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Note

High-performance liquid chromatographic determination of phenols as phenolates in a complex mixture

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Several coal gasification processes, such as underground (*in situ*) coal gasification, which do not occur at extremely high temperatures, produce substantial quantities of tar by-products. These tars contain a wide variety of organic compounds including aliphatic hydrocarbons, aromatic hydrocarbons, organic acids and azaarenes[1]. For the most part, these by-products stay underground following *in situ* coal gasification and pose a potential threat to the purity of ground-water supplies. Therefore, it is important to have facile means for the chemical determination of the organic by-product constituents. Among the more prominent of these constituents are the phenols, which despite their organophilic nature, are leachable into water, particularly at high pH; therefore, their chemical determination in complex tar–water samples is an important part of environmental monitoring associated with coal gasification.

Numerous analytical schemes covering a wide range of sophistication have been reported for the determination of phenols. The earliest and simplest of these are colorimetric methods for total phenols[2,3]; more recent highly sophisticated methods for determining individual phenols have made use of gas chromatography–mass spectrometry[4]. Liquid chromatography offers a number of advantages over gas chromatography for phenol determination. Reversed-phase high-performance liquid chromatography (RP-HPLC) is particularly useful for the separation and quantification of individual phenols. This technique has been used with UV detection at phenol absorption maxima at 215 and 272 nm[5]. The response ratios at 215 and 272 nm have also been used in the confirmation of phenols, cresols and xylenols[6].

The published methods for the determination of phenols have been found to be inadequate for their analysis in complex coal tar mixtures without prior fractionation. Available fractionation schemes are time consuming and may introduce anomalies into the samples. However, the monitoring of phenolic chromatographic effluents as phenolate anions can be sufficiently selective that prior separation is not necessary. This can be accomplished by virtue of the bathochromic shift of neutral phenol (–OH) absorption maxima from 215/272 nm to phenolate anion ($-O^-$) maxima

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at 235/290 nm. This report deals with the separation of phenols by RP-HPLC followed by UV detection of phenolate ions produced by post-column introduction of base. This combination provides a method for confirmatory determination of phenols in complex mixtures without prior fractionation.

EXPERIMENTAL

The components of the liquid chromatographic system used consisted of a microprocessor-controlled high-pressure pumping system capable of gradient elution,

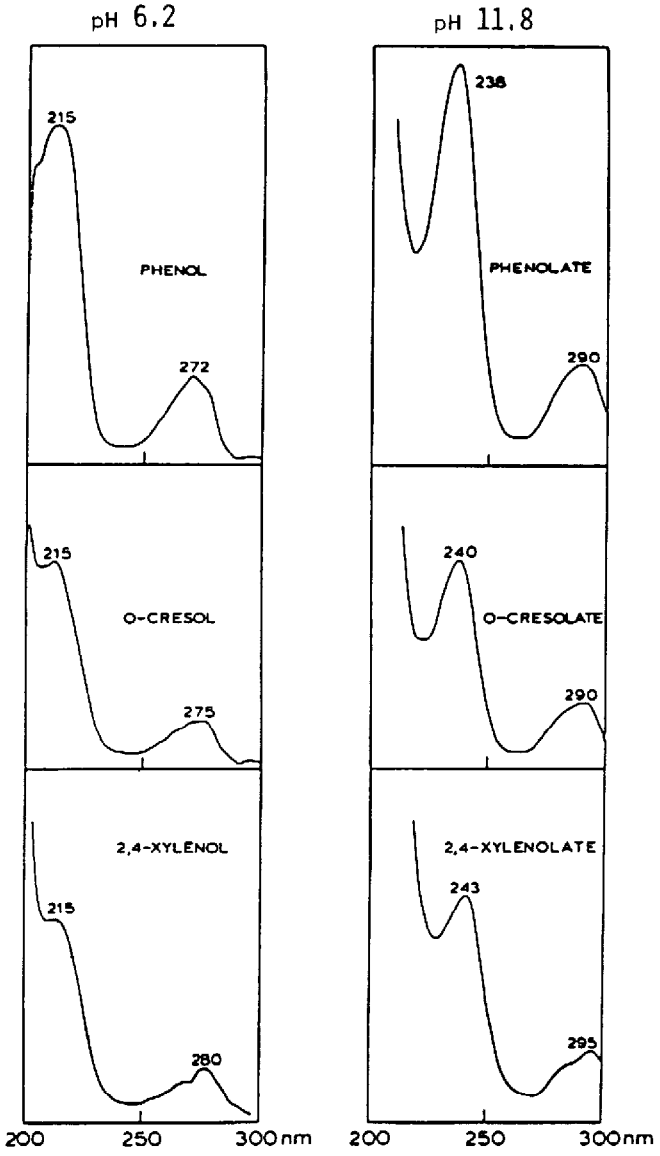

Fig. 1. UV absorption of neutral phenols (–OH) and corresponding phenolate anions ($-O^-$), from peaks trapped in the detector cell.

Model 3B (Perkin-Elmer, Norwalk, CT, U.S.A.), a 10-μl fixed-loop injector (Rheodyne, Cotati, CA, U.S.A.), a Waters Model 6000 pump for post-column addition of base (Waters Assoc., Milford, MA, U.S.A.) and a Model LC-75 scanning spectrophotometric detector (Perkin-Elmer). The chromatographic separation was carried out on a C_{18} bonded column (Supelco, Bellefonte, PA, U.S.A.). A low dead-volume "T" for post-column mixing of a base and column effluent was constructed to provide adequate mixing without excessive band broadening.

Solvent programming was employed. The composition of the eluent was changed from acetonitrile–water (40:60) to 100% acetonitrile by a three-step linear gradient program over a period of 25 min.

A pre-column packed with C_{18} bonded silica gel (particle size 35–40 μm) was used to prolong the life of the analytical column.

All solvents were of HPLC grade purity and were filtered through a 0.22-μm filter (Millipore, Bedford, MA, U.S.A.). The base added post-column was in the form of 0.04 *M* KOH in water–methanol (50:50).

The tar–water samples analyzed were collected as condensate from the gas

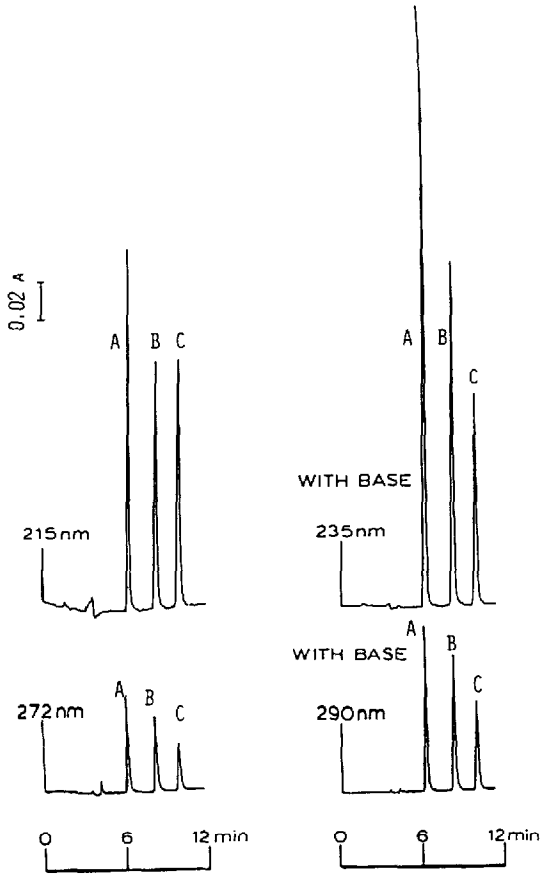

Fig. 2. Chromatograms of phenol (A), *o*-cresol (B) and 3,5-dimethylphenol (C) detected at absorption maxima for neutral phenols (215 and 272 nm) and with post-column addition of base to produce phenolate anions which were monitored at their absorption maxima (235 and 290 nm).

product of an experimental *in situ* coal gasification pilot plant (Hanna-IV) operated near Hanna, Wyoming.

For comparative studies a conventional solvent extraction scheme was used for fractionating tar components into acidic (mainly phenolic), basic and neutral fractions[7].

RESULTS AND DISCUSSION

The characteristic bathochromic shifts of the absorption maxima for phenol, *o*-cresol, 2,4-xylenol and corresponding anions are shown in Fig. 1. These spectra were obtained from chromatographic peaks retained in the detector cell of the chromatograph. It is seen that the absorption maxima for neutral phenols lies close to 215 nm, where optimum sensitivity for these compounds has been reported[6]. However, absorption maxima for a large number of other organic compounds also lie in this wavelength region, posing interference problems. Furthermore, at this wavelength the choice and quality of the solvents are crucial because of their absorption of 215-nm radiation. The bathochromic shift in absorption to 240 nm minimizes these problems.

The spectra on the right of Fig. 1 were obtained when 0.04 *M* KOH was added immediately post-column, and the resulting phenolate peaks were trapped in the detector. The pH of the column effluent after mixing with base was 11.8. This is high enough to convert essentially all neutral phenol species into phenolate anions, but not sufficiently high to be corrosive to the system. No damage was observed to the

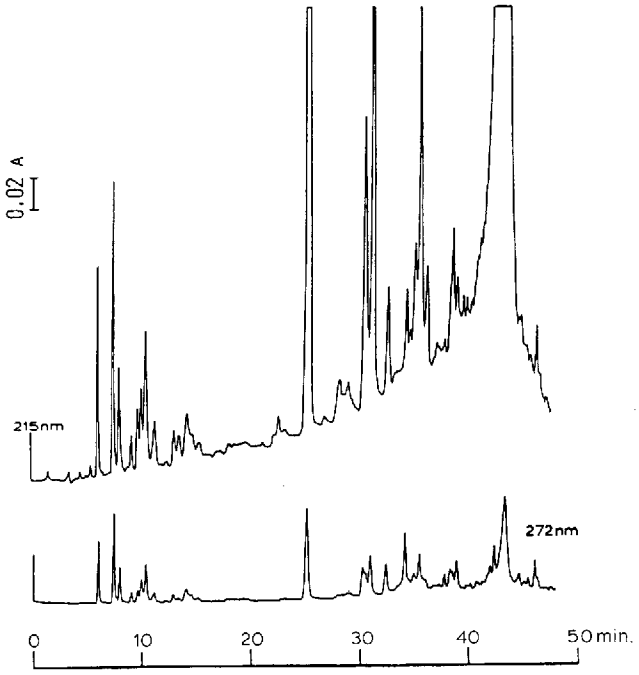

Fig. 3. RP-HPLC chromatograms of an unfractionated cyclohexane extract of a coal gasification tar-water sample monitored at 215/272 nm. Column effluent pH 6.2.

stainless-steel lines, quartz cell of the UV detector or other chromatograph components with post-column base addition after continuous use for several months.

HPLC peaks of neutral phenols are often monitored at 215 or 272 nm. Although the sensitivity is higher at 215 nm, better selectivity relative to other compounds, *e.g.*, aromatic hydrocarbons, is obtained at 272 nm. Gains made in both sensitivity and selectivity are obtained by monitoring the RP-HPLC effluents at 235–240 nm after converting the phenols into phenolate anions by post-column addition of base. The response for model compounds under these conditions is shown in Fig. 2 for a mixture of phenol, *o*-cresol and 3,5-dimethylphenol.

The separation of various components of an unfractionated cyclohexane extract of a coal gasification tar–water sample is shown in Figs. 3 and 4. The chromatogram in Fig. 3 was obtained by monitoring a pH 6.2 effluent at 215 nm. The larger peaks eluting late in the chromatogram were from aromatic hydrocarbons; the more polar phenols were eluted in the first 20 min. A chromatogram of the same extract with post-column addition of base and UV detection at 235 nm is illustrated in Fig. 4. As expected, the response of phenols (as phenolates) increased, whereas the response of the other constituents decreased. This characteristic shift in absorption maxima can be used along with chromatographic retention times for the confirmatory analysis of individual phenols. Several phenols were identified in the tar–water sample in this manner. Furthermore, this separation and detection technique can be used for the identification of non-phenolic polar constituents. This is demonstrated in Fig. 5 for four model polar compounds (*p*-hydroxybenzoic acid, *p-tert.*-butylben-

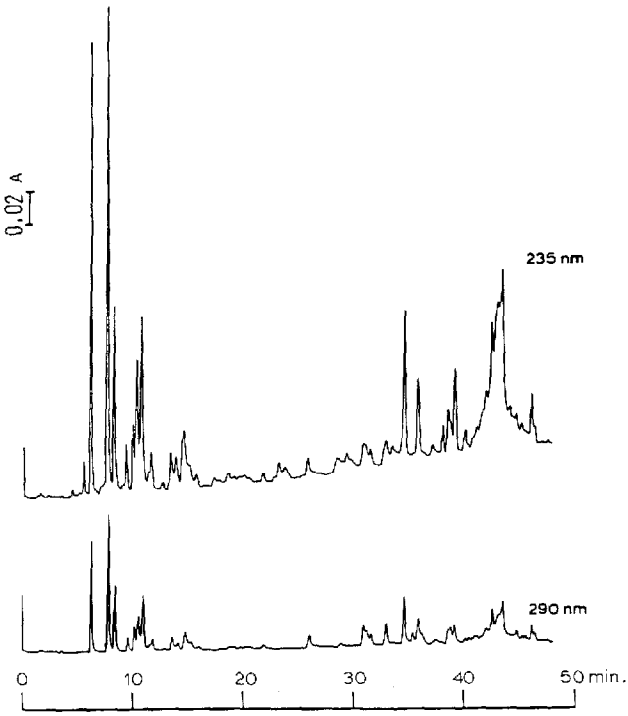

Fig. 4. RP-HPLC chromatograms of an unfractionated cyclohexane extract of a coal gasification tar-water sample monitored at 235/290 nm. Column effluent pH 11.8.

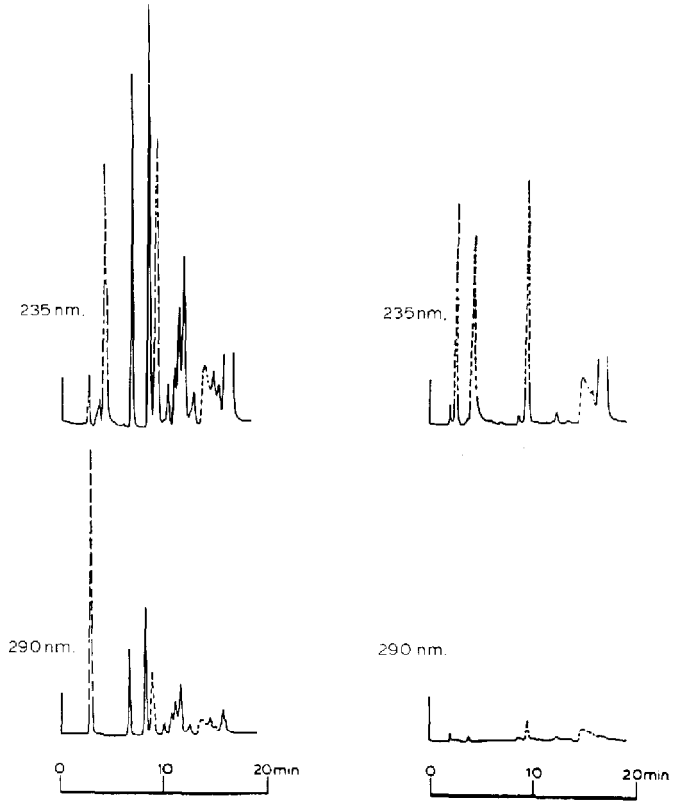

Fig. 5. RP-HPLC chromatograms of an unfractionated cyclohexane extract of a coal gasification by-product spiked with model compounds (see Fig. 6) (dashed peaks) monitored at 235 and 290 nm; left, pH 11.8 (with base); and right, pH 6.2 (without base).

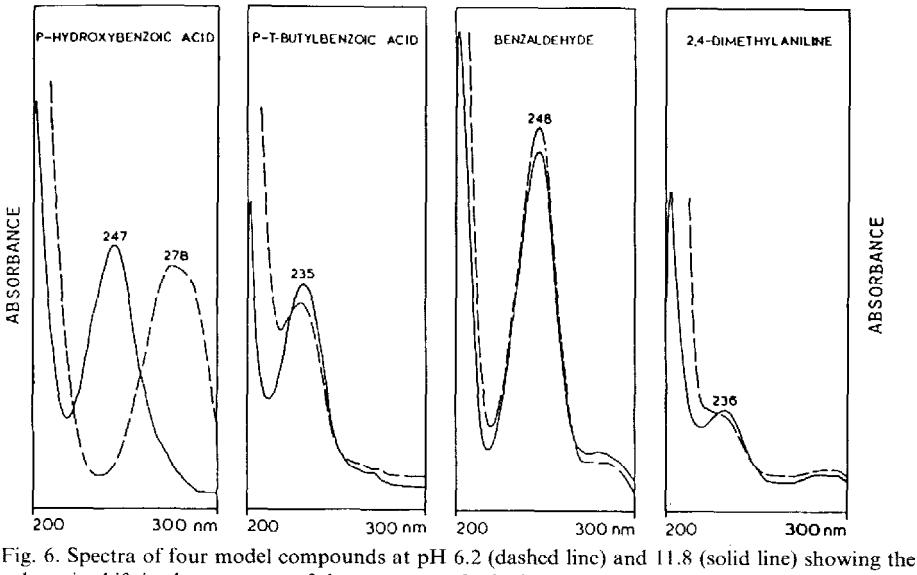

Fig. 6. Spectra of four model compounds at pH 6.2 (dashed line) and 11.8 (solid line) showing the bathochromic shift in the spectrum of the spectrum of *p*-hydroxybenzoic acid.

zoic acid, benzaldehyde, and 2,4-dimethylaniline) which were added to the tar–water extract and monitored with and without addition of base to the column effluent. As expected, the addition of base had little effect on the absorption maxima of *p-tert.*-butylbenzoic acid, benzaldehyde and 2,4-dimethylaniline, all of which lack phenolic –OH groups. However, as shown in Fig. 6, a characteristic shift was observed for *p*-hydroxybenzoic acid, which does have a phenolic –OH group. A clear distinction between these compounds and phenols can be obtained by monitoring the absorbance at 235 nm, with and without the addition of base to the column effluent as shown in Fig. 6.

These results show that both better sensitivity and selectivity can be obtained in the HPLC determination of phenols in complex mixtures by detection of these compounds in their anionic forms.

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