



ELSEVIER

Journal of Chromatography A, 777 (1997) 127–139

JOURNAL OF
CHROMATOGRAPHY A

Analysis of polar organic pollutants in the Elbe river by flow injection analysis and high-performance liquid chromatography with tandem mass spectrometry¹

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Abstract

Water extracts from the Elbe river and from one of its tributaries have been analyzed by gas chromatography–mass spectrometry (GC–MS) and by high-performance liquid chromatography combined with ultraviolet (UV) and/or MS detection. After column chromatography or flow injection analysis (FIA) bypassing the analytical column, ionization for MS was performed by either atmospheric pressure chemical ionization or electrospray. Since the reduction of the pollutant concentrations relative to the concentration of matrix components in the water samples had continued compared to earlier investigations [H.Fr. Schröder, *J. Chromatogr. A* 712 (1995) 123–140], substance-group-specific methods were applied for the screening for certain compound groups. For this purpose tandem mass spectrometry (MS–MS) was used to characterize the substance groups, with the help of parent-ion and neutral-loss scans. Identification then followed by means of daughter-ion spectra, which were generated by collisionally induced dissociation (CID) using FIA–MS–MS. The limitations of mixture analysis in the case of isomeric compounds present in the extracts are demonstrated. © 1997 Elsevier Science B.V.

Keywords: Aromatic sulfonic acids; Water analysis; Environmental analysis; Polar organic compounds; Anionic, cationic and nonionic surfactants

1. Introduction

The production of drinking water from surface water supplies more than 25% of the demand of Germany's population. A large part of the surface water is obtained from the Elbe river in the East and the Rhine river in the West. Apart from a few accidents, during the last years, the quality of Rhine water has reached a high standard. Also the water quality of the Elbe, which for a long time was one of

the most contaminated rivers in Central Europe, has considerably improved [1,2]. After the unification of the two German states in 1990, the number of sewage treatment plants has increased, and in parallel, industrial production in Eastern Germany has declined. This has led to a change in the quantity and quality of the pollutant spectrum in Elbe water [1–3]. The reduction in the pollutant spectrum has not effected nonpolar and polar organic compounds in the same way, but is observed disproportionately for nonpolar compounds. This reduction of the total pollution load makes drinking water treatment much easier. However, the concentration of polar compounds has only been reduced by a minimal amount

¹Dedicated to Professor Dr.-Ing. Böhnke on the occasion of his 75th birthday, 22 March 1997.

since these are unaffected by the bank filtration process employed as the main technique for water treatment. Therefore, other very expensive treatment steps are also necessary to remove these compounds from the raw- and drinking water.

In parallel with the reduction of pollutants, their detection became increasingly difficult. While GC–MS screening analysis was hardly effected, larger and larger water volumes have to be extracted for screening- and target analysis of polar organic constituents by flow injection analysis (FIA) and LC–MS. The reason for this is not only the general reduction of polar compounds, but also the shifting of the ratio of anthropogenic and biogenic compounds developed from anthropogenic compounds in favour of polar matrix compounds. Using atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) instead of thermospray (TSP) ionization [1], the detection sensitivity improves, which is helpful in target analysis performed using a LC separation prior to detection. But in FIA–MS analysis (carried out as a screening analysis) it is not helpful because the ratio of matrix and pollutants has changed in favour of the matrix. The ions of the pollutants are hidden by the matrix ions, preventing identification of pollutant ions on simple inspection of spectra.

For this reason, LC target analyses are often necessary for pollutant identification. This contribution deals with substance-group-specific screening methods for polar organic water constituents, which have been used to increase the specificity, i.e. to enable the identification of pollutants in the presence of matrix compounds. These methods had already been applied successfully for the examination of waste waters [4,5] and now have been optimized for the analysis of water samples from the Elbe and its tributaries, i.e. for surface waters [6].

2. Experimental

2.1. Materials

Water samples from the Elbe were taken from the Elbe monitoring station at Magdeburg. From the Saale (a tributary of the Elbe), samples were taken at various places along the river. Water pollutants were

extracted using solid-phase extraction (SPE) cartridges filled with 100, 500 or 1000 mg of C_{18} material from Baker (Deventer, Netherlands). Sodium azide for preservation was of analytical reagent grade (Merck, Germany). The standard blend Leomin AC 80 (fatty amine oxethylate) was a gift of Hoechst (Frankfurt, Germany).

SPE cartridges were conditioned as prescribed by the manufacturer. Glass-fibre and membrane filters used for the pretreatment of the water samples were obtained from Schleicher and Schüll (Dassel, Germany) or Sartorius (Göttingen, Germany). Before use, the glass-fibre and membrane filters were heated to 400°C or were treated with ultra-pure water obtained with a Milli-Q system from Millipore (Milford, MA, USA) for 24 h and then washed with 100 ml of the same water. Diethyl ether and methanol used for desorption of water pollutants from the solid-phase material and acetone and methanol for SPE-conditioning purposes were Nanograde solvents from Promo chem (Wesel, Germany). Acetonitrile, chloroform, methanol and dimethyl sulfoxide for column-cleaning purpose were of analytical grade (Merck, Germany). Nitrogen for drying of solid-phase cartridges was of 99.999% purity, nitrogen used as sheath gas in ESI ionization was of 5.0 purity, and argon used as collision gas was of technical grade (Linde, Germany).

LC separations were carried out using a Nucleosil C_{18} (5- μ m, spherical) column (25 cm \times 4.6 mm I.D.) (CS, Langerwehe, Germany). The mobile phase was acetonitrile (HPLC grade; Promochem) and Milli-Q-purified water. Ammonium acetate used in the APCI process, stored always at 4°C, was of analytical-reagent grade from Merck. Tetrabutylammonium hydrogensulfate (TBAHSO₄) and diammonium hydrogenphosphate were of analytical-reagent grade from Merck.

2.2. Sampling and sample preparation

All samples from the Elbe were taken as composite samples, the Saale samples were grab samples. All samples were taken and stored in glass bottles. Prior to use, the bottles were rinsed carefully with Nanograde acetone and methanol and dried at 105°C. The bottles were rinsed directly before use with several small portions of the same water that was

subsequently stored in them. Preservation was done adding sodium azide resulting in a concentration of 100 mg/l. The storage temperature was 4°C. The cold bottles from refrigerator storage were placed in an insulating packaging and were then transported by a parcel service within 24 h from the sampling point to the research laboratory, where they were immediately extracted by SPE.

Depending on the degree of pollution as monitored by measuring dissolved organic carbon (DOC) (as described in Section 2.3), different amounts of water were used for SPE. The quantity of water used for extraction was chosen in such a way that a maximum load of 7 mg DOC per 100 mg of SPE material was applied. Water samples for FIA- and LC-MS analysis were forced through the SPE cartridges after passage through a glass-fibre filter. The adsorbed pollutants were desorbed more or less separately. Solvents of different polarities (diethyl ether and methanol) were used for this purpose in combination with C₁₈ material. All eluates from the solid-phase extraction were evaporated to dryness with a nitrogen stream at 30°C. The residues were dissolved in acetonitrile and could be used for injection during FIA- and LC-MS analysis. The concentration factor in all cases was 5000. The quantity of water extracted and solvent used for elution were adapted to this concentration factor. The water samples of the Elbe used for the determination of aromatic sulfonic acids were handled as prescribed in literature [7] with the exception that sodium salts for ion-pairing elution purposes were substituted by ammonium compounds.

For GC-MS analysis, a mixture (1:1, v/v) of the diethyl ether and methanolic SPE eluates was used. The concentration factor was 5000. The solution could be used for injection into the GC-MS system.

2.3. Sum parameter analysis

The DOC content of the water samples was measured using a Dohrman total carbon analyzer DC 80 or a Ströhlein total carbon analyzer (C-MAT 5500). After filtration of the pretreated samples using a glass-fibre filter, wet oxidation with an acidic potassium persulfate solution in water assisted by UV radiation (DC 80) or the combustion miner-

alization was performed (C-MAT 5500), both combined with infrared detection.

2.4. Gas chromatographic system

A Varian (Darmstadt, Germany) Model 3400 GC system with a fused-silica capillary column was used. The conditions were as follows: carrier gas, helium; linear gas velocity, 15 cm/s; injector temperature, 250°C; transfer line temperature, 250°C; column, DB-35 ms (J&W), film thickness 0.25 µm (30 m×0.32 mm I.D.).

Combined with GC, electron impact (EI) ionization was applied with an ionization energy of 70 eV. Under these conditions the pressure in the ion source was $8 \cdot 10^{-6}$ Torr (1 Torr=133.322 Pa) and that in the vacuum system of the mass spectrometer $3 \cdot 10^{-2}$ Torr. The electron multiplier was operated at 1200 V with a conversion dynode voltage at 15 kV. The temperature in the ion source was 150°C.

2.5. Liquid chromatographic system

LC separations coupled with MS, MS-MS and UV detection were achieved with a Waters (Milford, MA, USA) Model 600 MS system. A Waters Model 510 pump was used for post-column addition of 0.1 M ammonium acetate solution in the APCI mode. A Waters 996 photodiode array detector system in combination with a Millennium 2010 data system (Millipore) was connected in-line with the APCI- or ESI interface. The conditions in FIA bypassing the analytical column were as follows: mobile phase methanol-water (30:70) containing 0.05 M ammonium acetate. The overall flow-rate was 0.6 ml/min.

The chromatographic separations on the analytical column were carried out after examination of optimized conditions for the separation of polar organic compounds in surface water extracts. The flow-rate for column separation using a gradient elution (solvent A: acetonitrile; solvent B: water) was 1.0 ml/min, the gradient was programmed as follows: Starting with A-B (10:90) the concentration was increased linearly to 90% A within 15 min. After passing the UV detector, 0.5 ml/min of 0.1 M ammonium acetate was added, which resulted in an overall flow-rate of 1.5 ml/min. The post-column

flow split ratio was 1:2 in favour of the MS in APCI and ESI mode or waste, respectively.

The reversed-phase column was cleaned several times a week with a mixture of acetonitrile–chloroform–methanol–dimethyl sulphoxide (3:3:3:1, v/v).

2.6. MS and MS–MS systems

A TSQ 700 mass spectrometer (Finnigan MAT, San Jose, CA, USA) combined with a DEC 5000/33 data station was used for research work. The APCI and ESI interface was obtained from Finnigan MAT.

For coupling the LC system with the mass spectrometer, the conditions for APCI ionization using ammonium acetate were chosen as: vaporizer temperature, 400°C, capillary temperature, 180°C. Corona voltage was operated at 5 kV. The potential of capillary, tube lens and API octapole were chosen as 50, 50 or –3 V, respectively. Sheath gas pressure was operated at 40 p.s.i. (1 p.s.i.=6894.76 Pa). ESI was operated at a capillary temperature of 200°C. Sprayer voltage was chosen as 4.5 kV. The potential of capillary, tube lens and API octapole were chosen as in APCI. Sheath gas pressure was operated at 40 psi.

Under the above conditions, the ion source pressure was 0.3 Torr, and the pressure in the vacuum system of the mass spectrometer was $2 \cdot 10^{-5}$ Torr.

The electron multiplier was operated at 1200 V and the conversion dynode at 15 kV. In the MS–MS mode the ion source pressure was also 0.5 Torr.

Under collision-induced dissociation (CID) conditions, the pressure in quadrupole 2 (collision cell) normally was 1.3 mTorr, unless otherwise specified in the captions of the figures. The collision energy was adjusted from –10 to –50 eV. The electron multiplier voltage in quadrupole 3 varied between 1200 and 1700 V with a conversion dynode voltage at 15 kV.

GC–MS analysis was performed by scanning at 1 s from 45 to 500 u.

FIA and LC analyses were applied, recording APCI or ESI mass spectra scanning from 150 to 1200 u at 1 or 3 s, respectively. FIA bypassing the analytical column with MS or MS–MS (daughter-, parent- and neutral loss-mode) detection was performed while accumulating a maximum of 50 scans after injection. The mass spectrum averaging the total ion current from the beginning of the signal up to the end in FIA–MS mode is called the ‘overview spectrum’.

APCI and ESI was normally carried out in positive and negative modes.

3. Results and discussion

The total ion current chromatogram (TIC) presented in Fig. 1 was obtained by GC–MS screening of a water sample from the Saale, a tributary of the Elbe. This sample was representative because of its DOC content. The water sample had been concen-

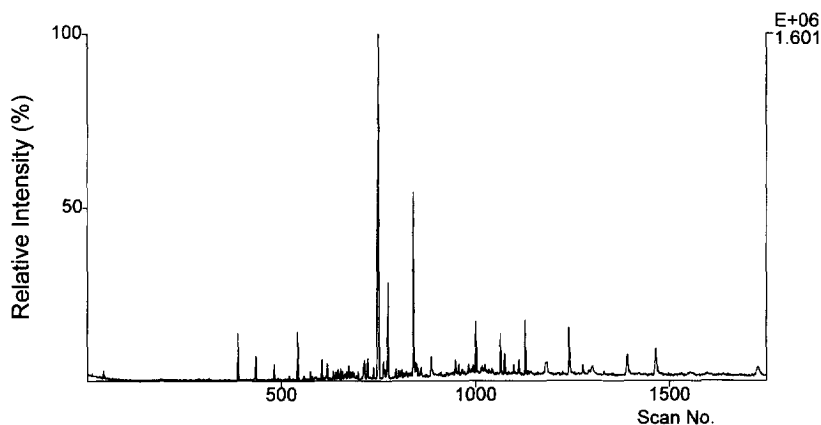


Fig. 1. GC–MS total-ion current tracing for water sample of the Saale river. C_{18} SPE; 1:1 (v/v) mixture of eluates; eluents, diethyl ether and methanol. For concentration factor, chromatographic and MS conditions, see Section 2.

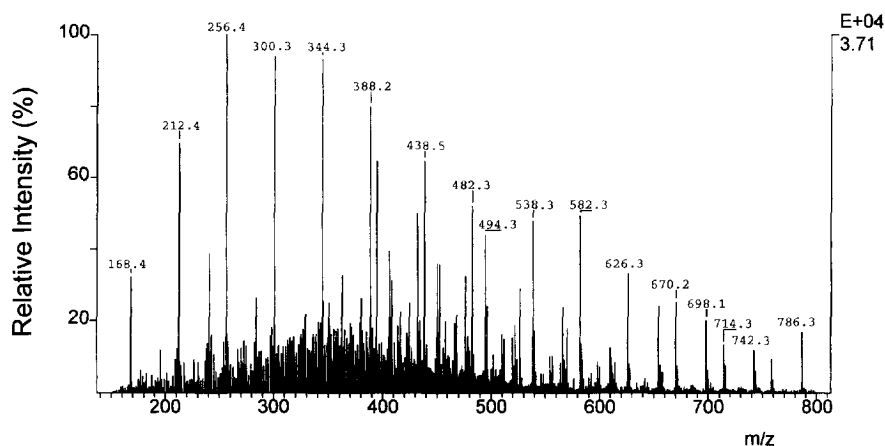


Fig. 2. APCI-MS loop injection spectrum for water sample of Saale river, obtained bypassing the analytical column (FIA-MS), subsequently called 'overview spectrum'. C_{18} SPE; eluent, diethyl ether. Positive APCI ionization. For FIA and MS conditions, see Section 2.

trated by C_{18} -SPE and then desorbed in succession by diethyl ether and methanol. The mixture (1:1) of the diethyl ether- and the methanol eluate was used for GC-MS analysis. Besides the signals of tributyl phosphate and butoxyethyl phosphate, both found ubiquitously, the TIC contained also short-chain polyethylenglycols (PEGs) and isomers of nonylphenol (NP). While the ester in the form detected here probably had already been present in the water, the majority of the nonylphenols must have developed from long-chain nonylphenolethoxylates (NPEOs) by thermal decomposition after injection

into the GC system. Considering the intensity of the ion current and the water volume used for extraction, this water sample can be regarded as not strongly polluted.

Using FIA-MS in combination with soft ionizing interfaces such as APCI or ESI bypassing the analytical column in order to quickly determine the load with polar pollutants, we obtained the overview spectra presented in the Figs. 2 and 3. They were recorded in FIA-MS(+) mode and show the fractions of the same water sample, eluted successively with diethyl ether and methanol. Besides the charac-

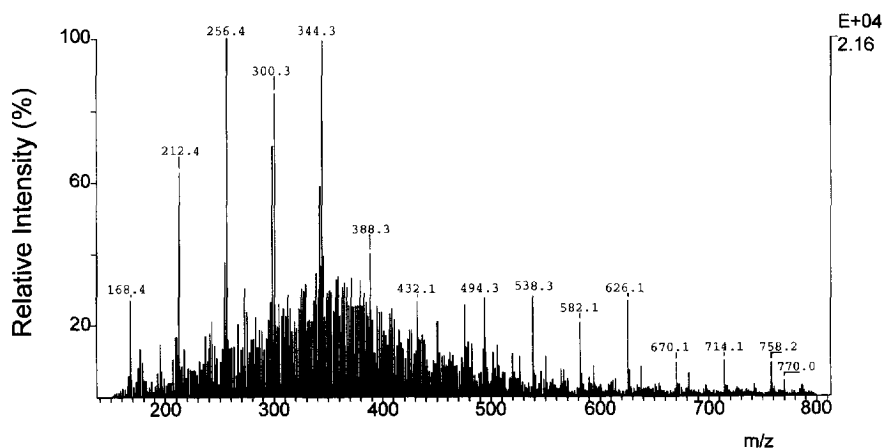


Fig. 3. APCI-MS overview spectrum as in Fig. 2. Eluent, methanol.

teristic signals for linear alkyl benzenesulfonic acids (LASs), the negative FIA–MS spectrum did not show the equidistant distribution of ions ($\Delta m/z$ 44), that can be observed in both of these figures. Comparing the results of this FIA–MS screening with GC–MS analysis data, it becomes obvious that (1) the organic load of 12 mg/l DOC found in the sample nearly exclusively is caused by the presence of polar organic compounds, and (2) for the examination of such samples only separation and detection methods are suited which do not require undecomposed volatility. Otherwise the constituents of the mixture have to be derivatized.

Regarding the pattern of the equidistant ions in the FIA–MS spectra and considering the thermolability of the sample material observed in GC–MS analysis, other compounds containing polyether components in their molecules seem to be present besides the NPEOs. After FIA–MS screening in positive and negative modes, we can presume with high probability that non-ionic or cationic surfactants containing a polyether group are present. Anionic surfactants with polyether components in the molecule, for example the alkylethersulfates (AESs), can be definitively excluded because the FIA–MS(–) spectrum did not show the equidistant distribution of negative ions ($\Delta m/z$ 44), characteristic for AESs [10]. This distribution being only observed in the positive ion spectra.

The result of this screening strengthens the presumption, based on a large number of analytical results from Elbe water samples [3], that the larger part of the anthropogenic polar pollution load consists of surface-active compounds. The origin of these compounds are detergents or their metabolites, i.e. PEG and its further degradation products. However, this finding cannot be verified by using FIA–MS screening only. The analyst has to try to get more information with the help of the retention behaviour of the compounds on the analytical column, using time-consuming high-performance liquid chromatography (HPLC) combined with MS detection (LC–MS) (Fig. 4a and b) which leads to long analysis times unlike FIA–MS which is very rapid.

If besides MS detection, an UV diode array detector, connected in series with the MS, is used, more information can be expected. UV spectra can be recorded and plotted (Fig. 4d), and the 3 D plot

(Fig. 5) gives an impression of the absorption behaviour of the compounds dependent on the wave length and the retention time. But the low informational content of this detector system in the determination of polar organic water constituents, described already several times [1,8], is demonstrated by the UV spectra (Fig. 4d) of selected signals in the UV trace 220 nm shown in Fig. 4c. Even the UV spectrum of the signal of nonylphenolethoxylate, recognizable only by the sharp signal in the mass chromatogram of m/z 458 (Fig. 4b), hardly differs from the UV spectra of selected neighbouring signals in the UV trace (Fig. 4c). By creating other mass chromatograms for ions, which from our experience can be associated with non-ionic surfactants, other surface-active compounds, PEG, and even polypropylenglycol (PPG) can be detected.

However, the same results can be obtained more easily, and above all, more quickly, if substance-group-specific screening by FIA–MS–MS is performed. This method was developed for the detection of polar compounds [3–5], based on a method for direct mixture analysis by MS–MS, used for the examination of complex multi-compound mixtures containing volatile organic compounds [9]. With the help of characteristic parent-ion scans, as listed in Table 1, several non-ionic surfactants and their biogenic degradation products as well as anionic surfactants can be easily recognized.

If the mixture presented already in Fig. 2 in the form of its FIA–MS spectrum is examined for example by FIA–MS–MS(+) using the parent-ion scan m/z 87, which is characteristic for metabolites of PEG or alkanol polyglycol ethers, specific statements are possible with the help of the parent-ion spectrum (Fig. 6). This is due to the fact that in the parent-ion spectrum, such ions are only now appearing which under CID conditions form, among others, the fragment ion m/z 87, i.e. in this case ions of polyether compounds, oxidized in terminal position to aldehyde, appear in the parent ion spectrum. The general structures of precursor compounds and metabolites as well as the fragmentation resulting in fragment of m/z 89 or 87 respectively are presented in Fig. 7. This type of compound normally represents metabolites from alkanol polyglycol ethers, but the compounds found here are mainly PEG metabolites resulting from the biochemical degradation of non-

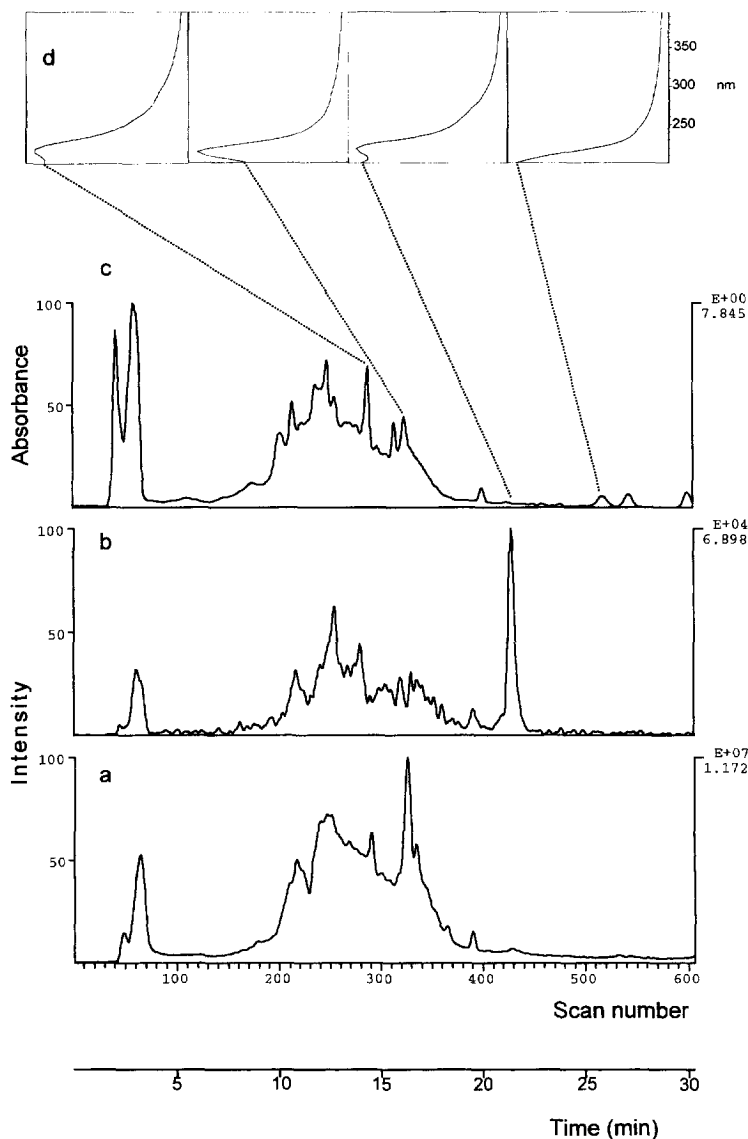


Fig. 4. (a) LC-MS total-ion current tracing water sample of Saale river. C_{18} SPE; mixture of eluates as in Fig. 1; positive APCI ionization; for concentration factor, chromatographic and MS conditions, see Section 2. (b) LC-MS mass trace m/z 458 of Saale river extract in (a) and (c) UV trace (220 nm) of (a). (d) UV spectra of marked peaks in (c); LC conditions as in (a).

ionic surfactants [8,10] prior to their further oxidation in the terminal position.

The result is even more impressive if substance-group-specific screening is used for the detection of the NPEOs, since these are not identifiable in the original FIA-MS spectrum (Fig. 2). By FIA-MS-MS(+), the parent-ion spectrum of m/z 291 presented in Fig. 8 is generated. This shows a series of

ions corresponding to $[M+NH_4]^+$ ions from the homologous series of NPEOs in this water sample. Besides insignificant impurities, only nonylphenolethoxylates are detected in this experiment. These data confirm that using parent scans makes characterization much easier.

Compared to LC-MS, the method described above (FIA-MS-MS) has the advantage that with

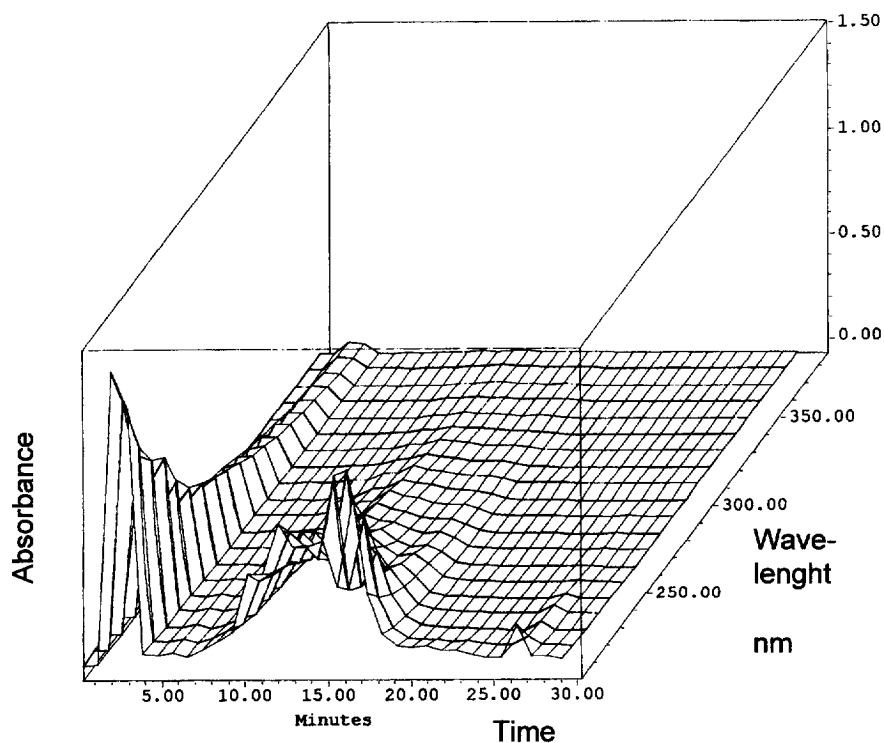


Fig. 5. UV tracing (three-dimensional plot) as in Fig. 4a.

the help of FIA, the analyst is able to examine compounds for which no LC separation method exists, i.e. which are neither eluted, retained nor eluted at all. The FIA–MS overview spectrum in Fig. 2 contains compounds which cannot be eluted from the column under the RPLC conditions chosen for

this LC separation. Under CID conditions, these compounds fragmented forming daughter-ions, which besides amine nitrogen also contained PEG chains with varying lengths, so that equidistant daughter-ions with $\Delta m/z$ 44 developed. Comparison of the daughter-ion spectra of the unknown com-

Table 1
Diagnostic FIA–MS–MS scans

Type of scan	m/z	u	pos./neg.	Characteristic for
Parents	87	–	+	Metabolites of PEG-type surfactants and PEG metabolites
Parents	89	–	+	PEG-type surfactants and PEG
Parents	106	–	+	Fatty acid diethanolamides
Parents	115	–	+	Metabolites of PPG-type surfactants and PPG metabolites
Parents	117	–	+	PPG-type surfactants and PPG
Parents	277	–	+	Octylphenoethoxylates
Parents	291	–	+	Nonylphenoethoxylates (NPEO)
Parents	80	–	–	Secondary alkane sulfonates (SAS)
Parents	97	–	–	Alkylsulfates
Parents	97	–	–	Alkylethersulfates
Parents	183	–	–	Alkylbenzenesulfonates (linear)
Parents	197	–	–	Alkylbenzenesulfonates (branched)
Neutral loss	–	64	–	Aromatic sulfonic acids with the exception of alkylbenzenesulfonates

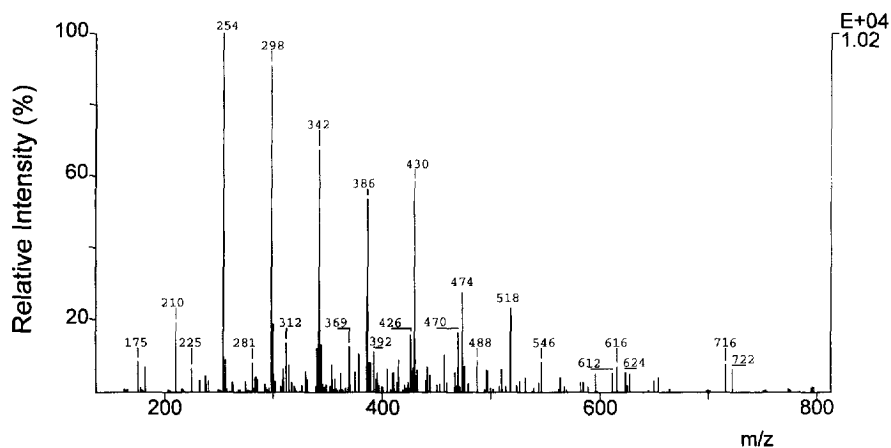


Fig. 6. Parent-ion mass spectrum (FIA-MS-MS) of daughter-ion m/z 87 generated from Saale river extract as in Fig. 2. For FIA and MS-MS conditions, see Section 2.

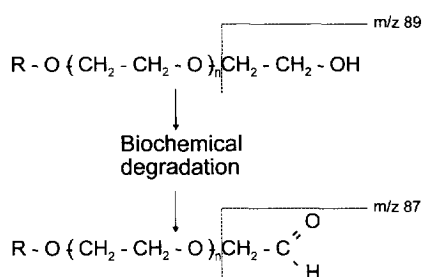


Fig. 7. General structures, biochemical degradation pathway and fragmentation behaviour of nonionic-surfactant of alkanol polyglycol ether type ($\text{R}=\text{C}_n\text{H}_{2n+1}-$) or polyethylen glycols ($\text{R}=\text{HO}-\text{CH}_2-\text{CH}_2-$) and their metabolites.

compound and a standard blend revealed that a cationic surfactants of the fatty amine ethoxylate type with the general structure $\text{C}_n\text{H}_{2n+1}\text{N(H)}-(\text{CH}_2-\text{CH}_2-\text{O})_x-\text{CH}_2-\text{CH}_2-\text{O}-\text{H}$ was present in the extract.

However, for the detection of the aromatic sulfonic acids, which in part are drinking-water relevant, a neutral loss scan (NL) has to be used. The neutral compound SO_2 can be eliminated under CID conditions from aromatic sulfonic acids. Here only ions of those compounds appear in the NL spectrum of 64 u. The linear alkyl benzene sulfonates as aromatic sulfonic acids, however, do not show this neutral loss, but can be identified with the help of a

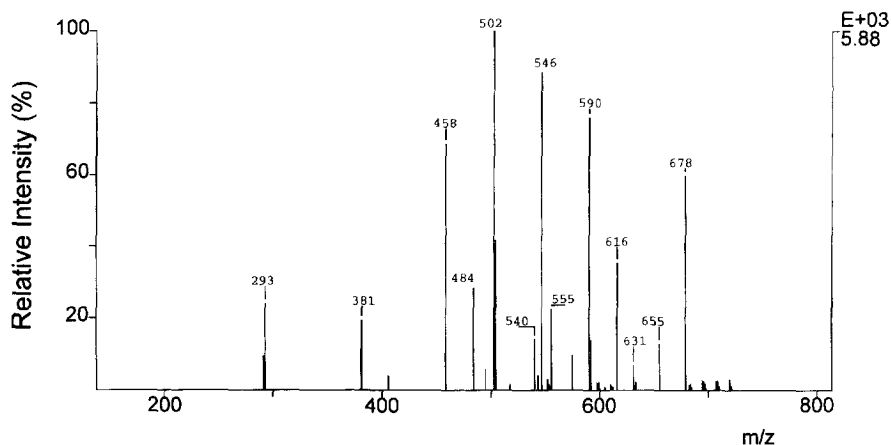


Fig. 8. Parent-ion mass spectrum (FIA-MS-MS) of daughter-ion m/z 291 from Saale river extract as in Fig. 2. For FIA and MS-MS conditions, see Section 2.

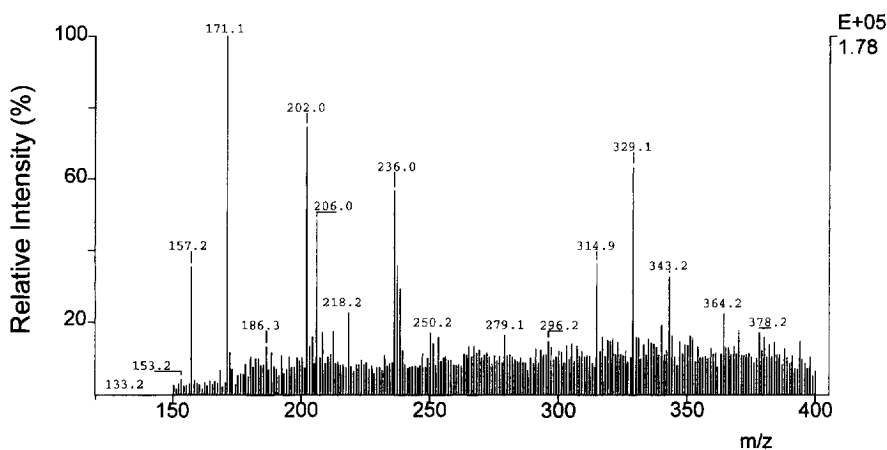


Fig. 9. ESI-MS loop injection spectrum obtained bypassing the analytical column (FIA-MS), for water sample No. 1 of Elbe river. C_{18} SPE; eluent, diethyl ether. Negative ionization. For FIA and MS conditions, see Section 2.

negative ion parent scan of 183 or 197, as shown in Table 1.

In Fig. 9, the FIA-MS(-) overview spectrum of an Elbe extract is presented where the ions of some of the sulfonic acids are recognizable. Aromatic sulfonic acids were monitored periodically in water samples of the Elbe with regard to quality and concentration [3]. Using parent-ion spectra NPEOs, octylphenoethoxylates or anionic surfactants show their characteristic ion patterns. Their repetitive structure is very striking and enables the identification of these compounds in mixtures. By contrast the aromatic sulfonic acids present did not exhibit such a conspicuous regular pattern in the NL spectrum. This

is because they are not present as homologous series. The molar mass of aromatic sulfonic acids depends on the different substituents and the varying number of sulfonic acid groups. Therefore daughter-ions have to be generated for identification following NL characterization. The results were verified by interpretation of the fragments or by comparison with daughter-ion spectra obtained from standards. The ions of the NL-active compounds presented in Fig. 10 could be assigned to benzenesulfonic - (m/z 157), toluenesulfonic - (m/z 171), nitrobenzenesulfonic - (m/z 202), aminochlorobenzenesulfonic - (m/z 206/208) and chloronitrobenzenesulfonic acid (m/z 236/238) respectively.

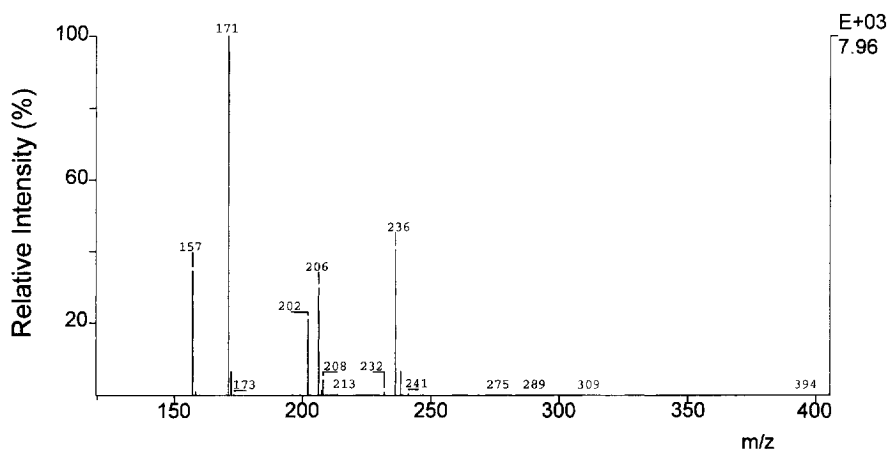


Fig. 10. Neutral loss spectrum (FIA-MS-MS) of NL 64 u active compounds as in Fig. 9. Negative ionization. For FIA and MS-MS conditions, see Section 2.

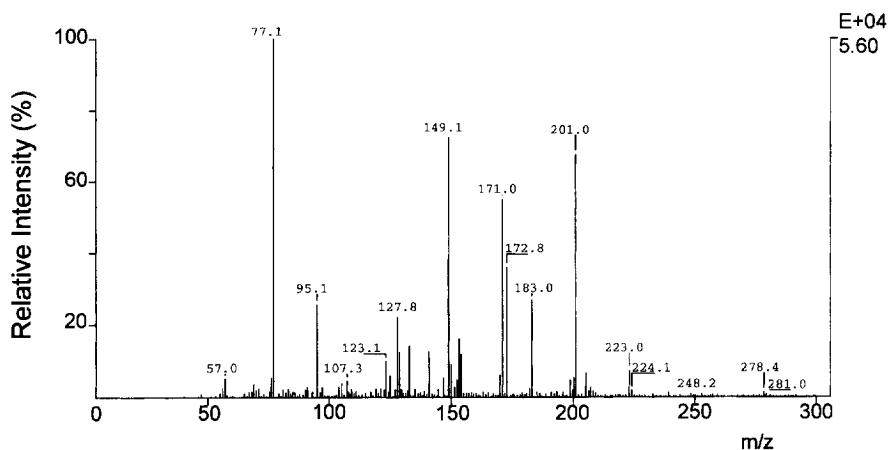


Fig. 11. Daughter-ion mass spectrum (FIA-MS-MS) of ion m/z 279 for water sample No. 2 of Elbe river. C_{18} SPE; eluent, methanol. Positive APCI ionization. For FIA and MS conditions, see Section 2.

FIA-MS and FIA-MS-MS methods, however, do not always lead to identification so quickly and unproblematically. As shown before, these analytical methods in part are complementary so that identification is largely possible. But if a water sample contains a mixture of differently structured components (isomers) with identical molar mass, mixed spectra inevitably result when daughter-ions are generated by FIA-MS-MS. Depending on the proportion of the different isomers in the composition of the starting mixture and on their fragmentation behaviour, the interpretation of this daughter-ion spectrum may become impossible. In this case, only by using LC separation with MS and/or MS-MS detection is it possible to separate and to identify the isomeric compounds. LC-MS provides the information on the molar mass and on the retention behaviour of individual components of the mixture. If the isomeric compounds with known molar mass but varying retention behaviour cannot be definitively identified by these parameters, daughter-ion spectra of the unknown compounds may be generated during the chromatographic separation (LC-MS-MS), which can then be used for identification purposes.

In the course of our investigations with Elbe water samples, this problem cropped up with the identification of the ion with m/z 279. Up to then, we had considered this ion to be the signal of the dibutylphthalate ion, which is ubiquitously detectable. But when we had examined such a compound

mixture at first by FIA-MS and then examined the ion at m/z 279 using a daughter-ion scan by FIA-MS-MS, we obtained a daughter-ion spectrum which could not be interpreted (see Fig. 11). The expected daughter-ion spectrum of a phthalate containing few fragments and the dominant fragment ion m/z 149 had given way to a spectrum with a large number of fragments, atypical of a phthalate. Subsequent LC separation (Fig. 12a) and the analysis of the mass trace 279 explained why the spectrum shown in Fig. 11 had given rise to problems. Two sharp signals were now observed in the mass trace 279 (Fig. 12b). Their daughter-ion spectra (Fig. 12c and Fig. 12d) were obtained by LC-MS-MS analysis. The compound eluting first was then identified as triphenylphosphineoxide (1), the compound eluting later as dibutyl phthalate (2).

4. Conclusions

Since the unification of the two German states, the water quality of the Elbe and its tributaries is continuously improving. This was observed definitively and without problems by sum [2] as well as single-compound parameter analysis [1,3]. Therefore it becomes increasingly difficult for the analyst to detect anthropogenic compounds in the presence of the matrix compounds contained in the water using FIA-MS as reported in this work. In spite of improved detection sensitivity of the soft ionizing

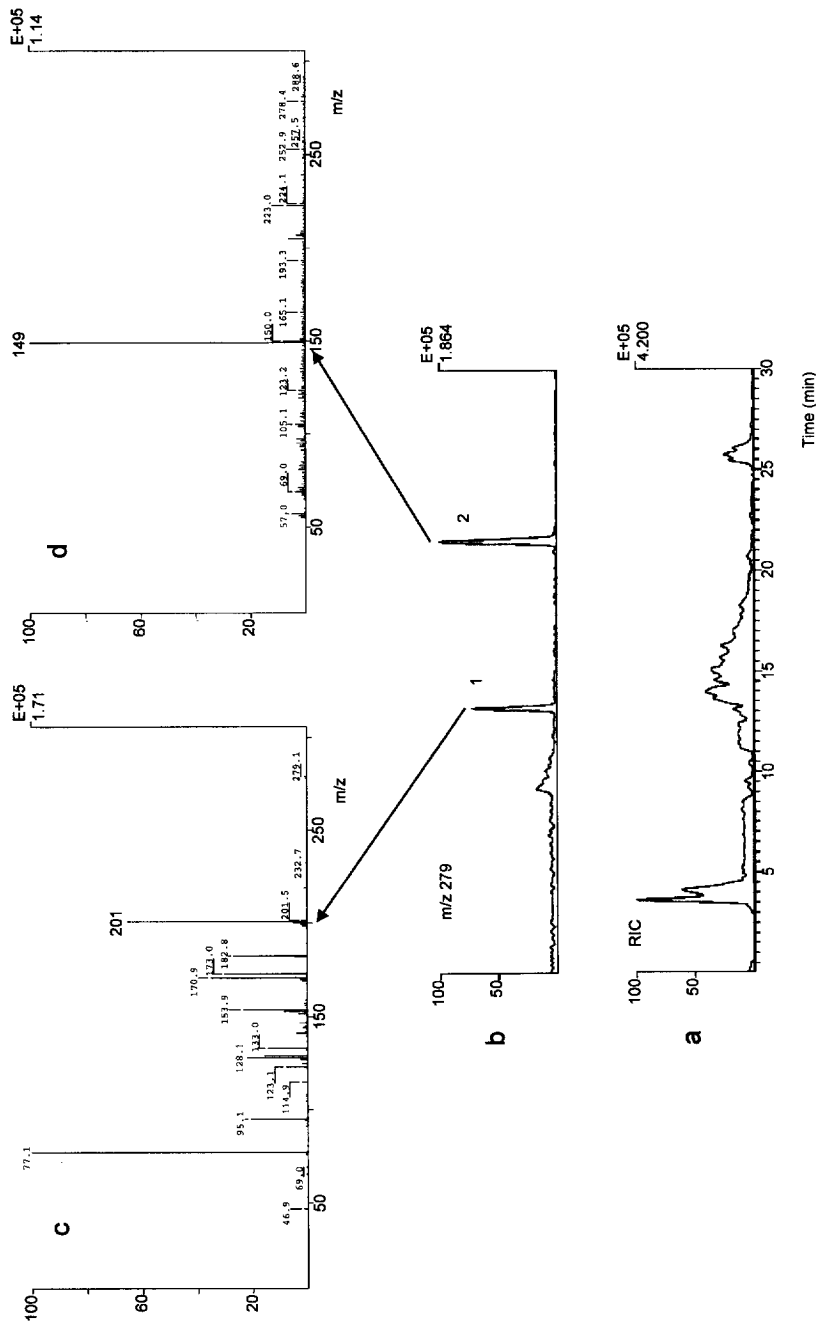


Fig. 12. (a) LC-MS total-ion current trace for water sample No. 2 of Elbe river as in Fig. 11; positive APCI ionization; chromatographic and MS conditions, see Section 2. (b) LC-MS mass trace m/z 279 of Elbe river extract in (a). (c, d) daughter-ion mass spectra (LC-MS-MS) of ion m/z 279 for water sample as in Fig. 11 (c) triphenylphosphineoxide, (d) dibutyl phthalate. Positive APCI ionization. For LC and MS-MS conditions, see Section 2.

MS interfaces applied in the past [1,8] and today—from TSP via APCI to ESI, the water volumes to be extracted have had to be continuously increased so that the amount of analyte obtained was not below the detection limits. This preconcentration, however, does not always lead to the expected success because the natural matrix compounds of the waters are concentrated at the same time, masking the anthropogenic compounds. By substance-group-specific screening methods using FIA–MS–MS, however, we were able to characterize polar organic compounds as non-ionic and anionic surfactants as well as aromatic sulfonic acids in surface water extracts. For identification, daughter-ion scans, in part, were applied successfully. To recognize the pollutants in spite of the complex natural matrix, positive and negative parent-ion scans and neutral loss scans, respectively, had to be carried out. However, using these FIA screening methods, identification becomes problematic if the mixtures contain isomeric compounds in comparable concentrations. The mixed daughter-ion spectra of at least two isomeric compounds developing allow no identification. In this case, final identification will be possible only after LC–MS–MS.

Acknowledgments

Generous financial support by the German Minis-

ter for Education and Science, Research and Technology (BMBF) in Project 02 WT 9358/2 is gratefully acknowledged. Moreover, the author thanks Mr. Dipl.-Ing. Gerlach and his coworker, Mr. Friedrich, of IWW, Mülheim/Ruhr, for the water samples from the Elbe river. The author thanks Mr. Scheduling for recording spectra and Mr. Gschwendtner for preparation of numerous samples.

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