

1. TITLE: MSD Analytical Method for Vapor Space Organics

2. PURPOSE:

- 2.1** This procedure provides steps and conditions for the determination of Vapor Space Organic Compounds in ground waters, and industrial waste waters.

3. SCOPE AND APPLICATION:

- 3.1** This method is used to analyze vapor space organics in samples prepared from all types of ground waters, and industrial waste water effluents.
- 3.2** The procedure applies to all documentation such as other Manuals and Standard Forms, which dictate quality control requirements for the determination of vapor space organics.

4.0 INTERFERENCES

- 4.1** Data from blank samples is collected to determine if interference is present during the preparation and or cleanup of the sample glassware, and if corrective action needs to be taken to eliminate the problem. Instrument blanks (as total integrated area) are to be less than one tenth of the total area found in the lowest standard, (30 PPM), used for instrument calibration.
- 4.2** Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. If carryover is suspected, the low-level sample should be reanalyzed.
- 4.3** Methane is a compound that may occur naturally in sewer samples. Positive contributions from methane are eliminated from the chromatogram by delaying detector data readings until after the methane peak has eluted. Alternatively, the value for methane can be manually subtracted from the total peak area.

5. REFERENCES

- 5.1.** MSD Analytical Method Vapor Space Organics, -January 28, 1984.

6. SAMPLE HANDLING AND PRESERVATIVES

- 6.1** All samples must be refrigerated at 4°C..
- 6.2** All samples must be analyzed within 14 days of collection.

6.3 Sampling Procedure

All samples will be grab samples

6.3.1 Sample vial preparation

Forty ml vials (as described in 44 FR 6946, 12-3-79) equipped with open top screw cap and teflon faced silicon septum. Vials must be washed with detergent, rinsed with tap water followed by distilled water and then dried at 105deg-C for a minimum of 1 hour. Ten mg Na₂S₂O₂ should be added to vials if the sample is suspected of containing an oxidant.

6.3.2 Sampling

A clean vial is immersed in the waste water and is filled until the liquid forms a convex surface with respect to the bottle. The bottle is capped and then inverted to check for air bubble(s). If a bubble is present, repeat the process until no bubbles are present in the inverted capped vial. Store the sample at 4 deg-C (ice) and transport to the laboratory

7 APPARATUS AND MATERIALS

7.1 GC SYSTEM

7.1.1 Shimadzu:

Gas Chromatograph GC-17A. The instrument has a temperature range that extends from (ambient +4 deg-C to ~ 450 deg C). The system includes a split / splitless injection port, an electronic flow controller, and uses a Flame Ionization Detector. The system is interfaced with a PC based Chromatography Data system.

7.1.2 GAS CHROMATOGRAPHY

The Gas Chromatograph is a Shimadzu GC-17A . The method parameters are as follows:

1. Injection port pressure is 25.2 psi
2. Total flow is 17.6 ml/min
3. Injector Splitless operation
4. Column flow 1.7 ml/min
5. Injection port A temperature 250 °C
6. Detector: Flame Ionization Detector (FID)
7. Detector temperature 250 C
8. Initial oven temperature 50 °C hold 3 minutes
9. Ramp at 10 °C/min to final temperature 190 C
10. Hold temp at 190C for 12.5 minutes
11. Helium flow rate 30 ml/min
12. Air flow rate 350 ml/min
13. Hydrogen flow rate 48 ml/min

7.1.3 COLUMN

Restek RT-UPLLOT, 15meter length, 0.53 I.D., 0.25um film thickness. Catalog number 19727.

7.1.4 DATA SYSTEM

The chromatography data system has the capability to view multiple chromatograms and allows for custom reporting which incorporates spread sheet options. The system complies with 21 CFR Part 11 Electronic Signature requirements and permits entire custom report exporting.

7.2 Hexane Standard Stock

A vapor standard is prepared by injecting 1.6 uL of hexane into a 1 liter bottle fitted with a septum stopper.

- a. Record the date, lab temperature, and barometric pressure
- b. Purge the standard liter bottle with air for 30 seconds
- c. Rinse a micro syringe about 6 times with hexane
- d. With the micro syringe needle in the hexane, pump the plunger several time to expel air from the needle. Then draw the plunger above the 2.5 uL mark
- e. Withdraw the micro syringe from the hexane, hold the syringe with the needle up, and tap to expel any bubbles.
- f. Gradually lower the plunger to the 1.5 to 1.6 uL mark. Pull the plunger back until all the hexane contents of the micro syringe are visible. There should be 2.7 to 2.8 uL of hexane in the micro syringe.
- g. Inject the hexane into the liter bottle, being careful not to lose the septum.
- h. After withdrawing the micro syringe from the septum, pull the plunger back to determine the amount of hexane left in the micro syringe. This should be about 0.8 uL.
- i. Subtract the remaining amount of hexane in the micro syringe from the amount in step f, This should yield approximately 1.5 to 1.6 uL of hexane. Record this value.
- j. The hexane is vaporized by heating the liter bottle to 100 deg-C for 8 minutes. The bottle is allowed cool to room temperature. A 1000uL aliquot of the vapor is removed with a gas tight syringe. The vapor is injected into the gas chromatograph . The area under the curve is integrated electronically.

8.0 Analytical Procedure

8.1 Analysis

A 40 ml vial containing the sample is removed from the refrigerator and warmed to room temperature. Using a glass syringe (20 ml or larger) remove 20 ml of liquid by piercing the septum. It will be necessary to replace the withdrawn liquid with gas. Nitrogen is preferred, but air is sufficient. The 20 ml of liquid removed can be discarded or injected into another 40 ml vial and used as a duplicate sample. It will be necessary to vent air from the second vial as it is filled. The vial is equilibrated as 21 deg-C +/- 3 deg-C for a minimum of 1 hour, vigorously shaken 30 times and held quiescent at 21 deg-C +/- 3deg-C for 10 min before analysis.

Using a gas tight syringe, withdraw a 1000 uL aliquot of headspace gas and inject into the GC. The column and temperature programming should be as specified for the hexane standard. The total peak area of the chromatogram will be used to calculate the total ppm of hexane to which the area is equivalent. The peak area of compounds eluting in less that 2 minutes will be considered as methane. The ppm equivalent to methane will be subtracted form the total ppm of hexane to yield the ppm of vapor space organics.

Samples with a vso value equivalent to or greater than 300 ppm may be analyzed by GC/MS to identify whether major peaks represent substances classified as priority pollutants by the EPA.

8.2 Calibration

A hexane standard is prepared fresh each day as described in 7.2. From the hexane standard, a 30 and a 300 ppm calibration sample are prepared and analyzed. For the 30 ppm standard, a 100ul aliquot of the vapor is removed from the standard bottle with a gas tight syringe. The vapor is injected into the GC. This procedure is repeated using a 1000ul aliquot for the 300 ppm standard. The total peak areas of the standard samples are then used to generate a calibration curve (9.6). Total peak areas of subsequent samples are compared to this curve to estimate the concentration of volatile organics in the headspace.

8.3 Method protocol for Sample Analysis

8.3.1 Analyzing a Sample: A sample run is carried out by the following steps: (1.) Select CONTROL from the menu bar (2.) Next select SINGLE RUN. This opens the acquisition screen where sample ID, Method, Data path, and data file are entered. The sample ID is entered as a LIMS number followed by the customer name i.e... AB04985 Reliant Chemicals. Method is a default path C:\CLASS.VP\Enterprise\Projects\Default\Method\vso.met. Data path is also a default setting C:\CLASS.VP\Enterprise\Projects\Default\Data. Data file is entered as month, year, and unique number, for example FEB07001. (3.) Once this is completed select START. The GC will step thru several system checks before flashing "Waiting for Trigger" the system is ready to accept a sample. (4.) Withdraw 1000 ul from the headspace of the sample, lock the valve, compress the plunger to approximately 200ul, inject the sample into GC. (5.) Press the start button on the GC keypad. The run time for this procedure is 32 minutes.

8.3.2 Integrating Peaks: *Often peaks need to be manually integrated. To do this highlight the chromatogram on the screen by dropping and dragging the mouse. Right click the mouse to display the graphing menu. Select GRAPHICAL PROGRAMMING left click on manual peak. Left click on the front of the peak and left click on the peak's end. Finally, when data analysis pops up, right click to establish the baseline. Repeat this for all unrecognized peaks.*

8.3.3 Printing Reports: *The final step is to generate a report. Select REPORTS from the menu bar. Select print and Method Custom Report. This prints a chromatogram, totals for peak areas, and a Area% report. This information is later used when calculating volatile organic concentrations in the headspace utilizing the equation outlined in 9.6.*

9.0 QUALITY CONTROL

- 9.1 A field blank will be run daily and will be considered as a zero standard.
- 9.2 A 30 ppm standard will be run daily. The total peak area must be 9.0 to 11.0 percent of the total peak area of the 300 ppm standard.
- 9.3 A 300 ppm standard will be run daily
- 9.4 Other standards may be run as necessary
- 9.5 A same vial duplicate will be run once for every 10 samples. The duplicates must have a margin of error less than 20 percent based on total hexane peak area

9.6 Calculations

The vapor concentration of the hexane standard is calculated as follows:

$$\text{ppm (V/V)} = ((W / MW) * 10^6) / (V/\underline{v})$$
$$\underline{v} = 24.47 * (760/P) * ((t + 273)/298)$$

W = weight of hexane (density * volume (ml))
MW = molecular weight of hexane
 \underline{v} = gram molar volume , liters
P = ambient pressure , mm Hg
T = ambient temperature , deg-C
V= volume of flask or bottle, liters

The concentration of total organics in the head space is calculated as follows:

$$\text{ppm} = (\text{ppm hexane std}) (\text{total peak area of sample}) / \text{total peak area of hexane std}$$

The concentration of the methane in the head space is calculated as follows:

$$\text{ppm} = (\text{ppm hexane standard}) (\text{total peak area of compounds with a retention time less than 2 minutes} / \text{total peak are of the hexane}$$

10.0 Safety

The laboratory is responsible for maintaining a reference file of material safety data handling sheets , available to all personnel involved in the chemical analysis.

Appropriate gloves should be worn when handling reagents. A fume hood should always be used when working with volatile solvents. Safety glasses should be worn during any operation where chemicals, glassware or any foreign object could accidentally enter the eye.

11. Documentation

11.1 Computer generated report information is stored on the C: drive of the MPC ClientPro 565 computer using the following file header protocol:

Sample field contains the AB(LIMS) number

Misc field contains the sample description

11.2 Each month's data is stored on the C: drive in file-folders using the following format

C:\CLASS-VP\Enterprise\Projects\Default\Data\((Month))

Where ((Month)) is in the following format month year

Example FEB07

11.3 Once data has been collected for two to three months, it is transferred to Cd-ROM dated and stored in a the desk drawer in room 210....

All relevant sample information is written in an appropriately dated record lab book.

11.5 All hard copies of reports, chromatograms, QA/QC are stored in respective folders, for each batch and stored in the desk filing cabinet, located in room 210.