2,6-DI-*t*-BUTYL-*p*-CRESOL(DBPC)* IN AIR

Measurements Support Branch

Analytical Method

Analyte: 2,6-Di-*t*-Butyl-*p*-Cresol (DBPC)*	**Method No.:** P&CAM 226
Matrix: Air	**Range:** 1 to 500 mg/m³ in a 10-liter sample of air
Procedure: Silica gel adsorption; methanol-carbon disulfide desorption; GC	**Precision (CV):** 0.05 (estimated analytical) over the above range
Date Issued: 6/30/76	**Classification:** D(Operational)
Date Revised:	

1. Principle of the Method

A known volume of air is drawn through a tube containing silica gel to trap the DBPC. The silica gel is transferred to a small, graduated test tube and desorbed with a mixed solvent, 5% (v/v) methanol in carbon disulfide. An aliquot of the solution is analyzed by gas chromatography with flame ionization detection (FID). The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 The calibration curve of peak area *versus* concentration is linear over the range of 0.02 to 10 mg/mℓ of DBPC in the mixed solvent. This range corresponds to 0.01 to 5 mg of DBPC in a sample, since the silica gel is extracted with 0.5 mℓ of the mixed solvent. A convenient working range for the sampling and analytical method is therefore 1 to 500 mg/m³ in a 10-liter sample of air.

2.2 The detection limit of the analytical method is 0.2 μg/mℓ of DBPC in the mixed solvent. This corresponds to 0.1 μg in a sample or 0.01 mg/m³ in a 10-liter sample of air.

3. Interferences

3.1 When the amount of water in the air is so great that condensation occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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*Also called butylated hydroxy toluene (BHT).

3.2 Any compound that has the same GC retention time as DBPC under the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a bulk sample of DBPC be submitted so that its composition can be established by other means. If the possibility of interference in the GC analysis exists, operating conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 No precision or accuracy data for the overall sampling and analytical method are available.

4.2 Although the precision of the analytical method has not been explicitly determined, the correlation coefficient is greater than 0.99 for the calibration curve in the linear concentration range.

4.3 The efficiency of desorption of 0.05 and 0.2 mg/tube of DBPC has been found to be 0.90, or greater, with coefficients of variation of 0.05 and 0.04, respectively.

5. Advantages and Disadvantages of the Method

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

5.2 One disadvantage of the method is that the amount of DBPC that can be collected on a tube without breakthrough is limited. When the procedure for the determination of desorption efficiency outlined in Section 8.4 was followed, at least 0.2 mg of DBPC was trapped in the front section without breakthrough. However, no detailed breakthrough study for this compound has been conducted. If the amount of DBPC found in the backup section exceeds 25% of that found in the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 **Sampling Pump**. An approved and calibrated personal sampling pump is required for personal samples. Each pump should be calibrated with a representative sorbent tube in the sampling line. A dry or wet test meter or glass rotameter that will determine the flow rate to within 5% may be used for the calibration. For an area sample any vacuum pump whose flow can be determined accurately for flow rates of 1 ℓ/min or less can be used.

6.2 **Sorbent Tubes.** Glass tubes, 7 cm long, 6 mm o.d., and 4 mm i.d., are packed with two sections of 45/60-mesh silica gel separated by a 2-mm plug of urethane foam. The front section contains 100 to 150 mg of silica gel and the backup section contains 50 to 75 mg. A 3-mm plug 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 the inlet end of the tube. The pressure drop across the tube must be less than 1 in. of Hg at a flow rate of 1 ℓ/min.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 A stainless steel GC column (10 ft by 0.125 in.) packed with 5% SE-30 on 60/80-mesh Chromosorb W, or an equivalent column.

6.5 A mechanical or electronic integrator or a recorder with a means of determining peak area.

6.6 Graduated glass-stoppered micro centrifuge tubes or 2-mℓ sealed sample vials for desorbing samples.

6.7 Microsyringes, 10 μℓ, and other sizes convenient for preparing standards.

6.8 Volumetric pipettes, 0.5 mℓ, or 1-mℓ pipettes graduated in 0.1 mℓ increments.

6.9 Volumetric flasks, 10 mℓ, and other sizes convenient for preparing standard solutions.

7. **Reagents**

7.1 Carbon disulfide and methanol, spectroquality. Prepare a solution containing 5% of methanol in carbon disulfide.

7.2 2,6-Di-*t*-butyl-*p*-cresol(DBPC), reagent grade.

7.3 Helium, Bureau of Mines Grade A, or prepurified nitrogen.

7.4 Hydrogen, prepurified.

7.5 Compressed air, filtered.

8. **Procedure**

8.1 **Cleaning of Equipment.** Wash all glassware with detergent solution and rinse thoroughly with tap water and distilled water.

8.2 **Collection and Shipping of Samples.**

8.2.1 Immediately before beginning the collection of a sample, break each end of the sorbent tube so as to provide openings at least half the inside diameter of the tubes.

8.2.2 Connect the backup end (smaller section of silica gel) of the sorbent tube to the pump and mount the tube vertically to prevent channeling, with the larger section of silica gel on top. Sample air must not pass through any hose or tubing before entering the sorbent tube.

8.2.3 Sample the air at 200 mℓ/min. A maximum sample volume of 10 liters is recommended. If very high concentrations of DBPC are known to be present, take smaller samples to minimize the possibility of breakthrough.

8.2.4 Cap the sorbent tubes with the plastic caps supplied immediately after sampling is completed. Do not use rubber caps.

8.2.5 One tube should be handled in the same manner as the sample tube (break, seal, and ship) except that no air is pumped through it. Label this tube as a blank.

8.2.6 Pack the capped tubes tightly in a suitable container to minimize breakage during transport to the laboratory.

8.2.7 Submit a sample of the bulk DBPC to the laboratory. Do not ship this bulk sample in the same container as the sample or blank tubes. If possible, ship a bulk air sample for qualitative identification purposes.

8.3 **Analysis of Samples**

8.3.1 **Preparation of Samples.** In preparation for analysis, score each sorbent tube with a file in front of the first section of silica gel and break it open. Transfer both the front glass fiber plug and the larger initial section of silica gel to a small stoppered test tube or sample vial. Tests indicate that the front glass fiber plug does trap some of the DBPC so it must be extracted with this first sorbent section. Remove and discard the separating section of foam; transfer the second smaller section of silica gel to another test tube. Analyze these two sections separately.

8.3.2 **Desorption of Samples.** Prior to analysis, pipette 0.5 mℓ of the mixed solvent into each test tube. (All work with carbon disulfide should be performed in a hood because of its toxicity.) Tests indicate that desorption is time dependent and requires at least 60 min with periodic agitation. The use of graduated, glass-stoppered micro centrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent; thus volume changes can occur during the desorption process depending on the surrounding temperature. Note the initial volume occupied by the silica gel plus the 0.5 mℓ of mixed solvent and make corresponding volume adjustments whenever necessary prior to GC analysis.

8.3.3 **GC Conditions.** Typical operating conditions for the gas chromatograph are:

- Helium carrier gas flow rate, 85 mℓ/min.
- Hydrogen gas flow rate to detector, 65 mℓ/min.
- Air flow rate to detector, 500 mℓ/min.
- Injector temperature, 200°C.
- Column temperature, 160°C.

8.3.4 **Injection.** The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. First flush the 10-μℓ syringe with solvent several times to wet the barrel and plunger. Draw 3 μℓ of mixed solvent into the syringe to increase the accuracy and reproducibility of the injected sample volume. Remove the needle from the solvent, and pull back the plunger about 0.2 μℓ to separate the solvent flush from the sample with a pocket of air to be used as a marker. Then immerse the needle into the sample, and withdraw a 5-μℓ aliquot, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. Remove the needle from the sample and pull back the plunger a short distance to minimize evaporation of the sample from the tip of the needle prior to injection. Make duplicate injections of each sample and standard. No more than a 3% difference in area is to be expected.

8.3.5 **Measurement of Area.** Measure the area of the sample peak with an electronic integrator or by some other suitable method of area measurement, and read preliminary results from a standard curve prepared as discussed below in Section 9.

8.4 Determination of Desorption Efficiency

8.4.1 **Importance of Determination.** The desorption efficiency of a particular compound can vary from one laboratory to another and possibly from one batch of silica gel to another. Thus, it is necessary to determine at least once the fraction of the specific compound that is removed in the desorption process. The Measurements Support Branch of NIOSH has found that the desorption efficiency for DBPC is 0.90 or greater down to levels of 0.05 mg.

8.4.2 **Procedure for Determining Desorption Efficiency.** Transfer an amount of silica gel equivalent to the amount in the first section of a sorbent tube (100 to 150 mg) into a 20-in., 4-mm i.d. glass tube, flame-sealed at one end. (This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused tubes.) Cap the open end of the tube with Parafilm. With a microliter syringe, inject directly into the silica gel a known amount of DBPC standard prepared in carbon disulfide. Cap the tube with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample of air at a concentration equal to the OSHA standard. Prepare at least six tubes in this manner and allow them to stand at least overnight to assure complete absorption of the DBPC by the silica gel. Treat a parallel blank tube in a similar manner, but add no DBPC standard to it. Desorb and analyze these standard and blank tubes as described in Section 8.3. Prepare two or three solution standards by injecting the same volume of DBPC into 0.5 mℓ of the mixed solvent with the same syringe used in the preparation of the silica gel-tube samples. Analyze these solution standards along with the tube samples. The desorption efficiency (D.E.) equals the difference between the average peak area for the tube samples and the peak area for the blank divided by the average peak area for the solution standards, or

$$\text{D.E.} = \frac{\text{tube sample area - blank area}}{\text{solution standard area}}$$

9. Calibration and Standards

9.1 Prepare a series of standards, varying in concentration over the range of interest. It is convenient to express the concentrations of standards in terms of milligrams of DBPC in 0.5 mℓ of desorbing solution. To minimize error caused by evaporation of the carbon disulfide, one can measure into 10 mℓ of the mixed solvent 20 times the weight of DBPC that would have been present in 0.5 mℓ. Analyze these standards under the same GC conditions and during the same time period as the unknown samples. Establish a calibration curve by plotting concentration (in mg/0.5 mℓ) versus peak area.

9.2 If no internal standard is used in the method, the standard solutions must be analyzed at the same time the sample analyses are done. This will minimize the effect of day-to-day variations and variations of FID response during the same day. However, it is recommended that a suitable internal standard be employed.

10. Calculations

10.1 From the standard curve, read the weight of DBPC (in mg) corresponding to the peak area for the particular sample. No volume corrections are needed, because the standard curve is based on mg/0.5 mℓ of extract, and the volume of sample injected into the GC is identical to the volume of the standards injected.

10.2 Make a correction for the blank for each sample.

$$\text{Corrected mg} = mg_s - mg_b$$

where: mg_s = mg found in front section of sample tube.

mg_b = mg found in front section of blank tube.

A similar procedure is followed for the backup section.

10.3 Add the corrected amounts present in the front and backup sections of the same sample tube to determine the total measured amount of DBPC in the sample.

10.4 Divide this total weight by the desorption efficiency (D.E.) to obtain the total amount, W (in mg), in each sample.

10.5 The concentration of DBPC in the air samples can be expressed in mg/m^3, which is numerically equal to $\mu g/\ell$:

$$mg/m^3 = \frac{W\ (mg) \times 1000\ \ (\mu g/mg)}{V\ (\ell)}$$

where: W = the total amount of DBPC collected in the sample.

V = volume of air sampled.

11. References

11.1 White, L. D., D. G. Taylor, P. A. Mauer, and R. E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," **Am. Ind. Hyg. Assoc. J.**, 31, 225 (1970).

11.2 Choy, T. K., J. J. Quattrone, Jr., and N. J. Alicino, "A Gas Chromatographic Method for the Determination of the Antioxidants BHA, BHT, and Ethoxyquin in Aqueous and in Hydrocarbon-Soluble Samples," **J. Chromotogr.**, 12, 171 (1963).

11.3 Grote, A. A., "Sampling and Analysis of 2,6-Di-*t*-Butyl-*p*-Cresol (DBPC) in an Industrial Atmosphere," presented at the American Industrial Hygiene Conference, Atlanta, Ga., May 1976.