o-sec-Butylphenol

Method number:	PV2128
Target concentration:	5 ppm (30 mg/m^3) OSHA TWA PEL
Procedure:	Samples are collected by drawing a known volume of air through and 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 Liters)
Status of method:	Partially Validated. 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 Technical Center has received many requests for a sampling and analytical procedure for o-sec-Butylphenol (OSBP). OSHA promulgated an exposure standard for o-sec-Butylphenol in January 1989, at a level of 5 ppm. OSHA method 32 recommends collection of phenol and cresol on XAD-7 tubes and desorption with methanol (Ref. 5.1). OSBP is related to these compounds, so this means of collection and analysis was tried and found to be successful. The storage, retention, and desorption studies all had recoveries above 94.9%.

1.1.2 Potential workplace exposure (Ref. 5.2)

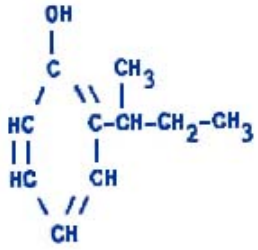
OSBP is used as a chemical intermediate, and in the manufacture of resins, plasticizers, and surface-active agents.

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)

OSBP is a skin and eye irritant. In reported occupational exposures, OSBP was a mild respiratory irritant. Skin exposures resulted in burns.

1.1.4 Physical properties (Re. 5.2):

Compound:



CAS:	89-72-5
IMIS:	B705
RTECS:	SJ8920000; 56581
DOT:	UN2228
Synonyms:	2-sec-Butylphenol
Molecular weight:	150.24
Melting point:	12 ºC
Boiling point:	226 ºC
Flash point:	107 ºC (225 ºF) (closed cup)
Odor:	Phenolic
Color:	Colorless to light yellow liquid
Molecular formula:	$C_{10}H_{14}O$

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 1 µg o-sec-Butylphenol. 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 technique

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 silanized glass wool plug, with a silanized glass wool plug before and at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 8-cm x 8-mm o.d., 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 the 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 tube.

2.2.5 Seal the XAD-7 tubes 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 paper work) 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 were spiked with loadings of 59.9 µg (0.487 ppm), 300 µg (2.44 ppm), and 599 µg (4.87 ppm) OSBP. They were allowed to equilibrate overnight at room temperature. They were then opened, each section placed into a separate 2 mL vial, desorbed with 1 mL of methanol with 1 µL/mL dimethyl formamide internal standard for 30 minutes with occasional shaking, and analyzed by GC-FID. The overall average was 94.9%. (Table 1)

Table 1
Desorption Efficiency

Tube #	% recovery		
	59.9 µg	300 µg	599 µg
1	95.2	96.1	93.4
2	95.3	95.3	93.8
3	96.0	94.4	93.7
4	94.0	95.5	94.5
5	95.9	94.6	93.3
6	97.6	95.6	04.0
average	95.7	95.3	93.8

overall average = 94.9
standard deviation = ±1.13

2.4 Retention efficiency

Six tubes were spiked with 599 µg (4.87 ppm) OSBP, allowed to equilibrate overnight, and then had 20 liters humid air (89% RH) pulled through them. They were opened desorbed and analyzed by GC-FID. The retention efficiency averaged 99.7%. There was no OSBP found on the backup portions of the tubes. The results were corrected for desorption efficiency. (Table 2)

Table 2
Retention Efficiency

tube #	% recovery "A"	% recovery "B"	total
1	101	0.0	101
2	100	0.0	100
3	99.3	0.0	99.3
4	101	0.0	101
5	97.7	0.0	97.7
6	99.2	0.0	99.2

average = 99.7

2.5 Storage

Tubes were spiked with 599 µg (4.87 ppm) OSBP and stored at room temperature until opened and analyzed. Since OSBP 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 98.5% for the 14 days stored. (Table 3)

2.6 Precision

Table 3
Storage Study

day	% recovered light	% recovered dark
7	100	100
7	96.6	101
7	lost	101
14	97.5	98.0
14	96.9	98.1
14	96.1	98.5

overall average = 98.5

The precision was calculated using the area counts from six injections of each standard at concentrations of 59.9, 300, 599, and 1198 µg/mL o-sec-Butylphenol in the desorbing solution. The pooled coefficient of variation was 0.00382 (Table 4)

Table 4
Precision Study

injection number	59.9 µg/mL	300 µg/mL	599 µg/mL	1198 µg/mL
1	18818	94167	188787	382116
2	18754	93814	188507	383068
3	18932	93727	188052	383614
4	18933	93357	189711	383533
5	18661	93463	189578	383214
6	18844	94214	189002	382807
average	18824	93790	188940	383059
standard deviation-	±105	±352	±633	±549
CV-	0.00558	0.00375	0.00335	0.00143
pooled CV-	0.00382			

Where:

$$CV\,(Coefficient\ of\ Variation) = \frac{Standard\ Deviation}{Average}$$

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

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficients of variation (CV's) 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.

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 30-m x 0.32-mm i.d. (0.25 µm d_f DB-225) capillary column and. 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 o-sec-Butylphenol, Reagent grade

3.2.3 Methanol, HPLC grade

3.2.4 Dimethyl Formamide, Reagent grade

3.2.5 Desorbing solution is 1 µL/mL Dimethyl Formamide internal standard in Methanol.

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, and 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 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 OSBP with the desorbing solution.

3.4.2 At least two separate stock standards should be made. Dilutions of the stock standards are prepared to bracket the samples. For this, study standards ranged from 1 to 1198 µg/mL.

3.5 Analysis

3.5.1 Gas chromatograph conditions 30-m x 0.32-mm i.d. (0.25 µm d_f 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 4 °C/min
Hydrogen (detector):	30		to 160 °C

Injection size: 1 µL
Elution time: 7.827 min

Chromatogram: (See Figure 1)

3.5.2 Gas chromatograph conditions 60-m x 0.32-mm i.d., (1.0 µm d_f DB-1) capillary column.

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

Injection size: 1 µL
Elution time: 14.58 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 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 curve with area counts versus concentration is constructed from the calibration standards.

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

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

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

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

$$\text{Volume of analyte at } 25\,^{o}C = (\text{moles analyte})(\text{molar vol } 25\,^{\circ}C \,\&\, 760 \text{ mmHg})$$

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

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula. Use this formula to calculate the ppm of analyte in the sample based on a 20-liter air sample.

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(20\,L)(DE)(MW)}$$

μg/mL = concentration of analyte in sample or standard
24.46 = molar volume (liters/mole) at 25 °C and 760 mmHg
MW = molecular weight
DV = desorption volume
20 L = sample air volume
DE = desorption efficiency

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 while working in the lab.

4 Recommendations for further study

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

5.2 "Documentation of the Threshold Limit Values and Biological Exposure Indices," Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986 p. 84.

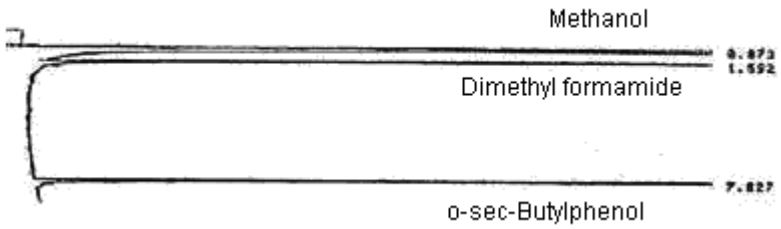


Figure 1.
An analytical standard of 300 µg/mL o-sec-Butylphenol in Methanol with 1 µL/mL Dimethyl Formamide internal standard analyzed on a 30 meter DB-225 capillary column.

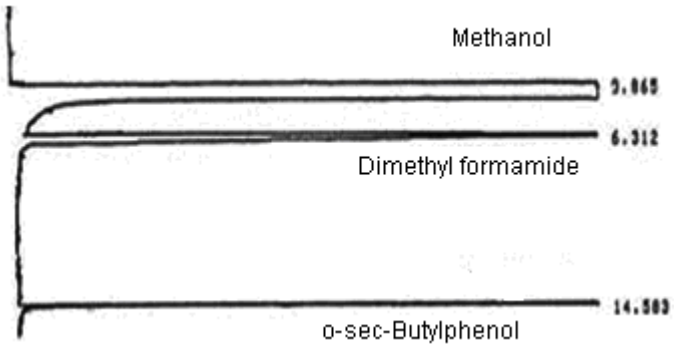


Figure 2.
An analytical standard of 300 µg/mL o-sec-Butylphenol in Methanol with 1 µL/mL Dimethyl Formamide internal standard analyzed on a 60 meter DB-1 capillary column.