p-tert-Butylphenol

Method Number:	PV2085
Target concentration:	5 ppm (30 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through an XAD-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 0.2 Lpm (20 L)
Status of method:	Partially validated method. This method has been only partially evaluated and is presented for information and trial use.

March 1992

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Technical Center has received many requests for a sampling and analytical procedure for p-tert-butylphenol (PTBP). OSHA method 32 recommends collection of phenol and cresol on XAD-7 tubes and desorption with methanol (Ref. 5.1). PTBP is related to these compounds, so this means of collection and analysis was tried and found to be successful. The desorption, retention and storage studies all had good recoveries.

1.1.2 Potential workplace exposure (Ref. 5.2)

PTBP is used as a plasticizer for cellulose acetate, intermediate for antioxidants, in oil soluble phenolic resins, as pour-point depressors, as emulsion breakers for petroleum oils and some plastics, as an intermediate in the manufacture of varnish and lacquer resins, and as a soap antioxidant.

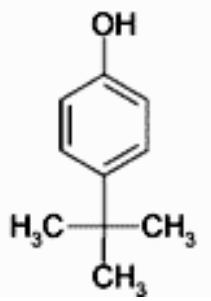
1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref. 5.3)

PTBP is a skin, eye, and mucous membrane irritant. It can cause skin burns, eye damage, and pulmonary edema.

1.1.4 Physical properties (Ref. 5.3):

CAS:	98-54-4
IMIS:	B109
RTECS:	SJ8925000; 56585
DOT:	UN2229
Synonyms:	4-tert-Butylphenol; Butylphen; 4-(1,1-Dimethylethyl) phenol; UCAR butylphenol 4-T
Molecular weight:	150.21
Melting point:	98 °C
Boiling point:	237 °C
Flash point:	107 °C (225 °F) (closed cup)
Odor:	phenolic
Color:	white crystals
Molecular formula:	$C_{10}H_{14}0$

Compound:



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 1 µg PTBP. This is the smallest amount that could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.008 ppm. (All ppm amounts in this study are based on a 20-liter air volume.)

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 XAD-7 tubes containing 15/50 mesh XAD-7 with a 100-mg adsorbing section with a 50-mg backup section separated by a silanized glass wool plug, with a silanized glass wool plug before and after the adsorbing sections. The ends are flame sealed and the glass tube containing the adsorbent is 8-cm x 8-mm o.d. x 6-mm i.d., SKC tubes, or equivalent.

2.2 Sampling technique

2.2.1 Open the ends of the XAD-7 tubes immediately before sampling.

2.2.2 Connect XAD-7 tubes 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 XAD-7 tubes.

2.2.5 Seal the XAD-7 tubes with plastic caps immediately after sampling. Seal each sample lengthwise with 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 container from other samples.

2.3 Desorption efficiency

Six tubes each were spiked at loadings of 60.9 µg (0.496 ppm), 304 µg (2.47 ppm), and 609 µg (4.96 ppm) PTBP. They were allowed to equilibrate overnight at room temperature.

They were then opened, each section placed in separate 2-mL vials, desorbed with 1 mL of the desorbing solution for 30 minutes, with occasional shaking, and analyzed by GC-FID. The overall average was 94.7 %. (Table 2.3)

Table 2.3
Desorption Efficiency

tube #	% recovered		
	60.9 µg	304 µg	609 µg
1	96.2	95.5	93.6
2	94.3	94.9	94.0
3	96.1	93.9	93.4
4	94.2	95.5	94.5
5	95.5	93.9	93.4
6	95.9	95.4	94.2
average	95.4	94.9	93.9

overall average = 94.7%
standard deviation = ±0.944

2.4 Retention efficiency

Six tubes were liquid spiked with 609 µg (4.96 ppm) PTBP, allowed to equilibrate overnight, and then had 20 liters humid air (89% RH) pulled through them at 0.2 L/min. They were then opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 99.1%. There was no PTBP found on the backup portions of the tubes. The values are desorption corrected. (Table 2.4)

Table 2.4
Retention Efficiency

tube #	% recovered		
	'A'	'B'	total
1	101	0.0	101
2	101	0.0	101
3	99.0	0.0	99.0
4	101	0.0	101
5	97.0	0.0	97.0
6	95.8	0.0	95.8

average = 99.1%

2.5 Storage

Twelve tubes were spiked with 609 µg (4.96 ppm) PTBP and stored at room temperature until opened and analyzed. Since PTBP may decompose in light, half of the tubes were stored under room light, and half were stored in darkness. The samples were found to be stable under both conditions. Results were corrected for desorption efficiency. The recoveries averaged 99.0% for the 14 days stored. (Table 2.5)

Table 2.5
Storage Study

day	% recovered	
	light	dark
7	101	101
7	96.8	101
7	lost	102
14	101	96.8
14	97.0	97.8
14	98.4	96.6

overall average = 99.0%

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 60.9, 304, 609, and 1218 µg/mL PTBP in the desorbing solution. The pooled coefficient of variation was 0.00593. (Table 2.6)

Table 2.6
Precision Study

injection #	60.9 µg/mL	304 µg/mL	609 µg/mL	1218 µg/mL
1	19812	97430	195843	395475
2	19483	97777	196784	399977
3	19667	97690	195049	396600
4	19724	97320	195991	399840
5	19657	96079	195486	399173
6	19896	96842	194083	399790
average	19707	97190	195539	398476
standard deviation –	±142	±636	±918	±1942
CV -	0.00721	0.00654	0.00469	0.00487

pooled CV = 0.00593

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

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

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficient of variation at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied was 20 liters.

2.7.2 The sampling rate studied was 0.2 liters 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 HP5890 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 30-m x 0.32-mm i.d. (0.25 µm d_f DB-225) capillary column. An alternate column is a 60-m x 0.32-mm i.d. (1.0 µm d_f DB-1) capillary column.

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

3.1.4 Two 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.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 p-tert-Butylphenol, Reagent grade

3.2.3 Methanol, HPLC grade

3.2.4 Dimethyl formamide, Reagent grade

3.2.5 Desorbing solution is methanol with 1 µL/mL dimethyl formamide used as the internal standard.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials. The front glass wool was placed in the vial containing the front section.

3.3.2 Each section is desorbed with 1 mL of the desorbing solution.

3.3.3 The vials are sealed immediately with PTFE-lined caps and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

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

3.4.2 At least two separate stock standards should be made. Dilutions of the stock standards are made to bracket the samples. The standards used in this study ranged

3.5 Analysis

3.5.1 Gas chromatograph conditions using a DB-225 capillary column.

Flow rates	**(mL/min)**	**Temperature**	**(°C)**
Nitrogen (makeup):	30	Injector:	240
Hydrogen (carrier):	1.5	Detector:	240
Air:	450	Column:	110 °C for 1 min then heated
Hydrogen (detector):	30		4 °C/min to 160 °C

Injection size: 1 µL
Elution time: 9.39 min
Chromatogram: (See Figure 1)

3.5.2 Gas chromatograph conditions using a DB-1 capillary column.

Flow rates	**(mL/min)**	**Temperature**	**(°C)**
Nitrogen (makeup):	30	Injector:	200
Hydrogen (carrier):	1.5	Detector:	240
Air:	450	Column:	80 °C for 0 min then heated
Hydrogen (detector):	30		10 °C/min to 220 °C

Injection size: 1 µL
Elution time: 14.87 min
Chromatogram: (See Figure 2)

3.5.3 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 A calibration curve with area counts versus concentration is prepared from the calibration standards.

3.7.2 The area counts for the samples are plotted on the calibration curve to obtain the concentration of PTBP in solution.

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

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

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

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

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

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula which is used to calculate the ppm of analyte in the sample based on a 20-liter air sample:

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

Where:

μg/mL = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (g/mole)
DV = Desorption volume, mL
20 L = Air volume, L
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 in laboratory areas.

4 Recommendations for further study

Collection studies need to be performed.

5 References

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

5.2 Windholz, M., "The Merck Index," Eleventh Edition, Merck & Co., Rahway N.J., 1989, p. 241.

5.3 Sax, N., Lewis, R., "Hawley's Condensed Chemical Dictionary," Eleventh Edition, Van Nostrand Reinhold Co., New York, 1987, p. 190.

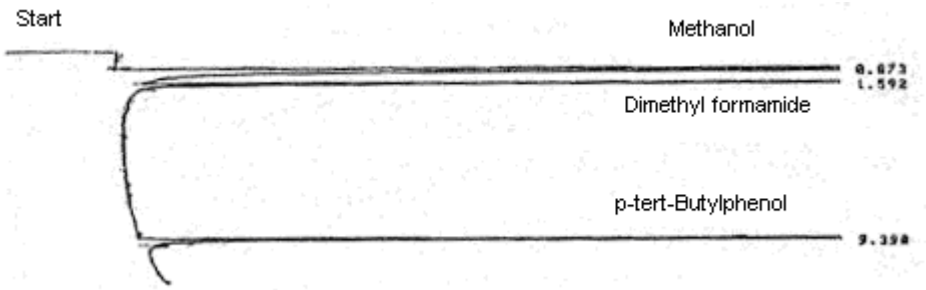


Figure 1. An analytical standard of 609-ug p-tert-butylphenol in methanol with 1 µL/mL dimethyl formamide internal standard, analyzed on a DB-225 capillary column.

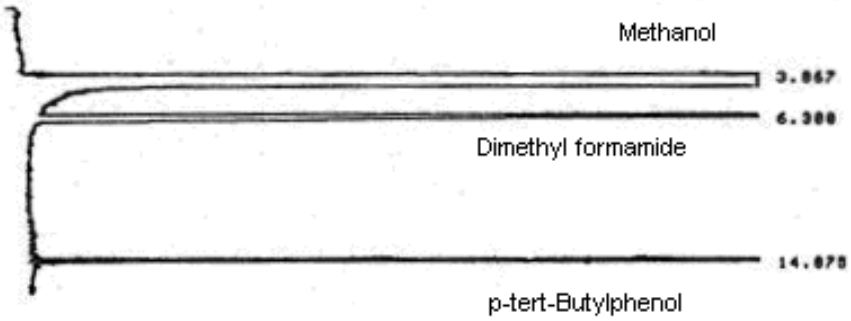


Figure 2. An analytical standard of 609-µg p-tert-butylphenol in methanol with 1 µL/mL dimethyl formamide internal standard, analyzed on a DB-1 capillary column.