Phenols In Industrial Wastewater

The extensive use of phenols in manufacturing and their generation as by-products and undesirable degradation products has led to regulation of these pollutants in wastewater effluent. In order to comply with the limits established by the Environmental Protection Agency, industries must routinely monitor their discharge into the water supply. A colorimetric analysis using 4-amino- antipyrene is the most widely used method for water samples(1). This procedure lacks specificity, however, and parasubstituted phenols cannot be measured. Methods using gas chromatography with the electron capture detector often require derivatization(2). Determination of phenolics in wastewater by liquid chromatography with ultraviolet detection has also been reported(3). This liquid chromatography/electrochemistry (LCEC) method offers rapid, accurate analysis of phenols which, at the same time, is also simple enough for screening purposes.

Materials

Reagents

0.2 M sodium perchlorate/0.005 M trisodium citrate buffer. Dissolve 28.10 g sodium perchlorate and 1.47 g sodium citrate in 1 L of deionized, distilled water. Adjust to pH 5.0 with glacial acetic acid.

Acetonitrile. Baker "Resi-Analyzed"

Phenol stock solution. Dissolve 10 mg of phenol in 100 mL of 10% CH_3CN/90% 0.2 M sodium perchlorate/0.005 M trisodium citrate buffer.

Wastewater samples were donated by an oil refinery.

Apparatus

Liquid Chromatograph. Bioanalytical Systems LC-304, BAS 400 or BAS 200 with a TL-5 glassy carbon working electrode.

MF-1 Microfilters (Bioanalytical Systems)

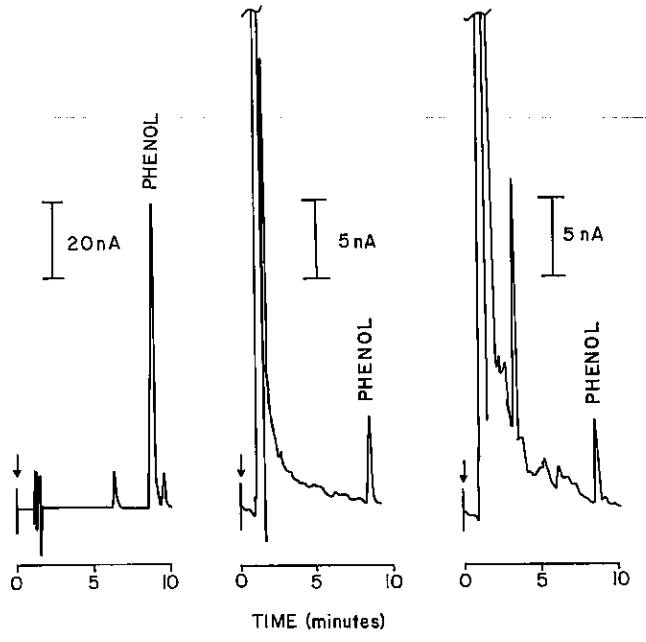

Figure 1. Chromatograms from various locations at an oil refinery. (A) 60 ppm foul-water stripper sample diluted 1:100, 30 ng injected (B) 23 ppb air flotation outlet sample, 2.3 ng injected (C) 20 ppb desalter water sample, 2.0 ng injected.

RC-58 membranes for Microfilters (Bioanalytical Systems)

Conditions

Liquid Chromatograph: LC-304, BAS 400 or BAS 200 (Bioanalytical Systems Inc.)
Mobile Phase: 15% CH_3CN in 0.2 M sodium perchlorate/0.005 M sodium citrate buffer, pH 5.00.
Stationary Phase: Biophase ODS 5 µm Column (250 x 4.6 mm)
Detector: LC-4A or LC-4B electronic controller with a glassy carbon working electrode.
Applied Potential: +900 mV vs. Ag/AgCl
Flow rate: 2 mL/min.
Temperature: ambient

Procedure

1. If necessary, dilute samples with the perchlorate/citrate buffer. This may be necessary if the expected concentrations exceed 1.5 ppm for any phenol.

2. Acidify samples to pH 3 with concentrated HCl.

3. Place 1 mL of sample into the sample compartment of a Microfilter equipped with RC-58 membranes. Centrifuge 5 minutes.

4. Inject 100 µL of the filtrate into the chromatograph.

Results

Samples obtained from various locations at an oil refinery were injected directly into the chromatograph. The selectivity of LCEC permits the analysis of phenol without extensive sample extractions. The highly sensitive method detects samples as low as 20 ppb without prior clean-up and requires dilution of samples above 1.5 ppm as shown by F1. Quantitation was accomplished by interpolation from a calibration curve and linearity was established for concentrations up to 160 ng injected.

References

1. M.C. Rand, A.E. Greenberg, and M.J. Taras (editor). Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D.C. 14th ed., 1976.

2. A.B. McKague, J. Chromatogr., 208(1981) 287-293.

3. C.M. Sparacino and D.J. Minick, Environmental Science and Technology. 14(1980) 880-882.