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Note

Determination of phenolic compounds in alternate fuel matrices

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The increased attention given alternate fuels, such as shale oil and solvent-refined coal, has given rise to the need for faster and more reliable methods of analysis for toxic compounds in these complex matrices. The high concentration of phenolic compounds found in these alternate fuels (relative to petroleum) has also increased the need for the development of reliable and rapid analytical procedures for these compounds.

The highly complex nature of the alternate fuel matrices requires high-resolution separation techniques to separate and identify the phenolic isomers present. Previous methods have involved the use of low-resolution packed columns[1–6], support-coated open-tubular (SCOT) columns[7], and wall-coated open-tubular (WCOT) columns[8–10], or the use of chemical derivatization and subsequent use of WCOT or packed columns[11–13].

In this paper we describe a method utilizing a high-resolution WCOT column for the separation and quantitation of phenols contained within a complex organic matrix. The utilization of this column, in combination with a simplified acid–base extraction scheme, produces a fast and reliable method for the quantitative analysis of phenols at μg/g (ppm) levels in alternate fuel matrices.

EXPERIMENTAL*

Two alternate fuels, a shale oil and a solvent-refined coal (SRC) liquid, were characterized in this work. The shale oil was supplied by the Oakridge National Laboratory, Oakridge, TN, U.S.A., and is from the Mahogany zone of the Colorado Green River formation. It had been processed in a 150-ton retort for *in situ* simulated combustion operated by the Laramie Energy Research Center, Laramie, WY, U.S.A. The shale oil had undergone centrifugation to separate water (40%) and sludge before being received at our laboratory. The shale oil was then filtered, homogenized, and stored in amber ampoules.

The SRC sample is a middle-to-heavy distillate from a fuel oil blend obtained

* In order to specify procedures adequately, it has been necessary to identify some commercial materials in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best available for the purpose.

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from the Pittsburg & Midway Coal Mining Co., Solvent-Refined Coal Pilot Plant, Dupont, WA, U.S.A. The SRC was similarly stored in amber ampoules for subsequent analysis.

Extraction

The alternate fuel sample (*ca.* 0.6 g) was accurately weighed into a small flask and dissolved in 50 ml of methylene chloride. An appropriate amount of *o*-chlorophenol, dissolved in methylene chloride, was then added to the sample as an internal standard. This solution was quantitatively transferred with an additional 50 ml of methylene chloride into a 250-ml separatory funnel. The acids were then isolated using an acid–base extraction procedure[14] adapted from Schmeltz[15]. Methylene chloride was substituted for ether in this procedure, because the stabilizing agent (2,6-di-*tert.*-butyl-*p*-cresol) in the ether interferred with final chromatographic quantitation. The resulting extract was dried over anhydrous sodium sulfate and concentrated under a stream of dry filtered nitrogen to 1 ml, in preparation for subsequent gas chromatographic (GC) analysis.

Column preparation

The analytical WCOT columns were prepared in our laboratory using the barium carbonate method of Grob *et al.*[16,17]. A 20 m × 0.3 mm I.D. capillary column was pulled from thick-walled borosilicate glass tubing. After the capillary had been acid-leached and dried, the inside surface was coated with $BaCO_3$ by forcing a saturated solution of barium hydroxide with CO_2 gas through the column. The column was then coated with a 20% solution of Pluronic L64 (Fluka, Buchs, Switzerland)[17] dissolved in methylene chloride. The column was conditioned at 220°C until it exhibited minimal bleed. Subsequent testing using the procedure described by Grob and Grob[18], revealed a film thickness of *ca.* 0.07 μm.

The gas chromatograph used for this work was equipped with a pressure-controlled capillary inlet system and a flame ionization detector. The chromatographic peaks were integrated using a digital integrator capable of internal standard calculations. The GC conditions used are listed in the caption of Fig. 1.

Qualitative analysis

Peak identification was accomplished utilizing a quadrupole GC–mass spectrometry (MS) system equipped with a 20 m × 0.3 mm I.D. Pluronic L64 WCOT column. GC conditions were identical with those used in quantitative analysis (see Fig. 1). The WCOT column was interfaced to the mass spectrometer through an "open-slit" fitting constructed out of nickel tubing (1/16 in. O.D. × 0.010 in. I.D.). The mass spectrometer was operated in the electron impact mode under the following conditions: electron energy, 70 eV; ionizing current, 1 mA; ion source manifold pressure, $1 \cdot 10^{-5}$ Torr; ion source temperature, 200°C; interface temperature, 250°C. Mass spectra were scanned repetitively every 2 sec under computer control for the entire GC run. Isomer identifications were verified by analysis of the mass spectra and comparisons of retention times of pure phenolic standards.

Quantitative analysis

Calibration factors of all the phenols relative to *o*-chlorophenol were deter-

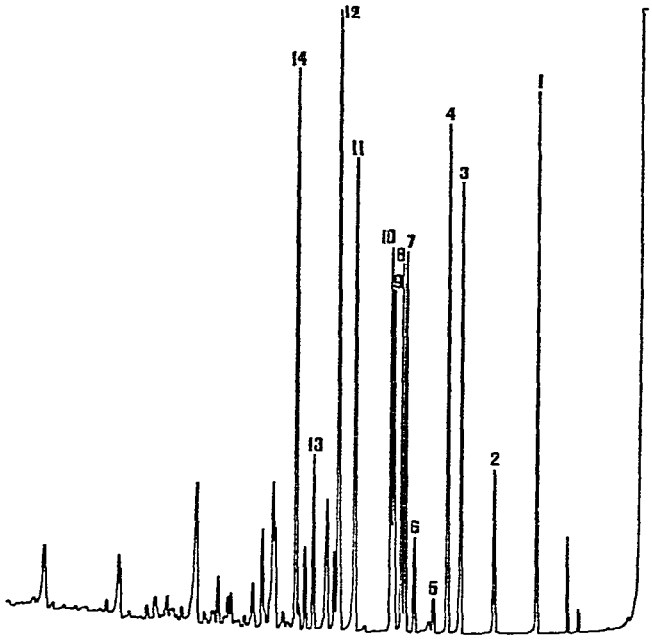

Fig. 1. Chromatogram of acidic fraction from shale oil. Column, 20 m × 0.3 mm I.D., Pluronic L64 WCOT; temperature program, 70°C to 160°C at 2°C/min; carrier gas, helium; split, 30:1; injector and detector temperatures, 300°C.

mined from a standard solution of gravimetrically prepared amounts of each of the analytes and *o*-chlorophenol in methylene chloride. Gold weighing boats were used in the preparation of standard solutions, after it was shown that using aluminium weighing boats introduced a large variability in the determination. The concentrations of the phenols in the standard solution were made to mimic the concentration of the phenols in the samples as closely as possible. An aliquot of this standard was extracted using the same procedure already described. Subsequent GC analyses yielded calibration factors which were then applied to the data from sample runs to yield quantitative results.

RESULTS AND DISCUSSION

A chromatogram of the shale oil acids on the Pluronic L64 WCOT column is shown in Fig. 1. The chromatogram contains over 50 peaks, most of which are sufficiently resolved for peak area integration with a precision of 5% or better. Peaks 1–14 were identified by GC–MS and retention indices, and are listed in Table I. Of particular note is the separation of all six dimethylphenol isomers (xylenols), the cresols, and phenol. This separation was achieved using a temperature program of 70°C initial, programmed to 150°C at 2°C/min. All the C_1–C_3 phenols in the sample eluted prior to a column temperature of 130°C. Retention on this liquid phase seems to be heavily dependent on the amount of steric hindrance, by adjacent methyl groups, around the polar hydroxy group. This is demonstrated by the elution of the dimethyl-

TABLE I

IDENTIFICATION OF PHENOLIC COMPOUNDS IN FIG. 2, BOILING POINTS, EXTRACTION EFFICIENCIES AND ANALYTICAL RESULTS

n = Not determined.

Compound	*Peak No. Fig. 1*	*B.p. (°C)* *	*Extraction efficiency*	*Concentration found (μg/g)* **	
				Shale oil	*SRC II fuel*
o-Chlorophenol	1	176	99.1	int. std.	int. std.
2,6-Dimethylphenol	2	212	74.9	168 ± 8	1450 ± 90
Phenol	3	182	99.3	401 ± 4	23,800 ± 1200
o-Cresol	4	191	98.1	384 ± 9	12,500 ± 500
2,4,6-Trimethylphenol	5	219***	n	n	n
2,3,6-Trimethylphenol	6	—	n	n	n
p-Cresol	7	202	99.3	273 ± 7	15,500 ± 800
m-Cresol	8	203	98.6	327 ± 10	29,100 ± 1900
2,5-Dimethylphenol	9	242	93.4	320 ± 12	8900 ± 500
2,4-Dimethylphenol	10	214	89.4	387 ± 17	8200 ± 600
2,3-Dimethylphenol	11	218	n	n	n
3,5-Dimethylphenol	12	219	n	n	n
3,4-Dimethylphenol	13	225	n	n	n
2,3,5-Trimethylphenol	14	233§	n	n	n

* Ref. 20.

** Uncertainties are ± 1σ.

*** Ref. 21.

§ Ref. 22.

substituted phenols. The sterically hindered 2,6-dimethylphenol (b.p., 212°C) elutes prior to phenol (b.p., 182°C), while the least hindered, 3,4-dimethylphenol (b.p., 225°C), is retained quite strongly.

The concentrations of several of the phenols in the shale oil and SRC are given in Table I. From this table it can be seen that the total phenolic contents of the shale oil and the SRC fuel oil are *ca.* 0.3 and 10%, respectively. The chromatogram of the SRC fuel oil is shown in Fig. 2. This chromatogram shows a very similar pattern of phenols to that of the shale oil. The individual concentrations, however, are approximately two orders of magnitude higher. These experimental results agreed with those determined by a method[14] using a liquid chromatographic pretreatment followed by GC–MS quantitation.

The extraction efficiencies were determined by the ratio of the peak areas of the residual phenols in the extracted organic solution of the standard phenols, with the phenols in the extract solution. The extraction efficiencies of these phenols are listed in Table I. All of the phenols showed an extraction efficiency in excess of 70%.

CONCLUSIONS

The method described in this paper has been shown to be both a rapid and straightforward method for the analysis of phenolic compounds in complex matrices, such as shale oil. The WCOT column used was shown to be capable of yielding highly reproducible quantitative separations.

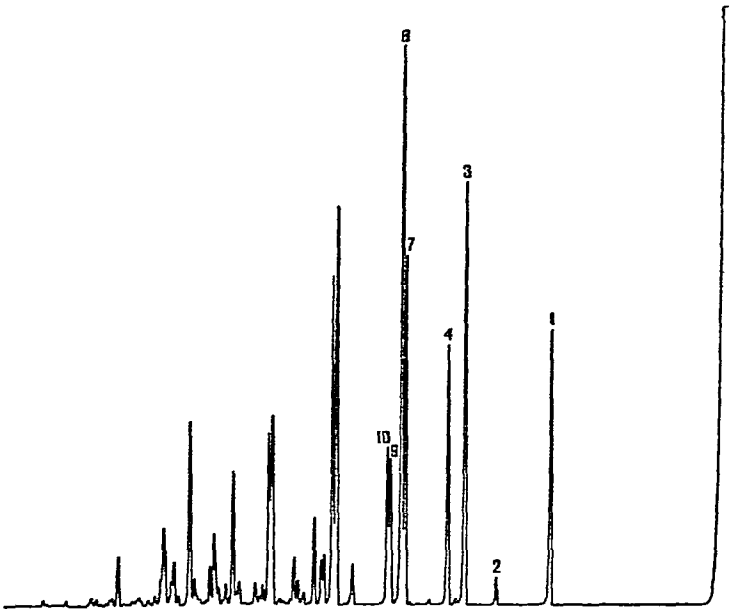

Fig. 2. Chromatogram of acidic fraction from a SRC II fuel oil. Same conditions as in Fig. 1.

It was experimentally determined that *ca.* 500 ng of phenol could be loaded onto the column without peak broadening or distortion. The large sample capacity and high resolving power exhibited by this column makes it ideal for GC–MS and GC Fourier transform infrared spectroscopic applications.

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