



Project Summary

Determination of Phenols in Industrial and Municipal Wastewaters

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This report describes the research conducted to develop an analytical test procedure for the analysis of specific organic toxic substances in effluent wastewaters. The test procedure is applicable to the analysis of 11 of the 114 priority pollutants identified by the EPA as Category 8—Phenols. The test procedure developed was originally published in the December 3, 1979 issue of the *Federal Register* as EPA Method 604 and subsequently included as one of the EPA Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.^{1,2}

The procedure consists of several steps, including extraction, concentration, and quantification by gas chromatography with flame-ionization detection. An optional derivatization step is presented, using pentafluorobenzyl bromide followed by column chromatography cleanup and quantification of the derivatives by gas chromatography with electron capture detection.

The final report describes the research leading to the selection of the procedural steps and includes the results of a literature search, sample preservation procedures, elution of the phenols on various gas chromatographic columns, several solvent extraction efficiencies versus pH, stability of the compounds in water-soluble solvents, sample extract cleanup procedures, and application of the procedures and effluent wastewaters.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research

project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) and the Amendments of 1977 (PS 95-217) required that the Administrator of the U.S. Environmental Protection Agency promulgate guidelines establishing test procedures for the analysis of the priority pollutants, which were separated into 12 categories. The final report fully describes the research required for the method developed for 11 of the priority pollutants in one of those categories: Category 8—Phenols.

The 11 compounds in Category 8—Phenols are phenol, 2,4-dimethylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 4-chloro-3-methylphenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, and 4,6-dinitro-2-methylphenol.

The research program included a literature search from 1960 through 1978, sample preservation studies, evaluation of solvents for liquid-liquid extraction, stability studies of the compounds in water-miscible solvents, and evaluation of sample and extract cleanup procedures.

The use of XAD-26 resin as a possible extraction and concentration step for all the priority pollutant phenolics in wastewater was evaluated and compared to liquid-liquid extraction.

The gas chromatographic characteristics data of the category compounds are presented and include information on

retention times with various gas chromatography columns at different temperatures, responses to both electron-capture and flame ionization detectors, linearity curves, and chemical data for all compounds, and minimum detection limits.

To enhance the electron-capture response of the phenols, two derivatization techniques were investigated with the results described in the full report. Pentafluorobenzyl bromide was selected as the derivatizing reagent for the final method.

Based on the information gathered during the research program, methods were proposed for the analyses of the Category 8 compounds in water. These proposed methods were then used to develop data on overall compound recoveries in spiked distilled water and wastewater effluent samples.

Conclusions and Recommendations

The results of the preservation study experiments indicate the samples are best preserved when buffered to a pH of 7 to 10, dechlorinated with 35 mg of sodium thiosulfate per mg/L of chlorine per liter of water, exposed to a minimum of UV light, and stored and shipped at a temperature of 4°C. When so handled, minimal change or loss of phenol concentrations are observed up to 7 days. The maximum loss seen during the studies was 50% for 4-nitrophenol while the minimum loss of 8% was observed for 2,4-dinitrophenol.

The adjustment of the water samples to pH 12, and extraction with dichloromethane was found to serve as a preliminary cleanup procedure. Most base/neutral extractable interferences are removed by this preliminary step, leaving the phenols in the water.

The extraction of one-liter water samples, with three 60-mL portions dichloromethane per liter, after adjustment to pH 2 with 1N H₂SO₄, was found to give the best overall extraction efficiencies for all the solvents studied. Optimum extraction efficiencies ranged from 42% to 100% for the phenols. The dichloromethane was concentrated in a Kuderna-Danish evaporator with solvent exchange to 2-propanol.

When the sample extracts require no further cleanup, they are best analyzed by flame ionization gas chromatography. The evaluation of several chromatographic columns led to the recommendation of Supelcoport* coated with 1% SP-1240DA.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Using this column, the response of the phenols by GC/FID was found to be linear throughout the low to high mg/L range. Table 1 summarizes the gas chromatographic operating conditions, retention times, and MDL obtained under these conditions. The separation of the 11 phenols achieved by this column is shown in Figure 1.

An alternate extraction and concentration step, the use of XAD-26 resin, was also evaluated. Results of this investigation indicate that the traditional solvent extraction/concentration procedure yields, average phenol recoveries that are 1.5 to 2 times the recoveries from the resin.

In confirmation of the results by flame ionization and as an aid in the elimination of interferences in the analysis of phenols in complex extracts, an optional derivatization and column chromatographic procedure was developed. Derivatization of the phenols with chloroacetic anhydride was unsuccessful due to poor reaction efficiencies and significant artifact formation. However, the phenols, in general, were successfully derivatized using pentachromobenzyl bromide in the presence of 18 Crown-6 catalyst. In order to eliminate extraneous peaks in the derivatized standard phenolic solution, a silica gel cleanup procedure was adopted.

Evaluation of gas chromatographic columns and conditions for the analyses of the phenol derivatives led to the recommended use of Chromosorb W-AW-DMCS coated with 5% OV-17 in conjunction with electron capture gas chromatography. Table 2 summarizes the

recommended gas chromatographic conditions and operating conditions. The table includes retention times and MDL obtained under these conditions. An example of the separation achieved by this column is shown in Figure 2.

The procedures developed during this study (Figure 3) were successfully applied to three treated industrial effluent samples and a municipal primary effluent sample which contained several of the phenols at concentration levels of 25 to 800 µg/L.

The accuracy of the complete method, based on spiked solutions of distilled deionized water expressed as percent of recovery, varied from 30% for 4-nitrophenol to 82% for 2-nitrophenol. The same experiment using spiked municipal wastewater gave an accuracy range from 50% for phenol to 76% for 4-chloro-3-methylphenol. The single operator coefficient of variation ranged from 10% for 2-nitrophenol to 54% for 2,6-dinitro-2-methylphenol in a spiked municipal wastewater sample.

References

- Guidelines Establishing Test Procedures for Analysis of Pollutants, Proposed Regulation. Federal Register. 44(223):69484-69489, December 3, 1979.
- Longbottom, J. E. and J. J. Lichtenberg. Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. EPA/600/4-82/057, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati. 1982.

Table 1. Chromatographic Conditions and Method Detection Limit

Parameter	Retention Time (min.)	Method Detection Limit (µg/L)
2-Chlorophenol	1.70	0.31
2-Nitrophenol	2.00	0.45
Phenol	3.01	0.14
2,4-Dimethylphenol	4.03	0.32
2,4-Dichlorophenol	4.30	0.39
2,4,6-Trichlorophenol	6.05	0.64
4-Chloro-3-Methylphenol	7.50	0.36
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-Dinitrophenol	10.24	16.0
Pentachlorophenol	12.42	7.4
4-Nitrophenol	24.25	2.8

Column conditions: Supelcoport (80/100 mesh) coated with 1% SP-1240 DA in 1.8 m long x 2 mm ID glass column with nitrogen carrier gas at a flow rate of 30 mL/min flow rate. Column temperature was 80°C at injection, programmed immediately at 8°C/min to 150°C final temperature. Method detection limits were determined with a flame ionization detector.

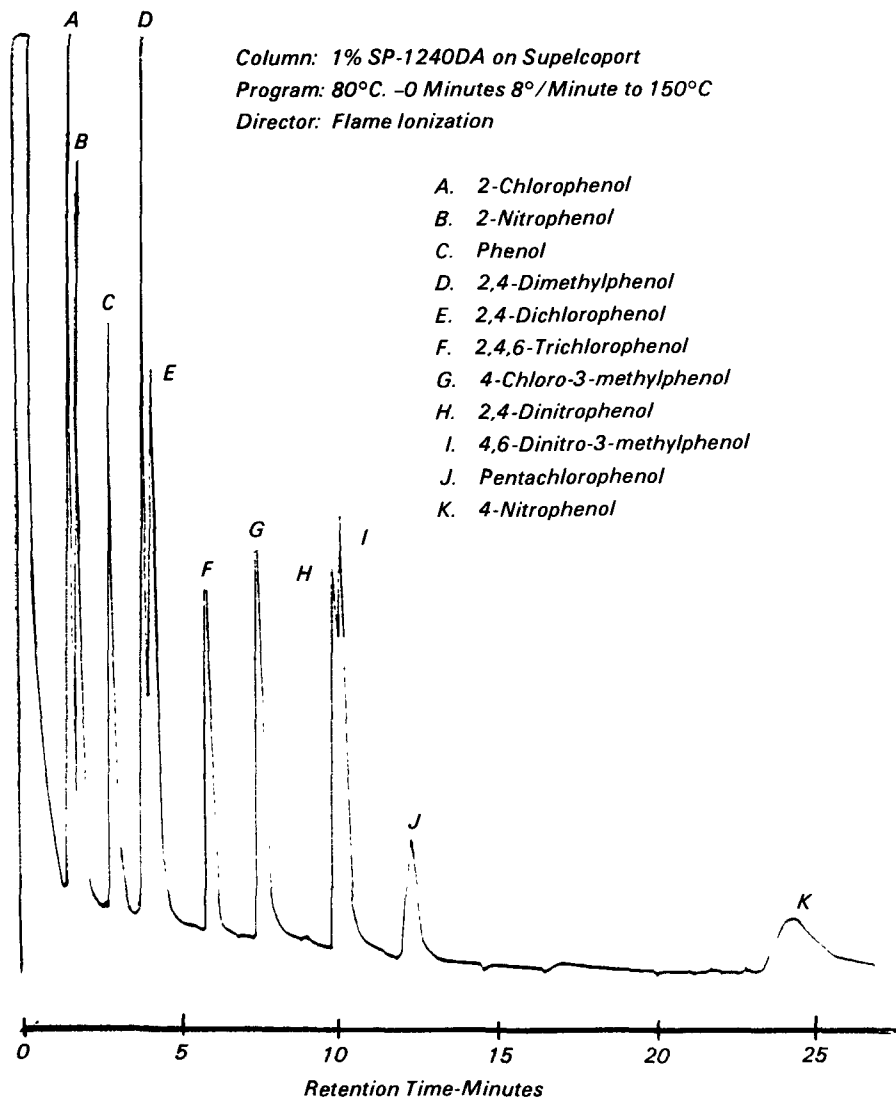


Figure 1. Gas chromatogram of phenols.

Table 2. Electron Capture Gas Chromatography of PFBB Derivatives

Parent Compound	Electron Capture	
	Retention Time (min.)	Method Detection Limit (µg/L)
2-Chlorophenol	3.3	0.58
2-Nitrophenol	9.1	0.77
Phenol	1.8	2.2
2,4-Dimethylphenol	2.9	0.63
2,4-Dichlorophenol	5.8	0.68
2,4,6-Trichlorophenol	7.0	0.58
4-Chloro-2-Methylphenol	4.8	1.8
Pentachlorophenol	28.8	0.59
4-Nitrophenol	14.0	0.70

Column conditions: Chromosorb W-AW-DMCS (80/100 mesh) coated with 5% OV-17 packed in a 1.8 m long x 2.0 mm ID glass column with 5% methane/95% argon carrier gas at a flow rate of 30 mL/min. Column temperature isothermal at 200°C.

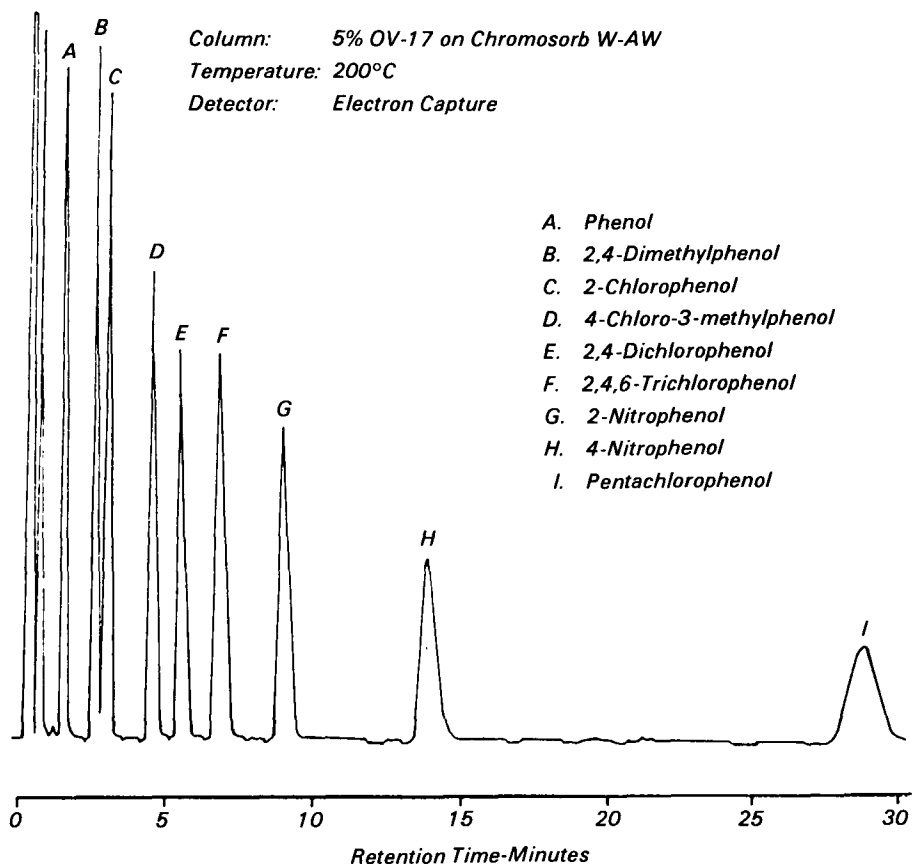


Figure 2. Gas chromatogram of PFBB derivatives of phenols.

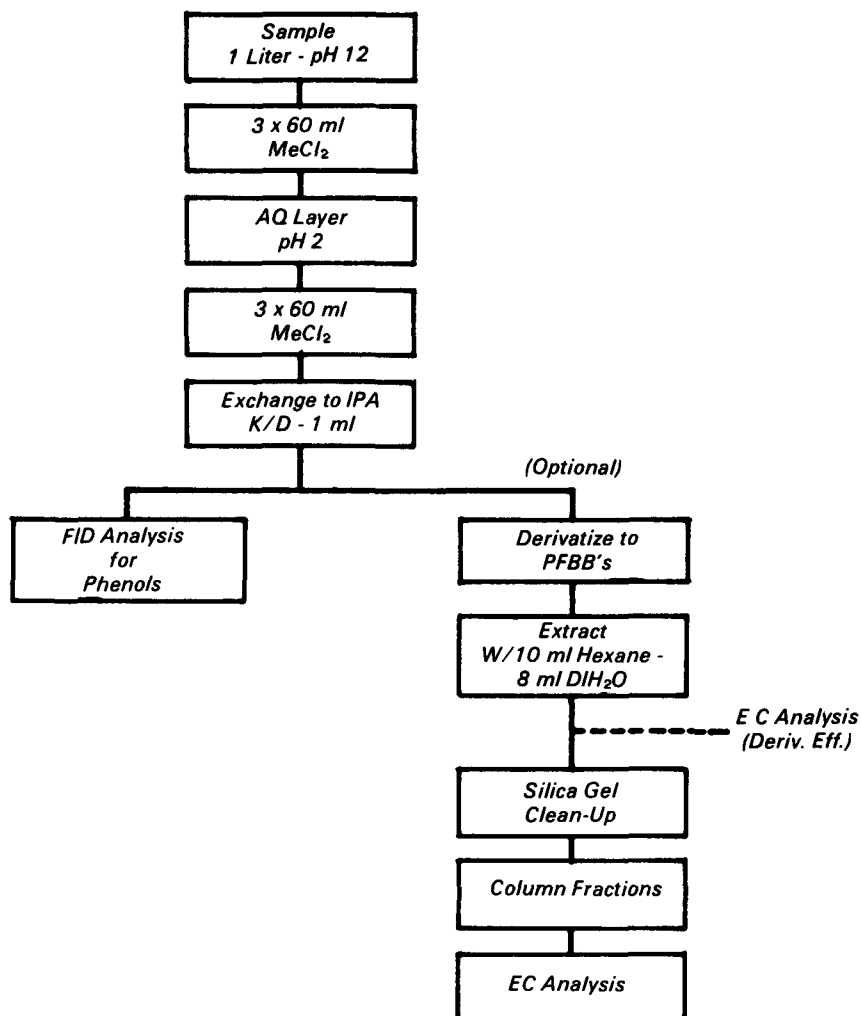


Figure 3. Analysis of phenols.

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James J. Lichtenberg is the EPA Project Officer (see below).

The complete report, entitled "Determination of Phenols in Industrial and Municipal Wastewaters," (Order No. PB 86-119 120/AS; Cost: \$16.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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