3M COMPANY

OCCUPATIONAL HEALTH & SAFETY PRODUCTS LABORATORY

Organic Vapor Analytical Method No. 2
January, 1979

DETERMINATION OF SELECTED ORGANIC VAPORS IN AIR

SCOPE

This is a procedure which covers the method of collecting and analyzing samples to determine the amount of a particular organic vapor(s) 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 Table 1. Also included in this Table is a suggested analytical column and desorption solvent. A calibration curve is generated for each compound of interest so that concentration ranges and sensitivities are known. Interferences will be treated in the Discussion Section.

SUMMARY OF METHOD

The organic vapors are adsorbed on high activity charcoal, desorbed with carbon disulfide and quantitated using a gas chromatograph equipped with a flame ionization detector.

APPARATUS

Organic Vapor Monitor - 3M brand No. 3500 and No. 3502 or equivalent. Additional information: The sample layer equals 160 mg. petroleum based charcoal. Features: Sampling rate determined by natural molecular diffusion.

Gas Chromatograph - Hewlett Packard, Model 5840A, or equivalent, equipped with a flame ionization detector - available from Hewlett Packard, 2400 North Prior, Roseville, Minnesota 55113.

Analytical Columns and Parameters - A list of suggested columns is given in Table 1. Column parameter should always be adjusted to produce sharp symmetrical peaks with as much resolution as possible from interfering components. Carrier gas flow rates are nominally set at 25 cm^3/min. for packed columns 1/8 inch in diameter.

Vials - Equipped with Teflon lined caps. Vials: Size - 3.2 mm x 1.1 mm volume - 1 ml. Part No. 3-3123

Cap Crimper - Part No. 3-3195 available from Supelco

REAGENTS

Carbon Disulfide - Spectroquality or equivalent.

Solvents - Preferably chromatoquality for all compounds listed in Table 1.

Gas Chromatograph Supplies - Pressurized bottles of:

1. Helium for carrier gas use must meet or exceed laboratory Grade D 99.995% pure.
2. Nitrogen for carrier gas use must meet or exceed laboratory Grade E 99.98% pure.
3. Hydrogen for flame detector must meet or exceed Grade A 99.8% pure.
4. Air for flame detector must meet or exceed industrial Grade Type 1.

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

Calibration Standards - A series of standard solutions are prepared for each solvent to be determined. A microliter syringe is used to inject an appropriate amount of a particular compound into a known volume of carbon disulfide or other suitable solvent. Nominally 10, 25, and 50 mL glass - stoppered volumetric flasks are used. For the more volatile compounds, known amounts are added to measured quantities of solvent contained in vials equipped with Teflon - lined caps. The vials are immediately inverted and left in that position until used. These solutions are used to prepare a reference calibration curve for the particular organic vapor of interest. Normally 2 uL of each of the standard solutions are injected into a gas chromatograph and the peak area for each concentration is recorded. A best fit line is calculated by the regression technique to correlate peak area with the weight of component(s) present. It is recommended that the calibration and monitor samples be the same size (2 uL) to avoid possible column overloading as well as factorial errors.

An alternate method to the regression line is to average the resultant sensitivity factors of three individually prepared standards. Sensitivity factors are determined by the ratio of weight to area units.

Caution: Carbon disulfide is toxic and should be handled in a hood. Standard solutions should be used as soon as possible. They may be stored in the laboratory refrigerator for no more than five days.

SAMPLING

The monitor is removed from the package and the exposure start time is recorded on the back of the badge. When personal sampling is being performed, the monitor should be attached near the breathing zone. For area sampling, the monitor should NOT be placed in a corner or along a wall where stagnant air may exist. At the conclusion of the sampling period, the badge is removed and the retaining ring along with the membrane are discarded. The elutriation cap is then immediately snapped on terminating monitor exposure and the end time is recorded on the back of the badge. The following information must be recorded for each sample:

1. Monitor number
2. Date exposed
3. Employee or Area I.D.
4. Organic vapor of interest along with suspected contaminants which could cause interference
5. Temperature and relative humidity of the monitored environment if considered extreme
6. Any comments or unusual circumstances

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 30 minutes, with occasional gentle agitation, the eluent is decanted into a marked auto-sampler vial where a 2 uL sized sample is automatically introduced into the gas chromatograph. Alternatively, a 2 uL aliquot is removed from the center port for manual injection. The resultant analysis is recorded on a chromatogram where area units of the desired component(s) are correlated with the amount (weight) present during the sampling period. The weight found is recorded and converted to mg/m^3 and/or ppm. If the total collected weight is determined to be greater than 16 milligrams, for strongly adsorbed materials, the monitor may have been overposed. In some cases over-exposure could occur at lower concentrations. Referring to the qualification data sheets for upper capacity limits will help determine if the monitor has been overexposed.

CALCULATION

The relationship between environmental contaminant concentrations and the weight of material collected by the monitor is given by equation (1).

(1) $M = D \frac{A}{L} C\ t$ where M = total mass of collected contaminant (ng)
D = molecular diffusion coefficient (cm^2/min)
A = diffusion path area (cm^2)
L = diffusion path length (cm)
C = environmental contaminant concentration ($ng/cm^3 = mg/m^3$)
t = sampling time (min)

When the (D A/L) term has been experimentally determined to be some value (K), equation (1) may be changed to equation (2)

(2) $M = KC\ t$ where K = sampling rate (cm^3/min); the time-weighted exposure level is then calculated by solving equation (2) the (C) term.

(3) $$\frac{mg}{m^3} = \frac{*\text{corrected nanograms found}}{\text{recovery coefficient} \times \text{sampling rate } (cm^3/min) \times \text{sampling time (min)}}$$

(4) $$ppm = \frac{mg}{m^3} \times \frac{22.41/mole}{M.W.\ g/mole} \times \frac{T°K}{273°K} \times \frac{760\ mm\ Hg}{P\ mm\ Hg}$$

where M.W. = molecular weight of the organic vapor
T°K = ambient temperature in degrees Kelvin
P = ambient atmospheric pressure in mm of Hg

DISCUSSION

Experience teaches that a single contaminant is rarely found by itself in a given industrial atmosphere. Depending on the number and nature of the contaminating organic vapors, it is possible that interferences may occur. To help insure the accuracy of an analytical result, a sample may be analyzed on two chemically different natured columns (Carbowax vs SE-30). If the results are essentially the same for both columns, there is a good chance no interferences are present. However, no absolute identification can be made for any contaminant(s) by retention time only, regardless of the number of analytical columns used.

*Corrected nanograms = (sample area - blank area) calibration factor.

It is good analytical practice to run a bulk sample of the solvents being used in the surrounding area. These samples will give the analyst some insight to the possible airborne matrix.

REFERENCES

1) Gilliland, E. R., Diffusion Coefficients in Gaseous Systems, Ind. and Eng. Chemistry, June, 1934

2) Procedure for Organic Solvents in Air from NIOSH Manual of Analytical Methods

H. E. Mullins
/ss

TABLE 1

COMPOUNDS AND SUGGESTED METHODS

Organic Vapor	Molecular Weight (g/mole)	Density (g/mL)	Desorption Solution	Analytical Column
Acetone	58.1	0.79	A	I
Acrylonitrile	53.1	0.81	A	I
Allyl Alcohol	58.1	0.85	B	II
Allyl Chloride	76.5	0.94	C	III
Benzene	78.11	0.88	A	IV, V
Benzyl Chloride	126.6	1.10	A	II
Bromoform	252.8	2.9	A	II
Butadiene	54.1	Gas	A	IV
2-Butanone (MEK)	72.1	0.81	A	II
2-Butoxy Ethanol	118.2	0.90	D	II
Butyl Acetate	116.2	0.88	A	VI
Butyl Alcohol	74.1	0.81	E	II
Carbon Disulfide	76.1	1.26	C	VII
Carbon Tetrachloride	153.8	1.59	A	II
Chlorobenzene	112.6	1.10	A	II
Chlorobromomethane	129.4	1.99	A	II
Chloroform	119.4	1.48	A	IV
Chlorotoluene	126.6	1.07	A	II
Cumene	120.2	0.86	A	II
Cyclohexane	84.2	0.78	A	III
Cyclohexanol	100.2	0.96	B	II

Organic Vapor	Molecular Weight (g/mole)	Density (g/mL)	Desorption Solution	Analytical Column
Cyclohexone	98.1	0.95	A	II
Cyclohexane	82.1	0.81	A	III
Decane	142.3	0.73	A	IV
Diacetone Alcohol	116.2	0.93	B	II
m-Dichlorobenzene	147.0	1.29	A	II
1,1-Dichloroethane	99.0	1.18	A	I, II
1,2-Dichloroethane	99.0	1.26	A	I, II
1,2-Dichloroethylene	97.0	1.28	A	II
Difluorodibromomethane	209.8	gas	F	II
Diisobutyl Ketone	142.2	0.81	A	II
Dioxane	88.1	1.03	A	IV
Dipropylene Glycol Methyl Ether	148.2	0.95	A	II
Epichlorohydrin	92.5	1.18	A	II
2-Ethoxyethyl Acetate	132.2	0.98	A	VI
Ethyl Acetate	88.1	0.90	A	VI
Ethyl Acrylate	100.1	0.94	A	VI
Ethyl Alcohol	46.1	0.80	G	II
Ethyl Benzene	106.2	0.87	A	II
Ethyl Bromide	109.0	1.45	F	II
Ethyl Butyl Ketone	114.2	0.82	H	II
Ethylene Chlorohydrin	80.5	1.20	B	II
Ethylene Dibromide	187.9	2.17	A	II
Ethylene Dichloride	99.0	1.26	A	VIII
Ethyl Ether	74.1	0.73	I	III
yl Formate	74.1	0.92	A	IV
Glycidol	74.1	1.11	J	II

Organic Vapor	Molecular Weight (g/mole)	Density (g/mL)	Desorption Solution	Analytical Column
Heptane	100.2	0.68	A	VIII
Hexane	86.2	0.66	A	IV
Hexanone	100.2	0.80	A	II
Isoamyl Acetate	130.2	0.88	A	VI
Isoamyl Alcohol	88.2	0.81	B	II
Isobutyl Acetate	116.2	0.87	A	VI
Isobutyl Alcohol	74.1	0.81	E	II
Isopropyl Acetate	102.1	0.87	A	VI
Isopropyl Alcohol	60.1	0.79	G	II
Isooctane	114.2	.70	A	IV
Mesityl Oxide	98.1	0.86	H	II
Methyl Acetate	74.1	0.93	A	IV
thyl Acrylate	86.1	0.96	A	VI
Methyl Bromide	94.9	1.73	A	II
Methyl Cellosolve	76.1	0.97	D	II
Methyl Cellosolve Acetate	118.1	1.0	A	VI
Methyl Chloroform	(See 1,1,1-Trichloroethane)			
Methyl Cyclohexane	98.2	0.77	A	IV
Methylene Chloride	84.9	1.33	A	IV
Methyl Ethyl Ketone	(See 2 - Butanone)			
Methyl Isobutyl Ketone	100.2	.80	A, H	I
Nitrobenzene	123.1	1.20	A	I
Octane	114.2	0.70	A	IX
Pentane	72.2	0.63	A	IX

Organic Vapor	Molecular Weight (g/mole)	Density (g/mL)	Desorption Solution	Analytical Column
Perchloroethylene	(See Tetrachloroethylene)			
n-Propyl Acetate	102.1	.84	A	VI
iso-Propyl Acetate	102.1	.87	A	VI
iso-Propyl Benzene	(See Cumene)			
Stoddard Solvent	148	0.78	A	X
Styrene	104.1	0.91	A	II
1,1,2,2-Tetrachloroethane	167.9	1.59	A	II
Tetrachloroethylene	165.9	1.63	A	VIII
Toluene	92.1	.87	A	IV
1,1,1-Trichloroethane	133.4	1.35	A	VIII
1,1,2-Trichloroethane	133.4	1.44	A	VIII
Trichloroethylene	131.4	1.47	A	VIII
Turpentine	256.0	0.85	A	X
Vinyl Chloride	62.5	Gas	A	III
Vinyl Toluene	118.1	0.89	A	II
Xylene	106.2	0.86	A	IV

Desorption Solution

Key

A Carbon disulfide
B Carbon disulfide containing 5% 2-propanol
C Benzene
D Methylene chloride containing 5% methanol
E Carbon disulfide containing 1% 2-propanol
F Isopropyl alcohol
G Carbon disulfide containing 1% 2-butanol
H Carbon disulfide containing 1% methanol
I Ethyl acetate
Tetrahydrofuran

Analytical Columns

Key	
I	15% carbowax 20m, Chromosorb W, 7.5 ft. x 1/8 in. SS
II	10% FFAP, Chromosorb W AW, 10 ft. x 1/8 in. SS
III	Porapak Q, 6 ft. x 1/8 in. SS
IV	10% FFAP, Chromosorb W AW, 20 ft. x 1/8 in. SS
V	25% CEF, Chromosorb P AW, 10 ft. x 1/8 in. SS
VI	5% FFAP, Supelcoport, 10 ft. x 1/8 in. SS
VII	5% OV-17, Supelcoport, 6 ft. x 4 mm glass
VIII	10% OV-101, Supelcoport, 10 ft. x 1/8 in. SS
IX	10% SP-2100, Supelcoport, 10 ft. x 1/8 in. SS
X	1.5% OV-101, Supelcoport, 6 ft. x 1/8 in. SS