

3M COMPANY
OCCUPATIONAL HEALTH & ENVIRONMENTAL SAFETY DIVISION
DETERMINATION OF SELECTED ORGANIC VAPORS IN AIR
USING 3M 3500/3520 ORGANIC VAPOR MONITORS
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SCOPE

This procedure covers the method of analyzing samples to determine the amount of organic vapor present in the air. More specifically, this procedure is to be used for those organic vapors which can be collected by 3M Organic Vapor Monitors and desorbed with carbon disulfide or other suitable solvents. A provisional list of organic vapors that can be determined is given in supplementary publications such as "3M Organic Vapor Monitor Sampling and Analysis Guide."

SUMMARY OF THE METHOD

The organic vapors are adsorbed on high activity charcoal, desorbed with carbon disulfide and quantified using a gas chromatograph equipped with a flame ionization detector (FID). There are certain compounds which have higher recoveries when desorbed with methylene chloride, acetonitrile or other suitable solvents. These are listed in the "3M Organic Vapor Monitor Sampling and Analysis Guide."

EQUIPMENT

The following or equivalent equipment is used:

Gas Chromatograph - Hewlett Packard, Model 5880A or 5890A equipped with a flame ionization detector (FID) and capillary capability.

Analytical Columns - J&W DB5 (nonpolar) (95% dimethyl 5% - diphenyl-polysiloxane), .25 um film thickness, .25 mm I.D., 30 m capillary; J&W DBWAX (polar) (polyethylene glycol), .25 um film thickness, .25 mm I.D., 30 m capillary; Restek Rtx-200 (trifluoropropylmethyl) 1 um film thickness, .25 mm I.D., 30 m capillary. Other appropriate columns such as J&W DB225 and DBFFAP may also be used.

REAGENTS/SUPPLIES

The following or equivalent reagents/supplies are used:

Organic Vapor Monitors - 3M Brand No. 3500 or 3520. Features: Sampling rate controlled by molecular diffusion. Each collection layer has about 180 milligrams of activated carbon in a Teflon matrix.

Autosampler Vials - 2 ml with Teflon lined caps.

Microliter Syringes - Hamilton (or equivalent) 1uL - 5 mL. These syringes are guaranteed accurate to +/-1% full scale and are used without further calibration.

Volumetric Flasks - Class A (10+/-0.02 mL, 25+/-0.03 mL, 50+/-0.05 mL, 100+/-0.08mL, etc.)

Carbon Disulfide - Aldrich # 27,066-0 (HPLC grade) or #34,227-0 (low benzene)

Solvents - Preferably reagent grade for all compounds of interest.

Compressed Gas Cylinders:

Helium for carrier gas (High Purity).

Hydrogen for FID (Ultra High Purity).

Argon-Methane for ECD (P5).

Caution: High pressure cylinders are hazardous and should be handled with care. Do not store in extreme heat.

Air for FID (house air meeting or exceeding industrial grade Type 1 purified with a Whatman Zero Air Generator.)

SAMPLING

The monitor is removed from the package. Detailed instructions for use of the monitor are enclosed in the package. The following information should be recorded:

1. Monitor number
2. Date of exposure
3. Employee or area identification
4. Temperature and relative humidity
5. Start and stop times
6. Any potential interferences
7. Any comments or unusual circumstances

When personal sampling is being performed, the monitor should be attached near the breathing zone. For area sampling, the monitor should be placed so that at least a 25 fpm face velocity is maintained. The monitor should not be placed in a corner or along a wall where stagnant air may exist.

After sampling with the 3M 3500 or 3520, the retaining ring and white barrier film are removed and discarded. The clear elution cap is snapped into place. The ports should be

securely sealed with the plugs. For the 3M 3520 monitor, the two monitor sections are separated. Snap the bottom cup into the bottom of the primary section. Snap an elution cap on the secondary body. A blank control sample should be prepared at the monitoring site and submitted with the samples.

CALIBRATION

Standards containing the compound(s) of interest are prepared (usually three to five) and run with each set of analysis samples. Standards are prepared by diluting an appropriate amount (1 to 100 uL) of the compound of interest to 1.5, 10 or 25 mL with CS₂ or other solvents such as acetonitrile, methylene chloride, isopropanol or 50% dimethylformamide in CS₂. When more dilute working standards are required, a 1:10 or 1:100 stock dilution is prepared first. Concentrations of standards are chosen to bracket the amount expected to be found. A sensitivity factor may be calculated by averaging the ug/unit area response for the standards, or a calibration curve may be prepared using Kaleidograph, Excel or other statistical program.

Appropriate quality control samples are run with each set of standards and samples.

Caution: Carbon disulfide is toxic and should be handled in a hood.

The standard solutions should be used as soon as possible. Standards may be stored in the laboratory refrigerator for no more than five days.

For example:

If a monitor is exposed to 50 ppm of toluene for 6 hours, the amount expected is:

$$mg = \frac{(ppm \times SR \times t \times MW \times 10^{-6})}{24.45} = \frac{(50 \times 31.4 \times 360 \times 92.14 \times 10^{-6})}{24.45} = 2.13$$

where:

SR = sampling rate (cm³/min)
 MW = molecular weight
 t = time (minutes)

If the monitor is eluted with 1.5 mL, the volume of pure toluene required in a 10 mL standard is:

$$uL = \frac{mg \times 10}{d \times 1.5} = \frac{2.13 \times 10}{0.865 \times 1.5} = 16.4$$

where:

d = density

Standards could be prepared to bracket this expected amount by diluting 10, 15 and 20 uL of pure toluene to 10 mL yielding standards of 0.865, 1.298, and 1.73 mg/mL.

Generally it is most convenient to prepare and plot the standard curve in either micrograms or milligrams per 1 ½ mL of CS₂. If the monitor is desorbed with 1 ½ mL, the amount found on the monitor can then be read directly from the standard curve. Otherwise, care must be taken to correct for the amount used for elution as shown in the calculations below.

SAMPLE ANALYSIS

Using a repipet or a syringe, add 1.5 mL of the desorption reagent to each monitor through the center port (the port is immediately resealed). After standing for 30 minutes with occasional gentle agitation, the eluent is decanted into a marked 2 mL vial, sealed and a 1 to 5 uL sized sample is automatically introduced into the gas chromatograph. The area of the peak of interest is recorded and the amount in mg or ug is determined from the standard curve. If the weight collected for a single contaminant is greater than the defined capacity listed in "3M Organic Vapor Monitor Sampling and Analysis Guide," then the validity of the sample should be questioned. When sampling multiple contaminants, the combined weights of the contaminants collected should not exceed the defined value for the single contaminant with lowest capacity.

CALCULATIONS

Determine the weight of contaminant(s) present in each sample by use of the calibration data (regression equation or sensitivity factor) generated from the prepared standards. The sample weight should always be corrected by subtracting any interfering contributions made from a control blank.

The time-weighted-average concentration of the environment sampled can be calculated by knowing the length of the sampling period, the contaminant weight determined by gas chromatography, the recovery coefficient and the molecular weight.

$$\text{ppm} = \frac{\left(\frac{\text{mg}}{\text{mL}}\right)(\text{mL})(24.45)}{(\text{SR})(t)(r)(\text{MW})(10^{-6})}$$

where:

mg/mL = amount found from calibration curve

mL = elution volume (usually 1.5 mL)
SR = sampling rate (cm³/min)
t = sampling time (min)
MW = molecular weight
r = recovery

Alternatively, the following simplified equations can be used when the amount found on the monitor is determined in micrograms.

The calculation constant A is used to calculate the concentration when expressed in units of milligrams per cubic meter (mg/m³) and constant B when expressed in units of parts per million (ppm). The calculation constants A and B have been determined for all the compounds listed in "3M Organic Vapor Monitor Sampling and Analysis Guide."

3500 Organic Vapor Monitor

The time-weighted-average concentration in milligrams per cubic meter (mg/m³) in the environment sampled can be calculated from the following expression:

$$C(\text{mg/m}^3) = \frac{W \times A}{r \times t}$$

The time-weighted-average concentration in parts per million (ppm) of the contaminant can be calculated from the following expression:

$$C(\text{ppm}) = \frac{W \times B}{r \times t}$$

where W = weight (ug) found (corrected for blank and sample elution volume)

r = recovery coefficient

t = length of sampling period (minutes)

A and B = calculation constants found in the Sampling and Analysis Guide or calculated as follows:

$$A = \frac{1000}{SR}$$

$$B = \frac{(1000)(24.45)}{(SR)(MW)}$$

Note: Each laboratory should determine their own recovery coefficients for greatest accuracy as described in the 3M bulletin "Recommended Procedure for Determination of

Recovery Coefficients." Typical recoveries determined in our laboratories are shown in the "3M Organic Vapor Monitor Sampling and Analysis Guide." Additional information on the determination of recoveries can be found in the 3M Monitor Validation Procedure.

The above expressions calculate the time-weighted-average concentrations at a sampling temperature of 25 °C and pressure of 760 mm Hg. When sampling at other environmental conditions, the previous expressions need to be corrected only for variations in temperature. If the temperature correction is desired, the time-weighted-average concentration can be calculated by multiplying the concentration calculated above by the temperature correction factor (CFt.)

Sampling Temperature		Correction Factor
(°C)	(°F)	(CFt)
44	111	.97
37	99	.98
31	88	.99
25	77	1.00
19	66	1.01
13	55	1.02
7	45	1.03
2	36	1.04
- 3	27	1.05
- 8	18	1.06

As shown in the above table, every 10-11 degrees above or below 77°F requires a one percent correction to the calculated time-weighted-average concentration. For every 10°F increment above 77°F, there is a decrease of about 1% in the time-weighted-average concentration. Below 77°F, there is an increase in the concentration.

Example Calculation (Trichloroethylene):

Length of sampling period (t): 465 minutes
 Temperature (T): 13 °C
 Calculation constant: A = 32.2 or B = 5.98
 Weight (W): 768 micrograms
 Recovery coefficient: 1.01

Using calculation constant (A):

$$C(\text{mg}/\text{m}^3) = (768 \times 32.2 \times 1.02) / (1.01 \times 465)$$

$$C = 53.7 \text{ mg/m}^3$$

Using calculation constant (B):

$$C(\text{ppm}) = (768 \times 5.98 \times 1.02)/(1.01 \times 465)$$

$$C = 10.0 \text{ ppm}$$

3520 Organic Vapor Monitor with back-up section.

Upon analysis of each section, the validity of the sample can be determined. The ratio of the contaminant weight (W_s) on the secondary section to the contaminant weight (W_p) on the primary section must meet the following criteria.

$$W_s/W_p < .50$$

The calculations for the 3520 and 3530 are as follows:

$$C \text{ (mg/m}^3\text{)} = \frac{(W_p + 2.2 \times W_s) \times A}{r \times t}$$

$$C \text{ (ppm)} = \frac{(W_p + 2.2 \times W_s) \times B}{r \times t}$$

where:

W_p = weight (ug) collected on the primary section (corrected for blank and sample elution volume)

W_s = weight (ug) collected on the secondary section (corrected for blank and sample elution volume)

A and B = calculation constants found in the Sampling and Analysis Guide

LIMIT OF QUANTITATION

The routine limit of quantitation (LOQ) for most single compounds is 2-3 ug. The routine LOQ for multi-component analytes like mineral spirits is 10-20 ug. The LOQ may be lowered if necessary by increasing the injection volume, reducing the split, using a splitless injection or using a more sensitive detector.

A LOQ of 3 ug of toluene would result in an air concentration of 0.05 ppm for an 8-hour sample and 1.7 ppm for a 15-minute sample.

APPENDIX A

Typical Parameters for HP5880 and HP5890 Gas Chromatographs:

OVM Analytical Method

Oven Temp 40 °C
Initial Time 3 min
Equib Time 0.5 to 2 min
Prgm Rate 10 °C/min
Final Value 180-225 °C
Final Time 3 min
Det Temp 250 °C
Inj Temp 225 °C

Chart Speed .50 cm/min
Attn 2³
%Offset 10
Threshold 0
Peak Width .04
Split Ratio 30:1 (15:1 may be used when very low levels are expected and
60:1 may be used when very high levels are expected)