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Review

Methods of analysis of polar aromatic sulfonates from aquatic environments

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Abstract

Methods for the analysis of aromatic sulfonates, such as linear alkylbenzene sulfonates (LAS) and (amino- and hydroxy-substituted) benzene and naphthalene sulfonates, from aqueous media are reviewed. All analytical steps including the extraction from water, clean-up from co-extracted substances, chromatographic separation and detection, and methods of identification of these compound classes are described and discussed. The techniques employed are solid-phase extraction, various modes of high-performance liquid chromatography (HPLC), capillary electrophoresis, gas chromatography (GC), GC–mass spectrometry, liquid chromatography–mass spectrometry, continuous flow- and flow injection–mass spectrometry, and spectroscopic methods. A remarkable gap becomes obvious between novel analytical methods developed with standard mixtures and those methods readily employable for environmental analysis. Finally, suggestions for future analytical developments are given.

Keywords: Reviews; Water analysis; Environmental analysis; Sulphonates, aromatic; Alkylbenzenesulphonates; Benzenesulphonates; Naphthalenesulphonates

Contents

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1. Introduction

During the last decade the occurrence, fate, and effects of linear alkyl benzene sulfonates (LAS) in aquatic environments were extensively studied, LAS thus represent the most prominent and best investigated group of aromatic sulfonates to date. In the last few years it was realized that many other groups of sulfonated aromatic compounds are applied in and subsequently released from industrial processes and that these compounds might also be of relevance for the aquatic environment.

Table 1 summarizes groups of sulfonated aromates, their structures and uses. Beside LAS [1], aromatic sulfonates are used in consumer detergent products and work as fluorescence whitening agents (FWA). Amino- and hydroxynaphthalenesulfonates (ANS, HNS) are employed as intermediates in dye-production. Alkylated napthalenesulfonates are used as suspending and wetting agents, dispersants, and stabilizers [2]. Condensation products, also referred to as sulfonated polyphenols, are applied as synthetic tanning agents [3] and sulfonated naphthalene formaldehyde condensates as superplasticisers for cement [4]. Lignosulfonates find applications as dispersing and flotation agents and are employed in enhanced oil recovery, as are petroleum sulfonates [2].

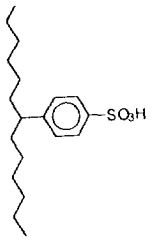
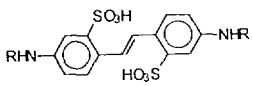
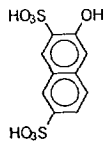
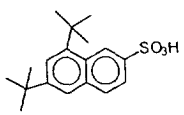
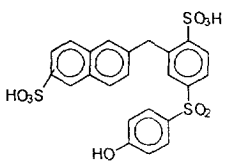
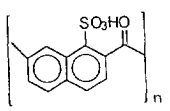
The limited attention previously paid towards aromatic sulfonates other than LAS within aquatic environments might be due to their apparently comforting ecotoxicological potential: the aquatic toxicity of aromatic sulfonates appears to be small, and the risk of bioaccumulation is limited, since the pK_{ow}-values typically range below 2 [5].

However, low K_{ow}-values are conversely indicative of a high mobility within the aquatic system. Contrary to LAS [6,7], polysulfonated aromates and substituted monosulfonated aromates exhibit only limited biodegradability [3,8]. Solubility enhancement of hydrophobic xenobiotics deposited within soils and sediments is a side-effect of surfactant release into aquatic systems that is presently being discussed [9–11]. These properties of sulfonated aromatic compounds make them potentially hazardous with respect to surface and groundwater and are of concern regarding drinking water quality. Intensified investigation of the occurrence and fate of sulfonated aromates in aquatic environments is required, calling for the development of appropriate analytical methods.

As mentioned above, investigations within the aquatic system concentrated on the occurrence and fate of LAS as did the development of analytical techniques. However, physical properties of sulfonated aromatic compounds differ widely, with pK_{ow}-values between 2.7 and −1.6 (Table 1), and methods of LAS analysis proved insufficient for the more polar sulfonates, as regards extraction, separation and identification. Modified procedures had to be developed, and use was made of novel analytical techniques such as capillary electrophoresis.

This review focusses on those groups of aromatic sulfonates dominated by the sulfonate substituent, such as LAS and naphthalenesulfonates. The analysis of complex substances bearing sulfonate moieties in addition to

Table 1
Groups of aromatic sulfonates: their structures, uses and octanol-water partition coefficients (pK_{ow}). References according to the text

	Compound class	Use	pK_{ow}
	linear alkylbenzene sulfonates (LAS)	detergents	1.2–2.7 [1]
	stilbene sulfonic acids etc.	fluorescent whitening agents (FWA) in detergent products	−4 to 1 [66]
	amino- and/or hydroxy-naphthalene sulfonates	intermediates in dye-production	~−1.6 [5]
	alkyl naphthalene sulfonates	suspending and wetting agents dispersants stabilizers	
	sulfonated polyphenols	synthetic tanning agents	<−0.8 [3]
	sulfonated naphthalene-formaldehyde condensates (SNF)	superplasticiers for cement	

many other functional groups, such as azo-dyes and FWA, will not be covered.

Although wastewater might not be considered an integral part of the aquatic environment, its analysis is incorporated into this review wherever indicated, since new analytical methods are frequently developed for wastewater analysis, before being applied to fresh- and seawater.

2. Extraction

2.1. LAS

Analogous to the colorimetric determination of anionic surfactants by the methylene blue active substances (MBAS) procedure [12], ion-pair liquid–liquid extraction (LLE) with the

methylene blue cation was employed for the extraction of LAS from river water [13]. The solvent sublation method of Wickbold [14] has never been of great importance in anionic surfactant extraction, but it is still being used for the analysis of LAS from seawater [15,16].

Within the last decade, solid-phase extraction (SPE) has been developed into the standard method of LAS extraction from wastewater and surface waters. C_{18} phases are most frequently employed [17–20], but C_8 is also reported [21,22]. Typical recovery rates from wastewater, wastewater treatment plant effluent, and receiving waters are above 90% for the total LAS amount [19,21], with some systematic differences between the homologues [23]. Most authors found 0.5–1 g l^{-1} of sorbent sufficient, while the use of 10 g for the extraction of 1 l of river water was very recently reported [24]. Extraction on C_{18} disks might be superior to cartridges in terms of extraction speed [25,26].

However, hydrophobic C_{18} and C_8 phases exhibit broad extraction properties. Co-extracted aromatic substances such as humic acids from surface waters or nonionic surfactants (NPEO) from wastewater might interfere with the chromatographic analysis of LAS. These difficulties increase with decreasing analyte concentrations, namely in surface waters. In these cases, a clean-up is required prior to LAS analysis, which might be performed by anion-exchange chromatography of the SPE eluates [27]. Some authors performed a second clean-up on C_{18} cartridges [24]; the sequence might also be inverted with C_8 prior to anion exchange [15]. Fujita et al. [19] employed gradient elution of the C_{18} extraction cartridge in order to remove more polar interferences prior to LAS elution. Co-extraction of less polar organics might be diminished by extraction on a less hydrophobic C_2 phase [27], but recovery of LAS was affected in some cases. An alternative procedure was presented by Marcomini and Giger [28]: HPLC analysis was optimized, so that co-extracted NPEO from wastewater are separated from LAS and parallelly detected.

Instead of silica-based reversed phases, Di Corcia et al. [29] used a deactivated charcoal (Carbopack B) for LAS extraction, which provides specific interaction with organic anions due to positively charged surface places. LAS were, therefore, quite specifically extracted with recovery rates of 91–96%, and a sample clean-up prior to analysis was unnecessary. However, due to the limited number of positive surface charges, these cartridges are easily overloaded [29].

Enrichment of LAS on XAD-resins [30,31] or a weak anion-exchanger [32] is reported. Field et al. [32] employed a complex isolation/clean-up procedure for LAS, dialkyltetralin sulfonates (DATS), and sulfophenyl carboxylates (SPC) from groundwater. Freeze-drying was sporadically employed [33].

2.2. Polar sulfonates

SPE, common for LAS, is less straightforward for more polar compounds lacking a hydrophobic alkyl chain such as naphthalene sulfonates (NS), benzene sulfonates (BS), and their amino- and hydroxy-derivatives. With K_{ow}-values up to four orders of magnitude below LAS, these substances exhibit no retention on C_{18} reversed-phase material. However, SPE is suitable if these sulfonates are paired with an organic cation such as tetraalkylammonium. Ion-pair formation with methylene blue [34] or tetrabutylammonium (TBA) [35,36] was also used for LLE of polar sulfonates and dyes.

Miyoshi et al. [37] invented the combination of ion-pairing (with cetyltrimethylammonium, CTMA) and SPE for the extraction of ANS from aqueous environments. Schullerer et al. [38] used TBA to extract eleven sulfonic and disulfonic acids from standard solutions. Recoveries were lowest for nitro- and diamino-substituted sulfonic acids (50–72%), while BS and NS reached 100%. The method was applied to surface water, bank filtrate, and wastewater effluents.

Brouwer et al. [39] implemented ion-pair extraction in their on-line trace enrichment system with PLRP-S. Recoveries were almost quantitative except for amino-substituted sulfonates (70–80%). However, interference from humic sub-

stances was observed, which was reduced by the addition of sodium chloride prior to extraction, but this affected the recovery of the most polar sulfonates. Ion-pairing with CTMA was reported [40], and recovery rates in the range of 80–110% from river water were obtained. With the more hydrophobic CTMA instead of TBA, amino-substitued sulfonates appear to be more effectively extracted [40]. Ion-pair SPE with TBA of various sulfonates worked poorly with spiked industrial wastewater of unknown source, though it worked well with synthetic samples [41]. Extraction of sulfonated polyphenols with TBA from tannery wastewater was not negatively affected by salt contents of up to 20 g l^{-1} [42].

Usually, the ion-pairing agent is added to the aqueous sample prior to extraction. Alternatively, Zerbinati and Ostacoli [43] saturated the solid phase with octyltrimethyl ammonium acetate, thereby producing an anion-exchange column, and applied the sample afterwards. Several anthraquinone sulfonates (AQS) and disulfonates (AQDS), naphthalene disulfonates (NDS), and hydroxynaphthalene disulfonates (HNDS) were obtained from standard solutions with 80–120% recovery, but the ion-exchange capacity and the breakthrough volume were low. The authors observed AQS to be incompletely desorbed from C_{18} cartridges, when the CTMA-cation was employed.

Lange et al. [44] determined eleven aromatic sulfonates, some of them being substituted with amino, hydroxy- and nitro-moieties, by on-line ion-pair extraction on C_{18} and applied this method to surface water and bank filtrate, media which are not hampered by high salt contents. Again, extraction of amino-substituted sulfonates proved problematic.

Although being a valuable tool for the extraction of aromatic sulfonates from aqueous media, ion-pair SPE suffers from three major drawbacks. (i) Co-extraction of interfering dissolved organic compounds is an even larger problem in ion-pair SPE than in conventional RP-SPE [41]. Thus, the need for sample clean-up prior to analysis is more urgent. The lack of interaction between polar aromatic sulfonates and C_{18}-material allows the use of a C_{18}-cartridge for the removal of less polar substances *prior* to ion-pair extraction [37,40,41]. (ii) It exhibits limited extraction efficiency for very polar sulfonates, namely amino- and amino-hydroxy-substituted derivatives [44]. The breakthrough volumes might be low when employing TBA as cation [45]. The use of CTMA might help to some extent [43]. (iii) High contents of inorganic salts might substantially affect recoveries. While a supporting salting-out effect is observed in conventional RP-SPE of LAS, inorganic anions compete with the sulfonate anions for the organic cation, thereby decreasing the extent of ion-pair formation of the sulfonates and their extraction efficiency. This is of concern in the analysis of industrial wastewater [41] and would hamper the extraction from seawater.

An alternative approach avoiding some of these problems was only recently presented. Altenbach and Giger [45] revealed that deactivated charcoal (Carbopack B) is also suitable for the specific extraction of polar aromatic sulfonates from industrial and domestic wastewater without ion-pairing. Like Di Corcia et al. [29], they suggested ionic interactions to be responsible for the specific adsorption of anionic species, thereby reducing the interference from humic substances. Ion-pair RPLC analysis could be performed without an intermediate clean-up. However, elution of amino sulfonates was difficult. Interferences by elevated salt contents appear to be weaker on Carbopack B than on ion-pair SPE. Chemically modified polystyrene–divinylbenzene resins [46], which have now become commercially available, might also offer suitable extraction properties for polar sulfonates.

Extraction of polar sulfonates by anion-exchange phases was unsuitable. While the extraction might be complete, polysulfonated aromates are only incompletely eluted from these phases [41,45]. Tsukioka [47] obtained 86–95% recovery of 0.2 μg l^{-1} amounts of AQS from spiked river water with a weak anion-exchange column. Lyophilization, followed by resolution in methanol and precipitation of inorganic salts by the addition of acetone might be suitable for the preparation of single extracts [48].

3. Liquid chromatography

3.1. Reversed-phase HPLC

To date, reversed-phase HPLC (RPLC) must be considered the routine method for LAS analysis.

3.1.1. Factors influencing RPLC

While the alkyl chain length homologues (predominantly C_{11} to C_{13}) are well resolved on C_{18} phases, the resolution of benzene ring isomers remains incomplete [15,17,18,20,21,28,49]. Even with 3-μm material the innermost phenyl isomers cannot be separated (Fig. 1). If it is not necessary to know the isomeric distribution of the homologues, less polar column material is favorable. C_8- [18,19,29] or C_1-material [27] was used instead of C_{18}, and all phenyl isomers co-elute under these conditions. This enhances sensitivity and simplifies distinguishing between the homologues. Acetonitrile [17-19,21,49] or methanol [15,29,50] is employed as the organic modifier. In all cases, LAS separation requires electrolyte addition to force interaction with the stationary phase. Sodium perchlorate (0.02 to 0.15 *M*) [21,23] has prevailed from the beginning, although other salts would provide the same effects [49].

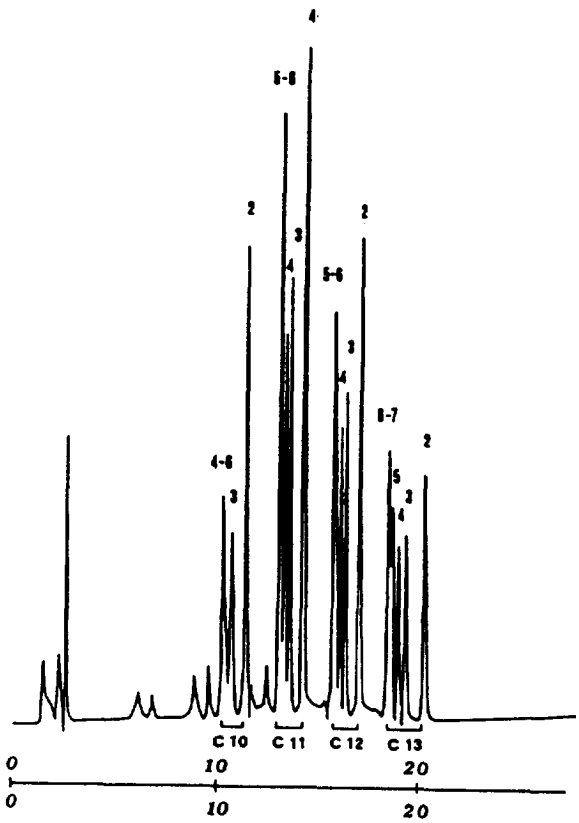


Fig. 1. RPLC chromatogram of a commercial LAS mixture. Spherisorb S3 ODS II column, 3 μm, 250 × 4 mm I.D.; fluorescence detection λ_{ex} 225 nm, λ_{em} 295 nm. Numbers refer to the benzene isomers, i.e., the position of the benzene ring at the alkyl chain. Reproduced with permission from Ref. [18].

Fluorescence detection (225 nm excitation, 290 nm emission) is to be preferred with respect to selectivity and sensitivity [15,17,18,20,27,29,50], but UV detection is sporadically employed [19,21].

3.1.2. Application to environmental analysis

RPLC with fluorescence detection was first used by Nakae et al. [50] for the analysis of LAS from river water by direct injection. This was possibly due to high LAS levels of 0.1–0.5 mg l^{-1}. Several reports are available on the determination of LAS in influents and effluents of wastewater treatment plants [20,21,23,24,27,29] and receiving waters [19,20,21,24,27,29] after SPE by RPLC. With fluorescence detection, method detection limits for total LAS range from 0.8–20 μg l^{-1} [23,27,29]. Seawater was only sporadically analyzed: Tokyo bay water was analyzed for LAS by Kikuchi et al. [17]. Employing SPE of 2-l samples, a detection limit of 0.1 μg l^{-1} for single components was obtained by RPLC with fluorescence detection. After solvent sublation and two clean-up steps, LAS were analyzed on C_{18} with fluorescence detection [15]. A detection limit of 0.4 μg l^{-1} from 1-l samples was reported, corresponding to 3 times the blank LAS content. Marcomini et al. [18] analyzed LAS in lagoon water. LAS analysis in groundwater influenced by landfill-leachate, together with its synthesis byproducts (DATS) and its metabolites (SPC), has been reported [32]. Meanwhile, numerous applications of the developed methods reviewed above have been published, but need not be discussed here.

3.2. Ion-pair RPLC

With increasing polarity of the sulfonates, e.g., due to substitution with amino- and hydroxy-groups or to polysulfonation, the interaction of the analytes with the reversed-phase column becomes too weak to obtain separation. Although separation of BS, ANS, hydroxybenzene sulfonates (HBS), other monosulfonates and dyes by RPLC was achieved with high inorganic modifier concentrations [51,52], ion-pair RPLC has become the method of choice. Since its invention, the underlying mechanisms have been a matter of debate. The following two fundamental retention mechanisms are proposed.

(i) The *ion-exchange mechanism*. Assuming that the stationary phase is saturated with the organic cation continuously delivered with the mobile phase, the analytes are separated according to the strength of ionic interaction with the fixed organic cation [53,54].

(ii) The *ion-pair formation and hydrophobic interaction*. A two-step retention mechanism is suggested: first, the sulfonates form ion-pairs with the organic cation dissolved in the mobile phase; secondly, these ion-pairs are separated due to hydrophobic interaction with the stationary phase [55]. Retention thus depends on the strength of ion-pair formation and the affinity of the ion-pairs towards the stationary phase.

Experimental evidence for both mechanisms was obtained [55,56]. Indeed, they might represent the pure theoretical extremes of the actual situation.

3.2.1. Factors influencing ion-pair RPLC

Numerous studies have been performed to investigate the parameters influencing the ion-pair RPLC separation of aromatic sulfonates. Most of them were performed with NS, NDS, BS, and AQS, and with various amino- (ANS, ABS) and hydroxy- (HNS, HNDS) substituted as well as mixed derivatives [38,43,54,57–61]. Ion-pair RPLC of sulphonated phenols [62] and sulfonated polyphenols [42] was also performed. The separation of LAS mixtures [31,57] and their degradation products sulfophenyl carboxylates (SPC) has been reported [31]. Sulfonated azo-dyes [63] and FWA [64–66] can also be separated by means of ion-pair RPLC. The following factors turned out to be of importance.

(i) The eluent pH [40,54,55,57] was frequently investigated and is recommended to be above the analytes' pK_a-value, in order to ensure dissociation of the acidic groups and strong ion-pair formation [57]. This effect was demonstrated with the weakly acidic SPC [31]. Although an increasing pH generally leads to increasing retention times, the processes involved appear to be complex, especially for polyfunctional sulfonates such as amino- and hydroxysulfonates. Typical pH-values vary from slightly acidic (pH 5) [57] to neutral [43]. For stable chromatographic conditions the eluents' pH should be selected within a range where small deviations in pH have only a limited effect on the retention of the analytes.

(ii) Several alkylammonium cations were compared [54,56,58,62]. The most frequently used ion-pair agents are CTMA [31,40,58] and TBA [38,39,41,42,44,45,56,57,59], with the symmetric TBA being favored to date. Effects of less hydrophobic cations such as tetramethyl- or tetraethylammonium might be too weak for substantial retention [56,62]. Bromide and hydrogensulfate are the typical anions, the latter being preferred for UV detection at low wavelengths.

(iii) Retention is further intensified by increasing counter-ion concentrations [55–59]. In the case of polysulfonated compounds, it additionally influences the elution order: if the concentration of the ion-pairing agent is sufficiently high to pair all sulfonate groups, monosulfonates elute first, followed by di- and trisulfonates. At low concentrations, however, only one sulfonate group per molecule is paired, and the elution order is inverted [56]. Drastic increases in retention were observed between 1 and 5 m*M* of TBA [57] (Fig. 2). Typical concentrations are, therefore, in the range of 5–10 m*M*.

(iv) Electrolyte concentration (inorganic modifier) further influences the retention. It decreases with increasing electrolyte concentration, since its inorganic anions compete with the analyte in ion-pair formation [55,56]. This effect has to be

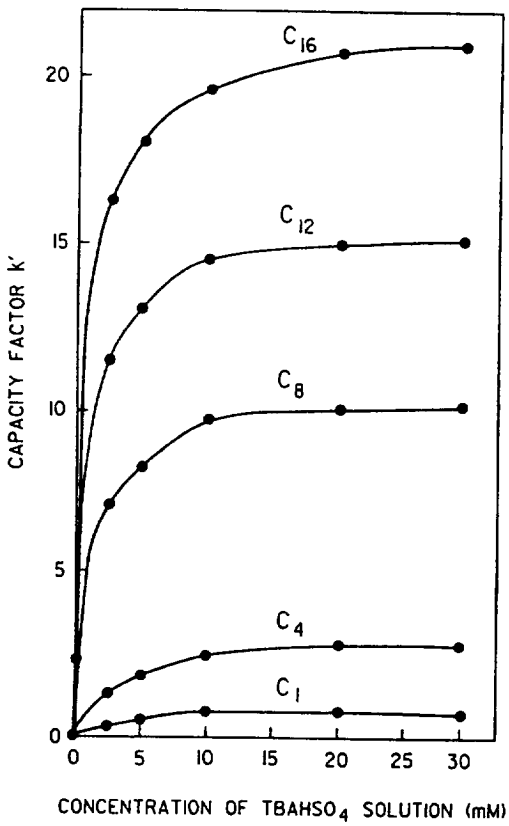


Fig. 2. Effect of TBA concentration on capacity factors of LAS in ion-pair RPLC. Reproduced with permission from Ref. [57].

considered if aqueous samples with high salt contents are analyzed directly.

(v) The effects of methanol or acetonitrile as organic modifiers have been frequently investigated [45,56,58–60,62]. The choice of a suitable organic modifier depends on the actual analytical task.

(vi) Little attention has been paid to column temperature, although it has a strong influence on separation [42,59]. Zou et al. [59] calculated ΔH^0 values from van't Hoff plots for various sulfonates in order to investigate the mechanisms underlying ion-pair RPLC. Since each ion pair has its own energy balance for ion-pair formation and adsorption processes, temperature variations not only influence total analysis time, but might alter the elution order of sulfonate mixtures.

On the one hand, the multitude of factors influencing separation in ion-pair RPLC provides a powerful means for the separation of polar aromatic sulfonates, although full use has not been made of it yet. On the other hand, all of the above-mentioned factors need to be carefully controlled in order to ensure reproducible chromatographic conditions.

3.2.2. Application to environmental analysis

While studies on the factors influencing ion-pair RPLC of aromatic sulfonates are frequently reported, reports of its application in environmental analysis are, although now increasing, still comparatively rare. Taylor and Nickless were among the first [31] to employ ion-pair RPLC for the separation of biodegradation products of LAS. Miyoshi et al. [37] reported the separation of several ANS extracted from waters and sediments. Schullerer et al. [38] analyzed sulfonated aromatic compounds in surface water, bank filtrate, and wastewater treatment plant effluents. Several signals were detected by means of UV and fluorescence detection, but only one of them could be ascribed to a certain compound. Brouwer et al. [39] provided an example of surface water monitoring with an ion-pair modification of their on-line trace enrichment system and identified AQDS in River Rhine water after an accidental spill in Germany. They reported detection limits of 0.2–3 $\mu g\ l^{-1}$ from 30-ml samples.

Zerbinati et al. [40,43] identified four aromatic sulfonates in river water by means of ion-pair RPLC with CTMA on a C_8-phase. Several unidentified sulfonates were also detected and detection limits of 1–60 $\mu g\ l^{-1}$ reported. Reemtsma et al. [42] determined sulfonated polyphenols in tannery wastewater and the effluent of a biological treatment pilot plant.

Only recently more extensive work on the determination of aromatic sulfonates was reported. Lange et al. [44] developed an automated system of on-line ion-pair extraction and ion-pair RPLC and obtained detection limits of 0.05–2 $\mu g\ l^{-1}$ from 50-ml samples. With this system, biologically treated wastewater, surface water, and various steps of drinking water preparation, such as bank filtration, ozonation, and activated

charcoal adsorption, were analyzed. NDS was identified as a dominant and persistent pollutant.

Altenbach and Giger [45] analyzed 25 sulfonic acids and 8 carboxylic acids by ion-pair RPLC (Fig. 3). Combined with SPE on Carbopack B, they applied this method to industrial wastewater, a wastewater treatment plant influent and effluent, as well as to surface water. Detection limits were in the range of 0.1–1 $\mu g\ l^{-1}$ from 100-ml samples. Nine sulfonic acids were identified in a wastewater treatment plant, which was dominated by wastewater from the textile industry.

3.3. Capillary electrophoresis

For several reasons, capillary electrophoresis (CE) has become an important technique for the separation of peptides, proteins, and other biomolecules. Some of these reasons are equally interesting for the application of CE in environmental analysis: (i) the extraordinarily high separation efficiency, which is due to the absence of a stationary phase; (ii) generally short separation times; and (iii) separation in aqueous media, which makes CE especially attractive for the analysis of aqueous samples. Nevertheless, the number of applications in this field is still limited.

Under conventional conditions, capillary zone electrophoresis (CZE) employs a negatively charged cathode as target electrode, and sulfonate anions would, thus, not reach the detector, if movement of the analytes within the electrical field (electrophoretic movement) was the only transport process. However, under suitable conditions, this process is superseded by electroosmotic flow (EOF), which is the movement of buffer solution towards the target electrode caused by the negatively charged capillary wall. Sulfonates are, therefore, separated by the superposition of the EOF towards the cathode and their own electrophoretic movement in the reverse direction. The elution order is, thus, the reverse of their electrophoretic mobility: large organic constituents result in a smaller electrophoretic mobility and in a shorter migration time [67], while electron-withdrawing substituents such as nitro and chloro exhibit longer migration times.

Williams et al. [68] compared the capacity of ion-pair RPLC and CZE in separating AQS and AQDS. The separation efficiency was one order of magnitude higher in CZE (100 000 theoretical plates), though this was not of great value in practice. CZE offers extremely low mass detection limits (3 pg), but due to the small sample

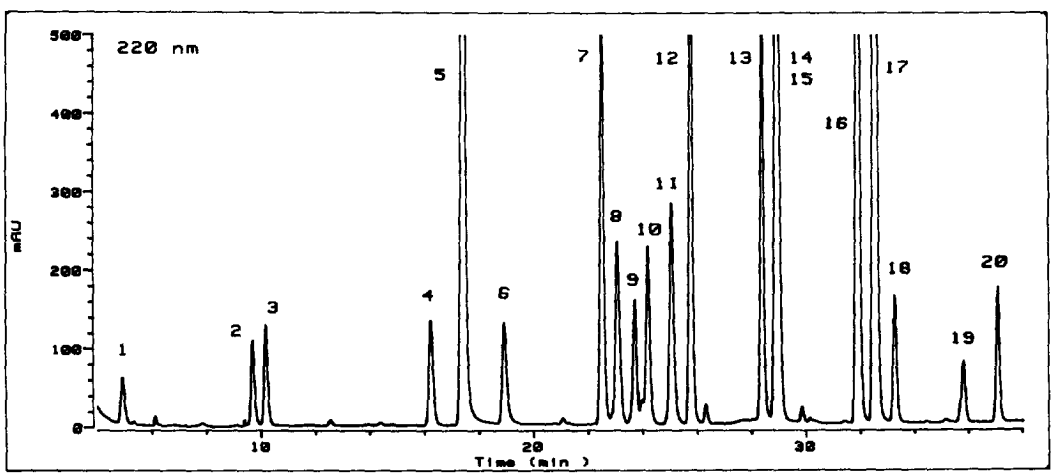


Fig. 3. Ion-pair RPLC chromatogram of aromatic sulfonates: (1) 4-ABS, (2) 3-ABS, (3) 4-HBS, (4) 4-COOH-BS, (5) 1-A-4-NS, (6) BS, (7) 2-A-4,8-NDS, (8) 2-A-1,5-NDS, (9) 2-A-5-NO_2-BS, (10) 3-NO_2-BS, (11) 4-Me-BS, (12) 2,7-NDS, (13) 2-H-3,6-NDS, (14) 4-Cl-BS, (15) 3-NO_2-5-Me-BS, (16) 1-NS, (17) 2-NS, (18) Diphenylamin-4-S, (19) 4-iPr-BS, (20) 2-AQS. Hypersil ODS column, 5 μm, 250 × 4 mm I.D.; UV detection 220 nm. Kindly provided by B. Altenbach.

volume applied (4 nl), the concentration detection limit was two orders of magnitude higher than in HPLC.

LAS and alkyl-BS were separated by CZE [69]. With acetonitrile as organic modifier, all phenyl isomers of LAS migrate together but alkyl homologues (C_2 to C_{12}) are baseline separated within 4 min.

Terabe and Isemura [70] separated NS and NDS by CZE. They addressed the problem of separating positional isomers of aromatic sulfonates under normal pH conditions due to their very similar electrophoretic mobilities. Instead of lowering the pH to the pK_a of the analytes, they added a polymeric cation [poly(diallyldimethylammonium)]. In this case, no electroosmotic flow is required; sulfonate anions are transported through the capillary imbedded in the cationic polymer solely by electrophoresis. The authors proposed the term ion-exchange electrokinetic chromatography. With this modification, positional isomers of NS and NDS were successfully separated.

AQS and largely differing positional isomers of AQDS (1.5- and 1.8-AQDS) were separated by CZE at pH 11 [68]. Garcia and Henion [71] employed capillary gel electrophoresis (CGE) for the separation of several BS, and NS and ANS coupled to a mass spectrometer. However, retention times appear to increase substantially in CGE compared with CZE with open tubular capillaries. Analysis time in this example was more than 40 min. Brumley [67] demonstrated two advantages of CZE (versatility and speed) by separating a mixture of LAS, alkyl-BS, NS, and chloro- and nitro-substituted BS within 4.5 min.

An alternate approach for separating isomeric aromatic sulfonates was presented by Pfeffer and Yeung [72]. They used electrochromatography (EC), which is instrumentally comparable to CE, with the plain silica capillary being replaced by a wall-coated, open-tubular capillary. This coating minimizes the EOF and introduces a chromatographic partitioning process; the driving force of analyte migration supplies their electrophoresis. This technique is viewed as a hybrid between CE and HPLC, with two major advantages over the latter, the flat rather than parabolic flow profile (corresponding to CE) and minimized mass transfer due to the stationary phase being a thin film instead of a packed bed. Sulfonates are separated as TBA^+ ion-pairs, and an efficient separation of ANS within an extraordinarily short analysis time is obtained (Fig. 4). Parallel to the discussion in RPLC (Section 3.2), ion-pair EC might be interpreted as ion-exchange EC [73].

3.3.1. Application to environmental analysis

When reviewing the available literature, it becomes obvious that the development of CE for environmental analysis is still continuing. While reports on the separation of standard compounds have long been available, CE applications to the analysis of samples from aqueous environments are scarce and need to be developed. However, CE was exemplarily applied to a landfill leachate [67], previously analyzed by anion-exchange chromatography [33]. Several distinct peaks were detected, but only one substance could be identified by means of CE–MS (Section 5.2).

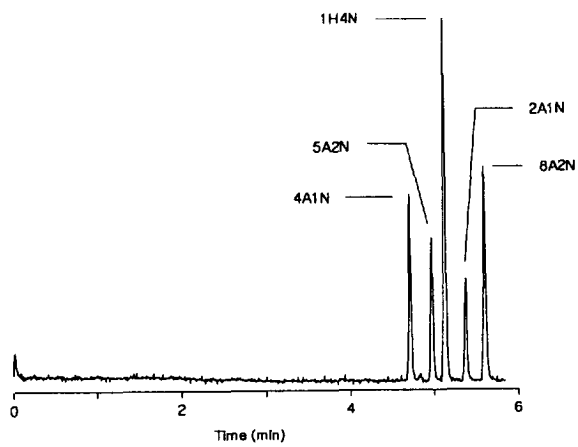


Fig. 4. Separation of ANS isomers by ion-pair electrochromatography. Fused-silica column coated with PS 264, 50 cm × 10 μm I.D., 40 cm separating distance; laser fluorescence detection, for details refer to Ref. [72]; 10 m*M* phosphate buffer, pH 7.0, 1.25 m*M* TBA; separation voltage +21 kV. Reproduced with permission from Ref. [72].

3.4. Other LC methods

Anion-exchange chromatography is of limited importance in the analysis of aromatic sulfonates since it has been found to be of low selectivity and to exhibit generally strong retention on styrol–divinylbenzol resins [51]. Nevertheless, Bear et al. [74] separated BS, benzene disulfonates (BDS), NS, and NDS by anion-exchange chromatography. Retention time windows for mono- and disulfonated and carboxylated derivatives were established, which allowed the determination of the degree of sulfonation in petroleum sulfonates. Kim et al. [33,48] employed anion-exchange chromatography coupled to MS to analyze aromatic sulfonates in landfill leachates.

3.5. Detection

As mentioned above, UV and fluorescence detection are routinely employed in RPLC of aromatic sulfonates. Generally, the benefit of aromatic sulfonate analysis from aquatic environments strongly depends on the availability of the appropriate reference compounds. Peak assignment might be supported by DAD detection and comparison of the UV spectra [38,39,44,45]. In the case of fluorescence-active substances, recording the fluorescence spectra might be helpful [40]. Comparison of the first deviation of the spectra might be useful in critical cases [40]. However, identification of substances not ascribed to a reference compound is impossible with these techniques, which is a major drawback for their application to environmental analysis. Identification of aromatic sulfonates requires either GC–MS (Section 5.1) or LC–MS coupling (Section 5.2).

Electrochemical desulfonation of aromatic sulfonic acids has been reported [75] and might permit the electrochemical detection of sulfonates in liquid chromatography. However, reductive electrochemical detection is easily hampered by dissolved oxygen and might not be advantageous. Hydroxy- and amino-substituents of sulfonates are amenable to oxidative electrochemical detection [76].

A sulfur-selective chemiluminescence detector coupled to HPLC was developed and an example of sulfonate analysis presented [77]. The use of sulfur- or sulfonate-selective detection methods would substantially diminish the interferences from co-extracted humic acids, from which UV and fluorescence detection suffer.

4. Gas chromatography

Gas chromatography generally provides higher separation efficiency than HPLC. For example, the phenyl-isomers of technical LAS-mixtures might be completely separated by GC. Additionally, GC with flame ionization detection (FID) allows the determination of aliphatic sulfonates such as secondary alkane sulfonates (SAS). An attractive aspect is the possibility to identify sulfonates by MS detection. However, the polarity of the sulfonate moiety requires derivatization prior to GC analysis.

4.1. Derivatization

Desulfonation in boiling phosphoric acid was the first method of LAS preparation for GC analyses [30,78]. Due to the rigidness of this procedure, the formation of artifacts might occur [78], and labile metabolites cannot be determined [31]. Therefore, several derivatization methods have been developed (Fig. 5).

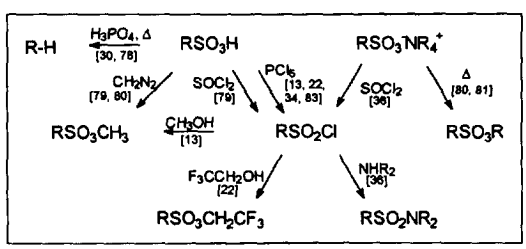


Fig. 5. Derivatization scheme for the GC analysis of aromatic monosulfonates. References according to the text.

Kirkland [79] analyzed LAS by GC–FID after esterification with diazomethane. Methylation of various sulfonates and disulfonates was reported by Heywood et al. [80] for the mass spectrometric analysis of pure compounds with direct inlet. They employed diazomethane or the tetramethylammonium cation as methylating agents, which reacted during heating of the MS system inlet. Esterification by the tetraalkylammonium cation was only recently employed for the injector-port derivatization of SAS and LAS [81].

Methylation of sulfonic groups in various dye intermediates was obtained by methyl fluorosulfate, which left amino and hydroxyl groups unaffected [35].

Sulfonyl chlorides are prepared from free sulfonic acids by thionylchloride [79] or phosphorous pentachloride [13,34] and might be analyzed by GC–FID, GC–ECD, or GC–MS. They were also selectively detected with GC–atomic emission spectroscopy (AES) [82] by their chlorine and sulfur traces. Sulfonyl chlorides are also amenable to tetraalkylammonium ion-pairs [36] and might be subsequently transformed to thermally and hydrolytically more stable sulfonamides by heating with dibutylamide [36]. Amer et al. [83] modified the chlorination with PCl_5 to a two-step procedure, allowing the analysis of amino-substituted sulfonates. Chlorination of AQS was performed by heating with HCl and sodium chlorate under reflux within 3 h [47]. Sulfonylchlorides might be transformed into methyl sulfonates by heating with methanol [13]. Significantly higher sensitivity in GC–MS analysis of LAS is obtained after esterification with trifluoroethanol under NCI conditions [22], which is also suitable for DATS detection.

The benefit of silylester formation remains ambiguous. Trimethylsilylesters of sulfonates were not detected by FID [84]. However, the reaction with TBDMSCl is reported to be suitable for sulfonate, hydroxy, and amino groups and to result in stable and FID-detectable products [85]. However, no application of this method has been published so far.

Most of the above-mentioned methods were developed for LAS analysis and are applicable to other monosulfonated aromates [22,79,80]. Derivatives of di- and polysulfonates, however, lack volatility and have even lower thermal stability than monosulfonates. They are, thus, not amenable to gas chromatographic separation. Furthermore, hydroxy- and amino-substituted sulfonates are only incompletely derivatized with most agents (e.g. methylation [80]). This, further, limits the applicability of GC–MS for the analysis of aromatic sulfonates.

4.2. Application to environmental analysis

Hon-Nami and Hanya [13] analyzed LAS from river water as sulfonyl chlorides by GC–MS in the EI-mode; no detection limits are given, but the lowest concentration reported is 3 $\mu g\ l^{-1}$ for single isomers. LAS analysis by FID and GC–MS (EI and CI) is reported by McEvoy and Giger [34]. Osburn [30] analyzed LAS from wastewater before and after biological treatment and from receiving waters after desulfonation by FID-detection. Trehy et al. [22], employing the trifluoroethanol esters, achieved a detection limit of 1 $\mu g\ l^{-1}$ from 50-ml samples; they applied their method to wastewater treatment plant effluents and river water.

Capillary columns of low polarity (up to 5% diphenyl in dimethylsiloxane) were used by all authors [22,30,34].

5. Mass spectrometry

5.1. GC–MS

GC–MS analysis was almost exclusively employed for the analysis of LAS. The base peak of LAS methyl esters analyzed under EI conditions is m/z 185, but the molecular ion remains visible. Fragmentation patterns of aromatic methylsulfonates are comparable to those of alkylbenzenes [13]. The position of the benzene ring is detectable by the fragments stemming from the α-fragmentation of the alkyl-chain [13].

The use of LAS chlorides is extensively discussed by McEvoy and Giger [34]. Significant fragments in the EI-mode are M^+ and $(M-35)^+$ due to the loss of chloride. Loss of alkyl-

fragments permits the localisation of the benzene ring within the alkyl chain. CI-MS gives rise to intensive $(M+1)^+$-ions. With the combination of EI and CI modes, co-eluting isomers of different homologues can be fully resolved (Fig. 6).

The trifluorethanol esters of sulfonates have the lowest detection limits when analyzed under NCI conditions [22]. Either the parent ion or $(M-100)^-$ (loss of trifluoroethanol) was employed for selected-ion monitoring. The fragment m/z 163 corresponds to $SO_3CH_2CH_3$ and is common to all sulfonates [22]. Trifluoroethanol esters are also detectable in the EI mode.

After silylation with MTBSTFA, $(M-57)^+$ was detectable from all TBDMS-derivatives even from threefold-silylated compounds [85]. Further fragmentations characteristic for sulfonate functions are $(M\text{-}SO_2(TBDMS))^+$ and $(M\text{-}SO_3(TBDMS))^+$. Amino groups are only silylated once.

LAS butyl esters, formed by flash injection of LAS and $TBA^+HSO_3^-$, were quantified by selected-ion monitoring of m/z 185 [26].

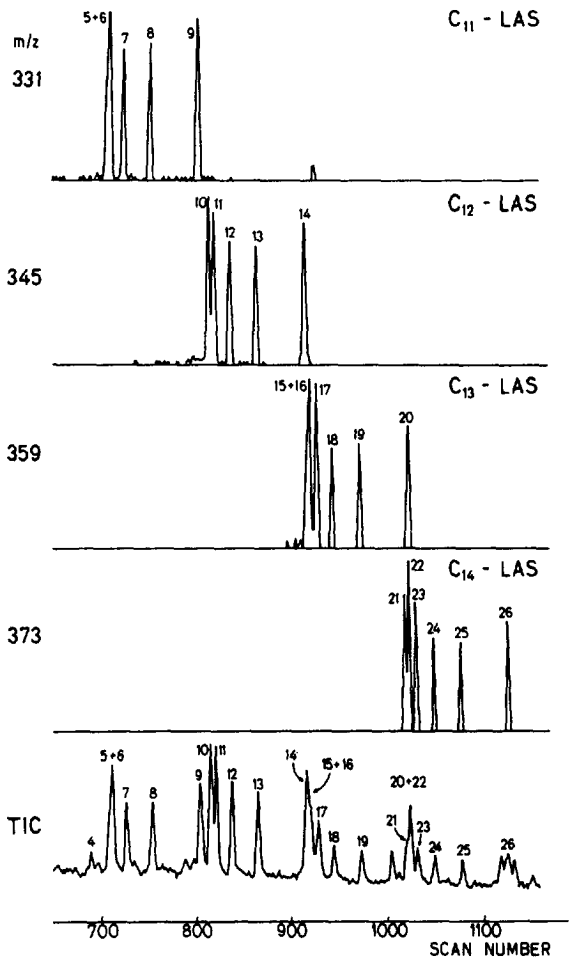


Fig. 6. Use of GC–MS (methane CI) for LAS identification: partial mass chromatograms and total ion current of LAS chlorides isolated from a sewage sludge. Numbers refer to the benzene ring isomers: pos. 7: 15, 21; pos. 6: 5, 10, 16, 20; pos 5: 6, 11, 17, 23; pos. 4: 7, 12, 18, 24; pos. 3: 8, 13, 19, 25; pos. 2: 9, 14, 20, 26. Reproduced with permission from Ref. [34].

5.2. LC–MS

Due to the above-mentioned restrictions of GC in separating polyfunctional sulfonates, GC–MS is only of limited value for the identification of aromatic sulfonated compounds other than LAS, and the coupling of liquid chromatography with MS is required. Unfortunately, ion-pair RPLC, the preferential mode for the separation of polar aromatic sulfonates (Section 3.2), is incompatible with MS coupling [86], as the ion-pair agents are not volatile enough to be removable within the liquid introduction interface between HPLC and MS. Therefore, the development of a new separation based on ammonium acetate would be necessary prior to the application of RPLC–MS.

All but the particle-beam interface result in chemical ionization mass spectra and provide information on the molecular mass only. For structural characterization, MS–MS analysis is required, with intermediate, collisionally induced dissociation [25,87].

RPLC–MS with a thermospray interface was employed by Schröder for the analysis of LAS in wastewater treatment plant effluents [87]. A combination of anion-exchange HPLC–MS was reported by Kim et al. [33,48]; they investigated chlorinated BS in a landfill leachate and BS, alkyl-BS, HBS, NS, and NDS from stock solutions with a particle-beam interface. The molecular ions as well as $(M-SO_2)^+$ and $(M-SO_3H)^+$ are characteristic fragments of aromatic sulfonates in the EI mode. However, even with SIM detection the limit of quantification was as

high as 250 ng. A CGE–MS [71] coupling was employed for the analysis of a standard mixture of BS, NS, and ANS with an ion-spray interface and NCI recording; $(M-H)^-$ was used for SIM detection. CZE–MS, as employed for the analysis of sulfonated dyes [88,89], should also be suitable for benzene and naphthalene sulfonates, but it has not been reported so far.

5.3. MS without chromatographic separation

Standards of aromatic sulfonates and polysulfonates were analyzed by fast atom bombardment (FAB)-MS [57,90]. Ventura et al. [91] identified LAS and other surfactant-derived substances in drinking water extracts with FAB–MS, after a prefractionation by HPLC.

The advent of MS–MS combinations allowed the development of continuous flow (CF)-MS analytical methods and related techniques, misleadingly referred to as flow injection (analysis)-MS (FIA-MS). No separation of the sample is performed, but the dissolved sample is transferred into the first mass spectrometer via a liquid interface. The primary MS system works as a mass filter, selecting parent ions of interest to be ionized and analyzed for daughter ions in the second MS [87,92]. Negative ionization is generally more specific than positive ionization, since only a minority of substances are able to stabilize negative charges. This is true for sulfur-containing molecules such as LAS, which are, thus, selectively determined best by NI-detection [92]. FIA–MS techniques proved capable of quantitative analysis of individual compounds out of complex mixtures [92]. Borderding and Hites employed CF FAB–MS for LAS analysis from wastewater treatment plant influents and effluents and from river water [25]. The $(M-H)^-$ and m/z 183 are characteristic for LAS, whereas m/z 197 proved typical for the branched alkylbenzene sulfonates (Fig. 7). Daughter-ion detection of m/z 183 provides the specificity necessary to quantify LAS from crude wastewater extracts. The detection limit was around 0.5 $\mu g\ l^{-1}$ for a 1-l sample volume, corresponding to 1 ng absolute [25] and is, thus, one order of magnitude higher than in conventional RPLC with fluorescence detection.

6. Spectroscopic methods

The application of spectroscopic methods in the field of organic residue analysis of environmental samples is unusual. It requires the liberation of the compounds of interest from the sample matrix to a much higher degree than for chromatographic analysis, and detection limits are often far above those needed. Nevertheless, a few applications of spectroscopic methods for the determination of aromatic sulfonates are reported. LAS and ABS were identified by ^{13}C-NMR in ground water extracts [93]. Field et al.

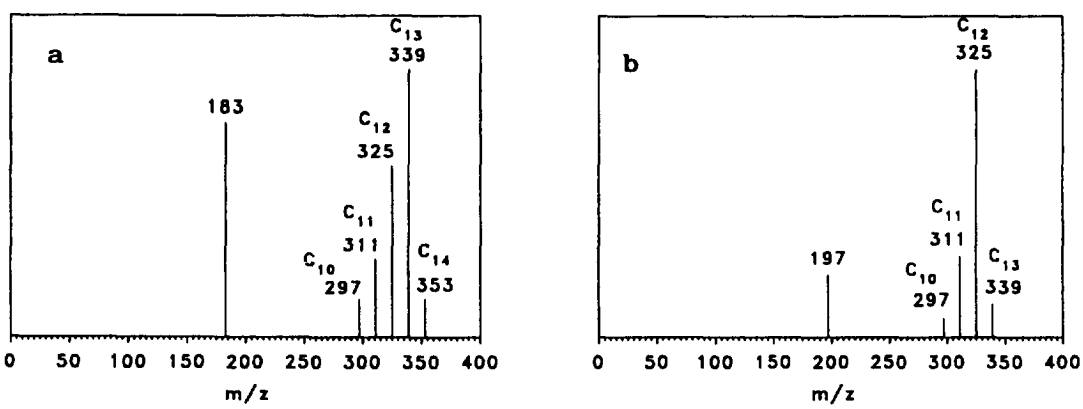


Fig. 7. Parent-ion mass spectrum of CF–FAB–MS–MS: (a) of LAS obtained by scanning the parents of m/z 183; (b) of ABS by scanning the parents of m/z 197. Reproduced with permission from Ref. [25].

[32] employed IR-spectroscopy, ^{1}H-NMR, and ^{13}C-NMR for the identification of LAS, DATS, and SPC also from groundwater extract. Signal identification was based on comparison with pure standards. However, as much as 5 mg of LAS were necessary to record ^{13}C-NMR spectra. Hellmann [94] developed a methodology for LAS determination and quantitation in surface waters based on second derivative IR-spectroscopy after extraction and TLC clean-up.

7. Summary

Analytical methods for aromatic sulfonates from water as well as their stage of development strongly differ between LAS and more polar sulfonated aromates.

The analytical methodology for LAS is, meanwhile, well established. Several combinations of SPE, clean-up and RPLC analysis with fluorescence detection have been investigated, and reliable methods for the analysis of wastewater, fresh and seawater have been available for nearly ten years. Analyte identification is based on GC–MS analysis of sulfonylchlorides or esters.

As opposed to this, the analysis of more polar aromatic sulfonates from aqueous media is still being developed. The majority of presently available reports is based on ion-pair extraction and ion-pair RPLC. This methodology has provided the first data on concentrations of polar aromatic sulfonates in wastewater, surface and ground water. However, ion-pair extraction turned out to be of limited efficiency for very polar, amino- and hydroxy-substituted aromatic sulfonates and is easily affected by high salt contents. Method development needs to be continued to allow the analysis of polar sulfonates from difficult matrices such as industrial wastewater and seawater. The use of other solid-phase sorbents such as deactivated charcoal might provide a solution.

The various modifications of CE (including EC) offer a promising potential for the separation of sulfonate mixtures and might become a powerful complementary separation technology to (ion-pair) RPLC. Very limited use has been made of this technology in the field of environmental analysis of sulfonates so far.

UV, DAD and fluorescence detection methods provide reasonable detection limits for routine analyses. However, detection methods specifically determining sulfur or the sulfonate group would diminish interferences from co-extracted substances, which presently hamper the analysis of polar sulfonates from surface waters.

Limited work has been done in the field of aromatic sulfonate identification from environmental samples. LC–MS–MS coupling or CF-MS–MS or FIA-MS–MS are needed for this, and particularly the last appears promising with respect to speed and versatility. However, the instrumental facilities are quite expensive, and their application is all but routine work in environmental laboratories.

Acknowledgements

The author is grateful to B. Altenbach for kindly providing the ion-pair RPLC chromatogram of aromatic sulfonates.

Abbreviations

ABS	Aminobenzene sulfonates
AQDS	Anthraquinone disulfonates
AQS	Anthraquinone sulfonates
ANDS	Aminonaphthalene disulfonates
ANS	Aminonaphthalene sulfonates
BDS	Benzene disulfonates
BS	Benzene sulfonates
C_1, C_2, C_8, C_{18}	Methyl-, ethyl, octyl-, octadecyl-coated silica gel
CE	Capillary electrophoresis
CF	Continuous flow
CGE	Capillary gel electrophoresis
CTMA	Cetyltrimethylammonium cation
CZE	Capillary zone electrophoresis
DAD	Diode-array detector
DATS	Dialkyltetraline sulfonates
EC	Electrochromatography
EOF	Electroosmotic flow
FAB	Fast atom bombardment

FIA	Flow injection analysis
FWA	Fluorescence whitening agents
HBS	Hydroxybenzene sulfonates
HNDS	Hydroxynaphthalene disulfonates
HNS	Hydroxynaphthalene sulfonates
K_{ow}	Octanol–water partition coefficient
LAS	Linear alkylbenzene sulfonates
LLE	Liquid–liquid extraction
MBAS	Methylene blue active substances (refers to the photometric determination of anionic surfactants [12])
MTBSTFA	N-Methyl-N-(*tert.*-butyldimethylsilyl)trifluoroacetamide
NCI	Negative-ion chemical ionization
NDS	Naphthalene disulfonates
NS	Naphthalene sulfonates
NPEO	Nonylphenolethoxylates
PLRP-S	Styrene–divinylbenzene copolymer
RPLC	Reversed-phase (high-performance) liquid chromatography
SAS	Secondary alkane sulfonates
SIM	Selected-ion monitoring
SPC	Sulfophenyl carboxylates
SPE	Solid-phase extraction
TBA	Tetrabutylammonium cation
TBDMS	*tert.*-Butyldimethylsilyl group
TBDMSCl	*tert.*-Butyldimethylsilyl chloride
TLC	Thin-layer chromatography

References

[1] V.C. Hand and G.K. Williams, Environ. Sci. Technol., 21 (1987) 370.

[2] A. Cahn and J.L. Lynn, in H.F. Mark et al. (Editors), Encyclopedia of Chemical Technology, Vol. 22, Wiley and Sons, New York, 3rd ed., 1983, p. 332.

[3] T. Reemtsma, J. Jochimsen and M. Jekel, Vom Wasser, 81 (1993) 353.

[4] V.T. Yilmaz, A. Kindness and F.P. Glasser, Cem. Concr. Res., 22 (1992) 663.

[5] H. Greim, J. Ahlers, R. Bias, B. Broecker, H. Hollander, H.-P. Gelbke, H.-J. Klimisch, I. Mangelsdorf, A. Paetz, N. Schöne, G. Stropp, R. Vogel, C. Weber, K. Ziegler-Skylakakis and E. Bayer, Chemosphere, 28 (1994) 2203.

[6] W. Giger, P.H. Brunner, M. Ahel, J. McEvoy, A. Marcomini and C. Schaffner, Gas Wasser Abwasser, 67 (1987) 111.

[7] L. Cavalli, A. Gellera and A. Landone, Environ. Toxicol. Chem., 12 (1993) 1777.

[8] B. Nörtemann, J. Baumgarten, H.G. Rast and H.-J. Knackmuss, Appl. Environ. Microbiol., 52 (1986) 1195.

[9] Z. Liu, S. Laha and R.G. Luthy, Wat. Sci. Technol., 23 (1991) 475.

[10] D.A. Edwards, Z. Liu and R.G. Luthy, J. Environ. Eng., 120 (1994) 5.

[11] Z. Ou, A. Yediler, H. He, A. Kettrup and T. Sun, Chemosphere, 30 (1995) 313.

[12] L.S. Clesseri, A.E. Greenberg and R.R. Trussell (Editors), Standard Methods for the Examination of Water and Wastewater, Am. Public Health Assoc., Washington, DC, 17th ed., 1989, p. 559.

[13] H. Hon-Nami and T. Hanya, J. Chromatogr., 161 (1978) 205.

[14] R. Wickbold, Tenside Deterg., 8 (1971) 61.

[15] E. Matthijs and M. Stalmans, Tens. Surfact. Deterg., 30 (1993) 29.

[16] S. Terzic, D. Hrsak and M. Ahel, Water Res., 26 (1992) 585.

[17] M. Kikuchi, A. Tokai and T. Yoshida, Water Res., 20 (1986) 643.

[18] A. Marcomini, S. Stelluto and B. Pavoni, Int. J. Environ. Anal. Chem., 35 (1989) 207.

[19] I. Fujita, Y. Ozasa, T. Tobino and T. Sugimura, Chem. Pharm. Bull., 38 (1990) 1425.

[20] A. Marcomini, A.D. Corcia, R. Samperi and S. Capri, J. Chromatogr., 644 (1993) 59.

[21] E. Matthijs and H. De Henau, Tens. Surfact. Deterg., 24 (1987) 193.

[22] M.L. Trehy, W.E. Gledhill and R.G. Orth, Anal. Chem., 62 (1990) 2581.

[23] A. Marcomini, S. Capri and W. Giger, J. Chromatogr., 403 (1987) 243.

[24] P. Schöberl, H. Kotz, R. Spilker and L. Nitschke, Tens. Surfact. Deterg., 31 (1994) 243.

[25] A.J. Borgerding and R.A. Hites, Anal. Chem., 64 (1992) 1449.

[26] J.A. Field, T.M. Field, T. Poliger and W. Giger, Environ. Sci. Technol., 28 (1994) 497.

[27] M.A. Castles, B.L. Moore and S.R. Ward, Anal. Chem., 61 (1989) 2534.

[28] A. Marcomini and W. Giger, Anal. Chem., 59 (1987) 1709.

[29] A. Di Corcia, M. Marchetti, R. Samperi and A. Marcomini, Anal. Chem., 63 (1991) 1179.

[30] Q.W. Osburn, J. Am. Oil Chem. Soc., 63(2) (1986) 257.

[31] P.W. Taylor and G. Nickless, J. Chromatogr., 178 (1979) 259.

[32] J.A. Field, J.A. Leenheer, K.A. Thorn, L.B.I. Barbar, C. Rostad, D.L. Macalady and S.R. Daniel, J. Contam. Hydrol., 9 (1992) 55.

[33] I.S. Kim, I. Sasinos, R.D. Stephens and M.A. Brown, Environ. Sci. Technol., 24 (1990) 1832.

[34] J. McEvoy and W. Giger, Environ. Sci. Technol., 20 (1986) 376.
[35] T. Sugiura and M.C. Whiting, J. Chem. Res., (M) (1980) 2426.
[36] H. Kataoka, T. Okazaki and M. Makita, J. Chromatogr., 473 (1989) 276.
[37] H. Miyoshi, T. Nagai and M. Ishikawa, Shizuoka Prefect. Inst. Public Health. Environ. Sci., 27 (1984) 45.
[38] S. Schullerer, H.-J. Brauch and F.H. Frimmel, Vom Wasser, 75 (1990) 83.
[39] E.R. Brouwer, J. Slobodnik, H. Lingeman and U.A.T. Brinkman, Analusis, 20 (1992) 121.
[40] O. Zerbinati, G. Ostacoli, D. Gastaldi and V. Zelano, J. Chromatogr., 640 (1993) 231.
[41] B. Bastian, T.P. Knepper, P. Hoffmann and H.M. Ortner, Fresenius J. Anal. Chem., 348 (1994) 674.
[42] T. Reemtsma and M. Jekel, J. Chromatogr. A, 660 (1994) 199.
[43] O. Zerbinati and G. Ostacoli, J. Chromatogr. A, 671 (1994) 217.
[44] F.T. Lange, M. Wenz and H.-J. Brauch, J. High Resolut. Chromatogr., 18 (1995) 243.
[45] B. Altenbach and W. Giger, Anal. Chem., 67 (1995) 2325.
[46] J.J. Sun and J.S. Fritz, J. Chromatogr., 590 (1992) 197.
[47] T. Tsukioka, H. Ozawa and T. Murakami, Anal. Sci., 7 (1991) 897.
[48] I.S. Kim, F.I. Sasinos, D.K. Rishi, R.D. Stephens and M.A. Brown, J. Chromatogr., 589 (1992) 177.
[49] A. Nakae, K. Tsuji and M. Yamanaka, Anal. Chem., 53 (1981) 1818.
[50] A. Nakae, K. Tsuji and M. Yamanaka, Anal. Chem., 52 (1980) 2275.
[51] P. Jandera, J. Churacek and J. Bartosova, Chromatographia, 13 (1980) 485.
[52] H. Grossenbacher, T. Thurnheer, D. Zürrer and A.M. Cook, J. Chromatogr., 360 (1986) 219.
[53] P.T. Kissinger, Anal. Chem., 49 (1976) 883.
[54] C. Pettersson and G. Schill, Chromatographia, 28 (1989) 437.
[55] C. Horvath, W. Melander, I. Molnar and P. Molnar, Anal. Chem., 49 (1977) 2295.
[56] P. Jandera, J. Churacek and B. Taraba, J. Chromatogr., 262 (1983) 121.
[57] G.R. Bear, J. Chromatogr., 371 (1986) 387.
[58] H. Sirén, R. Dammert and L. Huhanantti, Fresenius' Z. Anal. Chem., 332 (1988) 245.
[59] H.F. Zou, Y.K. Zhang and P.C. Lu, Chromatographia, 34 (1992) 15.
[60] H. Zou, Y. Zhang, M. Hong and P. Lu, J. Chromatogr., 644 (1993) 269.
[61] T.O. Crowley and R.A. Larson, J. Chromatogr. Sci., 32 (1994) 57.
[62] P.-O. Lagerstrom, J. Chromatogr., 250 (1982) 43.
[63] S.R. Camp and P.E. Sturrock, Water Res., 24 (1990) 1275.
[64] B.P. McPherson and N. Omelczenko, J. Am. Oil Chem. Soc., 57 (1980) 388.
[65] J.L. Jasperse and P.H. Steiger, J. Am. Oil Chem. Soc., 69 (1992) 621.
[66] T. Poiger, PhD Thesis, ETH Zürich (1994).
[67] W.C. Brumley, J. Chromatogr., 603 (1992) 267.
[68] S.J. Williams and D.M. Goodall, J. Chromatogr., 629 (1993) 379.
[69] P.L. Desbène, C. Rony, B. Desmazièrez and J.C. Jacquier, J. Chromatogr., 608 (1992) 375.
[70] S. Terabe and T. Isemura, Anal. Chem., 62 (1990) 652.
[71] F. Garcia and J.D. Henion, Anal. Chem., 64 (1992) 985.
[72] W.D. Pfeffer and E.S. Yeung, J. Chromatogr., 557 (1991) 125.
[73] T.W. Garner and E.S. Yeung, J. Chromatogr., 640 (1993) 397.
[74] G.R. Bear, C.W. Lawley and R.M. Riddle, J. Chromatogr., 302 (1984) 65.
[75] J. Simonet, in S. Patai and Z. Rappoport (Editors), The Chemistry of Sulphonic Acids, Esters and Their Derivatives, Wiley, Chichester, 1991, Ch. 14, p. 553.
[76] D.A. Roston and P.T. Kissinger, Anal. Chem., 54 (1982) 429.
[77] H.C.K. Chang and L.T. Taylor, Anal. Chem., 63 (1991) 486.
[78] R.D. Swisher, in M.J. Schick and F.M. Fowkes (Editors), Surfactant Biodegradation, Marcel Dekker, New York, 2nd ed., 1987.
[79] J.J. Kirkland, Anal. Chem., 32 (1960) 1388.
[80] A. Heywood, A. Mathias and A.E. Williams, Anal. Chem., 42 (1970) 1272.
[81] J.A. Field, D.J. Miller, T.M. Field, S.B. Hawthorne and W. Giger, Anal. Chem., 64 (1992) 3161.
[82] F. David, M. Verschuere and P. Sandra, Fresenius' J. Anal. Chem., 344 (1992) 479.
[83] A. Amer, E.G. Alley and C.U. Pittman Jr., J. Chromatogr., 362 (1986) 413.
[84] O. Stokke and P. Helland, J. Chromatogr., 146 (1978) 132.
[85] L.-K. Ng and M. Hupé, J. Chromatogr., 513 (1990) 61.
[86] P.O. Edlund, E.D. Lee, J.D. Henion and W.L. Budde, Biomed. Environ. Mass Spectrom., 18 (1989) 233.
[87] H.F. Schröder, J. Chromatogr., 647 (1993) 219.
[88] E.D. Lee, W. Mueck, J.D. Henion and T.R. Covey, Biomed. Environ. Mass Spectrom., 18 (1989) 253.
[89] E.D. Lee, W. Mueck, J.D. Henion and T.R. Covey, Biomed. Environ. Mass Spectrom., 18 (1989) 844.
[90] J.J. Monaghan, M. Barber, R.S. Bordoli, R.D. Sedgwick and A.N. Tyler, Org. Mass Spectrom., 17 (1982) 529.
[91] F. Ventura, J. Caixach, A. Figueras, I. Espalder, D. Fraisse and J. Rivera, Water Res., 23 (1989) 1191.
[92] H.F. Schroeder, Vom Wasser, 79 (1992) 193.
[93] E.M. Thurman, T. Willoughby, L.B. Barber and K.A. Thorn, Anal. Chem., 59 (1987) 1798.
[94] H. Hellmann, Z. Wasser Abwasser Forsch., 24 (1991) 178.