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Qualitative analysis of environmental samples for aromatic sulfonic acids by high-performance capillary electrophoresis

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ABSTRACT

High-performance capillary electrophoresis (HPCE) is investigated as a qualitative tool in the analysis of environmental samples for aromatic sulfonic acids and related compounds. Using standard borate buffer solutions, characteristic migration times define windows wherein certain compound types will be found. Eight aromatic sulfonic acids are separated as an example of the power of the technique. A leachate from a hazardous waste site is also subjected to HPCE. Qualitative identification may be approached by use of migration times and ancillary techniques such as continuous-flow fast atom bombardment mass spectrometry.

INTRODUCTION

Analytical interest in high-performance capillary electrophoresis (HPCE) has increased rapidly in the last few years [1–4], in part because it is a technique of high efficiency capable of generating theoretical plates above $1 \cdot 10^6$ [5]. Applications of CE to the determination of organic ions have centered largely in the biological and pharmaceutical areas [6]. Thus, peptides, proteins, and DNA fragments have been separated using CE [7–9]. In pharmaceutical applications of HPCE, issues such as purity and optical isomerism have been addressed [10–12]. Within this context, HPCE as a complementary tool to high-performance liquid chromatography has been emphasized [13].

In contrast, applications of HPCE to environmental analysis have been limited. Gaitonde and Pathak [14] used micellar electrokinetic CE to determine chlorophenols in wastewater. Separations of phenols and other compounds of environmental interest were reported [15–18]. Direct determination of small organic ions in the context of inorganic anion analysis was discussed [1]. This latter paper illustrated that an important role exists for CE in inorganic analysis, and one could extend the applicability to environmental problems.

On-column detection in HPCE is most often done by UV absorption in either the direct or indirect mode. Fluorescent detection is also widely used, and reports of electrochemical and other approaches have been reviewed [6]. Detection as a result of coupling CE to mass spectrometry (MS) has been the subject of several papers. Among the techniques employed include electrospray ionization and continuous-flow fast atom bombardment (CF-FAB) MS using either a coaxial or a liquid junction interface [19–22]. These techniques may be compared to approaches using ion chromatography. Ion chromatography in conjunction with particle-beam liquid chromatography–MS was used to identify 4-chlorobenzenesulfonic acid as a major com-

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ponent in the leachate from the Stringfellow Superfund site [23].

The extension of HPCE to the determination of non-volatile organics and water-soluble compounds of environmental interest seems obvious. The efficiency of HPCE in terms of the number of theoretical plates suggests a technique comparable to capillary gas chromatography. The great variety of chemistries to apply in HPCE enhances the prospect of sufficient selectivity for separations involving complex samples.

In this initial work, focus is placed on qualitative identification with the separation of eight aromatic sulfonic acids using a boric acid–borate buffer. This class of compounds presents a simple, common organic functional group that occurs in a variety of compounds. Azo dyes and anionic surfactants are two such classes of compounds that are of environmental interest. Additional results for selected azo dyes, aromatic carboxylic acids, and similar compounds defines functionally diverse moieties likely to be found in the migration window of interest. An electropherogram of the Stringfellow leachate is also presented. Finally, the qualitative identifications are supported by results from CF-FAB-MS used with direct CE interfacing and with flow-injection in an off-line mode.

EXPERIMENTAL

Chemicals

Compounds were used as received. Solutions of individual standards were made up at concentrations of approximately 0.5 mg/ml. Sodium dodecylbenzenesulfonate, sodium cumenesulfonate, sodium xylenesulfonate, and sodium toluenesulfonate were obtained from Chem Service (West Chester, PA, USA). Potassium phthalimide, sodium benzoate, sodium diphenylamine-4-sulfonate, orange II, boric acid, sodium tetraborate decahydrate, sodium salicylate, 4-chlorobenzenesulfonic acid, sodium 2-naphthalenesulfonate and sodium 3-nitrobenzenesulfonate were obtained from Aldrich (Milwaukee, WI, USA).

HPCE

A Beckman Model 2050 P/ACE system was used for all CE experiments; the instrument was controlled using the Windows-based operating system, version 2.0. A 57-cm (50 cm to the detector) × 0.050 mm capillary was used with UV detection at 214 nm. The buffer system was boric acid–borate at 50 m*M* (pH8.3). Generally, 5-s pressure injections were made followed by CE at 30.0 kV at a current of approximately 33 μA with temperature maintained at 25°C. Solutions were filtered through a 0.2-μm pore size nylon filter. Separations were carried out using a method that consisted of a 2.0-min rinse of buffer, 5.0-s pressure injection, separation, 2.0-min rinse of 0.1 *M* NaOH and 2.0-min rinse of deionized water.

To assess daily performance and reproducibility before running samples, a start-up sequence was established that began with 5.0-min rinses of 0.1 *M* NaOH followed by deionized water followed by buffer. Thereafter, a series of five runs of standards was made: two runs of Beckman's Test Mix A (benzoic acid, 4-hydroxybenzoic acid and 2-phenylacetic acid), two runs of toluenesulfonic acid and one run of pyridine. These runs provided information on separation, migration times, and electroosmotic flow.

CF-FAB-MS and CE–MS

A VG/Fisons 7070 EQ mass spectrometer with 11-250 (11/24 based, software B22) data system was used with a standard VG CF FAB probe. Flow injection analysis used a 0.25 mm I.D. fused-silica capillary (Polymicro Technologies, Phoenix, AZ, USA) with a flow of about 1 μl/min of FAB matrix consisting of 25% glycerol in water. Injections were made with a Valco valve (Model CI4W, Houston, TX, USA), and the flow was established with an Isco syringe pump (Model SFC-500, Lincoln, NE, USA).

Magnetic scans of 1 s/decade at an accelerating voltage of −6 kV were calibrated by using negative ions from the matrix or negative ions from polyethylene glycol. The FAB gun was operated at 8 kV, 1 mA. Accurate mass measurements were performed at a resolution of 3000 scanning at 3 s/decade.

CE–MS was performed using the coaxial arrangement [21]. A 0.020 mm I.D. × 0.144 mm O.D. capillary was used for CE and was about 110 cm long. The outer capillary (0.150 mm I.D. × 0.350 mm O.D.) carried the FAB matrix at a flow-rate of about 1 μl/min doped with ammonium acetate–triethylenetetramine (pH 9) to maintain electrical

continuity. A Glassman (Model PS/MJ30P, Whitehouse, NJ, USA) power supply was operated at 30kV (total voltage drop 36 kV) with currents generally below 15μA for 10 mM buffer of boric acid–borate or ammonium acetate (pH 8.3 using NH_3–water). Injections were electroosmotic at 30kV for 5–15 s. During injection, the CF-FAB probe was removed from the instrument to eliminate introduction of vacuum-induced air bubbles.

Leachate

A concentrated methanolic solution of leachate from the Stringfellow Superfund site was obtained from M. A. Brown (California Department of Health Services). Sample work-up was briefly as follows [23]. Aqueous samples (500–2000 ml) of leachate were concentrated by freeze-drying (24–72 h). The residue was redissolved in methanol (50–200 ml) and inorganic salts precipitated by adding an equal volume of acetone. After evaporation, the filtered residue was redissolved in methanol (1–20 ml).

RESULTS AND DISCUSSION

An electropherogram of eight aromatic sulfonic acids shows the power of the technique (Fig. 1). The inset in Fig. 1 illustrates the improved resolution of the last three sulfonic acids as a result of decreasing the injection time from 4.8 s to 1.2 s. The immediate application of HPCE to characterization of samples for aromatic sulfonic acids is obvious. A migration time window is defined from dodecylbenzenesulfonic acid to 4-chlorobenzenesulfonic acid of about 3.2–4.8 min under these conditions.

A migration time window in CE, like a retention

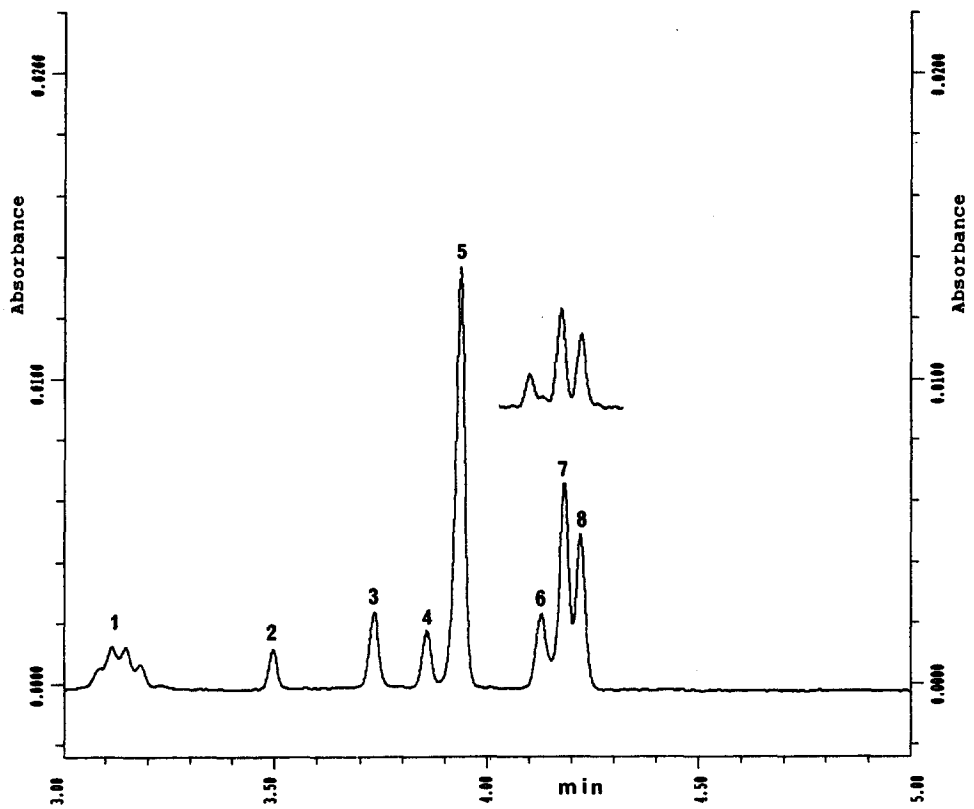

Fig. 1. Electropherogram of eight aromatic sulfonic acids using sodium borate–boric acid at pH 8.3, 57 cm (50 cm to detector) × 0.050 mm I.D. capillary, UV detection at 214 nm. Peaks: 1 = dodecylbenzenesulfonate; 2 = diphenylamine-4-sulfonate; 3 = cumenesulfonate; 4 = xylenesulfonate; 5 = 2-naphthalenesulfonate; 6 = toluenesulfonate; 7 = 4-nitrobenzenesulfonate; 8 = 4-chlorobenzenesulfonate. For inset, see text.

TABLE I

MIGRATION TIMES OF SELECTED ANIONS USING SODIUM BORATE–BORIC ACID BUFFER AT pH 8.3

Anion	Migration time (min)
Pyridine[a]	2.30
Orange II	3.42
Phthalimide	3.74
Benzoate	4.19
Salicylate	4.06
2-(4-Hydroxyphenyl)acetate	3.74
4-Hydroxybenzoate	4.03
Dodecylbenzenesulfonate (center)	3.13
Diphenylamine-4-sulfonate	3.50
Cumenesulfonate	3.73
Xylenesulfonate	3.86
2-Naphthalenesulfonate	3.94
Toluenesulfonate	4.12
4-Nitrobenzenesulfonate	4.18
4-Chlorobenzenesulfonate	4.22

[a] Neutral marker of electroosmotic flow.

time window in gas chromatography, can be used as a qualitative tool for the identification of compound types as well as specific isomers. The multiplet labeled as dodecylbenzenesulfonate indicates the many isomers present in the standard of this compound and the ability of HPCE to resolve them.

Anions with other organic functionalities undoubtedly will be found in this migration time window. For example, Table I gives migration times for the aromatic sulfonic acids and several aromatic carboxylic acids and related compounds that elute in this window under these experimental conditions. An azo dye is also included, and it produces a strongly fronting peak which may be indicative of mismatching mobilities with the buffer counter ions [1].

Within the class of sulfonic acids, it appears that large organic constituents result in a smaller electrophoretic mobility (*i.e.*, for anions moving in opposite direction to electroosmotic flow) and a shorter migration time. Conversely, electron-withdrawing substituents such as Cl and NO_2 and small organic substituents such as methyl result in longer migration times of the compounds illustrated. The azo dyes, with a large organic moiety, have some of the shortest migration times of the compounds studied. It therefore remains as an objective to develop CE conditions that are selective and appropriate for the high-efficiency separation of anions of very low mobility.

From an environmental perspective, the toxicity and other health effects associated with aromatic sulfonic acids and aromatic carboxylic acids may not be of primary concern. Nevertheless, the ability to characterize leachates or other matrices for these and similar compounds not readily amenable to gas chromatography–MS is of interest [23]. Such data help to account for total organic carbon and halogen in such matrices. An example of the potential of HPCE in this regard is the electropherogram of a leachate from Stringfellow Superfund site (Fig. 2). A large number of peaks are revealed under these buffer conditions. The simplicity and efficiency of HPCE compared with ion chromatography [23] are evident. Within the migration time window for sulfonic acids is one large peak and several lesser peaks that could indicate aromatic sulfonic or carboxylic acids of the type studied. The large peak corresponds to 4-chlorobenzenesulfonic acid [23], and this has been independently confirmed in this work by migration times of standards by HPCE, flow injection analysis using CF-FAB-MS, and by CE–MS as illustrated in Fig. 3. Differences in migration time between CE–MS and HPCE are a result of differences in column length, buffer concentrations and voltage.

The coaxial interface as presently implemented is difficult to use in practice, and further work is needed to put this approach on an equal footing with HPCE as usually carried out with commercial instruments. Comparisons of efficiencies indicate that standards and the leachate exhibit about 79 000 and 164 000 theoretical plates, respectively, for representative peaks. The CE–MS efficiency was never above 50 000 plates and ranged from 20 000 to 50 000 plates.

Medium resolution mass measurements have confirmed the elemental composition $C_6H_4SO_3Cl$ for the $(M - H)^-$ ion at m/z 191. The smaller peaks appear to be below the detection limit of the CE–MS techniques tried herein to date. Alternative approaches include automated peak collection with multiple runs followed by flow injection analysis using CF-FAB-MS.

Also evident in Fig. 2 are peaks eluting later than the aromatic sulfonic acids. These peaks likely con-

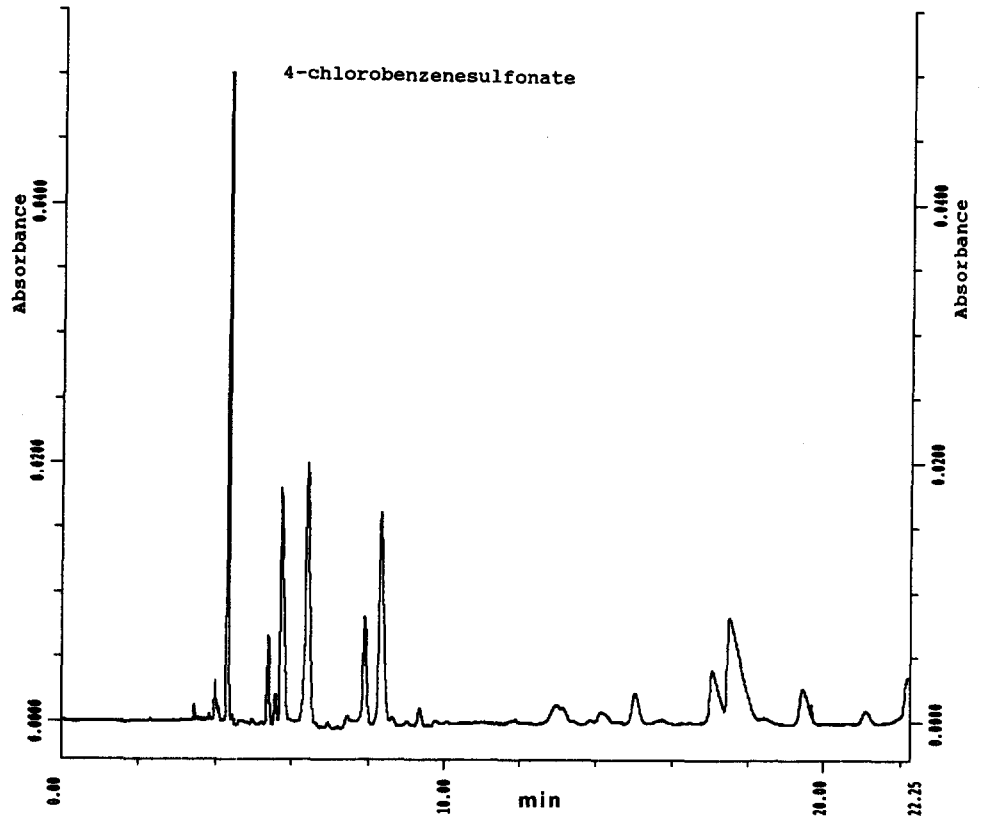

Fig. 2. Electropherogram of Stringfellow leachate using sodium borate–boric acid at pH 8.3.

sist of smaller organic anions of high mobility. The tailing evident in their peak shape again suggests an improper match with the mobility of the buffer counter ions [1]. The ability to identity these unknown ions remains an area of research.

Several issues involving analysis of environmental samples by HPCE need further investigation. Among these is the long-term reproducibility and comparability of migration times. Another issue concerns the long-term stability of calibration curves with appropriate corrections for on-column detection in quantitative analysis by CE. Essential quality assurance/quality control tools for assessing performance in the context of these issues will need to be developed.

The extension of HPCE to other pH conditions,

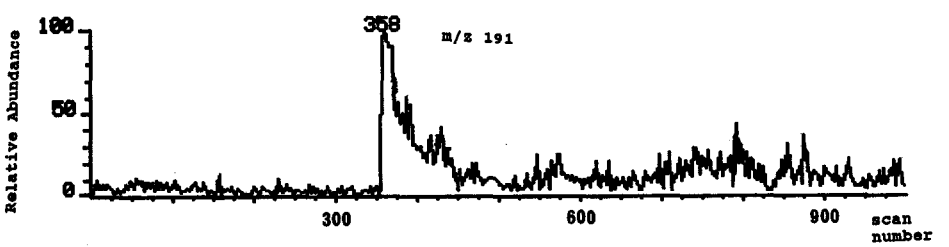

Fig. 3. Negative ion electropherogram of m/z 191 from the Stringfellow leachate using sodium borate–boric acid at pH 8.3.

buffers, and analytes within the context of environmental analysis remains an active pursuit. Whether as a stand-alone technique or as a complementary tool together with high-performance liquid chromatography and thin-layer chromatography, HPCE exhibits great potential for the separation and determination of non-volatile analytes and in characterizing environmental samples for such analytes.

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NOTICE

Although the research described in this report has been funded by the US Environmental Protection Agency, it has not been subjected to Agency review and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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