Method number:	PV2053
Target concentration:	10 ppm (45 mg/m^3) OSHA TWA PEL 20 ppm (90 mg/m^3) OSHA STEL (Note: These are the 1989 levels which have subsequently been rescinded.)
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:	60 minutes at 1.0 Lpm (60 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 Technical Center has received many requests for a sampling and analytical procedure for resorcinol. OSHA promulgated an exposure standard for resorcinol in January 1989, at a level of 10 ppm TWA, and 20 ppm STEL. OSHA method 32 recommends collection of phenol and cresol on XAD-7 tubes and desorption with methanol (Ref. 5.1). Resorcinol is related to these compounds, and resorcinol occurs as a particulate as well as a vapor, so an OVS-7 tube was tried. 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. The desorption, retention, and storage studies all had good recoveries.

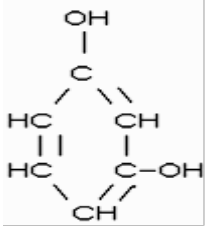
1.1.2 Potential workplace exposure (Ref. 5.2)

Resorcinol is used in the tanning and dyeing industries, in the manufacture of resins and resin adhesives, explosives, hexyl resorcinol, p-aminosalicylic acid, cosmetics, and as an antiseptic and topical antipruritic.

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)

Resorcinol is a skin, eye, and mucous membrane irritant. Exposure to resorcinol causes, with increasing exposure, skin burns, cyanosis, methemoglobinemia, convulsions, and death. It was found to be less toxic than phenol, but with similar toxic effects.

1.1.4 Physical properties (Ref. 5.2.):

CAS:	108-46-3
IMIS:	2221
RTECS:	VG962500; 76367
DOT:	UN2876 (Poison)
Synonyms:	1,3-Benzenediol; Resorcin; m-Dihydroxybenzene; C.I. 76505; C.I. Developer 4; C.I. Oxidation base 31; Developer O; developer R; Developer RS; Fouramine RS; Durafur developer G; Fourrine 79; Fourrine EW; m-Hydroquinone; 3-Hydroxycyclohexadiene-l-one; m-Hydroxyphenol
Molecular weight:	110.11
Melting point:	110 °C
Boiling point:	280 °C
Flash point:	127 °C (261 °F) (closed cup)
Odor:	phenolic
Color:	white, turns pink on exposure to light or air
Molecular formula:	$C_6H_6O_2$
Structure:	

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 8-µg resorcinol. This is the smallest amount that could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.0889 ppm. (All ppm amounts in this study are based on a 20 L 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 An OVS-7 tube is a 13-mm glass fiber filter in front of a 270-mg section of XAD-7 resin followed by a 140-mg section of XAD-7 resin 15/50 mesh, with foam plugs before and after the back XAD-7 section. The ends are sealed with plastic caps.

2.2 Sampling technique

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

2.2.2 Connect OVS-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 OVS-7 tubes.

2.2.5 Seal the OVS-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 (remove plastic end caps, reseal, & 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 and Extraction efficiency

2.3.1 Six glass fiber filters were spiked at loadings of 0.298 mg (1.10 ppm), 1.49 mg (5.51 ppm), 2.98 mg (11.0 ppm), and 5.96 mg (22.1 ppm) resorcinol. They were allowed to equilibrate overnight at room temperature. They were opened, desorbed with 2 mL of methanol for 30 minutes with shaking, and analyzed by GC-FID. The overall average was l00 %. (Table 1)

Table 1
Extraction Efficiency of GFF

filter #	% recovered			
	0.298 mg	1.49 mg	2.98 mg	5.96 mg
1	102	96.8	99.3	99.6
2	98.9	99.4	98.8	100
3	102	96.8	102	98.8
4	101	101	98.9	99.8
5	97.6	103	99.8	102
6	102	103	100	100
average	101	100	99.8	100

overall average = 100%
standard deviation = ±1.78

2.3.2 Six front portions of XAD-7 resin from the OVS-7 tubes were spiked at loadings of 89.9 µg (0.333 ppm), 450 µg (1.67 ppm), and 899 µg (3.33 ppm) resorcinol. They were allowed to equilibrate overnight at room temperature. They were opened, each section placed into a separate 2-mL vial, desorbed with 2 mL of methanol for 30 minutes with occasional shaking, and analyzed by GC-FID. The overall average was 100 %. (Table 2)

Table 2
Desorption Efficiency of XAD-7

tube #	% recovered		
	89.9 µg	450 µg	899 µg
1	101	98.3	100
2	98.0	96.8	101
3	99.4	100	102
4	102	101	99.2
5	97.3	102	99.6
6	102	102	101
average	100	100	100

overall average = 100%
standard deviation = ±1.71

2.4 Retention efficiency

Nine OVS-7 tubes had the glass fiber filter (GFF) removed and placed above the PTFE spacer (1/2" above the front XAD-7 resin section). The glass fiber filters were liquid spiked with 5.96 mg (22.1 ppm) resorcinol, allowed to equilibrate overnight, and then six tubes had 60 liters humid air (91% RH at 22 °C) and three had 180 liters humid air (87% RH at 21 °C) pulled through them. They were opened, desorbed, and analyzed by GC-FID. The retention efficiency

averaged 99.7%. There was no resorcinol found on the backup portions of the tubes. (Tables 3 and 4)

Table 3
Retention Efficiency with 60 L Humid Air

tube #	% recovered			total
	GFF	front XAD-7	back XAD-7	
1	96.9	2.4	0.0	99.3
2	98.6	2.6	0.0	101
3	94.1	5.7	0.0	99.8
4	96.8	2.8	0.0	99.6
5	95.6	2.9	0.0	98.5
6	97.5	2.4	0.0	99.7

average = 99.7%

Table 4
Retention Efficiency with 180 L Humid Air

tube #	% recovered			total
	GFF	front XAD-7	back XAD-7	
1	91.8	7.8	0.0	99.6
2	92.0	7.4	0.0	99.4
3	93.0	7.2	0.0	100

average = 99.7%

2.5 Storage

Tubes were spiked with 899 µg (9.98 ppm) resorcinol and stored at room temperature until opened and analyzed. Since resorcinol 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, for the 14 days stored, under both conditions. The recoveries averaged 98.5 %. (Table 5)

Table 5
Storage Study

days	% recovered	
	light	dark
7	101	101
7	98.1	96.1
7	lost	99.0
14	102	98.5
14	97.9	94.7
14	101	94.2

average = 98.5%

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 89.9, 450, 899, and 1798 µg/mL resorcinol in the desorbing solution. The pooled coefficient of variation was 0.00924. (Table 6)

Table 6
Precision Study

injection number	89.9 µg/mL	450 µg/mL	899 µg/mL	1798 µg/mL
1	15459	84017	157575	300122
2	15037	84092	157999	298006
3	15436	83171	156893	300985
4	15610	82527	158541	298940
5	15068	82572	156349	299382
6	15323	82670	158489	300375
average	15322	83175	157641	299635
standard deviation –	±228	±720	±882	±1078
CV -	0.0149	0.0086	0.00560	0.00360

pooled CV = 0.00924

Where:

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

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

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 is 60 liters.

2.7.2 The sampling rate studied is 1.0 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 Resorcinol, 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 an internal standard.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the glass fiber filter, front, and back sections of each tube are placed in separate 4-mL vials. If particulate analysis is not desired the glass fiber filter is added to the vial containing the front section.

3.3.2 Each section is desorbed with 2 mL of the desorbing solution.

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

3.3.4 An aliquot of each sample was removed and placed into 2-mL vials for analysis with the autosampler. This step may not be necessary, depending on the type of instrumentation used for analysis.

3.4 Standard preparation

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

3.4.2 At least two separate stock standards should be made, and dilutions bracketing the samples are prepared. In this study, the analytical standards ranged from 8 to 5960 µg/mL resorcinol in the desorbing solution.

3.5 Analysis

3.5.1 Gas chromatograph conditions 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 - 1 min then
Hydrogen (detector):	30		4 °C/min to 160 °C

Injection size: 1 µL
Elution time: 22.571 min

Chromatogram: (See Figure 1)

3.5.2 Gas chromatograph conditions 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 - 0 min then
Hydrogen (detector):	30		10 °C/min to 220 °C

Injection size: 1 µL
Elution time: 14.077 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 curve with area counts versus concentration is calculated from the calibration standards.

3.7.2 The area counts for the samples are plotted on the calibration curve to obtain the concentration of resorcinol 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. To calculate the ppm of analyte in the sample based on a 20-liter air sample:

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(60\ L)(DE)(MW)}$$

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 = 2 mL Desorption volume
60 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.

4 Recommendations for further study

A collection study should be performed.

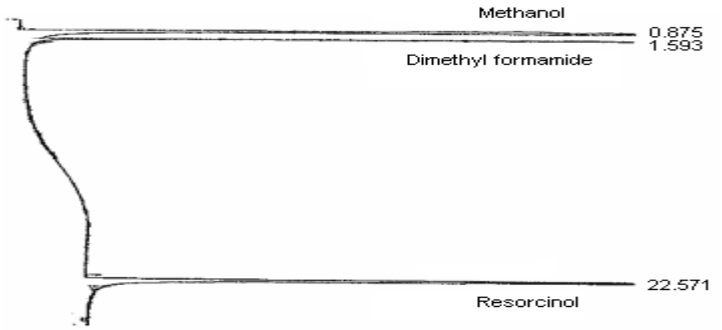


Figure 1. DB-225 Column - An analytical standard of 450 µg/mL resorcinol in methanol with 1 µL/mL dimethyl formamide internal standard.

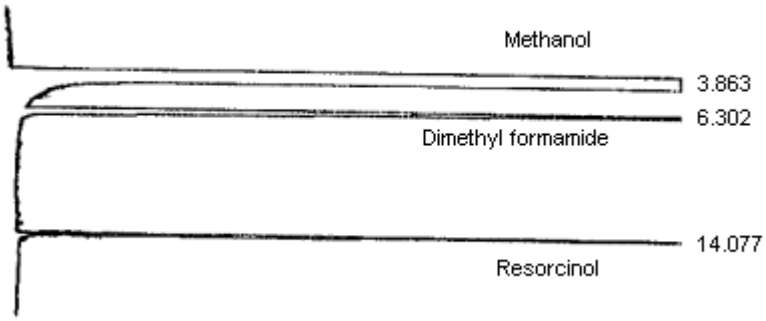


Figure 2. DB-1 Column - An analytical standard of 450 µg/mL resorcinol in methanol with 1 µL/mL dimethyl formamide internal standard.

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. 1176.

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. 511.