

Di-2-Ethylhexyl Phthalate*

Analyte:	Di-2-ethylhexyl phthalate	Method No.:	S40
Matrix:	Air	Range:	2.03 - 10.9 mg/cu m
OSHA Standard:	5 mg/cu m	Precision: ($\overline{CV}_T$):	0.057
Procedure:	Filter collection extraction with carbon disulfide, GC	Validation Date:	1/17/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a cellulose membrane filter to trap the organic aerosol present.
- 1.2 The filter in the cassette is transferred into a disposable glass pipet and eluted with carbon disulfide.
- 1.3 An aliquot of the eluted sample is injected into a gas chromatograph.
- 1.4 The area of the sample peak is determined and the concentration is determined from the calibration curve.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 2.03 - 10.9 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 32-liter sample. Under the conditions of sample size (30 liters), the probable useful range of this method is 0.5 - 15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 0.45 mg sample.
- 2.2 The upper limit of the range of the method is dependent on the filtration efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The filtration efficiency for di-2-ethylhexyl phthalate aerosol is greater than 95% when sampled for 30 minutes at 1 liter per minute from a test atmosphere containing 10 mg/cu m.

* Listed incorrectly as di-sec-octyl phthalate in 29 CFR 1910.93.

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3. Interference

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.03 - 10.9 mg/cu m is 0.057. This value corresponds to a standard deviation of 0.29 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 8% higher than the "true" values at the OSHA standard level.

These data are based on the validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

- 6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:
 - 6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37 mm 3-piece cassette filter holder.
 - 6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ (reference 11.2) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

- .2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (6-ft x 1/8-in stainless steel) packed with 5% OV-101 on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Assembly for sample elution.
 - 6.6.1 Extraction tube, Fisher brand disposable Pasteur pipet (Cat. No. 13-678-5A) modified as follows: cut off the upper 1-inch portion, i.e., just below the notch to eliminate the constricted portion, and flame seal the lower tapered end.
 - 6.6.2 Dumont No. 5 precision watchmakers tweezers, rustproof.
 - 6.6.3 Volumetric flask, 1 ml.
 - 6.6.4 Ultrasonic cleaner.
 - 6.6.5 Triangular file.
- 6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.
- 6.8 Volumetric flasks: 10-ml and other convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Di-2-ethylhexyl phthalate, reagent grade.
- 7.3 Tricosane, or other suitable internal standard.
- 7.4 Purified helium.
- 7.5 Prepurified hydrogen.
- 7.6 Filtered compressed air.

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8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples
- 8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.
- 8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.
- 8.3.4 A maximum sample size of 30 liters is recommended. Sample at a flow rate of 1.0 liter per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.5 Turn the pump on and begin sample collection. Since it is possible for filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.
- 8.3.6 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.
- 8.3.8 Carefully record sample identity and all relevant sample data.
- 8.3.9 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

- 8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

Analysis of Samples

8.4.1 Preparation of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad.
2. With the aid of the Dumont tweezers, carefully roll the filter into a narrow cylinder. To do so, place the filter (sample side upwards) on a clean surface such as a watch glass and imagine a tangent to any edge of the circular filter. Pinch the filter with the long, sharp prongs of the tweezers along a line parallel to the imaginary tangent and about 1 cm inwards from the tangential point and start rolling the filter by gradually and carefully turning the tweezers' handle.
3. Insert the rolled filter into the modified pipet.
4. Add a known aliquot of the internal standard solution in carbon disulfide (ca. 100 microliters only) to the filter.

Note: If the external standard method is used, this last step should be eliminated.

8.4.2 Extraction of Samples

1. Position pipets upright and add ca. 1 ml of carbon disulfide to the filter in the disposable pipet. Be sure that the entire filter is submerged in carbon disulfide and that there are no air bubbles trapped.
2. Seal the top of the pipet with a wad of glass wool to avoid sample contamination and loss during the next step.
3. Arrange the sample-containing pipets upright in a beaker and place the beaker in the ultrasonic vibrator for 30 minutes.
4. With a sharp file, very carefully score the tip (about 1 cm above the sealed end) of the pipet and break the tip inside the 1 ml volumetric flask. Allow the carbon disulfide eluent to drain completely into the flask. Apply air pressure, if necessary, to aid draining.

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5. Rinse the filter inside the pipet with more carbon disulfide by dropwise addition of solvent until the total volume of eluent collected is 1.0 ml. If the 1.0 ml mark is overshoot, concentrate sample to 1.0 ml by using a slow nitrogen flush.
6. If an automatic sample injector is used, transfer the sample extracts into the automatic sample injector vials prior to analysis.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 300°C injector temperature
5. 300°C manifold temperature (detector)
6. 230°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9 - 5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 termination of Sample Recovery

8.5.1 Need for determination. Since the extraction scheme may be dependent on operator skill, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicates and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining extraction efficiency. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within 5%.

For this validation study, an amount of the analyte equivalent to that present in a 30-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly and a known amount of internal standard was added to each filter prior to extraction. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The recovery values obtained were at least 95% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in mg recovered from the filter divided by the weight in mg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same conditions under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

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For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the OSHA standard level. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\begin{aligned}\text{mg sample} &= \text{mg found in sample filter} \\ \text{mg blank} &= \text{mg found in blank filter}\end{aligned}$$

10.3 Divide the total weight by the extraction efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg(Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

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where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.2 Final Report, NIOSH Contract HSM-99-71-31. "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

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