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## Note

# Portable liquid chromatograph for analysis of primary aromatic amines in coal-derived materials

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A significant part of the mutagenicity of synthetic fuel products is linked with organic bases, and particularly with primary aromatic amines (PAAs), especially those having two or three rings in their molecular structure[1–6]. Existing techniques for identifying and quantifying these compounds are expensive and time consuming, and require that samples be returned to the laboratory. Thus, an instrument or method suitable for performing on-site PAA analyses in suspect environments would be desirable. The possibility of developing a small, low-power PAA monitor based on liquid chromatography with electrochemical detection (LC–ED) has been established[7,8].

The PAAs are encountered in synthetic fuel processes in association with much higher concentrations of nonmutagenic or weakly mutagenic compounds, such as azaarenes, phenols, and neutral aromatic hydrocarbons. Low-pressure LC provides a partial separation of such complex mixtures. ED offers the sensitivity needed to determine the PAAs at part-per-billion*** levels because aromatic amines are easily oxidized electrochemically[9]. Also, ED offers the desired selectivity by eliminating the interference of the azaarenes and the electrochemically inactive polyaromatic hydrocarbons[8,9]. Moreover, electrochemical detectors are inexpensive and simple to operate, consume little power and can be more easily miniaturized than other high-sensitivity detection instruments, such as fluorescence or even chemiluminescence[10] detectors. This note reports the preliminary results of selective detection of PAAs by a portable LC–ED system assembled for this study. The PAAs were either in standard solutions or in materials derived from coal.

## EXPERIMENTAL

### *Portable LC–ED apparatus*

Fig. 1 is a schematic diagram of the portable LC–ED system, which consists of the following components: an FMI direct-current pump (Model RP-BG25, 12 V

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*** Throughout the article the American billion ($10^9$) is meant.

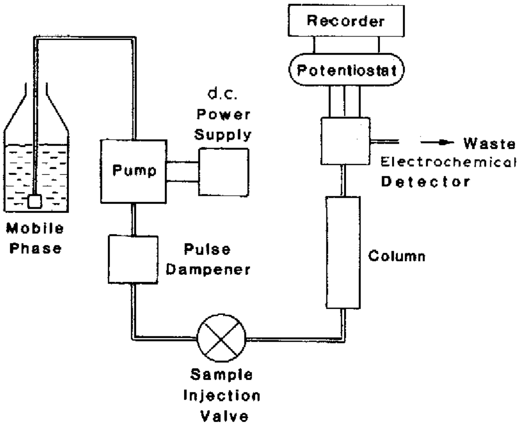

Fig. 1. Schematic diagram of the portable LC–ED system.

d.c., 60–100 mA, Fluid Metering, Oyster Bay, NY, U.S.A.) equipped with an RHOCKC pump head; an FMI pulse dampener with a built-in pressure gauge (Model PD-60-LF, Fluid Metering); an automatic sample injector (Model 7126, Rheodyne, Cotati, CA, U.S.A.) containing a 20-μl sample loop; a 3 cm × 4.6 mm I.D. C (10-μm) reversed-phase column (guard column cartridge, Brownlee Labs., Santa Clara, CA, U.S.A.); and a thin-layer transducer cell containing a glassy carbon working electrode. The pump was operated by a 6-V battery or a d.c. power supply (12.3 V, 5 A, Elpac Power Systems, Santa Ana, CA, U.S.A.) in conjunction with a variable autotransformer (Type 3PN1010, Energy Products, Dayton, OH, U.S.A.). The potential of the transducer cell was controlled by an LC-4B detector (Bioanalytical Systems, West Lafayette, IN, U.S.A.), and the current signals were recorded on a strip-chart recorder (Model 1243, Soltec Corp., Sun Valley, CA, U.S.A.).

The mobile phase was selected to give the highest sensitivities for PAAs and the least sensitivity for phenol[7,8]. Therefore, a solution of tetrahydrofuran–0.1 *M* sodium phosphate buffer (35:65), pH 2.2, was used. The potential of the working electrode was 0.9 V *vs.* Ag/AgCl, unless otherwise stated.

### *Preparation of solutions*

Chemicals were obtained from Aldrich (Milwaukee, WI, U.S.A.) and Sigma (St. Louis, MO, U.S.A.). Solutions of PAAs (5 ppm by weight) were prepared in 50% aqueous acetonitrile. Coal Oil A (a comparative research material designated as CRM-1) was first dissolved in benzene (3000 ppm) and then diluted to 600 ppm by adding acetonitrile. This coal liquefaction product was obtained from the U.S. Environmental Protection Agency/U.S. Department of Energy Fossil Fuels Research Materials Facility at Oak Ridge National Laboratory.

## RESULTS AND DISCUSSION

### *Effects of electrode potential*

The sensitivity of the electrochemical detector to PAAs and their isomers and phenol was studied at various potentials at a flow-rate of 0.58 ml/min. Fig. 2 shows

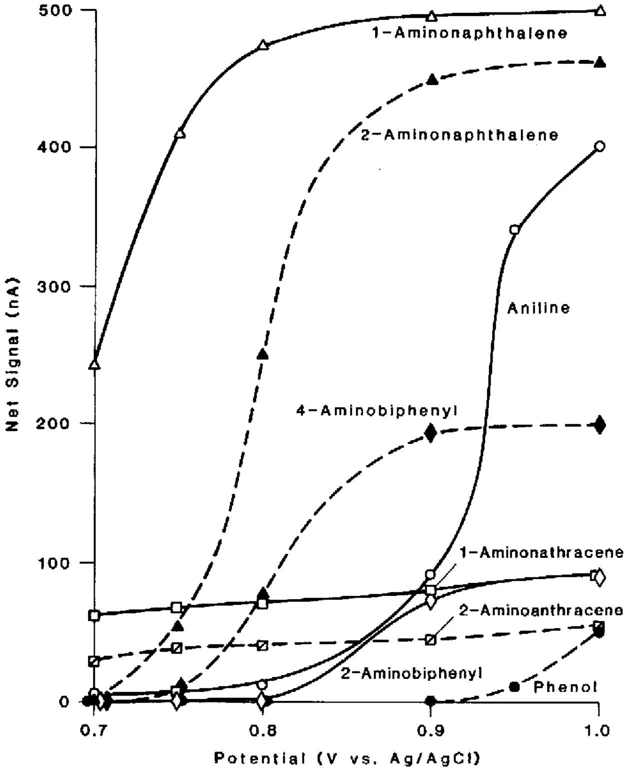

Fig. 2. Voltammograms obtained with tetrahydrofuran–0.1 *M* sodium phosphate, pH 2.2 (35:65). Flow-rate: 0.58 ml/min. Sample concentration: 5 ppm (by weight).

the results. Compared to the net signals obtained with a commercial LC–ED system under the same chromatographic conditions[8], those obtained in our experiments are up to three times greater for PAAs and about one-third smaller for phenol. This improvement can be attributed to the smaller dead volume of the portable LC–ED system.

Aminonaphthalenes and aminobiphenyls exhibit a mass-transport-limited behavior at high anodic potentials ($>$0.9 V *vs.* Ag/AgCl). Each PAA and phenol has a clearly different $E_{\frac{1}{2}}$ (half-wave potential) value. Therefore, each PAA and its isomer may be identifiable by differential pulse voltammetric techniques[11], even without any chromatographic column separation. Interference due to phenol (5–100 ppm) is negligible because the acidic phenol and the basic amine compounds are well resolved.

### *Effect of flow-rate*

Flow-rates were calibrated by measuring the input voltage and current of the d.c. pump. At least 3 V were necessary to operate the pump motor and thus produce a minimum usable flow-rate of 0.22 ml/min. The flow-rate, pressure and power to the pump were substantially proportional to the input voltage (3–8 V). Fluctuations in the flow-rate, which increased rapidly above 0.7 ml/min, were observed as oscillations in the back pressure of the column. When the pressure was reduced to *ca.* 60

p.s.i., a flow-rate of 0.6 ml/min was achieved with the portable LC–ED, which required only 0.22 W to operate the pump.

Fig. 3 illustrates the effects of flow-rate on net signal. The net signal for 1-aminonaphthalene increases linearly with flow-rate, confirming that the electrooxidation of 1-aminonaphthalene is controlled by a diffusion process (see Fig. 2). The signal for aniline is unaffected by flow-rate, confirming activation control at 0.9 V *vs.* Ag/AgCl (see Fig. 2), whereas the signal for 1-aminoanthracene increases only slightly with flow-rate. These variations in the effects of flow-rate on the signals caused by different compounds point to the necessity of maintaining a selected flow-rate to ensure accurate standardization and quantitation of unknown mixtures.

The magnitude of theoretical plate numbers (column efficiency) was comparable to that previously observed with a commercial LC–ED system under the same chromatographic conditions[8]. With the present portable LC–ED setup, the theoretical plate numbers increased slightly as flow-rates decreased. A flow-rate of 0.22 ml/min, which requires only *ca.* 30 p.s.i. (3 V and 0.12 W to operate the pump), gave the best chromatographic efficiency and separation. This feature is favorable for the development of a portable instrument.

Table I summarizes the chromatographic parameters for PAAs and phenol at two flow-rates. The reported parameters are the averaged values (with only two significant figures) determined from three runs per sample (concentration 5 ppm) at each flow-rate. Table I shows that phenol does not interfere with PAAs because its

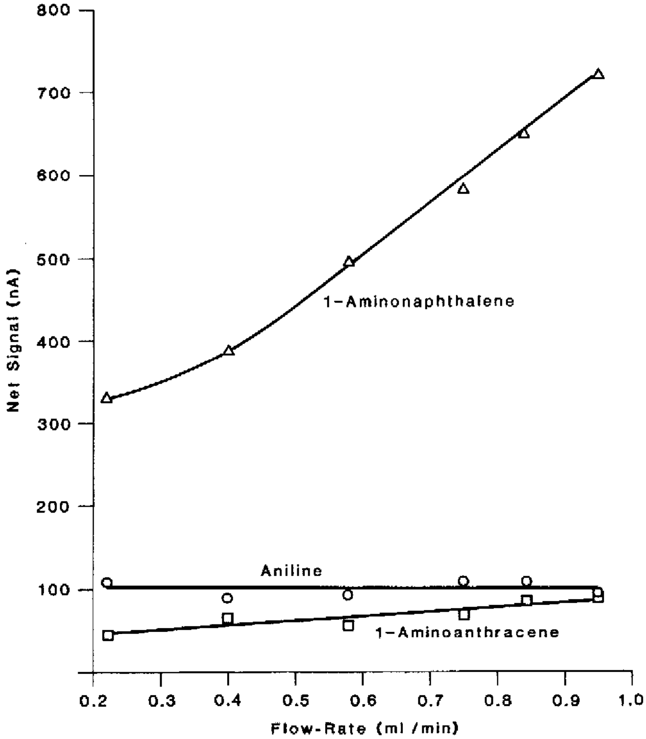

Fig. 3. Net signal for PAAs *vs.* flow-rate.Electrode potential: 0.9 V *vs.* Ag/AgCl.

TABLE I

CHROMATOGRAPHIC PARAMETERS FOR PAAs AND PHENOL OBTAINED WITH A PORTABLE LC–ED SYSTEM AT TWO FLOW-RATES

$E$ = 0.9 V *vs.* Ag/AgCl; $t_R$ = retention time; $i$ = sensitivity [signal (net current) divided by concentration]; and $N$ = theoretical plate number.

| *Compound* | *0.22 ml/min* | | | | *0.58 ml/min* | | | |
|---|---|---|---|---|---|---|---|---|
| | $t_R$ *(min)* | $i$ *(nA/ppm)* | $N$ | *Detection limit (ppb)* | $t_R$ *(min)* | $i$ *(nA/ppm)* | $N$ | *Detection limit (ppb)* |
| Aniline | 1.2 | 19 | 130 | 11 | 0.55 | 17 | 120 | 14 |
| 1-Aminonaphthalene | 2.1 | 70 | 550 | 2.9 | 0.95 | 100 | 500 | 2.4 |
| 2-Aminonaphthalene | 1.9 | 56 | 470 | 3.6 | 0.85 | 96 | 400 | 2.5 |
| 1-Aminoanthracene | 5.5 | 11 | 290 | 18 | 2.9 | 12 | 290 | 20 |
| 2-Aminoanthracene | 4.2 | 6 | 271 | 33 | 1.9 | 8.4 | 210 | 29 |
| 2-Aminobiphenyl | 4.0 | 11 | 550 | 18 | 1.7 | 15 | 470 | 16 |
| 4-Aminobiphenyl | 2.9 | 36 | 460 | 5.6 | 1.2 | 38 | 360 | 6.3 |
| Phenol | 7.9 | 0.5 | 700 | 400 | 3.4 | 0.5 | 520 | 480 |
| Benzene | — | 0 | — | — | — | 0 | — | — |
| Pyridine | — | 0 | — | — | — | 0 | — | — |
| Typical noise level (nA) | | 0.10 | | | | 0.12 | | |

retention time is much greater and its sensitivity is about 20–200 times lower than those for the PAAs studied here. The observed retention times for PAAs suggest that chromatographic separation of their isomer peak maxima (but not peak baselines) is possible at the flow-rate of 0.2 ml/min.

The minimum detectable quantity (detection limit) given in the last column of Table I was calculated as the value yielding a signal-to-noise ratio of 2 and is in the range of 3–33 ppb for PAAs at 0.22 ml/min. Other typical interferences (benzene and pyridine at concentrations of 100 ppm) gave no signals throughout the potential range studied (0.6–1.0 V *vs.* Ag/AgCl).

### *Analysis of raw coal oil sample*

The capabilities of the portable LC–ED system were tested by injecting a 600-ppm raw coal oil sample. Fig. 4 illustrates the results. At 0.58 ml/min (Fig. 4a), only a few major peaks are seen. Peaks 6 and 8 can be identified as aniline and 2-aminonaphthalene by comparison with the retention times in Table I. Peaks 1 through 5 represent some electroactive species lighter (or less adsorbable) than aniline present in the sample. After the signal for 2-aminonaphthalene, the response gradually returns to a low and noise-free baseline.

Better resolution was achieved at 0.22 ml/min (Fig. 4b). For example peak 12 for aniline is clearly better resolved. However, the number of peaks observed with the portable LC–ED system (18) is still much lower than that usually obtained by gas chromatography (GC) and GC–mass spectrometric analysis, which has revealed the presence of a least 130 components in the crude base fractions alone[4–6,12]. This

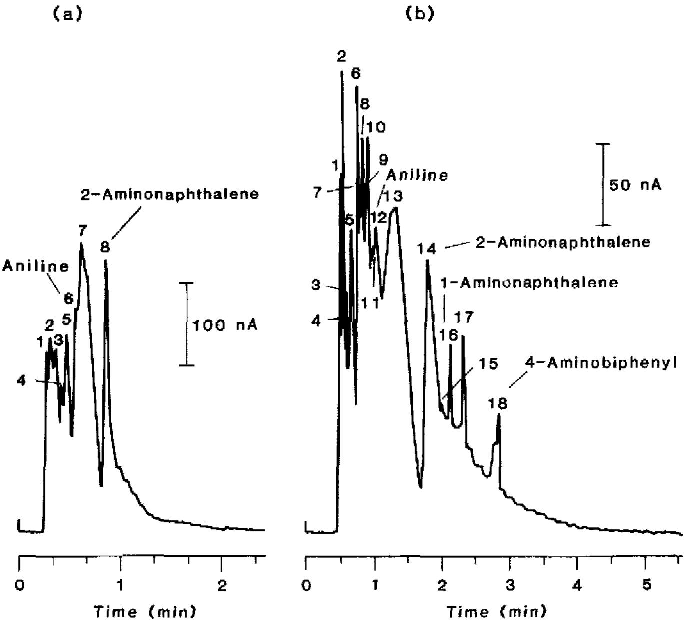

Fig. 4. Chromatograms of 600 ppm Coal Oil A (CRM-1) at (a) 0.58 ml/min and (b) 0.22 ml/min obtained with the portable LC–ED system. Electrode potential: 0.9 V *vs.* Ag/AgCl. Mobile phase: tetrahydrofuran–0.1 *M* sodium phosphate, pH 2.2 (35:65).

TABLE II

COMPOSITION OF PAAs IN CRM-1 ANALYZED BY A PORTABLE LC–ED SYSTEM AT 0.22 ml/min

| *Peak number* | *Component* | *LC-ED of 600-ppm sample* | | | *Original* ($^{0}/_{00}$)** | |
|---|---|---|---|---|---|---|
| | | $t_R$ *(min)* | *i* *(nA)* | *ppm** | *LC-ED* | *GC**** |
| 12 | Aniline | 1.2 | 186 | 9.8 | 16 | 5.1 |
| 14 | 2-Aminonaphthalene | 1.85 | 168 | 3.0 | 5.0 | 3.4 |
| 16 | 1-Aminonaphthalene | 2.2 | 128 | 1.8 | 3.0 | 2.4 |
| 18 | 4-Aminobiphenyl | 2.9 | 86 | 2.4 | 4.0 | 2.2 |

* Estimated using the sensitivity data in Table I.

** By GC analysis, refs. 4, 5 and 12.

*** Parts per thousand estimated to be present in the original CRM-1 sample material.

effect is partly due to the electrochemical detector's insensitivity to azaarenes and to most of the other much more abundant components[8]. The major peaks are identified according to the data in Table I, and the estimated concentrations of the identified components are given in Table II.

Fair agreement was obtained with the previously performed analysis of the base fraction of the same material by GC[4,5,12].The three-fold larger concentration of aniline estimated in this work indicates that peak 12 (see Fig. 4b) contains information not only for pure aniline but also for its derivatives, such as the methylanilines. Similarly, the 25–80% higher values for the three PAAs derived from peaks 14, 16 and 18 are probably caused by other PAAs, possibly including isomers or alkylated homologues of the listed compounds. Also, peak 13 may be associated with methylanilines or $C_n$-anilines ($n = 2$, 3, or 4).

The results show that a bench-top prototype of a portable LC–ED system with a battery-operated pump can identify PAAs in materials derived from coal tar. However, far more extensive measurements, including standard addition methods, are required to identify all of the observed peaks.

Future research activities using the portable LC–ED system should include:

(1) Analyzing additional standard samples, including the derivatives of the simpler PAAs and three- and four-ring PAAs.

(2) Analyzing the base/neutral fractions of CRM-1 and other coal tars to correlate their chemical composition with their mutagenic activity.

(3) Expanding the number of analyticl protocols that can be installed on a portable LC system (*i.e.*, a low-power, low-back-pressure system based on ED).

(4) Developing a portable LC system with automatic features for field applications.

(5) Analyzing vapor-phase PAAs (*e.g.*, 10 ppb to 10 ppm aniline in air), possibly in conjunction with a cryogenic sampler[13] in the presence of likely interferences, such as water, benzene, nitrobenzene, phenol and pyridine.

## CONCLUSION

The portable LC–ED system discussed here, combined with a cryogenic or other suitable sampler, could be useful in situations where inexpensive but selective field analyses are required.

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