ELSEVIER

Journal of Chromatography A, 854 (1999) 175–185

JOURNAL OF CHROMATOGRAPHY A

Use of volatile amines as ion-pairing agents for the high-performance liquid chromatographic–tandem mass spectrometric determination of aromatic sulfonates in industrial wastewater

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Abstract

The use of trialkylamines (triethylamine, *N*,*N*-dimethyl-*n*-butylamine, and tri-*n*-butylamine) as volatile ion-pairing agents for the high-performance liquid chromatographic separation of aromatic sulfonates was investigated. Negative ion electrospray tandem mass spectrometry was used to detect both singly and multiply charged analyte ions. Sensitivity of detection was strongly reduced by amine concentrations above 2.5 mmol l^{-1} in the eluent. With tributylamine as ion-pairing agent 19 aromatic sulfonic acids could be determined using time-scheduled selected reaction monitoring. Lowest orders of detection range from 3 to 74 μg l^{-1}. Several naphthalenesulfonic acids were determined in dyeing baths and textile wastewater in concentrations ranging from 0.1 mg l^{-1} to 2.1 mg l^{-1}. A degradation product of sulfonated azodyes was identified in the effluent of a laboratory treatment plant.

Keywords: Water analysis; Ion-pairing reagents; Environmental analysis; Amines; Sulfonic acids; Naphthalenesulfonic acids; Organic acids

1. Introduction

Aromatic sulfonates are widely applied in many industrial processes, including concrete furnishing [1,2] and the various steps of industrial textile processing [3,4]. Additionally, they are important intermediates in the production of dyes [5] and various other chemicals. Aromatic sulfonates are well soluble in water and many of them are resistant to microbial degradation [6]. Consequently, aromatic sulfonates have been found in wastewater as well as in surface water in many instances. They are thus of concern for environmental analysis, especially in the aquatic environment, a subject reviewed recently [7].

Ion-pair chromatography on reversed-phases is the most important technique among the different approaches in the analysis of aromatic sulfonates [5,8–12], although capillary electrophoresis [5,13,14] and ion chromatography [15] have been applied to some extent, the latter being one of the first instances to analyse naphthalenesulfonic acids in which a liquid separation technique is coupled to MS.

Common ion-pairing agents used for HPLC are tetraalkylammonium salts, for example tetrabutylammonium or trimethyloctadecylammonium salts, which are used mainly with UV or fluorescence detection. These modes of detection are, however, of limited use in the analysis of unknown compounds, and to obtain more structural information mass spectrometry is the method of choice.

Unfortunately, coupling of conventional ion-pair chromatography to mass spectrometry is obstructed

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0021-9673/99/$ – see front matter
PII: S0021-9673(99)00525-7

by contamination of the interface by the involatile tetraalkylammonium salts used as mobile phase modifiers. Additionally, sensitivity in HPLC–electrospray ionization (ESI) MS decreases rapidly with rising concentrations of tetraalkylammonium salts in the HPLC eluent. For the analysis of cyclic nucleotides Witters et al. [16] had to use rather low concentrations of ion pairing agent (less than 0.5 mmol l^{-1}), which did result in hardly sufficient retention for the more polar analytes. Another disadvantage of tetraalkylammonium salts as mobile phase modifiers in HPLC–ESI–MS is their tendency to form cluster ions with anionic analytes, which can further reduce sensitivity in selected ion monitoring (SIM)- or selected reaction monitoring (SRM)-detection modes [17].

For the coupling to mass spectrometry, volatile buffers should be prefered to enhance retention and peak shape. Ammonium acetate is well suited for this purpose, since it does not interfere with mass spectrometric detection in concentrations normally applied for HPLC [18]. It has consequently been used in several approaches to analyse sulfonated azodyes [19–21] and naphthalenesulfonic acids [17] by HPLC–MS. In an early example, Bruins et al. reported an ion spray HPLC–MS–MS method for mono- and disulfonated azodyes from fortified river water [19].

Apparently, higher sulfonated and thus very polar naphthalene sulfonates generally require more efficient ion pairing agents than ammonium acetate to obtain reasonable retention. Triethylamine was used in several applications for HPLC–MS, e.g. in the analysis of nucleotides and oligonucleotides [22] as well as for the analysis of linear alkylbenzene sulfonates (LASs) [23], but its suitability as ion-pairing agent for very polar compounds was never investigated.

For aromatic sulfonates, negative ion detection is the obvious mode for MS-analysis. It was used with different soft ionisation techniques, like fast atom bombardment (FAB) [24] or ESI [17–20,25]. With direct-probe ESI–MS diethylamine was reported to enhance ionisation of polysulfonates [25] and polyphosphates [26]. Addition of the amine suppressed multiply charged analyte ions in favour of singly charged ones, thus providing molecular mass information.

Thus, aliphatic amines seemed to be suitable to provide the necessary retention for HPLC and to enhance the ionisation of anionic analytes in HPLC–ESI–MS.

We therefore investigated the applicability of three aliphatic amines as mobile phase modifiers for the HPLC–ESI–MS–MS analysis of aromatic sulfonic acids. The volatility of these ion-pairing agents prevented many of the obstacles usually experienced with ion pairing agents in HPLC–MS. The retention behaviour as well as the influence of the concentration of the ion pairing on the mass spectrometric sensitivity of di- and trisulfonated aromatic compounds was studied. The potential of the final method is demonstrated by its application to the analysis of dyeing baths and textile processing wastewater.

2. Experimental

2.1. Chemicals

Naphthalene-2-sulfonic acid (95%, sodium salt) and toluenesulfonic (99%, sodium salt) acid were obtained from Merck (Darmstadt, Germany). Naphthalene-1,5-disulfonic acid (85%, disodium salt), 3-aminobenzenesulfonic acid (95%, sodium salt), 3-nitrobenzenesulfonic acid (95%, sodium salt), 1-hydroxynaphthalene-3,6-disulfonic acid (55%, sodium salt), 2-hydroxynaphthalene-3,6-disulfonic acid (95%, sodium salt), 4,5-dihydroxynaphthalene-2,7-disulfonic acid (99.5%, sodium salt) and naphthalene-1-sulfonic (75%, sodium salt) were obtained from Fluka (Deisenhofen, Germany). 1-Amino-8-hydroxynaphthalene-3,6-disulfonic acid (85%, sodium salt), naphthalene-2,6-disulfonic acid (80%, sodium salt) and anthraquinone-1,5-disulfonic acid (95%, sodium salt) were supplied by Aldrich (Steinheim, Germany), whereas naphthalene-2,7-disulfonic acid (95%, sodium salt) together with an isomeric mixture of naphthalenetrisulfonic acids (naphthalene-1,3,6-trisulfonic acid, naphthalene-1,3,5-trisulfonic acid, naphthalene-1,3,7-trisulfonic acid, 5:1:2; 95% for sulfonic acid content, sodium salts) were supplied by TCI/Chemos (Regenstauf, Germany). 7-Aminonaphthalene-1,3-disulfonic (85%)

and 7-amino-1,3,5-trisulfonic acids (70%) were gifts from Bayer (Ludwigshafen, Germany). Naphthalene-1,6-disulfonic acid (66%, sodium salt) and naphthalene-1,7-disulfonic acid (70%, sodium salt) were kindly provided by C. Redin (Research Center for Water Technology, Karlsruhe, Germany). Structures of the compounds together with the notation suggested by Kok et al. [13] can be found in Fig. 1.

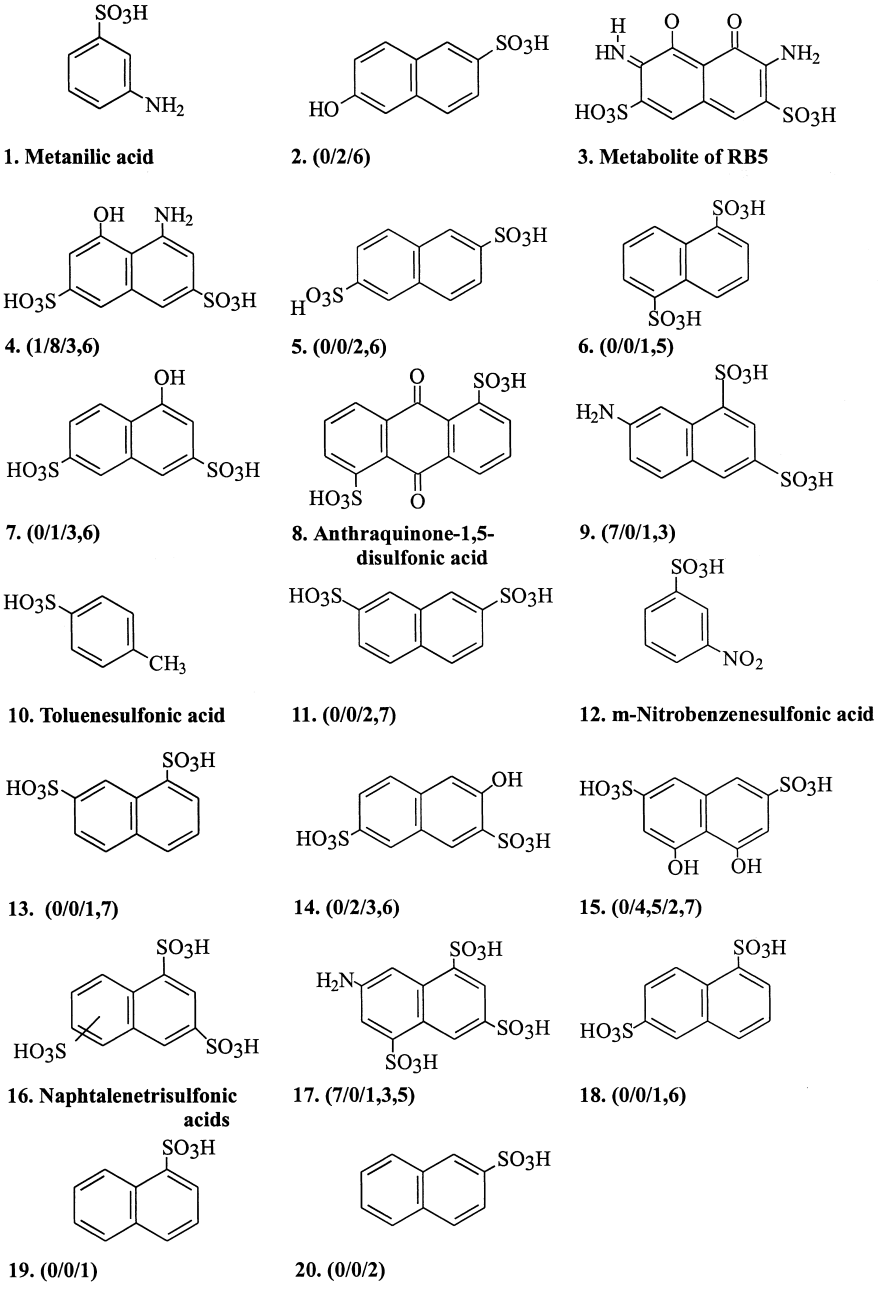

Fig. 1. Structures of the aromatic sulfonic acids examined. Notation scheme according to Kok et al. [13], with substituent positions on the naphthalene ring in parantheses (amino/hydroxy/sulfonate).

Stock solutions containing 1 mg ml^{-1} were prepared in ultrapure water, stored in the dark at 4°C and diluted to the desired concentrations prior to use.

Triethylamine (TEA), *N*,*N*-dimethyl-*n*-butylamine (DMBA), and tri-*n*-butylamine (TBA) were purchased from Fluka in the highest obtainable purity and distilled prior to use. The distilled amines were stored in the dark at 4°C. Acetic acid was of analytical grade from Fluka.

HPLC eluents were prepared from methanol (Baker ultra gradient grade) and water purified by an ELGA maxima HPLC ultra pure water unit (ELGA, Ubstadt–Weiher, Germany). The pH was adjusted with acetic acid using a WTW-microprocessor pH meter (WTW, Weilheim, Germany) together with a GAT ionode pH electrode (GAT, Berlin, Germany).

2.2. Samples

Textile wastewater was supplied by a textile dyehouse in Berlin, Germany. This wastewater was treated in a two step anaerobic/aerobic laboratory treatment facility [27]. Grab samples were taken from the influent, primary and secondary effluent. A sample from a spent dyeing-bath was provided by a plastic dyeing facility in South-eastern Germany. Samples were filtered through 13 mm diameter 0.2 μm nylon syringe filters (Alltech, Unterhaching, Germany) and injected without sample processing except for dilution in some cases.

2.3. Flow injection Liquid chromatography

A HP 1100 series liquid chromatograph (Hewlett–Packard, Waldbronn, Germany), consisting of a vacuum solvent degassing unit, a binary high-pressure gradient pump, an automatic sample injector, a column thermostat and a diode array detector was used for the flow injection analysis performed to evaluate the optimal mobile phase composition and for all LC separations.

Flow injections were performed using the HPLC system without an analytical column and injecting 20 μl of the analyte solution. To examine the effect of ion-pair concentration and pH on ionisation efficiency, the amines (TEA, DMBA, or TBA) were dissolved in water–methanol (1:1) in the desired concentration with the pH adjusted with acetic acid. Analyte solutions were prepared containing 1mg l^{-1} by diluting the aqueous stock solutions 1:1000 in the eluent, which should be tested.

HPLC separations were performed on a 150×2 mm Luna Phenyl-Hexyl (3 μm) column (Phenomenex, Eschborn, Germany), operated with a precolumn 30×2 mm containing the same sorbent. According to the manufacturer, this stationary phase offers excellent selectivities for aromatic analytes, together with a hydrophobicity comparable to conventional C_8 or even C_{18} material. The column temperature was maintained at 45°C and the flow-rate was set to 0.25 ml min^{-1}. Sample volumes of 20 μl were injected. Final chromatographic conditions were as follows: eluent A water–methanol (70:30) and eluent B water–methanol (30:70), both with 2.5 mmol l^{-1} TBA adjusted to pH 8 with acetic acid, linear gradient from 0% B to 75% B in 16 min, 2 min hold and 7 min equilibration.

2.4. Mass spectrometry

A Quattro-LC triple-stage-quadrupole mass spectrometer (Micromass, Manchester, UK) with a mass range up to m/z 4000 and equipped with the orthogonal Z-spray-electrospray interface was used for LC–MS–MS detection. Drying gas as well as nebulizing gas was nitrogen generated from pressurized air in a Whatman model 75-72 nitrogen generator (Whatman, Haverhill, USA). Collision gas was argon 5.0 (Messer, Berlin, Germany) with the pressure in the collision cell maintained at 1.1 to 1.3×10^{-3} mbar when operating in the MS–MS mode. Direct introduction was performed with an Model 11 single syringe pump (Harvard, Holliston, USA).

3. Results and discussion

3.1. Mass spectrometry of sulfonic acids

Upon ionisation with electrospray, naphthalenesulfonic acids produce easily interpretable spectra, consisting mainly of the molecular ions. Limited in-source-fragmentation is observed at low cone voltages, while considerable fragmentation occurs with cone voltages above 35 V. Among the frag-

ments, the SO_3^- radical anion at m/z 80 [19] as well as the $(M-SO_3-H)^-$ and the $(M-SO_2-H)^-$ are specific for aromatic sulfonates. The cone voltage (CV) has a strong influence on the intensities of the molecular ions as shown for naphthalene-1,5-disulfonic acid in Fig. 2. The dianion $(M-2H)^{2-}$ at m/z 143 is observed with maximum intensities at about 23 V applied to the cone, whereas the monoanion $(M-H)^-$ reaches its maximum intensity at about 43 V.

In heavily polluted wastewater from industrial processes, high concentrations of individual pollutants are likely to occur. For complex matrices like this, maximum selectivity rather than maximum sensitivity is desirable. Time-scheduled SRM was applied for this task. Optimal SRM conditions were established for all individual compounds under investigation, and the collision induced dissociation (CID) reactions chosen for detection in HPLC–MS–MS are given in Table 1 together with the respective cone voltages and collision energies. To enhance sensitivity in SRM detection, less than single mass resolution was used ($R=m/\Delta m=115$, as measured for the $(M-SO_2-H)^-$ ion at m/z 143 in the CID spectrum of naphthalene-2-sulfonic acid).

For confirmation purposes in the case of naphthalenedisulfonic acids, additional SRM reactions were selected. CID fragmentation of the dianion of naphthalenedisulfonic acids produces two main fragments, m/z 80 (SO_3^-) and m/z 206 $[(M-SO_3-2H)^-]$.

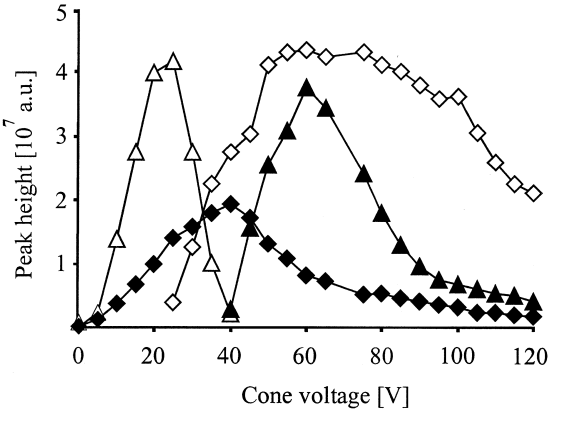

Fig. 2. Dependence of ionisation and fragmentation on cone voltage (CV) for naphthalene-1,5-disulfonic acid. ♦ m/z 287 (monoanion) △ m/z 143 (dianion) ◊ m/z 80 $(SO_3)^-$ ▲ m/z 207 [fragment $(M-H-SO_3)^-$].

Quantitation was performed with up to six SRM transitions in one time-frame, with dwell times of 0.2 s for each transition (quantitation method A). When naphthalenedisulfonic and naphthalenesulfonic acids were analysed exclusively, quantitation was performed with only two SRM transitions, m/z 287>m/z 207 and m/z 207>m/z 143. Thus, dwell times of 0.45 s could be used, which resulted in increased sensitivity (quantitation method B). The SRM transitions employed for each compound are given in Table 1. External calibration was performed with seven concentration levels (1, 5, 10, 50, 100, 500 and 1000 $\mu g\,l^{-1}$). Quadratic calibration graphs with regression coefficients from 0.96 to 0.996 were obtained.

3.2. Mobile phase optimization

3.2.1. MS detection

Ion yields in electrospray mass spectrometry are strongly dependent on the composition of the liquid phase, such as the concentration of the ion pairing agent and the pH value. To study the effect of amine concentration on ion yields of naphthalene-1,5-disulfonic acid and naphthalenetrisulfonic acid (mixture of isomers), eluents containing various concentrations of TEA, DMBA, and TBA were used for flow injection. Singly and multiply charged quasimolecular ions of the analytes were monitored in the SIM mode. For all ions and all three trialkylamines, the ion yield tends to decrease with increasing amine concentration, namely between 1 and 5 $mmol\,l^{-1}$ (Fig. 3a,b). In order to obtain the maximum sensitivity, the concentration of the ion-pairing agent should be kept as low as feasible for sufficient chromatographic retention.

Despite the general trend of decreasing intensities with increasing trialkylammonium concentrations, some instructive changes can be seen. The sensitivity decrease is generally much weaker for the monoanion than for the di- and trianions. These results are consistent with earlier findings of Ballantine et al. [25], who observed, that diethylamine increased the sensitivity of singly charged polysulfonates. They suggested, that this was due to the dissociation of the sulfonate–diethylammonium ion pairs into sulfonic

Table 1
Retention times (t_R), molecular masses (M_r), SRM-transitions, cone voltages (CV), collision energies (CE) and limits of detection (LOD) of the aromatic sulfonates investigated

	Compound[a]	t_R (min)	M_r	SRM	CV/CE (V/eV)	LOD[b] ($\mu g\,l^{-1}$)
1	Metanilic acid	4.93	173	172>80	35/24	12
2	(0/2/6)	9.36	224	223>158	43/31	8
3	Metabolite[c]	10.17	348	347>267	45/25	n.d.
4	(1/8/3,6)	10.38	319	318>238	46/23	27
5	(0/0/2,6)	10.81	288	287>207	46/24	9[d]
6	(0/0/1,5)	11.22	288	287>207	46/24	11[d]
7	(0/1/3,6)	11.33	304	303>223	43/21	23
8	Anthraquinone-1,5-disulfonic acid	11.37	368	368>195	48/41	31
9	(7/0/1,3)	11.52	303	302>222	46/23	29
10	Toluenesulfonic acid	12.35	172	171>107	38/21	3
11	(0/0/2,7)	12.44	288	287>207	46/24	12[d]
12	*m*-Nitrobenzenesulfonic acid	12.58	203	202>156	36/23	4
13	(0/0/1,7)	12.74	288	287>207	46/24	11[d]
14	(0/2/3,6)	13.33	304	303>223	43/21	35
15	(0/4.5/2,7)	14.39	320	319>239	46/22	37
16	(0/0/1,3,5) (0/0/1,3,6) (0/0/1,3,7)	14.70	368	367>206	61/31	51[e]
17	(7/0/1,3,5)	14.83	383	382>222	60/30	74
18	(0/0/1,6)	15.41	288	287>207	46/24	6[d]
19	(0/0/1)	16.70	208	207>143	43/26	5[d]
20	(0/0/2)	17.45	208	207>143	43/26	3[d]

[a] Notations according to Fig. 1.
[b] Determined for $S/N>5$, using quantitation method A, not corrected for purities of standards.
[c] Anaerobic degradation product of Reactive Black 5, refer to Fig. 1.
[d] Using quantitation method B, not corrected for purities of standards.
[e] Since the amounts of the isomers was not known, the LOD is given for the sum of the isomers.

acid and diethylamine during desolvation. It is, thus, reasonable to find an increasing portion of the monoanion compared to the di- and trianions with increasing trialkylammonium concentrations.

It should be noted, that an increase of the ion yields is found by increasing the amine concentration from 0.5 to 1 mmol l^{-1} in several instances. This effect is most pronounced for TBA. A comparable increase was found by Griffey et al. in the ESI–MS analysis of oligonucleotides [28]. With unaltered charge-state distribution of the oligonucleotide, they observed an 1.6-fold increase in intensity with 1 mmol l^{-1} glycine added to the sample, while a 2-fold decrease occured with a glycine concentration of 50 mmol l^{-1}. This phenomenon, however, is not fully understood and requires further investigation.

In general, sensitivity decreases with increasing number of sulfonate moieties. For example, the intensity of the monoanion of naphthalene trisulfonate comes up to 25% of the monoanion of the disulfonate (Fig. 3a), only.

The influence of the eluent-pH on ion yields was studied for TBA. Between pH 4.5 to pH 10 ion yields were not significantly altered for either of the two sulfonates. Since pK_a values of naphthalenesulfonic acids are very low [15], they are completely dissociated above pH 4. According to accepted theory, ions preformed in solution are the major source for ions in electrospray ionisation. Thus a pronounced pH-effect on ionisation efficiencies was not expected in the pH range investigated here.

A pH-value of 8 was selected for the final separation conditions used for quantitation, merely to prevent the acid-catalysed oxidation of TBA to the corresponding *N*-oxide.

3.2.2. Retention behaviour and quantitation

Fig. 4 shows the separation of 19 aromatic sul-

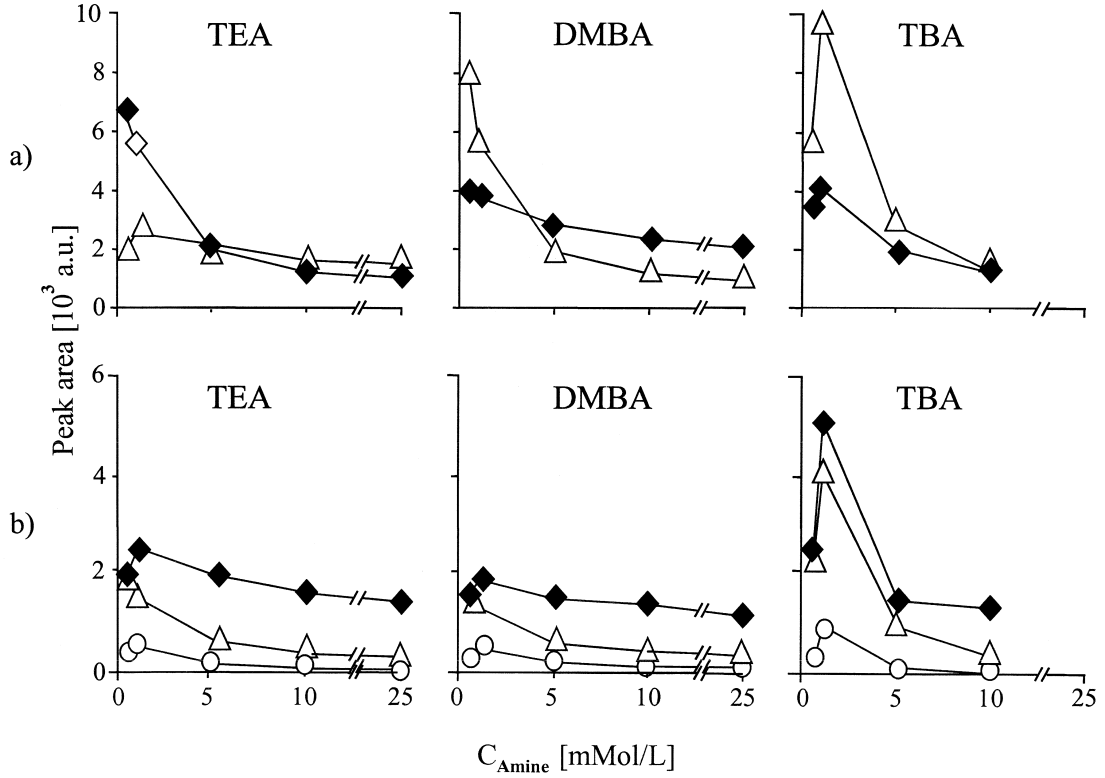

Fig. 3. Influence of amine concentrations on ionisation efficiencies as measured by flow injection of (a) naphthalene-1,5-disulfonic acid and (b) naphthalenetrisulfonic acid. (a)♦m/z 287 (monoanion) △m/z 143 (dianion) (b)♦m/z 367 (monoanion) △ m/z 183 (dianion) ○ m/z 121 (trianion)

fonic acids using TEA, DMBA and TBA as mobile phase modifiers with an amine concentration of 2.5 mmol l^{-1} at pH 7. TEA and DMBA provide sufficient retention for some monosulfonated compounds, such as naphthalene-1-sulfonic acid and naphthalene-2-sulfonic acid. However, the more polar di- and trisulfonated compounds, as well as the amino- and hydroxysubstituted naphthalenesulfonic acids, are poorly retained. Many of these compounds elute in the dead volume (Fig. 4a and b). With TBA even the most polar compounds exhibit strong retention under the same conditions (Fig. 4c). Thus, gradient elution can begin with a higher content of organic solvent in the mobile phase (Fig. 4d). This is expected to be beneficial for the ionization efficiency under electrospray ionisation conditions [29].

The retention behaviour of the naphthalenesulfonates is comparable to that observed in conventional ion pair chromatography with tetraalkylammonium salts, where the disulfonic acids are eluting before the trisulfonic acids, followed by naphthalene-1- and -2-sulfonate [8,10]. This suggests a comparable retention mechanisms for the separation with TBA.

With optimised chromatographic conditions and TBA as modifier, 19 naphthalenesulfonic acids could be analysed using time scheduled SRM-detection within a total analysis time of 25 min (Fig. 4d). Separation of five isomers of naphthalenedisulfonic acid, for which standard substances were available, was achieved. This is an essential prerequisite for the quantitation of isomers with identical mass spectrometric behaviour. The limits of detection (LODs, $S/N>5$) increase with the degree of sulfonation from 3 μg l^{-1} for naphthalene-2-sulfonic acid to 51 μg l^{-1} for naphthalenetrisulfonic acid. Aminosubstitution

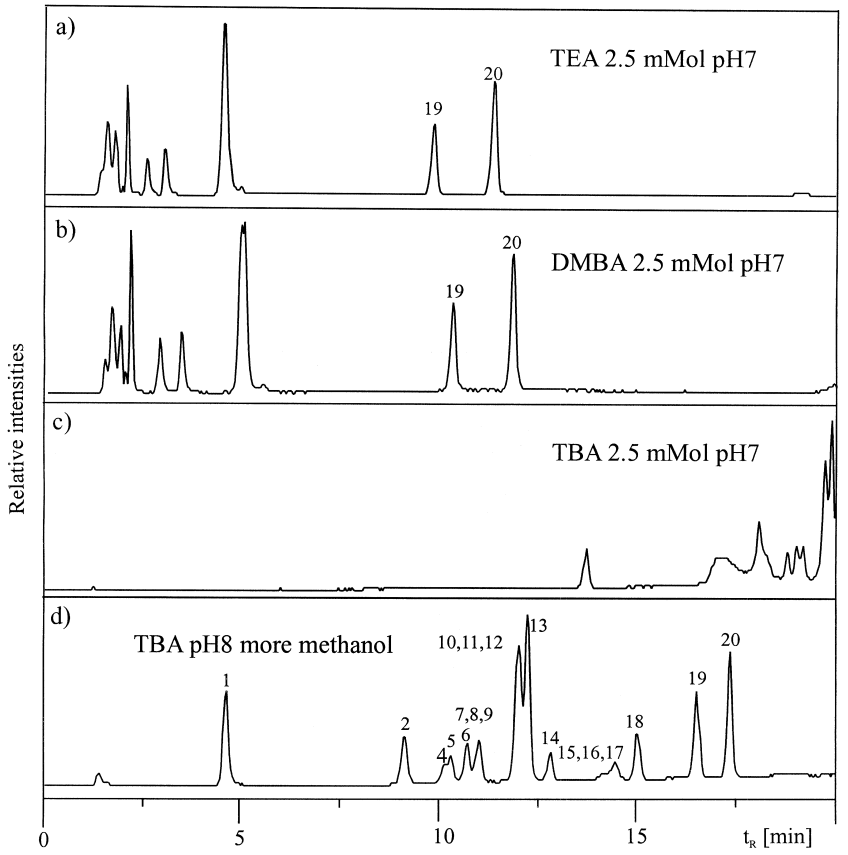

Fig. 4. Optimisation of chromatographic conditions using TEA, DMBA and TBA as mobile phase modifier. (a–c) Eluent A (10% methanol) and B (70% methanol) both containing 2.5 mmol l^{-1} amine. Linear gradient from 0% B to 75% B in 16 min, 2 min hold and 7 min reequilibration. (d) Accordingly, with 30% methanol in eluent A. Detection with SIM on all molecular masses in one detection window.

further increases the LOD to 74 μg l^{-1} in the case of 7-amino-naphthalene-1,3,5-trisulfonic acid. Further details are given in table 1. Although the LODs are higher than those reported for diode array or fluorescence detection, especially for higher sulfonated compounds [8,10], they are expected to be sufficient for the direct analysis of industrial wastewater. Lower concentrations would require an enrichment step such as solid-phase extraction in the analytical scheme.

3.3. Analysis of industrial wastewater

3.3.1. Naphthalenesulfonic acids

Fig. 5 shows an example for the determination of naphthalenesulfonic acids in a spent dyeing bath. Five isomers of naphthalenedisulfonic acid and two isomers of naphthalenesulfonic acid were identified in concentrations ranging from 0.1 to 2.1 mg l^{-1}.

To confirm the identity of the disulfonic acids, the transition m/z 143>m/z 206 was utilized. The sensitivity of this transition is considerably lower as compared to the transition m/z 287>m/z 207 applied for quantitation, because ionisation is not as efficient for the dianion under the conditions chosen. Nevertheless, identification of five naphthalenedisulfonic could be confirmed in this way (Fig. 5c and d). In addition, a compound was identified as another isomer of naphthalenedisulfonic acid (peak marked u in Fig. 5), although it was not possible to determine which isomer it was without standard substances.

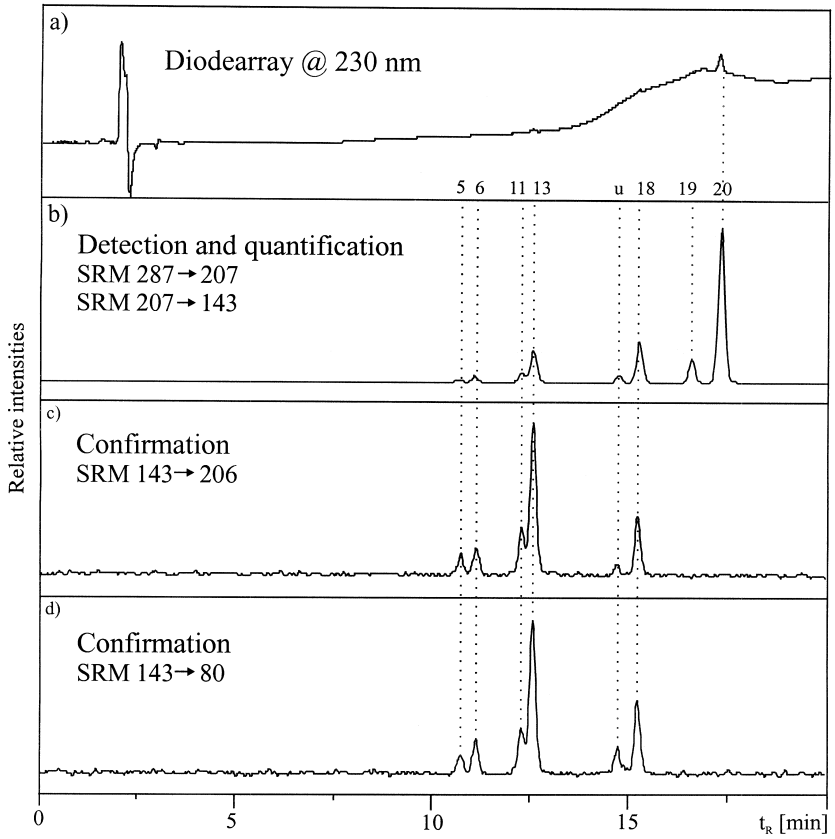

Fig. 5. Detection of naphthalenedisulfonic and naphthalenesulfonic acids in a spent dyeing bath. (a) diode array detection at 230 nm. (b) Detection with SRM on 287>207 and 207>143. (c and d) Confirmation using SRM on fragmentations of the dianions of naphthalenedisulfonic acids. For compound identities refer to Fig. 1, u: unknown isomer of naphthalenedisulfonic acid.

In textile wastewater, naphthalene-1- and naphthalene-2-sulfonic acid were identified together with three naphthalenedisulfonic acids in concentrations from 0.1 to 1 mg l^{-1}.

3.3.2. Dye degradation product

A degradation product of the sulfonated azodye Reactive Black 5 was identified in the effluent of an anaerobic laboratory reactor [26] by UV and mass spectra (Fig. 6). UV spectra and mass spectra were in accordance with those of a compound described by Kudlich [30] as an anaerobic degradation product of the sulfonated azo-dye Naphthol Black 6B (Fig. 1, compound 3). The product ion mass spectra confirmed the presence of two sulfonate groups by two successive losses of the specific mass m/z 80 (SO_3).

4. Conclusions

The method presented is well suited for the analysis of aromatic sulfonates in highly polluted wastewater. 19 aromatic sulfonates could be analysed by direct injection of 20 μl of the aqueous samples without further sample treatment steps except for filtration. Total analysis time was 25 min.

In contrast to conventional ion-pairing agents, e.g. tetraalkylammonium salts, the volatile amines TEA, DMBA and TBA are applicable in conjunction with mass spectrometric detection. Since the sensitivity is reduced by rising amine concentrations in the HPLC eluent, low concentrations of the ion-pairing agent are desirable. TBA provides the best retention for the separation of di- and trisulfonic acids at low amine

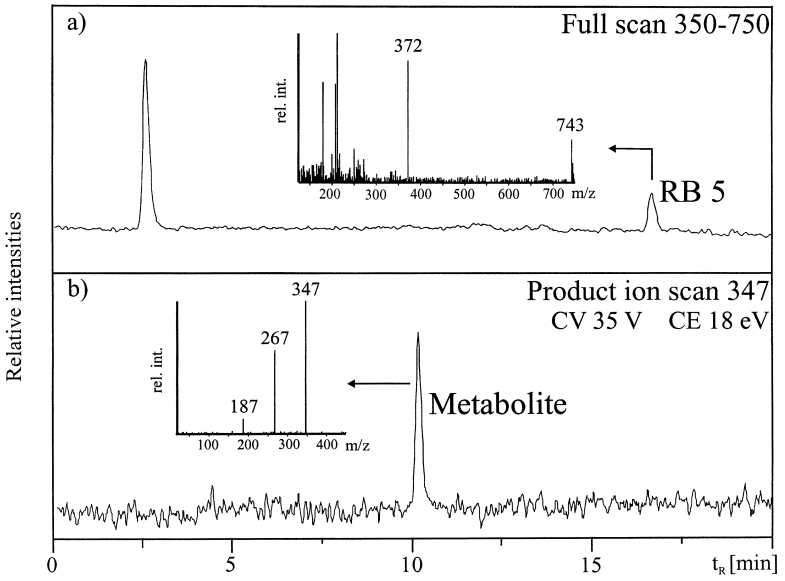

Fig. 6. Identification of a degradation product of the azodye Reactive Black 5 (RB 5) in the effluent of an anaerobic laboratory reactor. (a) Influent, summed intensities m/z 350–m/z 750, together with mass spectrum of RB 5. (b) Effluent, product ion scan of m/z 347, with product ion mass spectrum of the metabolite. Note that the fragments are separated by a mass difference of 80 (SO_3).

concentrations, and was accordingly chosen as ion pairing agent.

The limits of detection range from 3 $\mu g\,l^{-1}$ for naphthalenemonosulfonates to 74 $\mu g\,l^{-1}$ for an amino-substituted naphthalenetrisulfonate. For higher sulfonated compounds the limits of detection are generally higher than those obtained by diode array or fluorescence detection, but they are sufficient for the analysis of highly polluted industrial wastewater. Analysis of less polluted samples, for example surface water, would require preconcentration steps, such as solid-phase extraction, prior to analysis.

The main advantage of mass spectrometric detection for the analysis of highly polluted industrial wastewater is the high selectivity, especially when using SRM detection. In combination with good to moderate sensitivity, this proved to be very valuable to confirm peak assignments and to identify unknowns in highly polluted industrial wastewater.

Acknowledgements

Funding by the German Research Council through the ‘Sonderforschungsbereich 193 ‘Biological treatment of industrial wastewater’ TP A14’ is gratefully acknowledged. The authors wish to thank the Bayer AG (Leverkusen, Germany) and especially C. Redin (Research Center for Water Technology, Karlsruhe, Germany) for providing reference compounds. M. Borchert and J. Schürmann (Technical University Berlin, Germany) kindly provided samples of textile wastewater.

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