



Catechol (Pyrocatechol)

Method number: PV2014

Target concentration:
OSHA TWA PEL 5 ppm (20 mg/m³)

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: 100 minutes at 1.0 L/m. (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 catechol. OSHA promulgated an exposure standard for catechol of 5 ppm (20 mg/m³) TWA. OSHA Method 32 recommends collection of phenol and cresol on XAD-7 tubes and desorption with methanol (Ref. 5.1). Catechol 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. An OVS-7 tube contains a glass fiber filter, which would trap any particulates, followed by a 270 mg section of XAD-7 resin then a 140 mg section. Desorption, retention and storage recoveries were good using OVS-7 tubes.

1.1.2 Potential workplace exposure (Ref. 5.2 and 5.3)

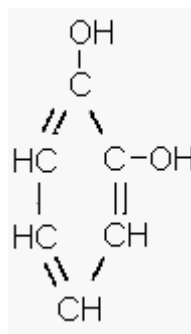
Catechol is used as a topical antiseptic, reagent, antifungal preservative on seed potato pieces, photographic developer, and developer in fur dyes. Catechol is used as an antioxidant in many industries including rubber, chemical, dye, photographic, pharmaceutical, fat, cosmetics, and oil.

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)

The lethal human dose of catechol is 50 to 500 grams/kilogram or 1 teaspoon to 1 ounce for a 70-kilogram (150 pound) person, with death resulting from pulmonary failure. Catechol is a skin, eye, mucous membrane, and pulmonary irritant. It is readily absorbed from the gastrointestinal tract, and through the skin. Catechol can cause elevated blood pressure through vasoconstriction, degeneration of the renal tubes in the kidneys, and diminished liver function.

1.1.4 Physical properties (Ref. 5.2):

Compound:



CAS: 120-80-9

IMIS: 0571

Synonyms: 1,2-Benzenediol; o-Benzenediol; Catechin; o-Dioxybenzene; 1,2-dihydroxybenzene; Fouramine 68; o-Hydroxyphenol; o-Hydroquinone; 2-Hydroxyphenol; CI Oxidation Base 26; Fouramine PCH; o-Diphenol; Durafur Developer C; Oxyphenic acid; o-Phenylenediol; Phthalhydroquinone; Pyrocatechin; pyrocatechol; Pyrocatechuic acid

Molecular weight:	110.11
Melting point:	105 °C
Boiling point:	245.5 °C
Flash point:	127 °C (261 °F)
Odor:	faintly musty phenolic
Color:	colorless to white crystals
Molecular formula:	C ₆ H ₆ O ₂
RTECS:	73250; UX1050000

1.2 Limit defining parameters

- 1.2.1 The detection limit of the analytical procedure is 2.1 µg/mL catechol 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 0.014-ppm catechol. (All ppm amounts in this study are based on a 100-liter air volume and 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 with the sampler attached.
- 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 and backup section, and after the backup section. The glass fiber filter is held next to the sampling section by a polytetrafluoroethylene (PTFE) retainer. (Figure 1) These tubes are commercially available through many sources.

2.2 Sampling technique

- 2.2.1 Remove the end caps from the OVS-7 tube immediately before sampling.
- 2.2.2 Connect the small end of the OVS-7 tube to the sampling pump with flexible tubing.

- 2.2.3 Place the tubes in a vertical position with the large end facing down to minimize channeling.
- 2.2.4 Air being sampled should not pass through any hose or tubing before entering the sample tube.
- 2.2.5 Seal the OVS-7 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 mailing container from the samples.

2.3 Desorption efficiency

- 2.3.1 Two hundred and seventy milligram portions of XAD-7 resin were placed into twenty-four separate 4-mL vials. Six vials were spiked at each loading of 0.205 mg (0.455 ppm), 1.02 mg (2.26 ppm), 2.05 mg (4.55 ppm), and 4.01 mg (8.9 ppm) catechol, and allowed to equilibrate overnight at room temperature. They were desorbed with 3 mL of the desorbing solution for 30 minutes with occasional shaking, and analyzed by GC-FID. The overall average desorption efficiency was 98.1%. (Table 1)

Table 1
Desorption Efficiency

portion #	% recovered			
	0.205 mg	1.02 mg	2.05 mg	4.01 mg
1	99.1	99.1	99.8	95.0
2	96.6	99.7	99.0	97.0
3	97.2	98.1	100	99.5
4	98.6	98.7	97.4	97.1
5	98.4	99.1	96.5	98.6
6	97.5	97.3	98.5	96.4
average	97.9	98.7	98.5	97.3

overall average = 98.1%
standard deviation = ±1.28

- 2.3.2 Twenty-four filters were placed into separate 4-mL vials and six each were spiked at a loading of 0.193 mg (0.429 ppm), 0.96 mg (2.13 ppm), 1.93 mg (4.29 ppm), and 4.00 mg (8.88 ppm) catechol and allowed to equilibrate overnight at room temperature. They were extracted with 3 mL of the desorbing solution for 30 minutes with occasional shaking, and were analyzed by GC-FID. The overall average desorption efficiency was 100 %. (Table 2)

Table 2
Desorption Efficiency

filter #	% recovered			
	0.193 mg	0.96 mg	1.93 mg	4.00 mg
1	100	102	98.7	98.6
2	100	99.3	100	98.9
3	99.8	99.9	101	99.9
4	102	99.8	101	99.9
5	101	99.9	101	99.4
6	98.0	100	99.7	99.9
average	100	100	100	99.6

overall average = 100%
standard deviation = ±0.998

2.4 Retention efficiency

The filters of six OVS-7 tubes were spiked with 2.0 mg (4.44 ppm) catechol, allowed to equilibrate overnight and then had 100 liters humid air (91% RH) pulled through them. The glass fiber filter was placed before the PTFE spacer to insure that no catechol spiked onto the filter was in contact with the XAD-7 sections before the humid air was drawn. They were then opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 98.6%. There was no catechol found on the backup portion of the tubes. The amount found on the front adsorbent portion of the OVS-7 tubes indicates that catechol is too volatile to be collected on glass fiber filters alone. (Table 3)

Table 3
Retention Efficiency

tube #	% recovered			
	filter	'A'	'B'	total
1	85.9	14.0	0.0	99.9
2	83.7	14.2	0.0	97.9
3	75.5	20.8	0.0	96.3
4	84.1	15.9	0.0	100
5	78.0	20.6	0.0	98.6
6	83.8	15.3	0.0	99.1

average = 98.6%

2.5 Storage

Glass fiber filters (GFF) from the OVS-7 tubes were removed and spiked with 2.23 mg (4.95 ppm) catechol and then placed in a 4-mL vial containing the front section of XAD-7 resin, and stored at room temperature until opened and analyzed. Catechol may degrade when exposed to light, so half of the vials were stored in room light and the other half were stored in a drawer. The recoveries averaged 98.6% for the 14 days stored, with little difference between the samples stored under room light and those stored in a drawer, indicating catechol is stable on OVS-7 tubes in the light. The catechol vaporized off the glass fiber filters and was adsorbed by the XAD-7 resin, with more of the catechol migrating to the XAD-7 resin on those filters which were in total contact with the resin, or the filter lying on top of the resin, than those with the filter beside the resin. The longer the samples were stored, the more of the catechol was adsorbed by the XAD-7 resin. (Table 4)

Table 4
Storage Study

day	% recovered light			% recovered dark		
	GFF	XAD-7	total	GFF	XAD-7	total
7	26.7	72.6	99.3	33.7	65.3	99.0
7	58.3	41.6	99.9	44.4	54.7	99.1
7	45.4	53.1	98.5	49.5	48.8	98.3
14	0.3	98.2	98.5	24.3	74.6	98.9
14	1.4	97.6	99.0	22.6	74.1	96.7
14	20.4	76.6	97.0	1.0	97.5	98.5

average = 98.7%

average = 98.4%

overall average = 98.6%

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 0.0644 mg/mL (0.429 ppm), 0.320 mg/mL (2.13 ppm), 0.644 mg/mL (4.29 ppm), and 1.33 mg/mL (8.86 ppm) catechol in the desorbing solvent. The pooled coefficient of variation was 0.0105. (Table 5)

Table 5
Precision Study

injection number	0.0644 (mg/mL)	0.320 (mg/mL)	0.644 (mg/mL)	1.33 (mg/mL)
1	1740	16279	42942	114630
2	1775	16018	43672	113338
3	1792	16124	43863	112695
4	1788	16380	43343	113710
5	1755	16325	42926	111274
6	1791	16165	43275	111157
average	1774	16215	43337	112801

standard deviation

±21.6

±136

±379

±1379

CV

0.0122

0.00839

0.00875

0.0122

pooled CV = 0.0105

Where:

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

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

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 100 liters.

2.7.2 The sampling rate studied is 1 liter per minute.

2.8 Interferences

Suspected interferences should be listed on the 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. An HP 5890 gas chromatograph was used in this study.

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

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

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

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

3.1.6 Pipettes for dispensing the desorbing solution. A 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 Catechol, Reagent grade

3.2.3 Methanol, reagent grade

3.2.4 Dimethyl formamide, Reagent grade

3.2.5 The desorbing solution was 0.25 μ L/mL dimethyl formamide in methanol.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the glass fiber filter and 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 analyses, 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 catechol 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 0.001 to 1.33 mg/mL of catechol in the desorbing solution.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

<u>Flow rates</u>	<u>(mL/min)</u>	<u>Temperature</u>	<u>(°C)</u>
Nitrogen (makeup):	30	Injector:	220
Hydrogen (carrier):	1.5	Detector:	250
Air:	450	Column:	90 °C 1 min, then programmed at 15 °C/min to 220 °C
Hydrogen (detector):	60		
Injection size:	1 µL		
Elution time:	8.912 min		
Chromatogram:	(See Figure 2)		

- 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 is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted, if necessary, to avoid interference.
- 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 generated from the calibration standards.
- 3.7.2 The area counts for the samples are plotted on the calibration curve to obtain the concentration of catechol in solution.
- 3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

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

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

$$\text{volume of analyte} = (\text{moles of analyte})(\text{molar volume})$$

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

* 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:

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

$\mu\text{g}/\text{mL}$ = 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, mL
 100 L = 100 liter air sample
 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 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.1272.

5.3 "Documentation of the Threshold Limit Values and Biological Exposure Indices," Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p. 112.

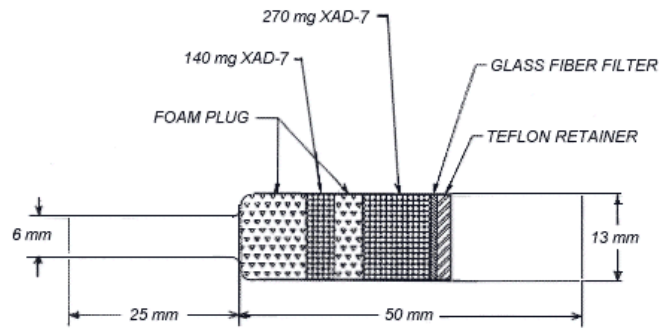


Figure 1. A diagram of an OVS-7 tube.

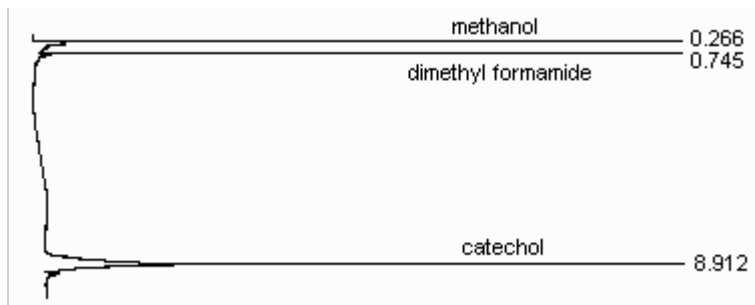


Figure 2. An analytical standard of 0.743 mg/mL catechol in methanol with 0.25 μ L/mL dimethyl formamide internal standard.