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ORGANIC VAPORS

(See Section 4)



Method no.: 07

Matrix: Air

OSHA PELs: Section 4

Procedure: Collection on charcoal, extraction with an organic solvent, and analysis by gas chromatography with flame ionization detector.

Recommended air volume and sample rate: Section 4

Status of method: This method has been used extensively in the OSHA Salt Lake Technical Center. With slight modification, this method is a generalized version of validated NIOSH methodology.

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1. General Discussion

1.1 Background

Background information on the analytes may be obtained from a number of sources such as NIOSH Criteria Documents, chemical dictionaries and industrial hygiene manuals. Solvents are used for degreasing, for dry cleaning, and in the manufacture of many materials ranging from paints, varnishes, shellacs, and lacquers to rubber and synthetic resins. When not being used as solvents, they may function as fuels or act as chemical intermediates with or without regard to their ability to put materials into solution. Toxic effects of the analytes vary with many acting as irritants or causing narcosis, and some having more hazardous effects.

1.2 Statistical parameters

1.2.1 Each analyte included in this general procedure has a validated NIOSH method, (Ref. 5.1) and/or a validated OSHA method. One of the NIOSH validation requirements is that the results obtained be within $\pm 25\%$ of the true values at the 95% confidence level at the air concentration equal to the OSHA standard. Although the OSHA evaluation procedure differs from that of NIOSH, the same validation requirements are used.

1.2.2 Refer to the validated NIOSH methods, (Ref. 5.1) for detailed information on individual analytes.

1.3 Advantages

1.3.1 The sampling device is small, portable, and involves no liquids.

1.3.2 The analysis is by a quick instrumental method.

1.3.3 Interferences can be eliminated by altering chromatographic conditions in most cases.

1.3.4 The method allows simultaneous analysis of two or more analytes.

1.4 Disadvantages

1.4.1 The air volume sampled is limited by the capacity of the charcoal tubes. Exceeding the capacity of the charcoal tube results in loss of sample. The adsorptive capacity is decreased by high humidity.

1.4.2 The method is limited by the reproducibility of the pressure drop across the tubes. The pressure drop affects the flow rate causing the air volume to be imprecise.

1.4.3 The analyst must work with toxic solvents.

1.4.4 When many components are present, elimination of interferences becomes difficult.

2. Sampling Procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate with the sampling device attached.

2.1.2 Charcoal tubes: Glass tubes with both ends flame sealed, 7 cm long with a 6-mm o.d. and 4-mm i.d., containing two sections of 20/40 mesh activated charcoal separated by a

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2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 in. of mercury at a flow rate of 1 L/min.

- 2.1.3 Certain analytes require petroleum base charcoal instead of coconut base charcoal. This requirement is specified in Section 4.

2.2 Reagents

None required in sampling procedure.

2.3 Technique

- 2.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 2.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.
- 2.3.3 The charcoal tube should be placed vertically during sampling to minimize channeling.
- 2.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
- 2.3.5 Do not exceed the recommended air volume.
- 2.3.6 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 2.3.7 One tube should be handled in the same manner as the sample tube (break, seal and transport) except that no air is sampled through this tube. This tube should be labeled as a blank.
- 2.3.8 Capped charcoal tubes should be wrapped end to end with official OSHA seals. They should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 2.3.9 For certain analytes where migration on the charcoal is a significant problem, it may be requested that two charcoal tubes be used in series in order that breakthrough may be distinguished from migration. These tubes must be separated and individually capped and sealed before shipping.

2.4 Breakthrough

Breakthrough data is presented on each analyte in its respective validated NIOSH method (Ref. 5.1).

2.5 Extraction efficiency

- 2.5.1 The back end of a charcoal tube is opened and the backup portion of activated charcoal is removed, leaving the front 100-mg portion of activated charcoal intact in the tube. The activated charcoal must be of the same lot as that in the tubes used to collect the

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samples. A known amount of analyte is injected directly into the activated charcoal with a microliter syringe and the tube is capped.

2.5.2 Six tubes at each of three concentration levels (0.5, 1, and 2 times the standard) are prepared by adding an amount of analyte equivalent to that present in a recommended air sample at the selected level. The tubes are allowed to stand at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no analyte is added to it. The sample and blank tubes are extracted and analyzed in exactly the same manner as the sampling tube described in Section 3.

2.5.3 The extraction efficiency (E_E) equals the average weight in milligrams recovered from the tube divided by the weight in milligrams added to the tube, or

$$E_E = \frac{M_R}{M_S}$$

where: E_E is extraction efficiency
 M_R is mass recovered
 M_S is mass spiked

2.5.4 If there is a significant change in extraction efficiency over the range of loadings studied, a plotted curve of E_E versus mass recovered must be used to correct for adsorption losses.

2.5.5 If there is no significant change in E_E over the range studied, reconfirmations need only be carried out at one loading in the middle of the range.

2.6 Recommended air volume and sample rate

See Section 4. for recommended air volume and sampling rate.

2.7 Interferences

2.7.1 It is important to be aware of other components in the atmosphere which may interfere with the collection of the analyte.

2.7.2 High relative humidity may significantly affect the collection of some analytes.

2.8 Safety precautions

2.8.1 Care must be taken when opening the sealed ends of charcoal tubes to avoid cuts to the hands.

2.8.2 Safety glasses should be worn when opening the sealed ends of charcoal tubes to avoid injury to the eyes from glass splinters.

3. Analytical procedure

3.1 Apparatus

3.1.1 Gas chromatograph equipped with flame ionization detector.

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- 3.1.2 Columns. A variety of columns are suitable. Two good selections are a 60-m \times 0.32 mm DB-1 capillary column with 1 μ m df or a 60-m \times 0.32 mm DB-Wax capillary column with 1 μ m df. Similar columns from other manufactures are acceptable.
- 3.1.3 A suitable method of measuring peak areas, such as an electronic integrator or data system.
- 3.1.4 Two-milliliter vials with either screw-on or crimp-on caps which contain PTFE-lined septa.
- 3.1.5 Microliter syringes; one-microliter for GC injections and 10- μ L for standard preparation, or other suitable sizes.
- 3.1.6 Pipets for dispensing extracting solvent (ES). A Glenco 1-mL reagent dispenser is adequate and convenient.
- 3.1.7 Volumetric Flasks. Five-milliliter and other convenient sizes.
- 3.1.8 Glass tubing cutter.
- 3.2 Reagents
 - 3.2.1 Chromatographic quality extracting solvent (ES). Although carbon disulfide is commonly used as the ES, certain analytes can be more effectively extracted with the use of alternate solvents or solvent solutions. These alternate ESs are listed in Chemical Sampling Information located at <http://www.osha.gov> and are normally used when the single analyte is requested or when the requested analytes are known to be effectively extracted with that ES. When analysis for a number of analytes requiring different extracting solutions is requested, the preferred ES will usually be carbon disulfide.
 - 3.2.2 Analyte standard, reagent grade.
 - 3.2.3 Internal standard, (optional) reagent grade. *p*-Cymene and *n*-hexylbenzene are suitable internal standards for many solvents.
 - 3.2.4 Chromatographic quality helium, nitrogen, hydrogen, and air.
- 3.3 Standard preparation
 - 3.3.1 Prepare analyte standard at a concentration of 1 μ L of analyte per milliliter of ES by adding 5 μ L of analyte to a 5-mL volumetric flask partially filled with ES. Fill the volumetric flask to the mark and invert 3 or 4 times for proper mixing. Other size volumetric flasks may also be used to prepare the 1 μ L/mL analyte standards. At least two standards at 1 μ L/mL are prepared. Standards must be used the day they are prepared. In some cases, analyte standards in concentrations other than 1 μ L/mL may be more suitable, especially with analytes that have extremely high or low OSHA standards.
 - 3.3.2 Injection of standards is accomplished with a 1- μ L or other suitable syringe. The syringe is rinsed thoroughly in carbon disulfide between standards. Injector septa should be checked for wear daily.
 - 3.3.3 Injection sizes other than 1- μ L and injection by means of a gas chromatograph autosampler are acceptable in most cases.

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3.4 Preparation of samples

- 3.4.1 The status of the seals on each charcoal tube is noted and recorded as intact, broken, or none.
- 3.4.2 The field identification number, the laboratory identification number and signature of the industrial hygienist on each sample seal are checked with those on the sample identification sheets.
- 3.4.3 The seal is removed and the charcoal tube is opened with a glass tubing cutter at the end containing the larger portion of charcoal. The front and back sections of charcoal are transferred to separate 2-mL capped vials. The glass wool plug and the small wad of urethane foam separating the two sections of charcoal are discarded.
- 3.4.4 The charcoal lot number is noted in order that the proper extraction efficiency is used in later calculations.
- 3.4.5 Gas chromatography parameters are set as recommended in the instruments manual. Oven temperature and column are varied until an optimum chromatogram is produced by the analyte standard.
- 3.4.6 Once the internal standard has been verified as not interfering with other peaks in the chromatogram, the samples are extracted. One milliliter of ES is dispensed into each sample vial. The vial is immediately sealed. Each vial is swirled periodically to increase the rate of extraction. Twenty to thirty minutes is typical for the extraction process.

3.5 Analysis

- 3.5.1 The data processor can be calibrated to provide results directly in units of mass. With a few of the analytes an additional similar correction may be necessary due to extraction efficiencies that change with concentration. The linear nature of the flame ionization detector allows the use of a point calibration, but the bracketing of samples with analytical standards is a good practice. The calculation of the equivalent air concentration for an analytical standard is detailed in Section 3.7.1.
- 3.5.2 Sample injection is accomplished with a 1- μ L or other suitable syringe. The syringe is rinsed thoroughly in carbon disulfide between samples. Injector septa should be checked for wear periodically. Injection by means of a gas chromatograph autosampler is acceptable.
- 3.5.3 Bracket the samples with analytical standards if detected concentrations are above the PEL.
- 3.5.4 When the identity of a suspected analyte peak is in question, it should be confirmed by GC/MS, GC/IR, or by retention time on at least two GC columns containing different packing material. The identity of the analyte should be considered suspect when detected concentrations are above the PEL.

3.6 Interferences

Interferences to the analytical method will in most cases appear as poor resolution of the analyte peak from other components. This may be overcome by prudent selection of a more suitable chromatographic condition or column.

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3.7 Calculations

- 3.7.1 An equivalent air concentration for analytical standards is used to calibrate the data processor such that analytical results are obtained directly in mass, mg.

$$W = V_s \times d$$

where W is weight of analyte in μg
 V_s is volume of analyte in μL
 d is density of analyte in $\mu\text{g}/\mu\text{L}$

$$C_v = \frac{V_M W}{M_r V E_E}$$

where C_v is air concentration reported to IH
 V_M is molar volume at 25°C and 760 mmHg, 24.46 L/mol
 W is weight of analyte
 M_r is molecular weight of the analyte
 V is air volume sampled
 E_E is extraction efficiency

- 3.7.2 The following example is the calculation for toluene:

$$W = 867 \mu\text{g} = 1 \mu\text{L} \times 867 \mu\text{g}/\mu\text{L}$$

$$C_v = 23.73 \text{ ppm} = \frac{(24.46 \text{ L/mol}) (867 \mu\text{g})}{(92.15 \text{ g/mol}) (10 \text{ L}) (0.97)}$$

The calculations should be considered an example only, and various parameters confirmed before used in actual analysis.

3.8 Safety precautions

- 3.8.1 Care must be taken when opening charcoal tubes to avoid cuts to the hands.
- 3.8.2 Safety glasses must be worn throughout the analytical procedure.
- 3.8.3 Work involving solvents open to the atmosphere must be performed in a hood.

3.9 Reporting results

- 3.9.1 When results uncorrected for air volume are greater than 10 ppm, three significant digits will be reported. For results below 10 ppm, the chemist will use his judgment, but in no cases report more than three significant digits.
- 3.9.2 The estimated detection limit based on the lowest mass per sample injected as a standard.
- 3.9.3 All concentration levels down to the detection limit are reported.

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- 3.9.4 If the concentration of analyte found on the back section of the charcoal tube is equal to or greater than 25% of the concentration found on the front section, the charcoal tube is considered to be saturated and reported as such on the analyst worksheet.
- 3.9.5 The presence of significant peaks caused by unrequested components in the sample is noted on the analyst worksheet and they are identified and quantitated if possible.
- 3.9.6 All data processor print-outs and chart recorder chromatograms are filed in a central file according to laboratory sample identification number.
- 3.9.7 Analytical data and results are checked by a fellow chemist before the completed analyst worksheets are given to the team leader.

4. Analytes

The following table contains those analytes which can be analyzed by this procedure. Standard size charcoal tubes containing coconut base charcoal are used unless specified otherwise in the table. Listed PELs are 8-h time weighted averages unless denoted as a ceiling concentration with a "(C)", before the PEL value. Before taking samples, the OSHA Chemical Sampling Information at <http://www.osha.gov> should be consulted for additional and more detailed information.

Table 4.
Recommended Sampling Parameters for Analytes Covered by This Procedure.

analyte	PEL (ppm)	air vol (L)	max rate (L/min)	NIOSH Method
Allyl alcohol	2	10	0.2	1402
Allyl chloride	1	48	0.2	1000
n-Amyl acetate	100	10	0.2	1450
sec-Amyl acetate	125	10	0.2	1450
Benzyl chloride	1	10	0.2	1003
Bromoform	0.5	10	0.2	1003
Butyl acetate	150	10	0.2	1450
sec-Butyl acetate	200	10	0.2	1450
tert-Butyl acetate	200	10	0.2	1450
Butyl alcohol	100	10	0.2	1401
sec-Butyl alcohol	150	10	0.2	1401
tert-Butyl alcohol	100	10	0.2	1400
n-Butyl glycidyl ether (BGE)	50	10	0.2	1616
p-tert-Butyltoluene	10	24	0.2	1501
Camphor	2 mg/m ³	24	0.2	1301
Carbon tetrachloride	10	15	0.2	1003
Chlorobenzene (monochlorobenzene)	75	10	0.2	1003
Chlorobromomethane	200	5	0.2	1003
Cumene	50	10	0.2	1501
Cyclohexane	300	5	0.2	1500
Cyclohexanol	50	10	0.2	1402
Cyclohexene	300	5	0.2	1500
Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)	50	10	0.2	1402
o-Dichlorobenzene	(C) 50	3	0.2	1003
p-Dichlorobenzene	75	3	0.05	1003
1,1-Dichloroethane	100	10	0.2	1003
1,2-Dichloroethylene	200	3	0.2	1003
Dichloroethyl ether	(C) 15	15	1.0	1004
1,1-Dichloro-1-nitroethane**	(C) 10	15	1.0	1601
Difluorodibromomethane (F-12-B2)*	100	10	0.2	1012
Diisobutyl ketone	50	10	0.2	1300
Dioxane (diethylene dioxide)	100	10	0.2	1602
Epichlorohydrin	5	20	0.2	1010
Ethyl acetate	400	6	0.2	1457

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Ethyl sec-amyl ketone (5-methyl-3-heptanone)	25	25	0.2	1301
Ethyl bromide	200	4	0.2	1011
Ethyl butyl ketone (3-heptanone)	50	25	0.2	1301
Ethylene chlorohydrin**	5	35	0.2	2513
Ethyl ether	400	3	0.2	1610
Ethyl formate	100	10	0.2	1452
Glycidol (2,3-epoxy-1-propanol)	50	50	1.0	1608
n-Heptane	500	4	0.2	1500
Hexachloroethane	1	10	0.2	1003
n-Hexane	500	4	0.2	1500
2-Hexanone (MBK)	100	10	0.2	1300
sec-Hexyl acetate	50	10	0.2	1450
Isoamyl acetate	100	10	0.2	1450
Isoamyl alcohol	100	10	0.2	1402
Isobutyl acetate	150	10	0.2	1450
Isobutyl alcohol	100	10	0.2	1401
Isophorone**	25	12	0.2	2508
Isopropyl acetate	250	8	0.2	1454
Isopropyl ether	500	3	0.05	1618
Isopropyl glycidyl ether	50	10	0.2	1620
Mesityl oxide	25	25	0.2	1301
Methyl acetate	200	7	0.2	1458
Methylal (dimethoxymethane)	1000	2	0.2	1611
Methyl-(n-amyl)ketone	100	25	0.2	1301
Methylcyclohexane	500	4	0.2	1500
Methyl isobutyl carbinol	25	10	0.2	1402
α -Methyl styrene	(C) 100	3	0.2	1501
Octane	500	4	0.1	1500
Pentane	1000	2	0.05	1500
2-Pentanone	200	10	0.2	1300
Phenyl glycidyl ether	10	50	0.1	1619
n-Propyl acetate	200	10	0.2	1450
Propyl alcohol	200	10	0.2	1401
Propylene dichloride	75	10	0.2	1013
n-Propyl nitrate**	25	70	0.1	S227
1,1,1,2-Tetrachloro-2,2-difluoroethane	500	2	0.035	1016
1,1,2, 2-Tetrachloro-1,2-difluoroethane	500	2	0.035	1016
1,1,2,2-Tetrachloroethane**	5	10	0.2	1019
Tetrahydrofuran	200	5	0.2	1609
Tetramethyl succinonitrile	0.5	48	0.2	155
1,2,3-Trichloropropane	50	10	0.2	1003
Vinyl toluene	100	24	0.2	1501

*Use two charcoal tubes in series for sampling.

**Use petroleum base charcoal for sampling.

5. References

- 5.1 "NIOSH Manual of Analytical Methods", ed. 4 Vol. 1-3 National Institute of Occupational Safety and Health, U.S. Government Printing Office, Washington, D.C. (1998)