

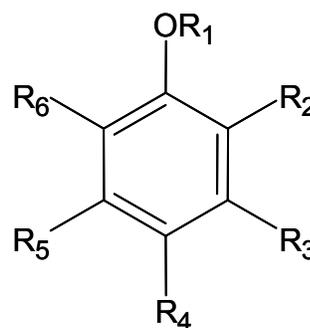
## Measurement of Priority Phenols in Water - Analytical Methodology

Priority phenols consist of a number of substituted phenolic compounds including halogenated (e.g., chlorophenol), nitrated (e.g., 2-nitrophenol), alkylated (e.g., 2,4-dimethylphenol) and ether (e.g., methoxyphenol) derivatives (Figure 1). Priority phenols are used (or produced) in several industrial processes. They are commonly used as preservatives, disinfectants, in pulp processing, in the manufacture of pesticides and other intermediates. Unfortunately, priority phenols are now common environmental pollutants found in potable water, sediments and soil.

Many priority phenols, especially the chlorophenols, are known for their toxicity, carcinogenicity, and persistence in the environment.<sup>1</sup> Pentachlorophenol is widely used as a wood preservative and has been found to be an indoor air contaminant.<sup>2</sup> Many phenol derivatives are now included in the lists of priority pollutants in many countries. The U.S. EPA lists eleven phenols on its list of priority pollutants. The European Union has set the maximum total and individual phenol permitted concentrations in water used for human consumption at 0.5 µg/L and 0.1 µg/L, respectively.<sup>1</sup>

U.S. EPA Method 528 provides procedures for the determination of phenols in finished drinking water. There are twelve compounds included in this method. In addition, the method uses tribromophenol, a surrogate, and tetrachlorophenol as an instrumental internal standard. The method employs Capillary Column GC separation and MS determination. Due to the poor sensitivity of the method, analytes are extracted by passing 1 Liter of water through a solid phase extraction cartridge.

High performance liquid chromatography (HPLC) is widely used for the determination of phenolic compounds. HPLC with electrochemical detection provides superior sensitivity for most of the phenols of interest with the exception of the dinitrophenols which are measured by UV absorbance. In the present method, coulometric electrochemical detection is combined with UV detection for the



Compound	R1	R2	R3	R4	R5	R6
2,4-Dinitrophenol	H	NO <sub>2</sub>	H	NO <sub>2</sub>	H	H
2-Methyl-4,6 Dinitrophenol	H	CH <sub>3</sub>	H	NO <sub>2</sub>	H	NO <sub>2</sub>
4-Nitrophenol	H	H	H	NO <sub>2</sub>	H	H
Phenol	H	H	H	H	H	H
2-Nitrophenol	H	NO <sub>2</sub>	H	H	H	H
2-Chlorophenol	H	Cl	H	H	H	H
2,4,6-Trichlorophenol	H	Cl	H	Cl	H	Cl
2,4-Dimethylphenol	H	CH <sub>3</sub>	H	CH <sub>3</sub>	H	H
Pentachlorophenol	H	Cl	Cl	Cl	Cl	Cl
4-Chloro-3-methylphenol	H	H	CH <sub>3</sub>	Cl	H	H
2,4-Dichlorophenol	H	Cl	H	Cl	H	H
Methoxyphenol (4-methylguaiaicol)	CH <sub>3</sub>	H	H	H	H	H
p-Cresol	H	H	H	CH <sub>3</sub>	H	H
2-Methoxy-4-methylphenol	H	OCH <sub>3</sub>	H	CH <sub>3</sub>	H	H
o-Cresol	H	CH <sub>3</sub>	H	H	H	H
4-Ethylphenol	H	H	H	CH <sub>2</sub> CH <sub>3</sub>	H	H
4-Ethyl Methoxyphenol	CH <sub>3</sub>	H	H	CH <sub>2</sub> CH <sub>3</sub>	H	H
2-Ethylphenol	H	CH <sub>2</sub> CH <sub>3</sub>	H	H	H	H
Tetrachlorophenol (IS)	H	Cl	Cl	Cl	Cl	H
Tribromophenol (MS)	H	Br	H	Br	H	Br

**Figure 1.** Chemical Structures of Priority Phenols, Internal Standard (IS) and Method Surrogate (MS).

determination of the 11 EPA priority pollutant phenols as well as 7 other phenols of interest. Like the EPA Method 528, tribromophenol is used as a surrogate and tetrachlorophenol as an instrumental internal standard. The combination of EC Array and UV detection provides qualitative as well as quantitative information. The unrivaled sensitivity of this method will enable simplified sample preparation without the need for laborious organic extractions and the need to process large volumes of water samples.

## Materials and Methods

The gradient HPLC system consisted of two pumps, a dynamic mixer, a refrigerated autosampler, a thermostatic organizer, a twelve channel CoulArray detector and a UV detector.

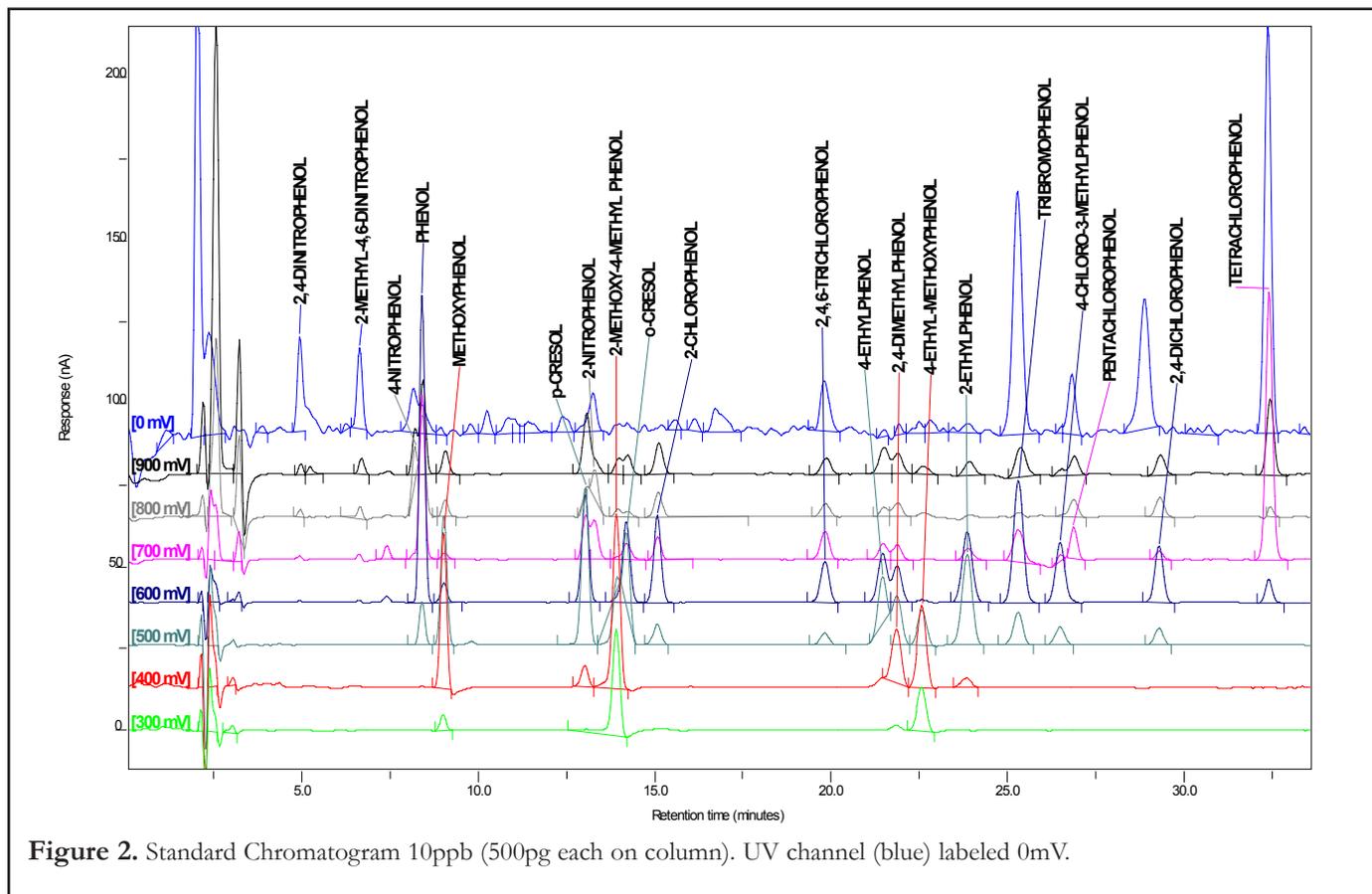
### LC Conditions:

Column: Capcell Pak C18 MG (4.6 x 250 mm; 5 $\mu$ )  
Temperature: 25°C  
Mobile Phase A: 25 mM Potassium Phosphate Buffer  
20 % Acetonitrile  
10 % Methanol  
pH 7.40  
Mobile Phase B: 25 mM Potassium Phosphate Buffer  
50 % Acetonitrile  
10 % Methanol  
pH 7.40

Gradient Conditions: Isocratic 20% B from 0-1 min. Linear increase of phase B from 20% to 40% from 1 – 20 min. Linear increase of phase B from 40% to 100% from 20-34 min. Isocratic 20% B from 35 – 40 min.  
Flow Rate: 1.0  $\mu$ L/min  
Injection Volume: 50  $\mu$ L (tray at 4°C)

### Detector and Conditions:

Detector: Model 5600A CoulArray  
Applied Potentials: 200 to +900mV (vs. Pd) in 100 mV increments  
UV Detector: Models 520 or 522  
Wavelength: 240 nm



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### Results and Discussion

The gradient method enables the separation and detection of twenty different phenols in a 32 minute run (Figure 2). The combination of EC and UV detection provides qualitative as well as quantitative information. In the case of EC detection, the use of an eight channel EC array allows for highly specific determination of each of the phenols. The first two channels of the EC array are used as screening electrodes to remove interfering compounds. The different phenols appear on different channels across the array depending upon their electrochemical response. For example, the methoxy substituted phenols are relatively easily oxidized and appear at the lower channels (400 mV), the alkyl substituted phenols appear at slightly higher potentials 500-600 mV, the monochlorophenols at 600-700mV while the polychlorinated phenols and nitrophenols oxidize at the highest potentials 700-900 mV. UV detection is needed in order to detect the dinitrophenols and also provide some qualitative information.

The maximum allowable concentration of individual phenols in drinking water is 0.1 µg/L. In order to achieve this detection limit, pre-concentration of the sample is required. In EPA Method 528 sample preparation involves Solid Phase Extraction. In the SPE procedure one liter of water is passed through a 6 mL SPE column. The phenols are eluted with dichloromethane and the solvent is concentrated to a final volume of 1 mL (1000X concentration). This degree of concentration is necessary due to the poor sensitivity of the GC/MS method. The improved sensitivity of the present method makes it possible to measure phenols at 0.1 µg/L using a concentration factor of x10 or x20. Thus all of the compounds of interest could be measured at 0.1 µg/L by passing a 20 mL sample of water through the SPE method.

Numerous methods have been described for the SPE extraction of phenols including EPA Method 528. In addition to the references below, several different methods for extracting phenols from water can be obtained from the JTBaker.com Technical Library.

The limit of detection ranged from 5–100 pg on column for the compounds detected by EC. The detection limit for the compounds (dinitrophenols) detected by UV was 75 pg on column (s/n 3:1). The method was linear up to 5000 pg on column with correlation coefficients of >0.999

Compound	RT 1	RT 2	Height 1	Height 2
Phenol	7.09	7.12	163 na	164 na
4-Nitrophenol	6.65	6.70	52.5	55.8
Methoxyphenol	7.50	7.52	215	194
2-Chlorophenol	12.38	12.30	67.4	66.6
2,4,6-Trichlorophenol	15.76	15.93	30.9	31.8
Dimethylphenol	18.60	18.75	47.9	51.6
Pentachlorophenol	22.95	23.18	12.4	12.7
Dichlorophenol	28.78	29.09	18.6	18.6

**Table 1.** Variation in Retention Time (RT, mins) and Peak Height (nA) for some Priority Phenols over a 28hr Period.

for all of the phenols with the exception of 4-nitrophenol which was 0.989. Table 1 gives the retention time and peak height response variation for a number of the phenols over a 28 hour period.

This gradient HPLC array/UV method is highly sensitive, permits the measurement of numerous priority phenols (as well as an internal standard and method surrogate) in under 32 minutes and uses each analyte's voltammetric behavior across the array to verify compound purity and identity.

### References

<sup>1</sup>Penalver, A., Pocurull, E., Borrull, F. and Marce, R.M. (2002). Solid-phase microextraction coupled to high-performance liquid chromatography to determine phenolic compounds in water samples. *J. Chrom. A*, **953**, 79-87.

<sup>2</sup>Sarrion, M.N., Santos, F.J., and Galceran, M.T. (2002). Determination of chlorophenols by solid-phase microextraction and liquid chromatography with electrochemical detection. *J.Chrom. A*, **947**, 155-165.

Munch, J.W. (2000). EPA Method 528: Determination of phenols in drinking water by solid phase extraction and capillary column gas chromatography/mass spectrometry (GC/MS). U.S. EPA.

# Application note

## Measurement of Priority Phenols in Water - Analytical Methodology

Puig, D. and Barcelo, D. (1997). Determination of polar priority phenols at the parts per trillion levels in water using on-line liquid-solid extraction followed by liquid chromatography with coulometric detection. *J. Chrom. A*, **778**, 313-319.

Ruana, J. and Urbe, I. (1993). Determination of phenols at the ng/L level in drinking and river waters by liquid chromatography with UV and electrochemical detection. *J. Chrom A*, **655**, 217-226.

Standard Methods for the Examination of Water and Wasterwater (1985). American Public Health Association, Washington, D.C. 16<sup>th</sup> edition.

### Ordering Information

Description	Part Number
CoulArray, Model 5600A - 12 channel	70-4330
Pump, Model 582	70-4050
Gradient Upgrade	70-4051
CoulArray Organizer with Temperature Control	70-4340T
Autosampler, Model 540	70-1484
UV detector(s), Model 520 or (522)	70-1909
	(70-4130)
Column, Shiseido Capcell Pak C18 MG	88-90104



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