Di-tert-butyl-p-Cresol

Method no.:	PV2108
Target concentration:	10 mg/m³ OSHA TWA PEL
Procedure:	Samples are collected by drawing a known volume of air through an OVS-7 tube. Samples are desorbed with methanol and analyzed by gas chromatography with a flame ionization detector (GC-FID).
Air volume and sampling rate studied:	100 minutes at 1.0 L/min (100 L)
Status of method:	Partially Validated Method. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Salt Lake Technical Center has received many requests for a sampling and analytical procedure for di-tert-butyl-p-cresol (BHT). OSHA promulgated an exposure standard on January 1989, for BHT at a level of 10 mg/m³ TWA. There is a NIOSH method 226 for collection of BHT on silica gel tubes and desorption by (5/95) methanol/carbon disulfide, and analysis by GC-FID (Ref. 5.1). This is a partially validated method with no retention or collection studies performed. The lab performed a retention study with 10 liters of 89% RH air, on silica gel tubes spiked with 100 µg BHT. The average recovery was 30.9%, so another means of collection was explored. OSHA Method 32 collects phenol and cresol on XAD-7 tubes and desorbs them with methanol (Ref. 5.2). BHT is related to these compounds, and is a solid at room temperature, so a modification of method 32 was tried, using an OVS-7 tube instead of the XAD-7, and found to be successful. An OVS-7 tube is a glass fiber filter in front of a 270 mg section of XAD-7 resin followed by a 140 mg section of XAD-7 resin. Desorption, retention, and storage recoveries were good using OVS-7 tubes.

1.1.2 Potential workplace exposure (Ref. 5.3)

BHT is used as an antioxidant for food, animal feed, petroleum products, synthetic rubbers, plastics, animal and vegetable oils, and soaps. BHT is used as an antiskinning agent for paints and inks.

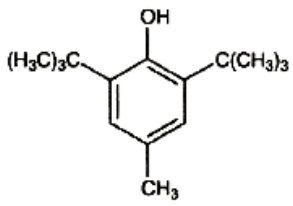
1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref. 5.4)

BHT is a skin and eye irritant. Levels of 5 to 10 times the level in processed foods caused brain and behavioral changes in mice; the treated mice fought more and slept less than the control group. Large doses of BHT in the food of rats, mice, cats, and dogs caused liver weight increase, which was reversible in the rat study where 500 mg/kg/day was given for two weeks. The LD_{50} for male rats was 1.7 g/kg. The FDA limits the BHT level in food to 2 ppm.

1.1.4 Physical properties (Ref. 5.3):

CAS:	128-37-0
IMIS:	2683
Synonyms:	Butylated hydroxytoluene; 2,6-Bis (1,1-dimethyl- ethyl)-4-methyl phenol; BHT; DBPC; Antracine 8; 2, 6-di- tert-butyl-4-methyl phenol; Tenox BHT; Annual CP; Sustane; Dalpac; Impruvol; Vianol
Molecular weight:	220.34
Melting point:	70 °C
Boiling point:	265 °C
Flash point:	127 °C (261 °F)
Odor:	light cresylic
Color:	white to pale yellow crystals
Molecular formula:	$C_{15}H_{24}O$
RTECS:	27354; G07875000

Structure:



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 333 µg/mL BHT in the desorbing solvent. This is the smallest amount that could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.01 mg/m³ BHT. (All mg/m³ amounts in this study are based on a 100-liter air volume and a 3-mL desorption.)

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

None known.

2 Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow.

2.1.2 The sampling media consists of OVS-7 tubes. The OVS-7 tubes are specially made 13-mm o.d. glass tubes that are tapered to 6-mm o.d. These tubes are packed with a 13-mm diameter glass fiber filter then a 270-mg sampling section followed by a 140-mg backup section of purified XAD-7 resin, available from Alltech. There is a foam plug between the sampling section and backup section and after the backup section. The glass fiber filter is held next to the sampling section by a polytetrafluoroethylene (PTFE) retainer. These tubes are commercially available through many sources.

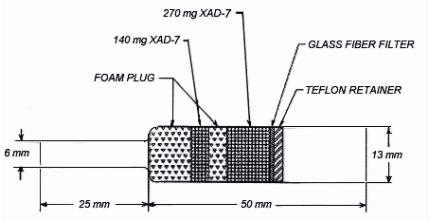


Figure 1. A diagram of an OVS-7 tube.

2.2 Sampling technique

2.2.1 Remove the end caps of the OVS-7, immediately before sampling.

2.2.2 Connect the OVS-7 to the sampling pump with flexible tubing.

2.2.3 Place the tubes in a vertical position to minimize channeling, with the smaller section, towards the pump.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the OVS-7 tube.

2.2.5 Seal the OVS-7 with plastic caps immediately after sampling. Seal each sample lengthwise with a Form OSHA-21 seal.

2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a separate mailing container from other samples.

2.3 Desorption efficiency

2.3.1 Two hundred and seventy milligram portions of XAD-7 resin were placed into separate 4-mL vials and six portions were spiked at each loading of 0.1 mg (1 mg/m³), 0.5 mg (5 mg/m³), 1 mg (10 mg/m³), and 2 mg (20 mg/m³) BHT. They were allowed to equilibrate overnight at room temperature. They were desorbed with 3 mL of the desorbing solution for 30 minutes with shaking, and were analyzed by GC-FID. The overall average recovery was 96.6%. (Table 2.3.1)

Table 2.3.1
Desorption Efficiency

portion #	% recovered			
	0.1 mg	0.5 mg	1.0 mg	2.0 mg
1	94.2	97.6	96.3	97.4
2	94.3	94.8	96.4	98.3
3	95.4	96.7	96.4	97.0
4	97.2	96.3	95.6	97.1
5	95.7	97.0	98.8	98.8
6	96.2	96.2	97.7	96.8
average	95.5	96.4	96.9	97.6

overall average = 96.6%
standard deviation = ±1.23

2.3.2 Six filters were placed into separate 4-mL vials and spiked at each loading of 0.1 mg (1 mg/m³), 0.5 mg (5 mg/m³), 1 mg (10 mg/m³), and 2 mg (20 mg/m³) BHT. They were allowed to equilibrate overnight at room temperature. They were then extracted with 3 mL of the desorbing solution for 30 minutes with shaking, and were analyzed by GC-FID. The overall average recovery was 100%. (Table 2.3.2)

Table 2.3.2
Desorption Efficiency

filter #	% recovery			
	0.1 mg	0.5 mg	1.0 mg	2.0 mg
1	99.3	99.5	101	100
2	99.4	99.5	99.2	100
3	101	99.9	101	101
4	101	101	99.0	101
5	100	99.3	98.5	101
6	100	100	98.7	98.7
average	100	99.9	99.6	100

overall average = 100%
standard deviation = ±0.863

2.4 Retention efficiency

The filters of six OVS-7 tubes were spiked with 1.0 mg (10 mg/m³) BHT, allowed to equilibrate for 6 hours, and had 100 liters humid air (89% RH) pulled through them. The glass fiber filter was placed before the PTFE spacer to insure that no BHT spiked onto the filter was in contact with the XAD-7 sections before the humid air was drawn. They were opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 99.3%. There was no BHT found on the backup portion of the tubes. The amount found on the front adsorbent portion of the OVS-7 tubes indicates that BHT is too volatile to be collected on glass fiber filters. (Table 2.4)

Table 2.4
Retention Efficiency

tube #	% recovered			
	filter	'A'	'B'	total
1	65.7	34.4	0.0	100
2	65.9	34.3	0.0	100
3	53.1	44.7	0.0	97.8
4	65.9	34.5	0.0	100
5	71.7	28.5	0.0	100
6	73.2	25.0	0.0	98.2

average = 99.3%

2.5 Storage

Glass fiber filters (GFF) from the OVS-7 tubes were removed and spiked with 1.0 mg (10 mg/m³) BHT and were placed in a 4-mL vial containing the front section of the XAD-7 resin from the OVS-7 tube, and stored at room temperature, in room light, until opened and analyzed. The recovery averaged 98.5% for the 14 days stored. The BHT vaporized off of the glass fiber filters and was absorbed by the XAD-7 resin. The longer the samples were stored, the more of the BHT was absorbed by the XAD-7 resin. (Table 2.5)

Table 2.5
Storage Study

day	% recovered		
	GFF	XAD-7	total
7	0.1	98.5	98.6
7	0.1	97.6	97.7
7	0.0	98.7	98.7
14	0.0	96.4	96.4
14	0.0	99.7	99.7
14	0.0	100	100
average = 98.5%			

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 33.3 µg/mL (1 mg/m³), 167 µg/mL (5 mg/m³), 333 µg/mL (10 mg/m³), and 667 µg/mL (20 mg/m³) BHT in the desorbing solvent. The pooled coefficient of variation was 0.00904. (Table 2.6)

Table 2.6
Precision Study

injection number	33.3 µg/mL	167 µg/mL	333 µg/mL	667 µg/mL
1	13243	64377	129549	261860
2	13093	63760	129074	259408
3	13313	63894	130334	258086
4	13170	65779	132099	261404
5	13229	64064	130739	262641
6	13118	64332	132667	260757
average	13194	64368	130774	260693
standard deviation –	±82.9	±732	±1408	±1680
CV -	0.00628	0.0114	0.0108	0.00644
pooled CV	0.00904			

$$CV\ \left(Coefficient\ of\ Variation\right) = \frac{\left(standard\ deviation\right)}{\left(average\right)}$$

$$Pooled\ CV = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

Where: A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = coefficients at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied is 100 liters.

2.7.2 The sampling rate studied is 1 liter per minute.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times in designated areas.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector. A HP 5890 gas chromatograph was used in this study.

3.1.2 GC column capable of separating the analyte and an internal standard from any interference. The column used in this study was a 15-m x 0.32-mm i.d., (0.25-µm d_f DB-WAX) capillary column.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 Two and four milliliter vials with PTFE-lined caps.

3.1.5 A 1-µL syringe or other convenient size for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.7 Volumetric flasks - 5 mL, and other convenient sizes for preparing standards.

3.1.8 An analytical balance capable of weighing to the nearest 0.01 mg.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Di-tert-Butyl-p-Cresol, Reagent grade.

3.2.3 Methanol, HPLC grade.

3.2.4 Dimethyl formamide, Reagent grade.

3.2.5 The desorbing solution is 0.25 µL/mL dimethyl formamide in methanol.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the glass fiber filter, the front, and back section of each tube are placed in separate 4-mL vials.

3.3.2 Each section is desorbed with 3 mL of the desorbing solution.

3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes on a shaker, a roto-rack, or a sample rocker.

3.3.4 Samples were transferred to two-milliliter vials for analysis, as this was the size needed to fit in the autosampler.

3.4 Standard preparation

3.4.1 Standards are prepared by diluting a known quantity of BHT with the desorbing solution.

3.4.2 At least two separate stock standards should be made. Dilutions of the stock standards are prepared covering the concentrations in the samples. The analytical standards used in this study ranged from 0.333 µg/mL to 1.0 mg/mL of BHT in the desorbing solution.

3.5 Analysis

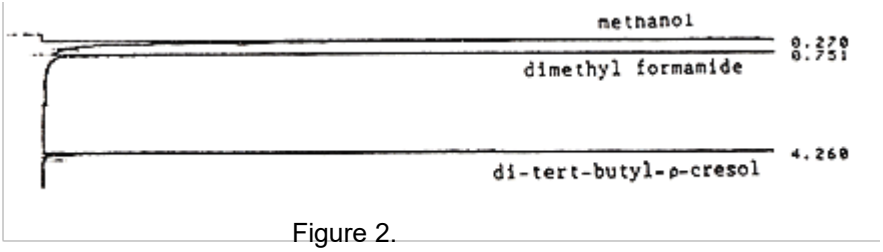


Figure 2.
An analytical standard of 333 µg/mL BHT in methanol with 0.25 µL/mL dimethyl formamide internal standard.

3.5.1 Gas chromatograph conditions.

Flow rates	**(mL/min)**	**Temperature**	**(°C)**
Nitrogen (makeup):	30	Injector:	220
Hydrogen (carrier):	1.5	Detector:	250
Air:	450	Column:	90 °C - 1 min, then 10 °C/min to 150 °C
Hydrogen (detector):	60		

Injection size: 1 µL
Elution time: 4.26 min
Chromatogram: Figure 2 above

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted if necessary so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 The instrument was calibrated with a standard of 0.667 mg/mL BHT in the desorbing solution. The linearity of the calibration is checked with standards ranging from 0.333 µg/mL to 1 mg/mL BHT in the desorbing solution.

3.7.2 If the calibration is non-linear, a calibration curve is plotted. The area counts for the samples are plotted with the calibration curve to obtain the concentration of BHT in solution.

3.7.3 To calculate the concentration of analyte in the air sample, the following formulas are used:

$$mass\ of\ analyte,\ \mu g = \frac{(\mu g / mL)(desorption\ volume,\ mL)}{(desorption\ efficiency,\ decimal)}$$

$$number\ of\ moles = \frac{(mass\ of\ analyte,\ \mu g)(1\ g)}{(molecular\ weight)(10^6\ \mu g)}$$

$$volume\ of\ analyte = (moles\ of\ analyte)(molar\ volume)$$

$$ppm = \frac{(volume\ of\ analyte,\ L)(10^6)^*}{(air\ volume,\ L)}$$

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 100-liter air sample:

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(100\ L)(DE)(MW)}$$

µg/mL = concentration of analyte in sample or standard
24.46 = Molar volume (liters/mole at 25°C and 760 mmHg)
MW = Molecular weight (g/mole)
DV = Desorption volume, 3 mL
100 L = 100-liter air sample collected
DE = Desorption efficiency, decimal

3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all chemicals.

3.8.3 Wear safety glasses, gloves, and a lab coat at all times.

4 Recommendations for further study

Collection studies need to be performed.

5 References

5.1 "NIOSH Manual of Analytical Methods," U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1976, Method 226.

5.2 Cummins, K., Method 32, "Phenol and Cresol," Organic Methods Evaluation Branch, OSHA Salt Lake Technical Center, 1986.

5.3 Windholz, M., "The Merck Index," Eleventh Edition, Merck & Co., Rahway N.J., 1989, p.238.

5.4 "Documentation of the Threshold Limit Values and Biological Exposure Indices," Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p. 227.