detection (LOD) is determined annually.

8 CALCULATIONS

The weight fraction of analyte in the product is calculated as follows:

$$\text{Weight Fraction of Analyte} = \left(\frac{\text{analyte}\,(\text{mg/mL})}{\text{sample dilution}\,(\text{g})} \right) \times 10^{-2}$$

Appendix A

ANALYSIS FOR ACETONE/ALCOHOL

Calibration Standard Stock: The stock standard consists of 40 g each of the following compounds, which are placed in a 500 mL volumetric flask and prepared, as follows: methanol, ethanol, acetone, methyl acetate, isopropanol, 1-propanol, isobutane, perchloroethylene, and limonene.

Bring to volume with MPA and mix. Aliquot the solution into 20 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

Control/Check Stock: The control/check stock is a 25% acetone solution prepared by weighing 50 g each of acetone and water into a 200 mL volumetric flask. Bring to volume with MPA and mix. Aliquot the control/check stock in individual 5 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

1 Load Method:

1.1 Under ***Method***, select ***Load Method***.

1.2 Click on ***ACETONE.m***; then ***OK***.

2 Load Sequence:

2.1 Under ***Sequence***, select ***Load Sequence***.

2.2 Click on ***ACETONE.S***; then ***OK***.

3 Modifying Sequence:

3.1 Under ***Sequence***, select ***Sequence Parameters*** to create a subdirectory for the data.

3.2 Input sequence parameters:

3.2.1 **Operator Name** – enter your initials.

3.2.1.1 For newer model GC software, enter initials under ***Sequence Comments***.

3.2.2 **Data Files** – select ***Auto***.

3.2.3 **Subdirectory** – enter the two decimal month, day, year (December 5, 2007

would be entered as ***120507***); a letter can be put at the end to distinguish specific analyses run on the same day.

3.2.4 **Part of method to run** – select ***According to Runtime Checklist***.

3.2.5 **Sequence Comment** – enter set sample numbers, and any other pertinent information.

3.3 Click on ***OK***.

4 Sequence Table:

4.1 Under ***Sequence***, select ***Sequence Table***.

4.2 Input sequence information:

4.2.1 **Sample Name** – enter the following, in order: MPA blank, the five standards, MPA blank, control, trip sample and the samples.

4.2.1.1 An entry for MPA blank followed by a check is made after every ten samples and again at the end of the run.

4.2.2 **Method Name** – select ***ACETONE*** from the pull-down menu.

4.2.3 **Vial** – vial number corresponds to the position of the vial on the autosampler tray.

4.2.3.1 Each entry for the blank will reference the same blank vial.

4.2.3.2 Each entry for check will reference the control vial.

4.2.4 **Inj/Vial** – enter 1, for all samples.

4.2.5 **Sample Type** – select ***Sample*** from the pull down menu for all lines except for the five calibration lines; for these lines select ***Calibration***.

4.2.6 For the calibration lines only:

4.2.6.1 **Cal Level** – enter 1,2,3,4,5, respectively.

4.2.6.2 **Update RF** – select ***Replace*** from the pull down menu.

4.2.6.3 **Update RT** – select ***Average*** from the pull down menu.

4.3 Click on ***OK***.

5 Save Sequence:

5.1 Under ***Sequence***, select ***Save Sequence***.

6 Print Sequence:

6.1 Under ***Sequence***, select ***Print Sequence***.

6.2 Check ***Method and Injection Info Part***; then click on ***Print***.

6.3 Verify that the sequence matches the vial placement on the autosampler.

6.4 Place sequence printout in the sequence binder.

7 Starting Sequence:

7.1 Under ***Run Control***, select ***Run Sequence***.

8 During the Sequence Run:

8.1 Print out the calibration curve for the standards.

8.1.1 Under ***View***, select ***Data Analysis***. This should be done in off-line mode.

8.1.2 Under ***File***, select ***Print***, ***Calib Table + Curves.***

8.2 Verify the correlation coefficient for each compound present in the calibration is greater than 0.98.

8.2.1 If the calibration fails, the sequence is stopped and corrective action taken.

8.3 Verify the trip sample recoveries.

8.4 Verify control and check values are within control limits.

9 After Sequence Completion:

9.1 Review the chromatograms. Verify the MPA peak is of a consistent area throughout the entire sequence. If a sample was misinjected, the problem will most likely show up in the MPA peak.

10 Note any problems in the lab instrument notebook.

Appendix B

ANALYSIS FOR DICHLOROMETHANE AND TRICHLOROETHANE

Calibration Standard Stock: The stock standard consists of 40 g each of the following compounds, which are placed in a 500 mL volumetric flask and prepared, as follows: Dichloromethane, Ethyl acetate, 1,1,1-Trichloroethane, Toluene, Ethyl benzene, m-Xylene, o-Xylene, and Pinene.

Bring to volume with MPA and mix. Aliquot the solution into 20 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

Control/Check Stock: The control/check stock is a 25% dichloromethane (DCM) solution prepared by weighing 25 g of DCM into a 100 mL volumetric flask. Bring to volume with MPA and mix. Aliquot the control/check stock in individual 5 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

1 Load Method:

1.1 Under ***Method***, select ***Load Method***.

1.2 Click on ***DCM.m***; then ***OK***.

2 Load Sequence:

2.1 Under ***Sequence***, select ***Load Sequence***.

2.2 Click on ***DCM.S***; then ***OK***.

3 Modifying Sequence:

3.1 Under ***Sequence***, select ***Sequence Parameters*** to create a subdirectory for the data.

3.2 Input sequence parameters:

3.2.1 **Operator Name** – enter your initials.

3.2.1.1 For newer model GC software, enter initials under ***Sequence Comments***.

3.2.2 **Data Files** – select ***Auto***.

3.2.3 **Subdirectory** – enter the two decimal month, day, year (December 5, 2007

would be entered as ***120507***); a letter can be put at the end to distinguish specific analyses run on the same day.

3.2.4 **Part of method to run** – select ***According to Runtime Checklist***.

3.2.5 **Sequence Comment** – enter set sample numbers, and any other pertinent information.

3.3 Click on ***OK***.

4 Sequence Table:

4.1 Under ***Sequence***, select ***Sequence Table***.

4.2 Input sequence information.

4.2.1 **Sample Name** – enter the following, in order: MPA blank, the five standards, MPA blank, control, and the samples.

4.2.1.1 An entry for MPA blank followed by a check is made after every ten samples and again at the end of the run.

4.2.2 **Method Name** – select ***DCM*** from the pull-down menu.

4.2.3 **Vial** – vial number corresponds to the position of the vial on the autosampler tray.

4.2.3.1 Each entry for the blank will reference the same blank vial.

4.2.3.2 Each entry for check will reference the control vial.

4.2.4 **Inj/Vial** – "1".

4.2.5 **Sample Type** – select ***Sample*** from the pull down menu for all lines except for the five calibration lines; for these select ***Calibration***.

4.2.6 For the calibration lines only:

4.2.6.1 **Cal Level** – enter 1,2,3,4,5, respectively.

4.2.6.2 **Update RF** – select ***Replace*** from the pull down menu.

4.2.6.3 **Update RT** – select ***Average*** from the pull down menu.

4.3 Click on ***OK***.

5 Save Sequence:

5.1 Under ***Sequence***, select ***Save Sequence***.

6 Print Sequence:

6.1 Under ***Sequence***, select ***Print Sequence***.

6.2 Check ***Method and Injection Info Part***; then click on ***Print***.

6.3 Verify that the sequence matches the vial placement on the autosampler.

6.4 Place sequence printout in the sequence binder.

7 Starting Sequence:

7.1 Under ***Run Control***, select ***Run Sequence***.

8 During the Sequence Run:

8.1 Print out the calibration curve for the standards.

8.1.1 Under ***View***, select ***Data Analysis***. This should be done in off-line mode.

8.1.2 Under ***File***, select ***Print***, ***Calib Table + Curves***.

8.2 Verify the correlation coefficient for each compound present in the calibration is greater than 0.98.

8.2.1 If the calibration fails, the sequence is stopped and corrective action taken.

8.3 Verify control and check values are within control limits.

9 After Sequence Completion:

9.1 Review the chromatograms. Verify the MPA peak is of a consistent area throughout the entire sequence. If a sample was misinjected, the problem will most likely show up in the MPA peak.

10 Note any problems in the lab instrument notebook.

Appendix C

ANALYSIS FOR SILOXANES

Calibration Standard Stock. The stock standard consists of 40 g each of the following compounds, which are placed in a 500 mL volumetric flask and prepared, as follows: Hexamethyldisiloxane, Hexamethylcyclotrisiloxane, Octamethyltrisiloxane, Octamethylcyclotetrasiloxane, Decamethyltetrasiloxane, Benzyl Alcohol, Decamethylcyclopentasiloxane.

Bring to volume with MPA and mix. Aliquot the solution into 20 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

Control/Check Stock: The control/check stock is a 25% hexamethyldisiloxane (HMDS) solution prepared by weighing 25 g of HMDS into a 100 mL volumetric flask. Bring to volume with MPA and mix. Aliquot the control/check stock in individual 5 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

1 Load Method:

1.1 Under ***Method***, select ***Load Method***.

1.2 Click on ***SILOX.m***; then ***OK***.

2 Load Sequence:

2.1 Under ***Sequence***, select ***Load Sequence***.

2.2 Click on ***SILOX.S***; then ***OK***.

3 Modifying Sequence:

3.1 Under ***Sequence***, select ***Sequence Parameters*** to create a subdirectory for the data.

3.2 Input sequence parameters:

3.2.1 **Operator Name** – enter your initials.

3.2.1.1 For newer model GC software, enter initials under ***Sequence Comments***.

3.2.2 **Data Files** – select ***Auto***.

3.2.3 **Subdirectory** – enter the two decimal month, day, year (December 5, 2007 would be entered as ***120507***); a letter can be put at the end to distinguish specific analyses run on the same day.

3.2.4 **Part of method to run** – select ***According to Runtime Checklist***.

3.2.5 **Sequence Comment** – enter set sample numbers, and any other pertinent information.

3.3 Click on ***OK***.

4 Sequence Table:

4.1 Under ***Sequence***, select ***Sequence Table***.

4.2 Input sequence information.

4.2.1 **Sample Name** – enter the following, in order: MPA blank, the five standards, MPA blank, control, and the samples.

4.2.1.1 An entry for MPA blank followed by a check is made after every ten samples and again at the end of the run.

4.2.2 **Method Name** – select ***SILOX*** from the pull-down menu.

4.2.3 **Vial** – vial number corresponds to the position of the vial on the autosampler tray.

4.2.3.1 Each entry for the blank will reference the same blank vial.

4.2.3.2 Each entry for check will reference the control vial.

4.2.4 **Inj/Vial** – "1".

4.2.5 **Sample Type** – select ***Sample*** from the pull down menu for all lines except for the five calibration lines; for these select lines ***Calibration***.

4.2.6 For calibration lines only:

4.2.6.1 **Cal Level** – enter 1,2,3,4,5, respectively.

4.2.6.2 **Update RF** – select ***Replace*** from the pull down menu.

4.2.6.3 **Update RT** – select ***Average*** from the pull down menu.

4.3 Click on ***OK***.

5 Save Sequence:

5.1 Under ***Sequence***, select ***Save Sequence***.

6 Print Sequence:

6.1 Under ***Sequence***, select ***Print Sequence***.

6.2 Check ***Method and Injection Info Part***; then click on ***Print***.

6.3 Verify that the sequence matches the vial placement on the autosampler.

6.4 Place sequence printout in the sequence binder.

7 Starting Sequence:

7.1 Under ***Run Control***, select ***Run Sequence***.

8 During the Sequence Run:

8.1 Print out the calibration curve for the standards.

8.1.1 Under ***View***, select ***Data Analysis***. This should be done in off-line mode.

8.1.2 Under ***File***, select ***Print***, ***Calib Table + Curves***.

8.2 Verify the correlation coefficient for each compound present in the calibration is greater than 0.98.

8.2.1 If the calibration fails, the sequence is stopped and corrective action taken.

8.3 Verify control and check values are within control limits.

9 After Sequence Completion:

9.1 Review the chromatograms. Verify the MPA peak is of a consistent area throughout the entire sequence. If a sample was misinjected, the problem will most likely show up in the MPA peak.

10 Note any problems in the lab instrument notebook.

Appendix D

ANALYSIS FOR METHYL ETHYL KETONE AND p-CHLOROBENZOTRIFLUORIDE

Calibration Standard Stock: The 80 mg/mL stock standard consists of 40 g each of the following compounds, which are placed in a 500 mL volumetric flask and prepared, as follows: Methyl Ethyl Ketone, p-Chlorobenzotrifluoride, PM Acetate (Propylene Glycol Methyl Ether Acetate**)**, 2-Butoxyethanol.

Bring to volume with MPA and mix. Aliquot the solution into 20 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

Control/Check Stock: The control/check stock is a 25% methyl ethyl ketone (MEK) solution prepared by weighing 25 g of MEK into a 100 mL volumetric flask. Bring to volume with MPA and mix. Aliquot the control/check stock in individual 5 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

1 Load Method:

1.1 Under ***Method***, select ***Load Method***.

1.2 Click on ***MEK.m***; then ***OK***.

2 Load Sequence:

2.1 Under ***Sequence***, select ***Load Sequence***.

2.2 Click on ***MEK.S***; then ***OK***.

3 Modifying Sequence:

3.1 Under ***Sequence***, select ***Sequence Parameters*** to create a subdirectory for the data.

3.2 Input sequence parameters:

3.2.1 **Operator Name** – enter your initials.

3.2.1.1 For newer model GC software, enter initials under ***Sequence Comments***.

3.2.2 **Data Files** – select ***Auto***.

3.2.3 **Subdirectory** – enter the two decimal month, day, year (December 5, 2007 would be entered as ***120507***); a letter can be put at the end to distinguish specific analyses run on the same day.

3.2.4 **Part of method to run** – select ***According to Runtime Checklist***.

3.2.5 **Sequence Comment** – enter set sample numbers, and any other pertinent information.

3.3 Click on ***OK***.

4 Sequence Table:

4.1 Under ***Sequence***, select ***Sequence Table***.

4.2 Input sequence information:

4.2.1 **Sample Name** – enter the following, in order: MPA blank, the five standards, MPA blank, control, and the samples.

4.2.1.1 An entry for MPA blank followed by a check is made after every ten samples and again at the end of the run.

4.2.2 **Method Name** – select ***MEK*** from the pull-down menu.

4.2.3 **Vial** – vial number corresponds to the position of the vial on the autosampler tray.

4.2.3.1 Each entry for the blank will reference the same blank vial.

4.2.3.2 Each entry for check will reference the control vial.

4.2.4 **Inj/Vial** – "1".

4.2.5 **Sample Type** – select ***Sample*** from the pull down menu for all lines except for the five calibration lines; for these select lines ***Calibration***.

4.2.6 For calibration lines only:

4.2.6.1 **Cal Level** – enter 1,2,3,4,5, respectively.

4.2.6.2 **Update RF** – select ***Replace*** from the pull down menu.

4.2.6.3 **Update RT** – select ***Average*** from the pull down menu.

4.3 Click on ***OK***.

5 Save Sequence:

5.1 Under ***Sequence***, select ***Save Sequence***.

6 Print Sequence:

6.1 Under ***Sequence***, select ***Print Sequence***.

6.2 Check ***Method and Injection Info Part***; then click on ***Print***.

6.3 Verify that the sequence matches the vial placement on the autosampler.

6.4 Place sequence printout in the sequence binder.

7 Starting Sequence:

7.1 Under ***Run Control***, select ***Run Sequence***.

8 During the Sequence Run:

8.1 Print out the calibration curve for the standards.

8.1.1 Under ***View***, select ***Data Analysis***. This should be done in off-line mode.

8.1.2 Under ***File***, select ***Print, Calib Table + Curves***.

8.2 Verify the correlation coefficient for each compound present in the calibration is greater than 0.98.

8.2.1 If the calibration fails, the sequence is stopped and corrective action taken.

8.3 Verify control and check values are within control limits.

9 After Sequence Completion:

9.1 Review the chromatograms. Verify the MPA peak is of a consistent area throughout the entire sequence. If a sample was misinjected, the problem will most likely show up in the MPA peak.

10 Note any problems in the lab instrument notebook.

Appendix E

ANALYSIS FOR GLYCOL COMPOUNDS

This appendix covers six different glycol compounds, separated into three different methods:

- **PEGLYCOL** for analysis of propylene glycol and ethylene glycol
- **CBPGLY** for carbitol, butyl carbitol, and propylene carbonate.
- **DIPROP** for dipropylene glycol.

Calibration Standard Stock: The 80 mg/mL stock standard consists of 40 g each of the following compounds, which are placed in a 500 mL volumetric flask and prepared, as follows:

- **PEGLYCOL** prepared using propylene glycol and ethylene glycol
- **CBPGLY** prepared using carbitol, butyl carbitol, and propylene carbonate.
- **DIPROP** prepared using dipropylene glycol.

Bring to volume with MPA and mix. Aliquot the solution into 20 mL screw capped vials then date, label and store the vials in the Standards refrigerator.

Control/Check Stock: The control/check stock for the each method prepared by weighing 25 g of the specified compound into a 100 mL volumetric flask, as follows:

- **PEGLYCOL** is prepared using propylene glycol
- **CBPGLY** is prepared butyl carbitol.
- **DIPROP** is prepared using dipropylene glycol.

Bring to volume with MPA and mix. Aliquot the control/check stock in individual 5 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

1 Load Method:

1.1 Under ***Method***, select ***Load Method***.

1.2 Click on ***[insert method designation here – PEGLYCOL, CBPGLY or DIPROP].m***; then ***OK***.

2 Load Sequence:

2.1 Under ***Sequence***, select ***Load Sequence***.

2.2 Click on ***[insert sequence designation here].S***; then ***OK***.

3 Modifying Sequence:

3.1 Under ***Sequence***, select ***Sequence Parameters*** to create a subdirectory for the data.

3.2 Input sequence parameters:

3.2.1 **Operator Name** – enter your initials.

3.2.1.1 For newer model GC software, enter initials under ***Sequence Comments***.

3.2.2 **Data Files** – select ***Auto***.

3.2.3 **Subdirectory** – enter the two decimal month, day, year (December 5, 2007 would be entered as ***120507***); a letter can be put at the end to distinguish specific analyses run on the same day.

3.2.4 **Part of method to run** – select ***According to Runtime Checklist***.

3.3 Click on ***OK***.

4 Sequence Table:

4.1 Under ***Sequence***, select ***Sequence Table***.

4.2 Input sequence information:

4.2.1 **Sample Name** – enter the following, in order: MPA blank, the five standards, MPA blank, control, and the samples.

4.2.1.1 An entry for MPA blank followed by a check is made after every ten

samples and again at the end of the run.

4.2.2 **Method Name** – select appropriate method name from the pull-down menu.

4.2.3 **Vial** – vial number corresponds to the position of the vial on the autosampler tray.

4.2.3.1 Each entry for the blank will reference the same blank vial.

4.2.3.2 Each entry for check will reference the control vial.

4.2.4 **Inj/Vial** – "1".

4.2.5 **Sample Type** – select ***Sample*** from the pull down menu for all lines except for the five calibration lines; for these lines select ***Calibration***.

4.2.6 For calibration lines only:

4.2.6.1 **Cal Level** – enter 1,2,3,4,5, respectively.

4.2.6.2 **Update RF** – select ***Replace*** from the pull down menu.

4.2.6.3 **Update RT** – select ***Average*** from the pull down menu.

4.3 Click on ***OK***.

5 Save Sequence:

5.1 Under ***Sequence***, select ***Save Sequence***.

6 Print Sequence:

6.1 Under ***Sequence***, select ***Print Sequence***.

6.2 Check ***Method and Injection Info Part***; then click on ***Print***.

6.3 Verify that the sequence matches the vial placement on the autosampler.

6.4 Place sequence printout in the sequence binder.

7 Starting Sequence:

7.1 Under ***Run Control***, select ***Run Sequence***.

8 During the Sequence Run:

8.1 Print out the calibration curve for the standards.

8.1.1 Under ***View***, select ***Data Analysis***. This should be done in off-line mode.

8.1.2 Under ***File***, select ***Print***, ***Calib Table + Curves***.

8.2 Verify the correlation coefficient for each compound present in the calibration is greater than 0.98.

8.2.1 If the calibration fails, the sequence is stopped and corrective action taken.

8.3 Verify control and check values are within control limits.

9 After Sequence Completion:

9.1 Review the chromatograms. Verify the MPA peak is of a consistent area throughout the entire sequence. If a sample was misinjected, the problem will most likely show up in the MPA peak.

10 Note any problems in the lab instrument notebook.

Appendix F

ANALYSIS FOR HEXYLENE GLYCOL

Calibration Standard Stock: The 80 mg/mL stock standard consists of 40 g of hexylene glycol placed in a 500 mL volumetric flask. Bring to volume with MPA and mix. Aliquot the solution into 20 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

Control/Check Stock: The control/check stock is a 25% hexylene glycol (HXGLY) solution prepared by weighing 25 g of HXGLY into a 100 mL volumetric flask. Bring to volume with MPA and mix. Aliquot the control/check stock in individual 5 mL screw-capped vials then date, label and store the vials in the Standards refrigerator.

1 Load Method:

1.1 Under ***Method***, select ***Load Method***.

1.2 Click on ***HXGLY.m***; then ***OK***.

2 Load Sequence:

2.1 Under ***Sequence***, select ***Load Sequence***.

2.2 Click on ***HXGLY.S***; then ***OK***.

3 Modifying Sequence:

3.1 Under ***Sequence***, select ***Sequence Parameters*** to create a subdirectory for the data.

3.2 Input sequence parameters:

3.2.1 **Operator Name** – enter your initials.

3.2.1.1 For newer model GC software, enter initials under ***Sequence Comments***.

3.2.2 **Data Files** – select ***Auto***.

3.2.3 **Subdirectory** – enter the two decimal month, day, year (December 5, 2007 would be entered as ***120507***); a letter can be put at the end to distinguish specific analyses run on the same day.

3.2.4 **Part of method to run** – select ***According to Runtime Checklist***.

3.2.5 **Sequence Comment** – enter set sample numbers, and any other pertinent information.

3.3 Click on ***OK***.

4 Sequence Table:

4.1 Under ***Sequence***, select ***Sequence Table***.

4.2 Input sequence information.

4.2.1 **Sample Name** – enter the following, in order: MPA blank, the five standards, MPA blank, control, and the samples.

4.2.1.1 An entry for MPA blank followed by a check is made after every ten samples and again at the end of the run.

4.2.2 **Method Name** – select ***HXGLY*** from the pull-down menu.

4.2.3 **Vial** – vial number corresponds to the position of the vial on the autosampler tray.

4.2.3.1 Each entry for the blank will reference the same blank vial.

4.2.3.2 Each entry for check will reference the control vial.

4.2.4 **Inj/Vial** – "1".

4.2.5 **Sample Type** – select ***Sample*** from the pull down menu for all lines except for the five calibration lines; for these select ***Calibration***.

4.2.6 For calibration lines only:

4.2.6.1 **Cal Level** – enter 1,2,3,4,5, respectively.

4.2.6.2 **Update RF** – select ***Replace*** from the pull down menu.

4.2.6.3 **Update RT** – select ***Average*** from the pull down menu.

4.3 Click on ***OK***.

5 Save Sequence:

5.1 Under ***Sequence***, select ***Save Sequence***.

6 Print Sequence:

6.1 Under ***Sequence***, select ***Print Sequence***.

6.2 Check ***Method and Injection Info Part***; then click on ***Print***.

6.3 Verify that the sequence matches the vial placement on the autosampler.

6.4 Place sequence printout in the sequence binder.

7 Starting Sequence:

7.1 Under ***Run Control***, select ***Run Sequence***.

8 During the Sequence Run:

8.1 Print out the calibration curve for the standards.

8.1.1 Under ***View***, select ***Data Analysis***. This should be done in off-line mode.

8.1.2 Under ***File***, select ***Print, Calib Table + Curves***.

8.2 Verify the correlation coefficient for each compound present in the calibration is greater than 0.98.

8.2.1 If the calibration fails, the sequence is stopped and corrective action taken.

8.3 Verify control and check values are within control limits.

9 After Sequence Completion:

9.1 Review the chromatograms. Verify the MPA peak is of a consistent area, throughout the entire sequence. If a sample was misinjected, the problem will most likely show up in the MPA peak.

10 Note any problems in the lab instrument notebook.

SOP Revision History

DATE	VERSION	NOTES
March 10, 1998	1.1	Adjusted document font to Times New Roman 12. Inserted appendix B formerly a stand-alone document.
February 3, 1999	1.2	Addition of exempt compounds in the calibration files. This also includes modifications to Appendix A to include additional analyses for some less common exempts and aromatic hydrocarbons.
February 4, 2003	1.3	Inserted Appendix C the Siloxane procedure and Appendix D the MEK procedure. Renamed the DCM procedure Appendix B, and renamed the Acetone procedure Appendix A. Adjusted document font to Times New Roman 12. Renumbered to new section number.
April 3, 2003	1.4	Modified all Appendices to reflect calibration curve changes, and calibration standard preparation. Modified calibration range for MEK and Siloxane, now to include a high point of 80 and 50 percent respectively. Modified Acetone/Alcohol standard prep exception including ethanol and isopropanol. Current neat ethanol is denatured with methanol.
January 7, 2005	1.5	Inserted Appendix E, the Glycol procedure. Retitled to reflect the scope covered by SOP. Changed document font to Arial 12. Corrected revision enumeration.
January 18, 2005	1.6	Added Glycerol and Butyl Carbitol to the Glycol procedure (Appendix E).
June 1, 2007	1.7	Update for all methods. Revised Glycols which now uses a different column and is itself divided into 2 methods.
August 20, 2010	1.8	Update of methods. Addition of hexylene glycol analysis, as Appendix F.
August 28, 2012	1.9	Update of methods. Addition of dipropylene glycol analysis to Appendix E.