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## **Separation and detection of non-chromophoric, anionic surfactants**

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### **ABSTRACT**

The newly developed Solid Phase Reagent (SPR) permits the conductivity detection of various alkylsulfonates and alkylsulfates. In its present version, SPR is an aqueous suspension of submicron particles of a polymeric cation exchange material in the hydrogen form. The SPR is pumped into the eluent stream coming from the separation column. The post-column reaction transforms the tetrabutylammonium alkyl sulfate or sulfonate into the corresponding free acid. This changes the analytes into more conductive species. At the same time the tetrabutylammonium borate eluent is converted to the low conducting boric acid. Both types of post-column reactions greatly increase the sensitivity of detection by conductivity. The conductivity detection method with the help of SPR also makes it possible to employ gradient elution for separations of complex mixtures of alkylsulfates or sulfonates. Such gradient separations are preferably carried out on silica based reversed-phase columns, rather than on polymeric based reversed-phase columns. The latter type of columns shows better tolerance to increased levels of the organic solvents as well as higher separation efficiency.

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### **INTRODUCTION**

Solid Phase Reagent (SPR) has been introduced recently as a new method of post-column conductivity enhancement [1,2]. In its most common version, it is used as a highly dilute aqueous suspension (1% and less) of sulfonated submicron polymeric beads. SPR is capable of removing highly conductive countercations from the ion chromatographic eluents on their way from the separator column to a conductivity detector. The removal of alkaline cations from carbonate, borate or hydroxide solutions and the formation of non-conductive carbonic acid, boric acid and water leads to pronounced decrease of background conductivity contributed by the eluent. At the same time, the mostly strongly acidic analyte anions are converted from a salt form into a fully dissociated acid. Both types of ion-exchange reactions occurring on the surface of SPR beads have been shown to increase the sensitivity of detection for low-molecular-weight anionic species [3,4].

Low-molecular-weight anions, such as the anionic surfactants carrying sulfate or sulfonate functional groups have traditionally presented a great challenge to analytical chemists. These types of compounds, used in a large number of personal care products and in a variety of industrial processes are usually synthesized in rather

complicated reaction mixtures. Correspondingly, there is a great need to determine the composition of synthetic mixtures and the purity of commercial products.

Most anionic surfactant mixtures can be separated on liquid chromatographic (LC) reversed-phase columns using an ion pairing agent and an organic solvent (acetonitrile, methanol tetrahydrofuran)–water gradient. The chromophoric components of such mixtures can then be easily monitored by UV detection. This approach has been shown to be applicable for example to the determination of alkyl chain distribution of alkylbenzenesulfonates [5]. Highly sensitive detection of linear alkylsulfonates was also demonstrated using fluorescence detection [6].

Post-column derivatization followed by UV detection was reported for some non-chromophoric anionic surfactants [7,8]. Simultaneous detection of chromophoric and non-chromophoric surfactants was shown to be feasible with the help of a newly developed evaporative light scattering detector [9]. Other approaches to the universal detection of surfactants included conductivity [10] and indirect UV [11].

The post-column addition of SPR discussed in this article converts the alkylammonium borate eluent into nearly non-conducting boric acid and the anionic surfactants from low conducting alkylammonium salts to highly conductive alkylsulfuric and alkylsulfonic acids. This type of conversion for the enhancement of conductivity signals can be carried out without difficulty in gradient mobile phases containing high levels of an organic solvent. Use of silica based reversed-phase columns also allows a greater range of concentrations of an organic solvent in gradient separations.

## EXPERIMENTAL

### *Instrumentation*

The LC system used in our experiments consisted of Waters Action Analyzer (Waters Chromatography Division of Millipore, Milford, MA, U.S.A.), the Waters Novapak C<sub>18</sub> separation column and Waters Reagent Delivery Module (RDM) for the post-column addition of aqueous suspension of the Solid Phase Reagent (SPR). Waters 431 conductivity and programmable 490 UV detectors were connected in series for most of the experiments. The UV detector was placed between the column outlet and the mixing tee for the addition of SPR.

### *Chemicals*

The eluents were: (A) Milli Q water (used also to prepare all other aqueous solution for this investigation; Millipore, Bedford, MA, U.S.A.) containing 0.5 mM tetrabutylammonium borate (TBAB), and (B) acetonitrile (HPLC grade, J. T. Baker, Phillipsburg, NJ, U.S.A.) containing 0.5 mM TBAB. A concentrate containing 25 mM TBAB was used for the preparation of eluents. This concentrate was prepared by neutralizing a 40% aqueous solution of tetrabutylammonium hydroxide (Aldrich Chemical Company, Milwaukee, WI, U.S.A.) with a dilute reagent grade boric acid (J. T. Baker) and by final dilution to 25 mM using the Milli Q water.

Standards of alkyl and arylsulfonates were obtained from the following sources: Chem Service, West Chester, PA, U.S.A.; Eastman-Kodak, Rochester, NY, U.S.A.; Fluka Chemie, Buchs, Switzerland; and Aldrich.

*Solid Phase Reagent<sup>a</sup>*

The SPR was obtained from Waters as a concentrate containing *ca.* 12% solids (SPR-H<sup>+</sup>) and diluted for use to contain *ca.* 1% solids and a cation-exchange capacity of not less than *ca.* 50 mequiv./l. A complete description of various applications of this new reagent is given elsewhere [1-3]. The efficient removal of tetrabutylammonium ions by SPR was verified by <sup>1</sup>H NMR. After the addition of the same volume of 1% SPR suspension in <sup>2</sup>H<sub>2</sub>O to 5 mM solutions of TBAB in <sup>2</sup>H<sub>2</sub>O, corresponding proton signals (between 0.9 and 3.3 ppm) decreased below the detection limit of the NMR method.

The enhancement of the conductivity signal by SPR was confirmed by the series of measurements shown in Table I.

TABLE I  
ENHANCEMENT OF CONDUCTIVITY SIGNAL BY SPR

Solution	Conductance ( $\mu$ S)	$\Delta\mu$ S	% Change
a Water	0.68		
b SPR-water (1:9)	12.0		
c 0.5 mM TBAB	29.4		
d b + c (1:3)	6.99		
d - c		22.41	- 76.2
e d containing 1 $\mu$ g/ml C <sub>12</sub> SO <sub>3</sub> Na	8.64		
e - d		1.65	23.6
f c containing 1 $\mu$ g/ml C <sub>12</sub> SO <sub>3</sub> Na	30.4		
f - c		1.0	3.4

The concentration of dodecylsulfonate in solutions e and f was chosen to correspond approximately to an average concentration in a peak zone after a 500-ng injection (10 ppm in 50  $\mu$ l). The expected reduction of the conductivity background due to eluent and the enhancement of the analyte signal (from 3 to 23% for dodecylsulfonate) are thus confirmed.

## RESULTS AND DISCUSSION

*Separations of standard mixtures of alkyl and arylsulfonates*

The separation of a standard mixture of linear alkyl sulfonates is shown in Fig. 1. The gradient curves have been overlaid on this and the following chromatogram. The concentration of acetonitrile in the eluent is increased linearly from 15 to 60%, while the concentration of the tetrabutylammonium borate remains unchanged. The two unknown peaks occurring around 5 min and between the pentane and hexane sulfonates in Fig. 1 were combined impurities stemming from one batch of tetrabutylammonium hydroxide.

Without the employment of the post-column reaction replacing the tetrabutylammonium cation by hydronium ions by means of ion-exchange groups on the surface of SPR, the conductivity detector would register only high background signal

<sup>a</sup> Patent pending.

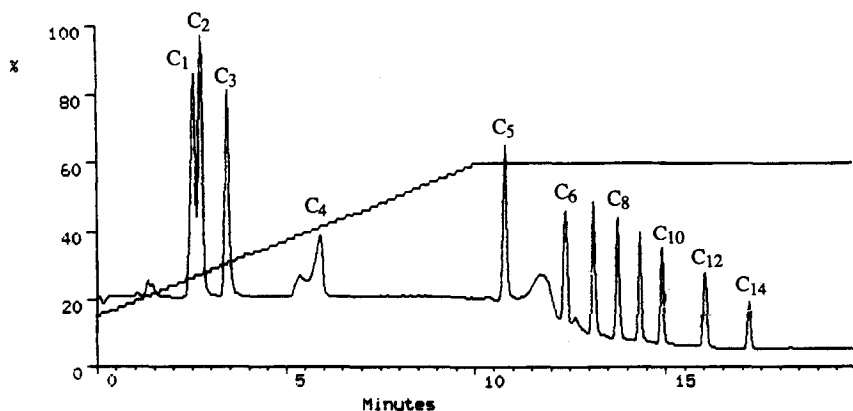


Fig. 1. Linear alkylsulfonate standards [methanesulfonate-(C<sub>1</sub>) to tetradecylsulfonate(C<sub>14</sub>)]. The gradient curve is overlaid on the chromatogram. Initial conditions: 85% A-15% B, A: aqueous 0.5 mM tetrabutylammonium borate (TBAB), B: 0.5 mM TBAB in acetonitrile. Column: Novapak C<sub>18</sub>. Flow-rates: 1 ml/min A + B, 0.3 ml/min SPR diluted to 50 mequiv./l. Detection by conductivity. Injection: 100  $\mu$ l standard solution containing *ca.* 10 ppm of sulfonates.

due to borate, and the separated peak zones due to 5–10 ppm alkylsulfonates would remain undetected. The submicroscopic particles of SPR (*ca.* 0.2  $\mu$ m) are too large to participate to any extent in the transport of electric charge that would affect the conductivity of the solution. After the attachment of the tetrabutylammonium ions to the surface functionalities on the beads, both the beads and the alkylammonium cations pass through the conductivity cell undetected. By exchanging the alkylammonium cations for hydronium ions, the conductivity background of borate is lowered to a level enabling a sensitive detection at ppm concentrations. At the same time, the sulfonates are converted by SPR to their more readily detectable free acid form.

A simultaneous separation of alkylsulfates and alkylsulfonates is presented in Fig. 2. The sulfates were added at a lower concentration than the sulfonates for ease

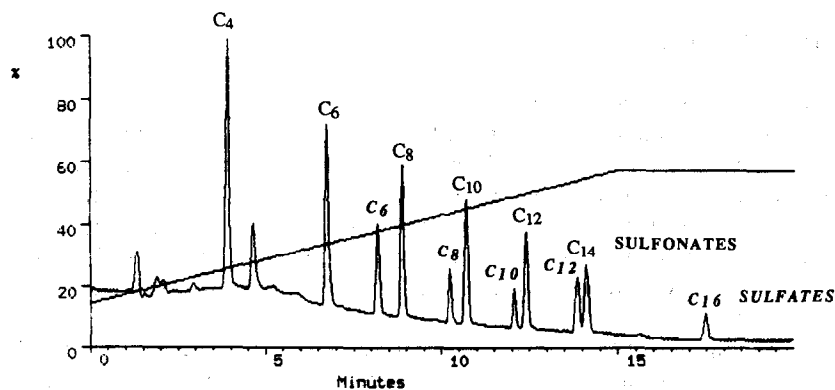


Fig. 2. Mixture of linear alkylsulfonates and alkylsulfates. Injection: 100  $\mu$ l of standard solution containing 5 ppm sulfates and 10 ppm sulfonates. The gradient curve is overlaid on the chromatogram. Other conditions were as indicated in Fig. 1.

of identification. The gradient range remained the same as in Fig. 1 (15 to 60%), but the gradient curve is not as steep as in the previous chromatogram: the composition of 60% acetonitrile is reached after 15 min, not in 10 min as in Fig. 1. This change of gradient conditions makes it possible to improve the resolution of the three closely eluting peak pairs in the standard mixture of sulfates and sulfonates. It can be noted that all sulfonates included in the standard mixture show a weaker retention than the corresponding homologous sulfates. This is directly attributable to their relatively higher polarity and to their lower tendency to ion pair with the tetrabutylammonium cation. The peak eluting after the butanesulfonate is an unidentified impurity.

Figs. 1 and 2 illustrate both, the capabilities and limitations of chromatographic separations of anionic surfactant mixtures. Organic chemistry describes a multitude of ways by which polarity and ion pairing behavior of compounds containing an identical number of carbon atoms can be broadly modified. Even the least significant of these modifications will have a pronounced influence on the retention behavior on chromatographic columns.

The separation in Fig. 3 which was obtained by using UV and SPR-conductivity detection simultaneously, is another example of varying retention times for sulfo-

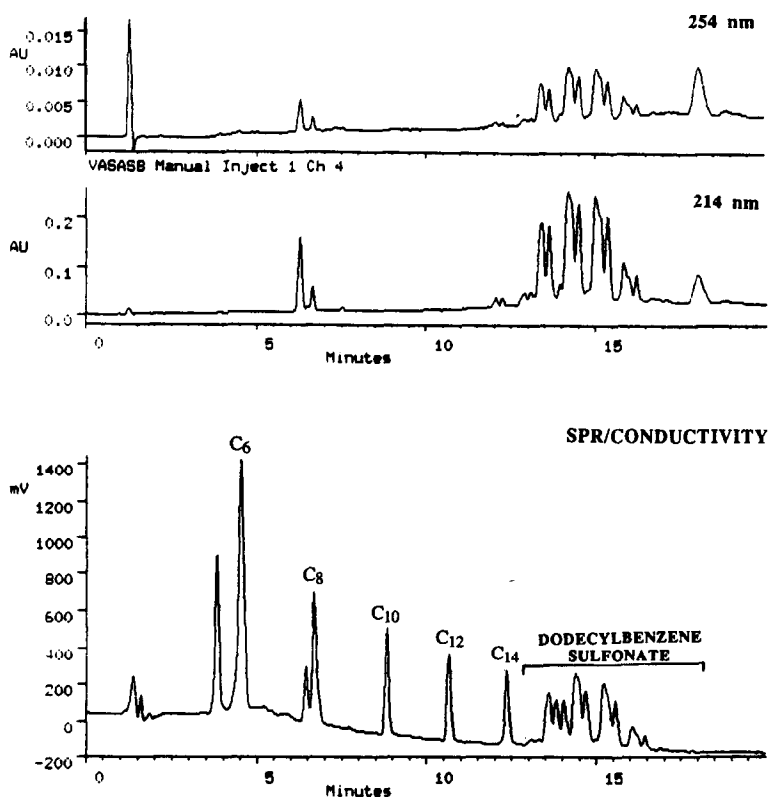


Fig. 3. Mixture of linear alkylsulfonate with dodecylbenzenesulfonate standards. The upper two chromatograms were obtained with UV detection at 254 and 214 nm. Linear gradient from 15%B to 60%B. Injection: 100  $\mu$ l standard with all components at 10 ppm. Other conditions as in Fig. 1.

nates having the same number of carbon atoms. The dodecylbenzenesulfonate which was added to the mixture of alkylsulfonates is not a single compound as indicated by its manufacturer, but rather a mixture of at least eight different structural isomers.

The simultaneous use of SPR-conductivity and UV detection offers several advantages in the analysis of complex mixtures of organic sulfates and sulfonates. It is possible by this approach to distinguish between the aromatic and non-aromatic

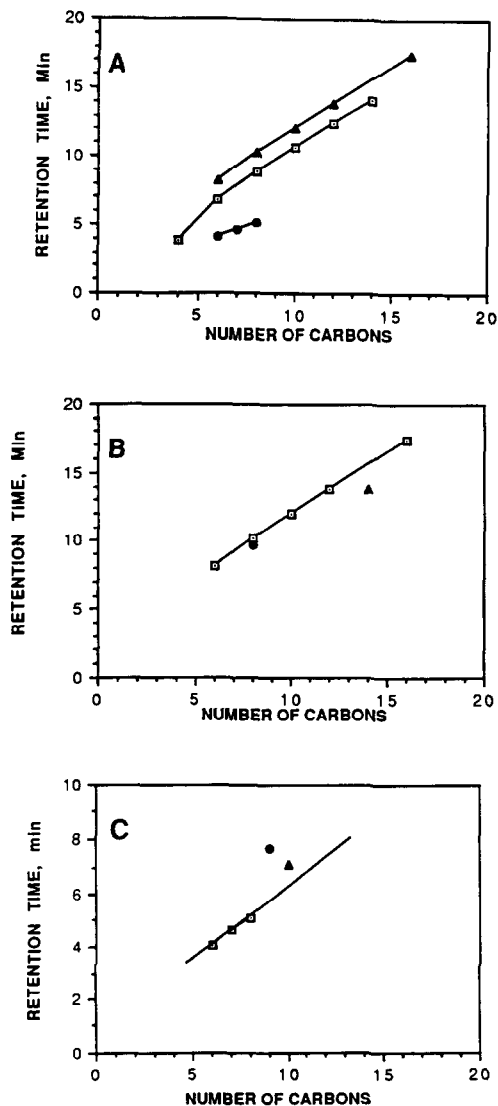


Fig. 4. (A) Methyl group addition to alkylsulfonates (□), alkylsulfates (▲) and arylsulfonates (●). (B) Effect of chain branching of alkylsulfates (□) on retention behaviour (● = 2-ethylhexylsulfate; ▲ = *sec*-tetradecylsulfate). (C) Effect of carbon addition to benzenesulfonate (□) on retention behaviour (● = cumenesulfonate; ▲ = naphthalensulfonate). Chromatographic conditions as in Fig. 2.

components. Comparisons of UV and conductivity recordings can also reveal the presence of impurities that would otherwise remain undetected. Furthermore, the two different detection modes provide useful information about the possible composition of unknown impurities. Consider for example, the unknown peak preceding the peak of hexanesulfonate in the conductivity trace in Fig. 3. Its absence in the UV recordings, together with the relatively short observed retention time, can be taken as a first indication of the possibility, that this signal may be due to an isomeric alkylsulfonate.

Additional results summarizing the influence of isomeric modifications on the retention behavior are listed in Fig. 4A–B,C. Fig. 4A compares the homologous series of alkylsulfates and sulfonates from Fig. 2 with benzene, toluene and xylenesulfonates. The Fig. 4B compares the influence of two different types of branching of alkyl chains on the retention behavior of corresponding alkylsulfates. It appears from this limited experimental data, that the relative position of secondary carbon atoms in respect to the sulfate group plays an important role. The secondary tetradecylsulfates is observed to deviate more from the homologous series than the 2-ethylhexylsulfate. As seen in Fig. 4C both, naphthalenesulfonate and cumenesulfonate have longer retention times than the benzenesulfonate indicating two other possible types of homologous series influencing the retention behavior of arylsulfonates.

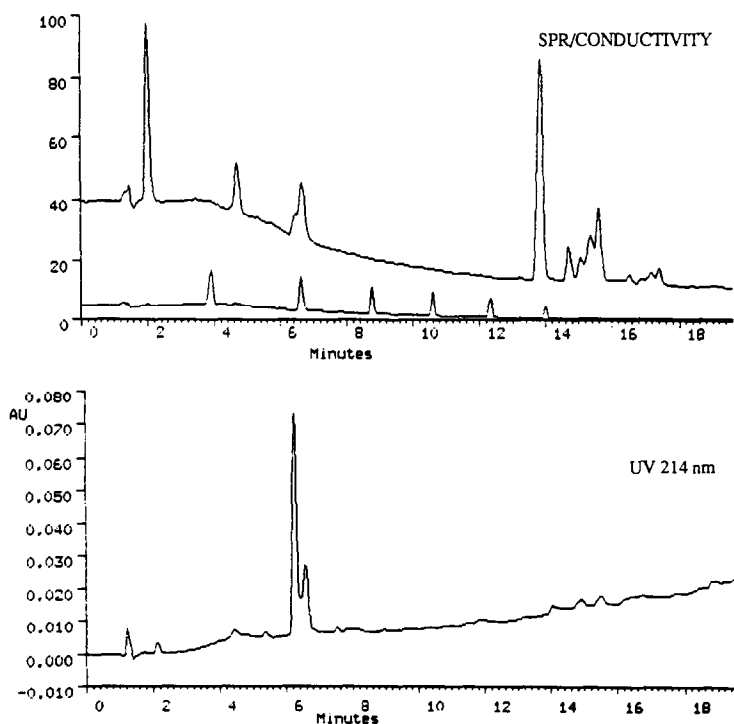


Fig. 5. Separation of components of a commercial shampoo (1:1000 dilution, 100  $\mu$ l injected). Both UV and SPR-conductivity were used for detection. The overlaid standard shows the peaks for C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub> and C<sub>14</sub> linear alkylsulfonates. Chromatographic conditions as in Fig. 2.

There are 3314 possible structural isomers for the homologous series of alkylsulfonates ( $C_4$  to  $C_{14}$ ) separated in Fig. 2. This number, perhaps better than anything else, shows why the retention times from a LC method can not be used as the only proof of identity of unknown peaks.

#### *Synthetic mixtures of organic sulfonates*

The next two chromatograms show separations of two different types of commercial surfactant mixtures—a hair shampoo (Fig. 5) and a common laundry detergent (Fig. 6). The high resolving power of the discussed method can be put to a good use in the quality control and other assays carried out by industrial laboratories. “Good” production results could possibly be correlated to a certain shape of the “finger print” separations. Possible fluctuations of quality of production could then be easily detected by an observed emergence of additional peaks or by shifts in the concentration ratios among the existing peaks.

Simultaneous use of SPR–conductivity and UV detection generates additional information for the analysis of unknown mixtures. Non-aromatic or aromatic components can be easily recognized from the relative signal intensities by conductivity and UV. Overlaid separations of homologous alkyl series ( $C_4$  to  $C_{14}$ ) make it possible

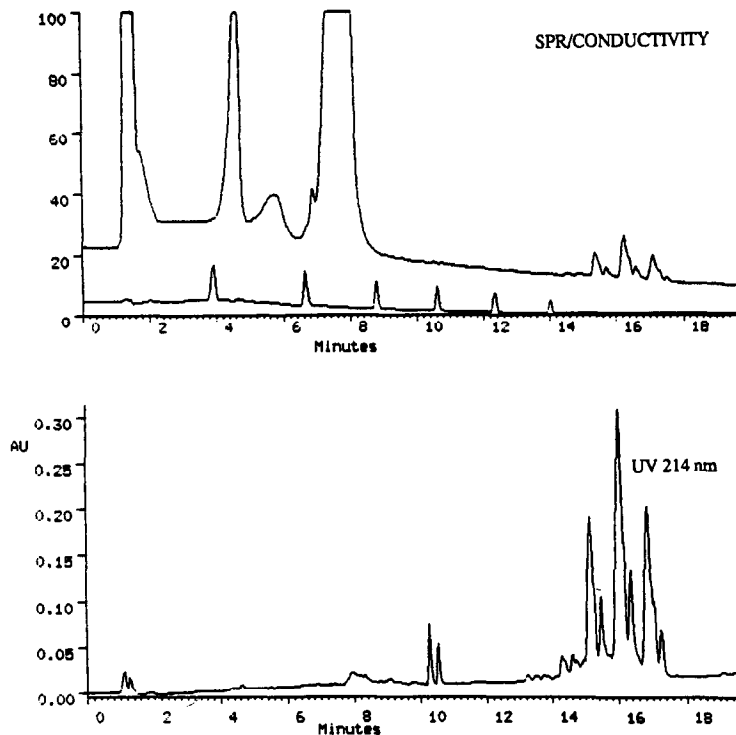


Fig. 6. Common laundry detergent after 1:1000 dilution with UV and SPR–conductivity detection. The overlaid standard shows the peaks for  $C_4$ ,  $C_6$ ,  $C_8$ ,  $C_{10}$ ,  $C_{12}$  and  $C_{14}$  linear alkylsulfonates. Chromatographic conditions as in Fig. 2.



to estimate the approximate molecular weight of the unknown components in the reaction mixture.

## CONCLUSIONS

Combined use of solvent gradients on silica based reversed-phase columns and SPR-conductivity detection provide a new approach to the analysis of complicated organic sulfonate and sulfate mixtures. Additional information can be gained by a simultaneous utilization of UV detection in series with the SPR-conductivity detection.

The nearly limitless number of structural parameters influencing the retention behavior makes it very difficult to utilize this method for positive identification of unknown components in complex mixtures. However, the technique can be highly useful in the fingerprinting of synthetic mixtures and in the assay of commercial detergent products.

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