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Pollutants in drinking water and waste water

Horst Fr. Schröder

Institut für Siedlungswasserwirtschaft, Technical University of Aachen, Templergraben 55, D-52056 Aachen (Germany)

ABSTRACT

Extracts of drinking water and effluents from municipal and industrial sewage treatment plants were analysed by gas chromatography–mass spectrometry and by high-performance liquid chromatography combined with ultraviolet and/or mass spectrometric detection. After column chromatography or flow-injection analysis bypassing the analytical column, ionization was performed by a thermospray interface. Identification of the pollutants was carried out by tandem mass spectrometry, generating daughter-ion spectra by collision-induced dissociation. Most pollutants in drinking water and in the effluents of waste water treatment plants are surface-active compounds of anthropogenic origin or their biochemical degradation products. Difficulties encountered during separation, detection and identification are presented and discussed and techniques for solving these problems are proposed.

INTRODUCTION

Although the number of biological waste water treatment plants in Germany has doubled within the last 20 years [1], the pollution of the river Rhine as the most important drinking water reservoir did not decrease correspondingly [2]. Using this water for the drinking water treatment process, some pollutants cannot be completely eliminated from the water, even by large-scale treatment processes such as soil filtration, ozone or hydrogen peroxide combined with UV radiation, activated carbon filtration and others. These so-called drinking-water-relevant compounds (poorly degradable polar pesticides [3], detergents [4,5] and their metabolites [6,7] or non-biodegradable, non-target compounds from chemical synthesis [8]) can be found in high concentrations in the raw river water and drinking water produced from it [4,5].

Important changes concerning the range of pollutants spectrum can be observed in the last decade. Legislation has regimented the use of certain substances, and the efficiency of biological waste water treatment has increased. Especially polar, non-volatile, persistent compounds [9,10] can be found in the waste water, owing to the substitution of soaps by detergents in washing and cleaning agents. Although so-called "biologically degradable" detergents are widely applied, the portion of the original compounds and their primary degradation products in the pollution of these surface waters may be high. So far there has been a lack of data in this field, because surface and waste water analysis dealing with polar compounds is relatively new. Substance-class-specific methods have been applied, which, however, turned out to be inefficient in many instance because of the extremely complex matrix. Only the use of substance-specific methods such as HPLC combined with UV or fluorescence [11,12], refraction [13] or conductivity detection [14] or HPLC–flow-injection analysis (FIA) coupled by thermospray (TSP) with MS–MS [4,5,9,15–17] or fast atom bombardment (FAB) MS [6,7] improved the detection of anthropogenic and biogenic pollutants in water. In spite of the introduction and improvement of these methods in recent years, great difficulties remain.

We have attempted to develop substance-specific analytical methods, not only by using conventional separation techniques coupled with MS-detection but also by mixture analysis, using the FIA technique and selective MS–MS separation and detec-

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tion (FIA–TSP-MS–MS) to determine and characterize these pollutants from a complex matrix. These techniques should enable us to state which pollutants, especially detergents are eliminated from the water phase, *i.e.*, adsorbed, primarily degraded or even mineralized during soil filtration in the drinking water treatment process or during biological waste water treatment.

EXPERIMENTAL

Materials

Drinking water samples were taken from a drinking water treatment plant of a German city located on the river Rhine. Waste water samples were taken from two different waste water treatment plants in Aachen or from a treatment plant of a German chemical company located on the Rhine. The waste water for laboratory experiments was taken from one of Aachen's treatment plants (Aachen-Soers).

Water pollutants were extracted using either continuous liquid–liquid extraction or solid-phase extraction cartridges from Baker (Deventer, Netherlands). Solid-phase extraction materials were conditioned as prescribed by the manufacturer. Glass-fibre and membrane filters used for the pretreatment of the water samples were obtained from Schleicher & Schüll (Dassel, 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 (Waters, Milford, MA, USA) for 24 h and then washed with 100 ml of the same water. Hexane, diethyl ether and methanol used for the liquid–liquid extraction or desorption of water pollutants from the solid-phase material were Nanograde solvents from Promochem (Wesel, Germany). Acetonitrile, chloroform, dimethyl sulphoxide and methanol used for column-cleaning purposes were of analytical-reagent grade from Merck (Darmstadt, Germany). Nitrogen for drying of solid-phase cartridges was of 99.999% purity (Linde). All surfactant standards for the identification via daughter-ion spectra library and for waste water spiking purposes were gifts from the producers (Hüls, Marl; Hoechst, Frankfurt; and BASF, Ludwigshafen, Germany) and were of technical grade.

GC analyses were performed with a DB 1701 fused-silica column (J&W Scientific, Folsom, CA, USA) and helium of 99.999% purity (Linde) was used as the carrier gas. HPLC separations were carried out with a μBondapak C_{18} (5 μm) column (30 cm × 3.9 mm I.D.) (Waters) or on a Hyperchrome NC NH_2 (5 μm) column (25 cm × 4.6 mm I.D.) (Bischoff). The mobile phase was methanol (HPLC grade) from Promochem and Milli-Q-purified water or hexane and 2-propanol (HPLC grade), respectively. Ammonium acetate for TSP ionization was of analytical-reagent grade from Merck.

Sampling and sample preparation

All samples from the waste water and the drinking water treatment plant were taken as grab samples in glass bottles. The bottles were rinsed carefully with several portions of the same water that was subsequently stored in them. The storage temperature was 4°C.

Depending on the degree of pollution, different amounts of water were used for liquid–liquid and solid-phase extraction. Water samples for LC–MS analysis were forced through the solid-phase extraction cartridges after passage through a glass-fibre filter. To ensure complete adsorption, the water samples were forced through two cartridges in series. The adsorbed pollutants were desorbed separately. Solvents of different polarities (hexane, hexane–diethyl ether, diethyl ether, water–methanol and methanol) were used for this purpose. All eluates except those with methanol and methanol–water were evaporated to dryness with a stream of nitrogen, and the residue was dissolved in methanol. The samples were rinsed into glass bottles after solid-phase extraction, and freeze-drying was applied to enrich non-C_{18}-adsorbable compounds. After freeze-drying, the samples were dissolved in methanol and used for LC–MS investigations. Liquid–liquid extracts were dried with anhydrous sodium sulphate, filtered and concentrated by rotatory evaporation.

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-1701, film thickness 0.25 μm, 30 m × 0.32 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 in the manifold $3 \cdot 10^{-2}$ Torr. The electron multiplier was operated at 1200 V with a dynode voltage of 5 kV. The temperature in the ion source was 150°C.

Liquid chromatographic (LC) system

LC separations coupled with MS, MS–MS and UV detection were achieved with a Waters Model 60 MS system. A Waters Model 510 pump was used for postcolumn addition of 0.1 *M* ammonium acetate solution in the TSP mode. A Waters Model 490 MS UV detector was connected in-line with the TSP interface. The conditions in FIA bypassing the analytical column were as follows: mobile phase I, methanol–water (60:40); mobile phase II, 0.1 *M* ammonium acetate in water; overall flow-rate 1.5 ml/min, with a ratio of 0.8 ml/min of mobile phase I and 0.7 ml/min of mobile phase II.

The chromatographic separations on the analytical columns were carried out after optimization of the conditions by a standardized method, shown in Table I; if they differ from this gradient, they are specified in the legends of the figures.

The flow-rate for column separation was 1.0 ml/min of mobile phase I. After passing the UV detector, 0.5 ml/min of mobile phase II was added, which resulted in an overall flowe-rate of 1.5 ml/min.

The reversed-phase column was cleaned with acetonitrile–chloroform–methanol–dimethyl sulphoxide (3:3:3:1, v/v) after finishing analysis and before equilibration for a new separation.

TABLE I

GRADIENT ELUTION SCHEME AND COMPOSITION OF MOBILE PHASE I

A = acetonitrile; B = water–methanol (80/20, v/v).

Time (min)	Solvent A (%)	Solvent B (%)
0	10	90
10	30	70
25	60	40
35	90	10

MS and MS–MS systems

The mass spectrometer was a TSQ 70 combined with a PDP 11/73 data station. The TSP interface was obtained from Finnigan MAT. For coupling the HPLC system with the mass spectrometer, the conditions for TSP ionization using ammonium acetate were vaporizer temperature 90°C and jet block temperature 250°C. The conditions varied during the analytical separations. Under the above conditions the ion source pressure was 0.5 Torr and the pressure in the manifold was $2 \cdot 10^{-5}$ Torr.

Using discharge ionization and hexane–2-propanol as isocratic eluent, the conditions were changed to vaporizer temperature 70°C and jet block temperature 250°C. The discharge electrode was operated at 700 V, the electron multiplier at 1200 V and the dynode at 5 kV. In the MS–MS mode the ion source pressure was 0.5 Torr. Under collision-induced dissociation (CID) conditions the pressure in quadrupole 2 (collision cell) normally was 1.3 Torr or is specified in the legends of the figures. The collison energy was adjusted to −15 eV. The electron multiplier voltage in quadrupole 3 was 1500 V with a dynode voltage of 5 kV.

FIA and column separation analysis were applied, recording TSP mass spectra beginning at *m/z* 150 and ending at *m/z* 1200.

RESULTS AND DISCUSSION

The liquid chromatographic separation of drinking, surface or waste water extracts is one of the most difficult applications of HPLC if no clean-up procedures as in pesticide, polychlorinated biphenyl (PCB) or polychlorinated dioxin and furan (PCDD/PCDF) analysis have been applied in advance. Using the same analytical column, the difficulties normally increase dramatically on going from drinking water to waste water. Drinking water has passed through several clean-up steps during the treatment process and contains only non-degradable drinking-water-relevant compounds at concentrations worth mentioning. In our experience [4], these compounds often cannot be determined using UV or fluorescence detectors because of a missing chromophore in the molecule. If they are registered as a signal by these detectors, however, they cannot be identified.

Using a mass spectrometer as detector coupled

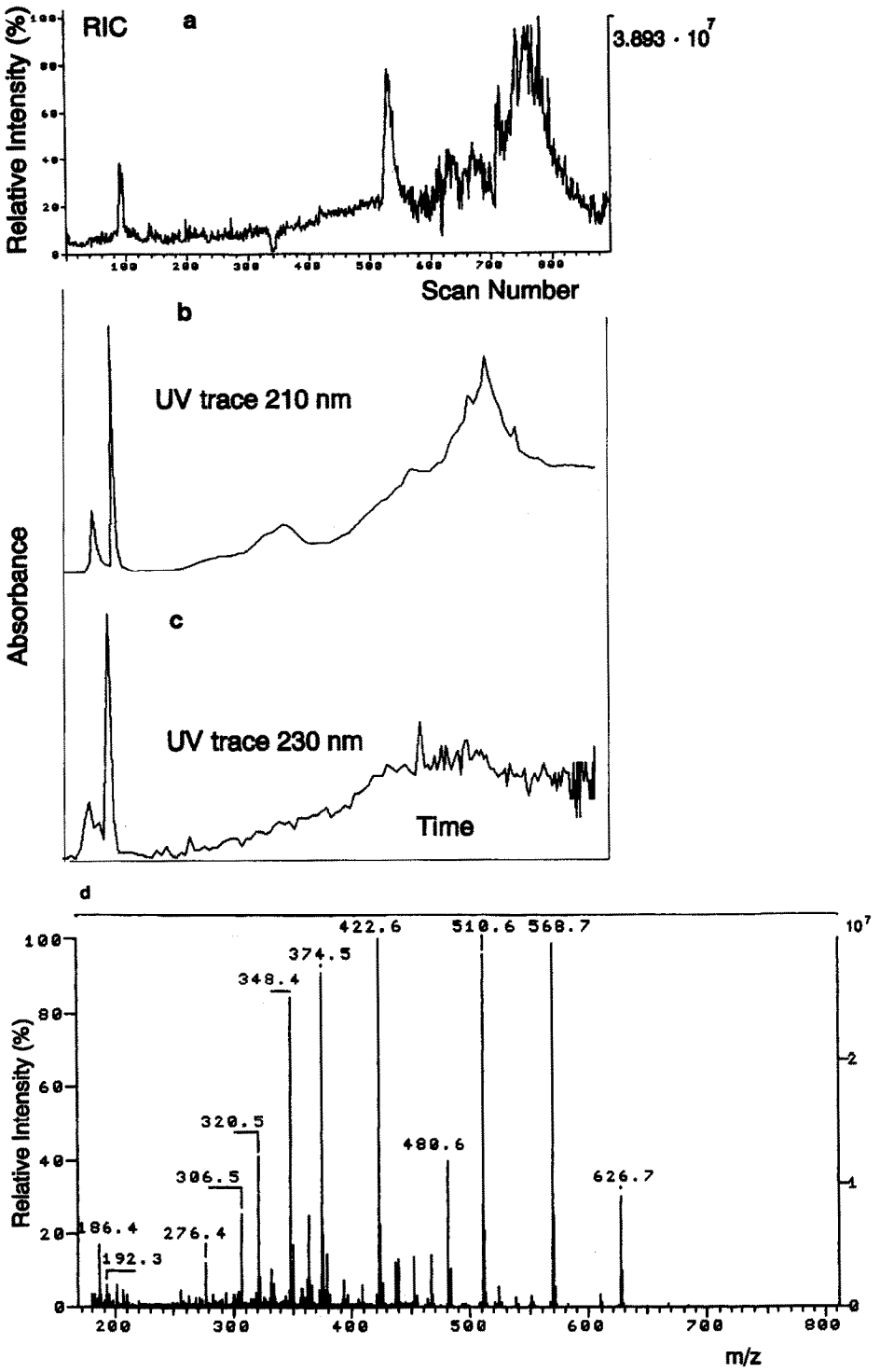

Fig. 1. (a) LC–TSP–MS total ion current trace from an activated carbon filtrate (drinking water). C_{18} solid-phase extract, eluent methanol; C_{18} column, mobile phase methanol–water, gradient from 100% water to 100% methanol in 30 min at 1 ml/min; 0.5 ml/min 0.1 *M* ammonium acetate in water was added after column separation and UV detection. (b) UV (210 nm) and (c) UV (230 nm) traces of drinking water extract in (a). LC conditions as in (a). (d) Selected mass spectra (scans 752–763) from (a).

with a soft ionizing interface to generate only molecular or cluster ions but no fragments, it can be recognized that drinking water analysis by FIA will lead to many ions in the region of 150–500 u, *i.e.*, every mass in this region is occupied by the signal of at least one ion type [4]. In spite of great efforts to obtain an optimized separation by varying the chromatographic conditions, the result was a chromatographic separation shown with the reconstructed ion current (RIC) being recorded in Fig. 1a. The chromatogram consists of unresolved peaks which often contain a mixture of several eluates, as the mass spectrum of a selected peak of this total ion current (TIC) proves (Fig. 1d). The UV traces in Fig. 1b and c, recorded at 210 and 230 nm, respectively, in parallel to the ion current, show only very poor separation and either no or no distinct absorption.

During the separation of this slightly polluted water (drinking water) on an analytical column we observed that the retention times of the eluting substances after two injections of the same sample have changed markedly, so that identification by standard retention time comparison would not have been possible.

This showed that even such small portions of surface-active compounds (non-ionic detergents of the alkanol polypropylene glycol ether type [4] which had been in the drinking water extract) were adsorbed irreversibly under these chromatographic conditions, interfering with the chromatographic potential of the reversed-phase material on the analytical column. Reproducible retention times of the pollutants on this column could only be observed after a time-consuming clean-up procedure with an organic solvent mixture described under Experimental. The same problems, but on a larger scale, will arise if waste water samples which normally contain detergents are to be separated by column chromatography. The reason is that even after the described "selective elution" [4] the number of waste water compounds in these fractionated samples is still extremely high. Retention time shifts of two identical samples analysed one after the other, as shown in the RICs in Fig. 2a and b, cannot be recognized without a selective detector such as a mass spectrometer. Analysing UV or fluorescence traces by standard retention time comparison of the signals after a chromatographic separation would lead to considereable misinterpretations of the results. This is demonstrated in Fig. 2c and d, comparing selected mass traces (m/z 256 and 476) of the RICs in Fig. 2a and b. Large retention time shifts of the same compounds in the same sample could be observed if no procedure to clean up the analytical column had been applied before starting the second run.

Taking this behaviour of waste water extracts into account, a chromatographic separation is possible without problems [18] even in the presence of non-ionic detergents of the alkanol polypropylene glycol ether type, which had been detected by FIA–MS and identified by FIA–MS–MS. Separation occurs depending on the length of the polypropylene glycol ether chain (Fig. 3). Only TSP–MS detection was possible; UV detection recording traces at 190 or 220 nm failed because of a missing chromophore in the molecules.

In the biological waste water treatment process this type of detergent molecule may be biochemically degraded if the waste water biocoenosis has been adapted. No mineralization occurs but only a small change in the molecular structure takes place: the terminal hydroxyle function of the polypropylene glycol ether chain will be converted into an aldehyde function by biochemical oxidation, as shown in Fig. 4. The presence of this biochemical oxidation product in addition to the precursor compound "detergent" can be recognized in the FIA–MS trace bypassing the analytical column (overview spectrum) by the cluster ions at m/z 248, 306, 364, 422, etc., for the metabolite ions and at m/z 250, 308, 366, 424, etc., for the precursor compound ions (Fig. 5). This mixture of pollutants (metabolites and precursor compounds in addition to matrix compounds) can also be separated by time-consuming chromatographic methods. Under optimized conditions the TIC in Fig. 6a after chromatographic separation on a C_{18} column could be recorded. The mass spectra of the two selected peaks [m/z 308 (detergent), m/z 306 (metabolite)] of this RIC together with their characteristic CID spectra (see Fig. 6b and c) demonstrate that an excellent separation under these conditions has taken place, although the structural differences of the detergent and metabolite molecules caused by biochemical oxidation are not very impressive (compare structures in Fig. 4).

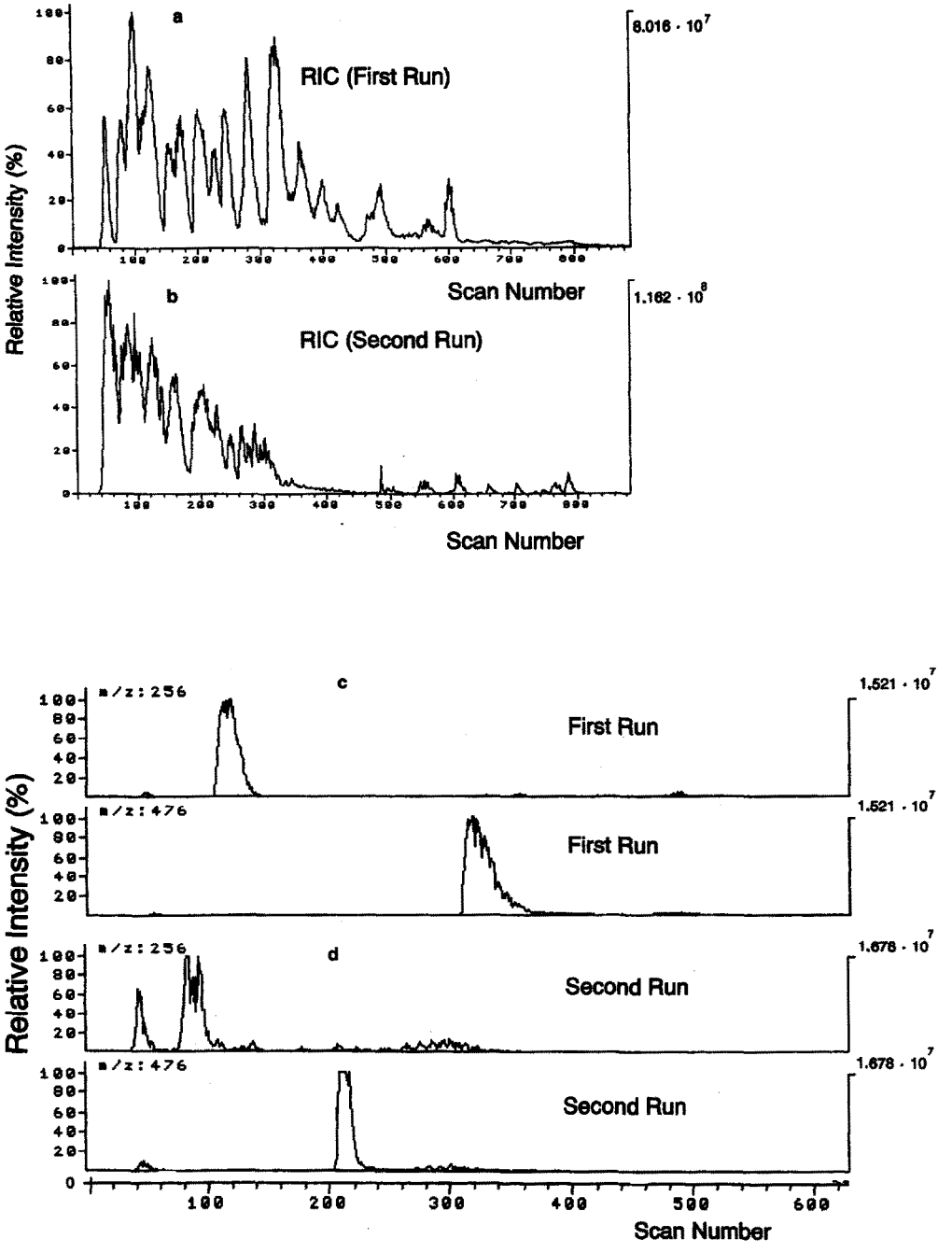

Fig. 2. (a) LC–TSP-MS total ion current trace from waste water extract containing a non-ionic detergent. C_{18} solid-phase extract, eluent methanol; C_{18} column, chromatographic conditions as under Experimental and in Table I. (b) The same extract separated under the same LC conditions as in (a). (c) Selected mass traces of (a). (d) Selected mass traces of (b).

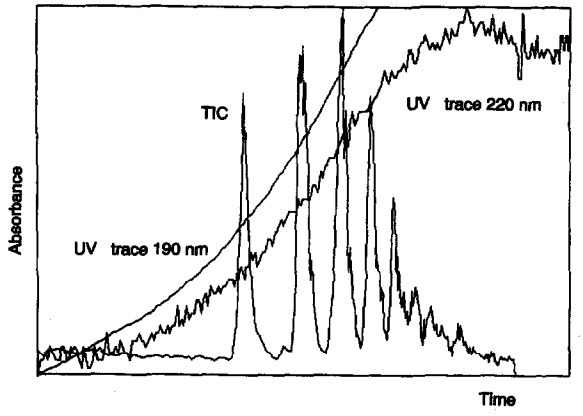

Fig. 3. LC–TSP-MS total ion current trace and UV traces (190 and 220 nm) from waste water extract containing a non-ionic detergent of the alkanol polypropylene glycol ether type shown in Fig. 4a. C_{18} solid-phase extract, eluent methanol; C_{18} column, chromatographic conditions as in Fig. 2a.

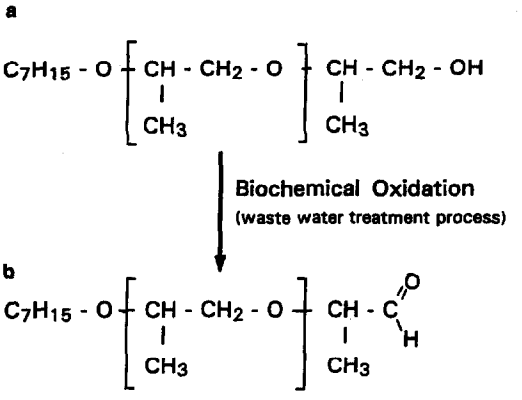

Fig. 4. (a) Non-ionic detergent (alkanol polypropylene glycol ether). (b) Biochemical oxidation product of a waste water treatment process (metabolite).

While the described biochemical oxidation of the alkanol polypropylene glycol ether led to a terminal aldhyde function in the glycol ether chain, another non-ionic detergent of the alkanol polyethylene glycol ether type was biochemically degraded to a carboxylic compounds. This biochemical oxidation process could be observed in the waste water of a treatment plant in Aachen. Starting from this non-ionic detergent, which had been detected by FIA–MS in the overview spectrum of the treatment plant influent (see Fig. 7) and identified by the equally spaced signals ($\Delta m/z$ 44) and its CID mass-spectrum, the biochemically hardly degradable metabolite molecule, shown in Fig. 8a, was formed by mi-

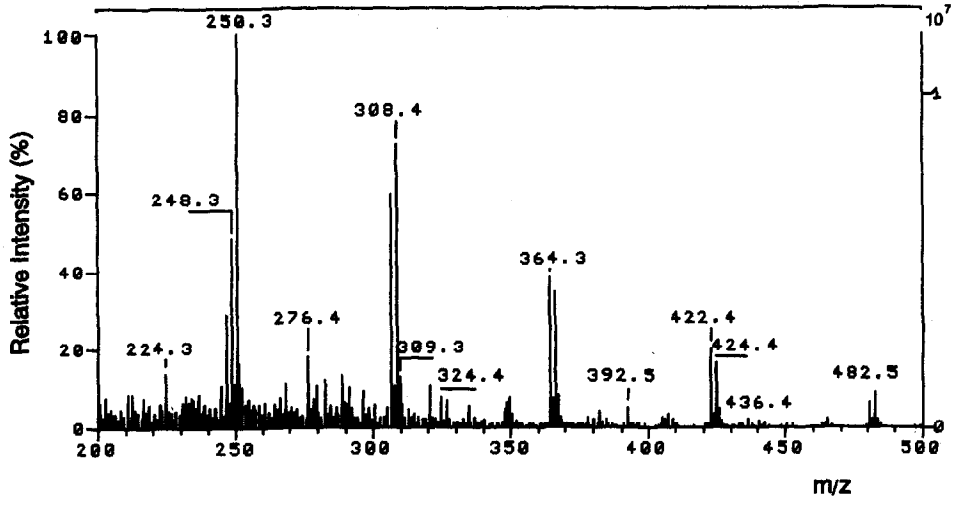

Fig. 5. FIA–LC–MS of waste water extract containing non-ionic detergents (m/z 250, 308, 366, 424, 482) and their metabolites (m/z 248, 306, 364, 422, 480). C_{18} solid-phase extract, eluent diethyl ether. For FIA conditions, see Experimental.

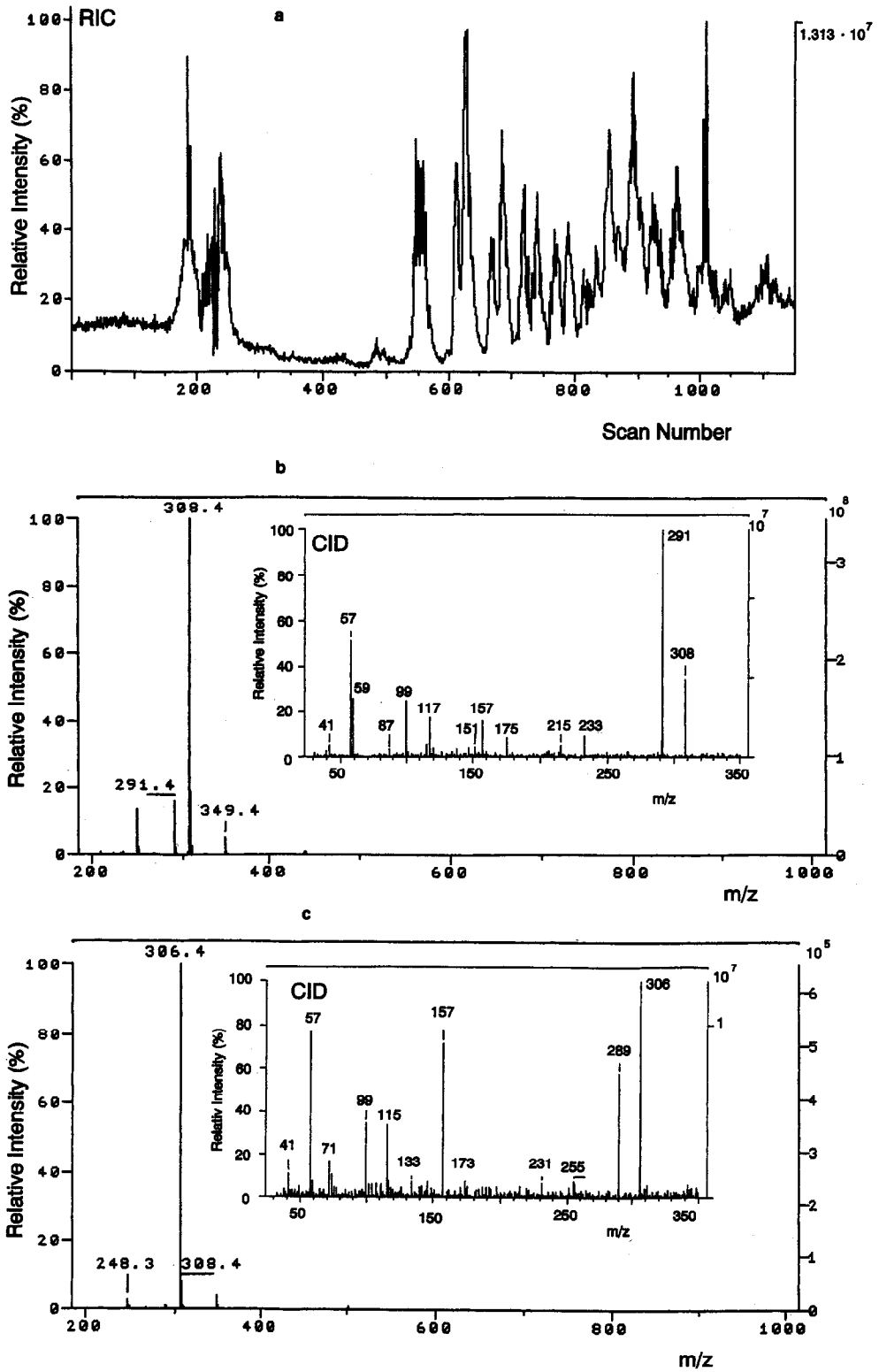

Fig. 6. (a) LC–TSP-MS total ion current trace from waste water extract in Fig. 5. C_{18} column, chromatographic conditions as under Experimental and in Table I. (b) Mass spectrum and daughter-ion mass spectrum (FIA–LC–TSP-MS) of detergent after column separation [scans 605–616 of TIC in (a)]. (c) Mass spectrum and CID spectrum (FIA–LC–TSP-MS–MS) of metabolite (scans 624–632); compare with (b).

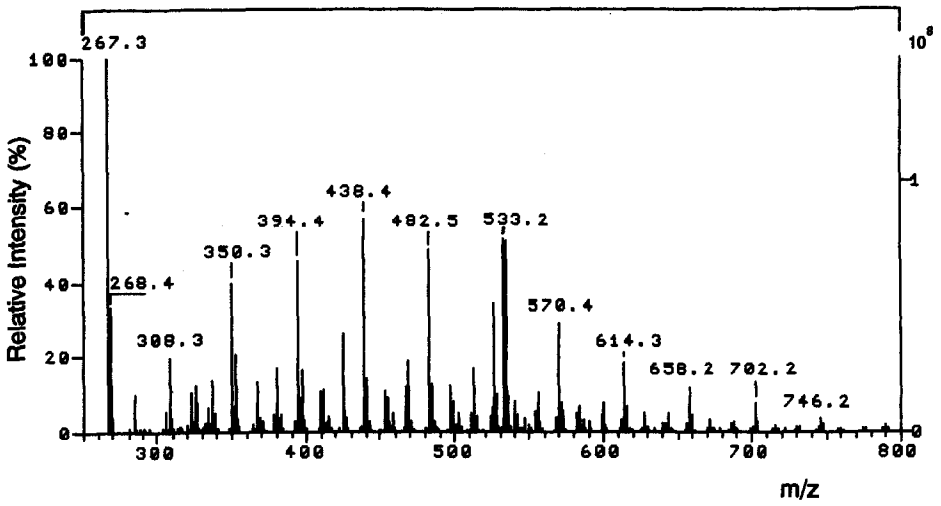

Fig. 7. FIA–LC–MS of waste water extract containing non-ionic detergents. C_{18} solid-phase extract, eluent methanol. FIA conditions as in Fig. 5.

a

$C_{13}H_{27} - O \left[CH_2 - CH_2 - O \right]_n CH_2 - C(=O)OH \quad * NH_4^+$

n = 1; m/z = 320
n = 2; m/z = 364
n = 3; m/z = 408

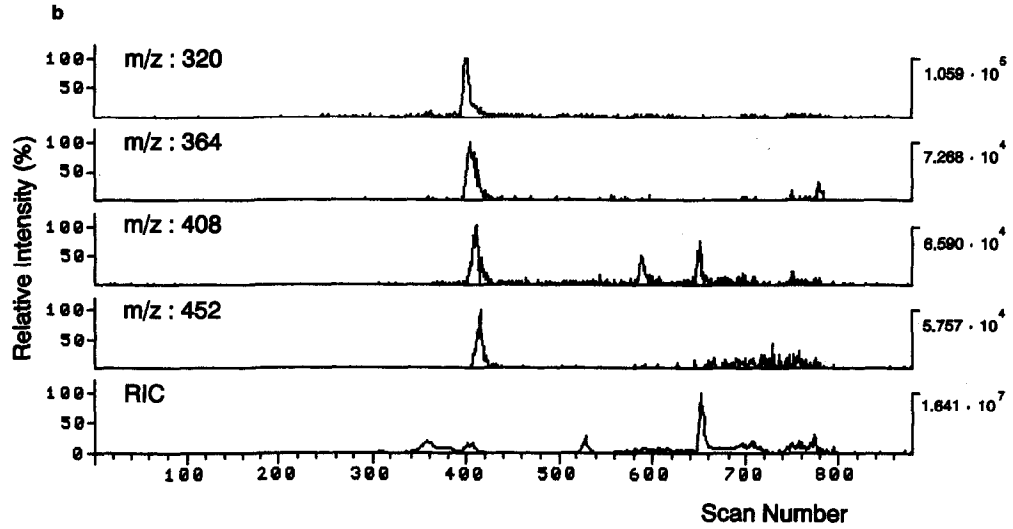

Fig. 8. (a) Structural formula of primary degradation products (metabolites) of detergent mixture in Fig. 7. (b) LC–TSP-MS traces of metabolite in (a) and RIC of waste water extract. C_{18} solid-phase extract, eluent diethyl ether; C_{18} column, chromatographic conditions as in Fig. 2a.

crobiological primary degradation. This metabolite molecule can be separated from the waste water matrix and the precursor compounds on an analytical column, as the mass traces at *m/z* 320, 364, 408 and 452 in the scan region 393–422 in Fig. 8b demonstrate. The same behaviour in the biological waste water treatment process could be observed when a fluorine-containing, non-ionic detergent of the polyethylene glycol type (Fig. 9a) was biochemically degraded [17]. This detergent, partially fluorinated in the alkanol chain, resists chemical and physico-chemical treatments such as hydrolysis, strongly oxidizing acids or mineralization in a hydrogen–oxygen flame. However, biochemical degradation could be observed in the waste water treatment process resulting in the metabolite shown in Fig. 9b. The polyethylene glycol ether chain in this molecule is shortened in parallel. This primary degradation product resists further biochemical degradation. In a batch reactor there is no significant degradation within a period of 10 days.

The precursor compound of this biochemical oxidation and the primary degradation product can be identified using their typically different daughter-ion spectra in Fig. 9a and b. Separation of the non-ionic detergents and the metabolites on a C_{18} column, depending on the different lengths of the fluorine-containing alkyl chains, is successful as the

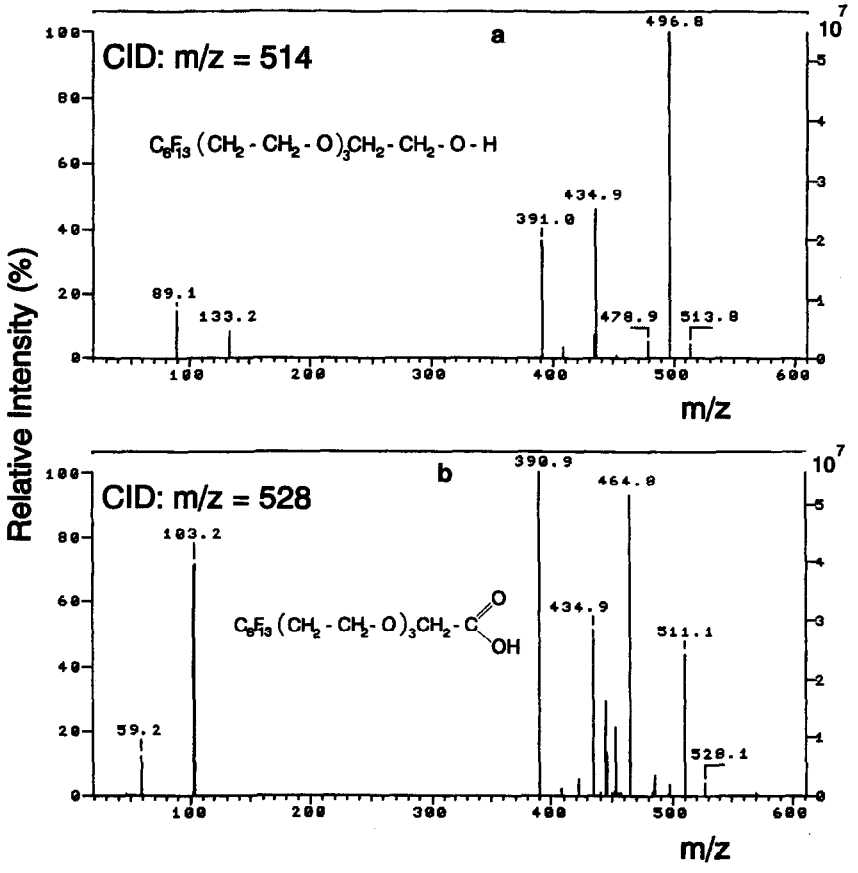

Fig. 9. (a) Daughter-ion mass spectrum (FIA–LC–TSP-MS–MS) and formula of fluorine-containing detergent from waste water extract. C_{18} solid-phase extract, eluent diethyl ether. FIA conditions as in Fig. 5. For CID conditions, see Experimental. (b) Daughter-ion mass spectrum as in (a) and formula of metabolite of detergent in (a) from waste water extract. C_{18} solid-phase extract, eluent hexane–diethyl ether (6:4, v/v); FIA and CID conditions as in (a).

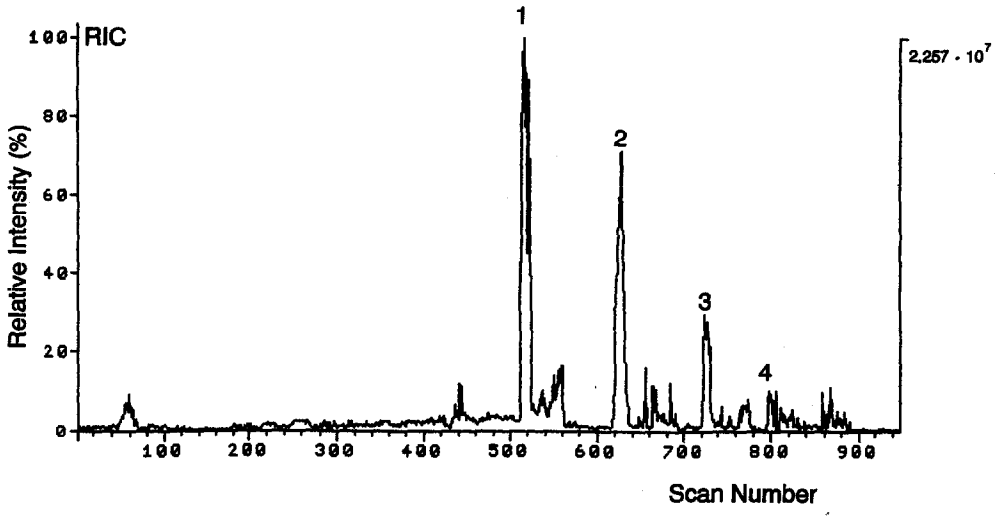

Fig. 10. LC–TSP–MS total-ion current of waste water extract containing the fluorine detergent in Fig. 9a and its metabolite (Fig. 9b). C_{18} solid-phase extract, eluent methanol; C_{18} column, chromatographic conditions as in Fig. 2a. 1 = Metabolite; 2 = detergent [Perfluoro alkyl group (R_f) = C_6F_{13}]; 3 = detergent (R_f = C_8F_{17}); 4 = detergent (R_f = $C_{10}F_{21}$).

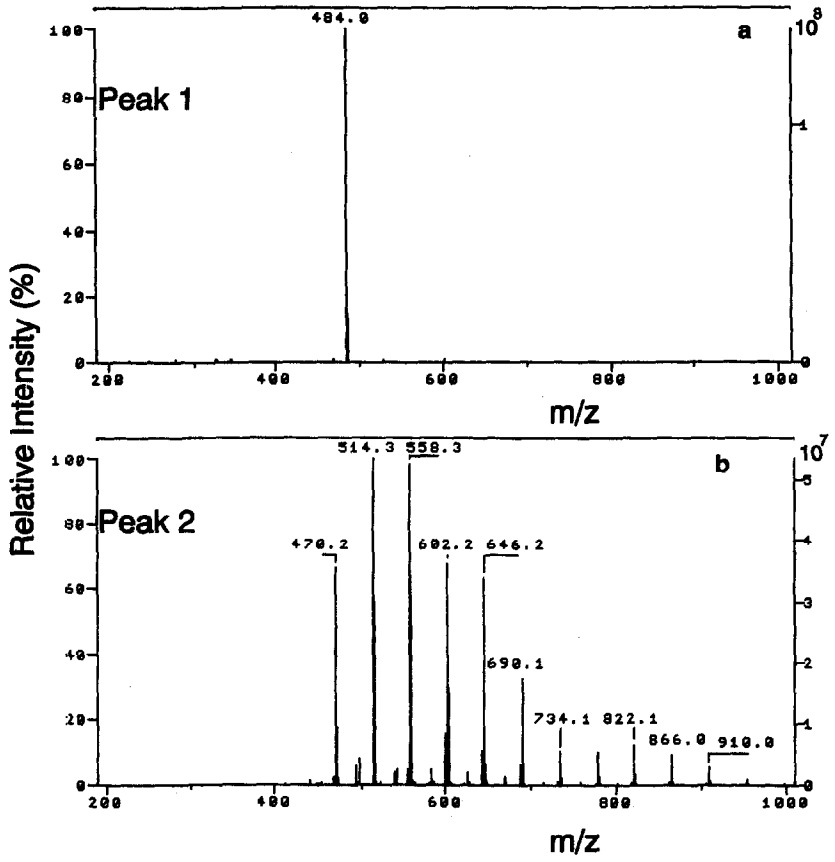

Fig. 11. LC–TSP mass spectra of (a) peak 1 and (b) peak 2 in Fig. 10.

LC–MS-TIC of the waste water extract shows (see Fig. 10). Mass spectra of selected peaks in the RIC (Fig. 10) demonstrate the separation efficiency for the metabolite (Fig. 11a) and the detergents (Fig. 11b) from this mixture. UV detection of these compounds was not possible because they did not show any absorbance in the region >210 nm.

Extracts from influents of waste water treatment plants nowadays contain non-ionic detergents of the fatty acid diethanolamide type in high concentrations. Analysis of effluent samples from these plants demonstrated the elimination of these pollutants, *i.e.*, complete degradation or adsorption on the sludge seems to occur very quickly without the formation of hardly or non-biodegradable metabolites. However, high concentrations of these pollutants in the influent make the elimination capacity insufficient [9]. Even after an intensified biological waste water treatment process, waste water extracts from the effluent of a laboratory-scale treatment plant spiked with 2 mg of detergent per litre of waste water in the influent [3] contain the single isomers of the fatty acid diethanolamide. These compounds could be easily identified in the overview spectrum by their characteristic molecular ion patterns, which appear depending on the length of the alkyl chain at m/z 232 (C_7H_{15}), 260 (C_9H_{19}), 288 ($C_{11}H_{23}$) and 316 ($C_{13}H_{27}$) and by their daughter-ion specra (CID) obtained by FIA–LC–MS or FIA–LC–MS–MS (Fig. 12).

Chromatographic separation of these compounds in the effluent from a laboratory-scale plant is possibly on a C_{18} column. Even the separation of a much more problematic waste water extract from the influent of a municiple sewage treatment plant in Aachen was successful, as the TIC in Fig. 13b shows. The peaks in this RIC marked 1, 2 and 3 are the ion-current signals for the molecular ions at m/z 232, 260 and 288. The excellent separation from all other compounds in the mixture can be recognized in the mass spectrum of peak 3 in Fig. 13c. The molecular structure of this surfactant type in Fig. 13c shows the reason why this molecule could be ionized without forming an ammonia cluster ion. The nitrogen atom in the molecule is able to carry the positive charge necessary for ionization.

The signal in the RIC (Fig. 13b) in the scan region 345–389 could be characterized as a non-ionic detergent of the alkanol polyethylene glycol ether type because of its equidistant masses of $\Delta m/z$ 44 and its daughter-ion spectrum of the selected ion with m/z 336 (Fig. 13d).

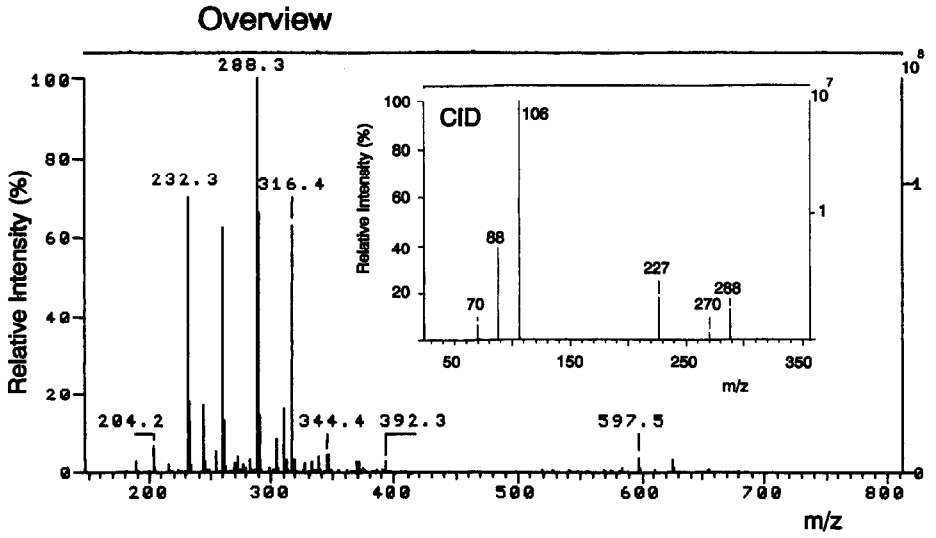

Fig. 12. FIA–LC–MS and FIA–LC–MS–MS (m/z 288) of waste water extract containing fatty acid diethanolamide; C_{18} solid phase extract, eluent diethyl ether; FIA and CID conditions as in Fig. 9a.

The 210-nm UV trace plotted in Fig. 13a recorded in parallel to the LC–TSP–MS TIC proves that this non-ionic detergent of the fatty acid diethanolamide type shows an absorbance at 210 nm. Many other pollutants contained in the waste water extract which cannot be ionized by TSP ionization can be detected because of their strong UV absorbance at 210 nm. The identification of these pollutants was not possible.

Another important topic, in spite of all the diffi-

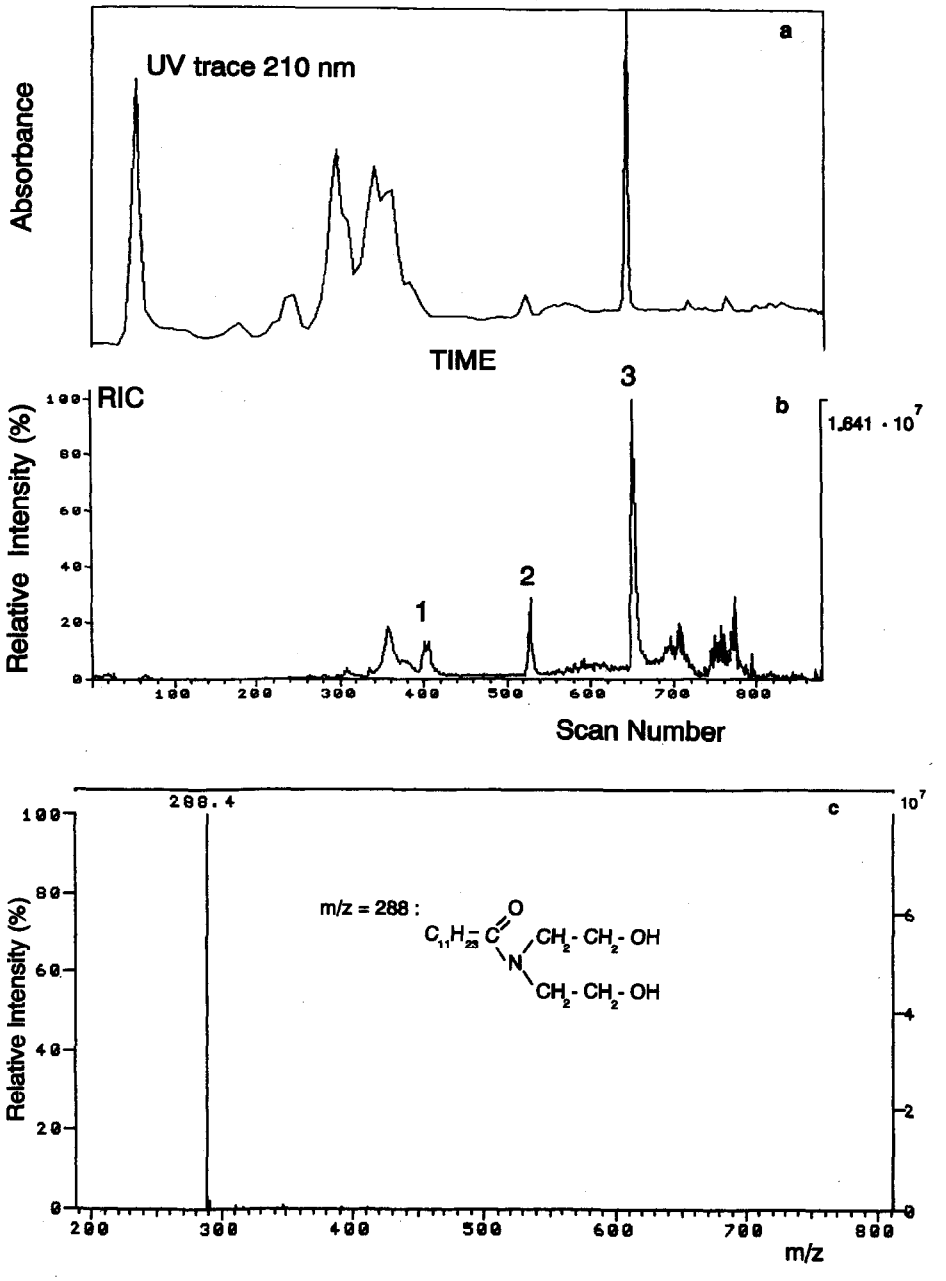

Fig. 13.

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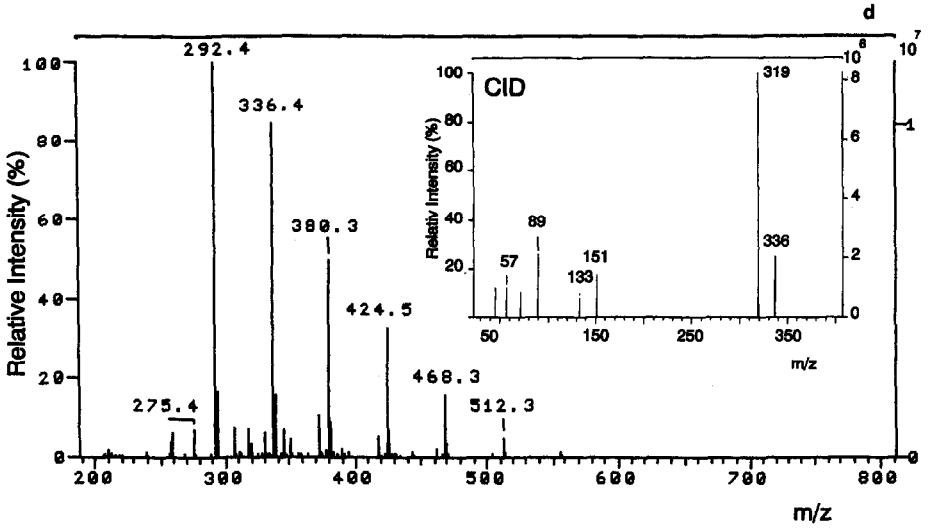

Fig. 13. (a) UV trace (210 nm) of waste water extract containing fatty acid diethanolamide. C_{18} solid-phase extract, eluent methanol; C_{18} column, chromatographic conditions as in Fig. 2a. (b) RIC of waste water extract of (a). LC conditions as in (a). (c) Mass spectrum of peak 3 in (b) and structural formula of coconut fatty acid diethanolamide (*m/z* 288). (d) LC–TSP-MS and CID spectrum of non-ionic detergent of RIC in (b) (scans 345–389).

culties, is the analysis of waste waters in the chemical industry containing large amounts of such pollutants. The complexicity of municipal waste water even in the influent is exceeded substantially by waste water in the effluent from these sewage treatment plants. This becomes obvious by GC–MS analysis of extracts of municipal and industrial waste water treatment plant effluents after an optimized biological treatment process. Very low concentrations of volatile compounds can be detected in municipal sewage treatment plant effluents [5]. In contrast, we found many volatile organic compounds in the hexane extract of chemical industry waste water discharging into the river Rhine. The TIC of this GC–MS analysis is shown in Fig. 14a. Enrichment of compounds from this waste water by C_{18} solid-phase extraction was used for examination of polar and low-volatile compounds. The methanol eluate from this extraction procedure was analysed by LC–TPS–MS on a C_{18} column using the above-described chromatographic conditions and showed a good separation (Fig. 14b). Some of the pollutants could be identified as tributyl phosphate (*m/z* 267), phthalate (*m/z* 279) and alkanol polyglycol ether (*m/z* 240, 284, 328, 372 and 416) by MS–MS. Target analysis for toxic compounds using the mass traces at *m/z* 326, 370, 414, etc., to look for the ammonia adduct ions of nonylphenol ethoxylates showed that these precursor compounds of nonylphenol were present in the effluent in low concentration. However, as the chromatographic separation on a reversed-phase column was not satisfactory (Fig. 14b) and the response of these compounds was very low with TSP ionization, normal-phase chromatography was applied to test for the presence of nonylphenol ethoxylates. Separation was obtained on a an amino-bonded packing with an organic eluent (hexane–2-propanol) [11] and recording RIC and UV traces at 254 nm in parallel. Comparison of the RIC and UV traces showed that under these chromatographic conditions nonylphenol ethoxylates could be detected much better by UV detection at 254 nm (see Fig. 15a) than by LC–TSP–MS using the discharge electrode (see Fig. 15b). However, evidence about the identity of the signals in the RIC can only be obtained from the selectivity of the mass spectrum of the selected peak 1 from the RIC in Fig. 15b. The plotted mass spectrum of *m/z* 441 in Fig. 15b belongs to the molecular ion ($[M + H]^+$) of a nonylphenol ethoxylate with five PEG units in the ether chain.

The practicability of this method using an organ-

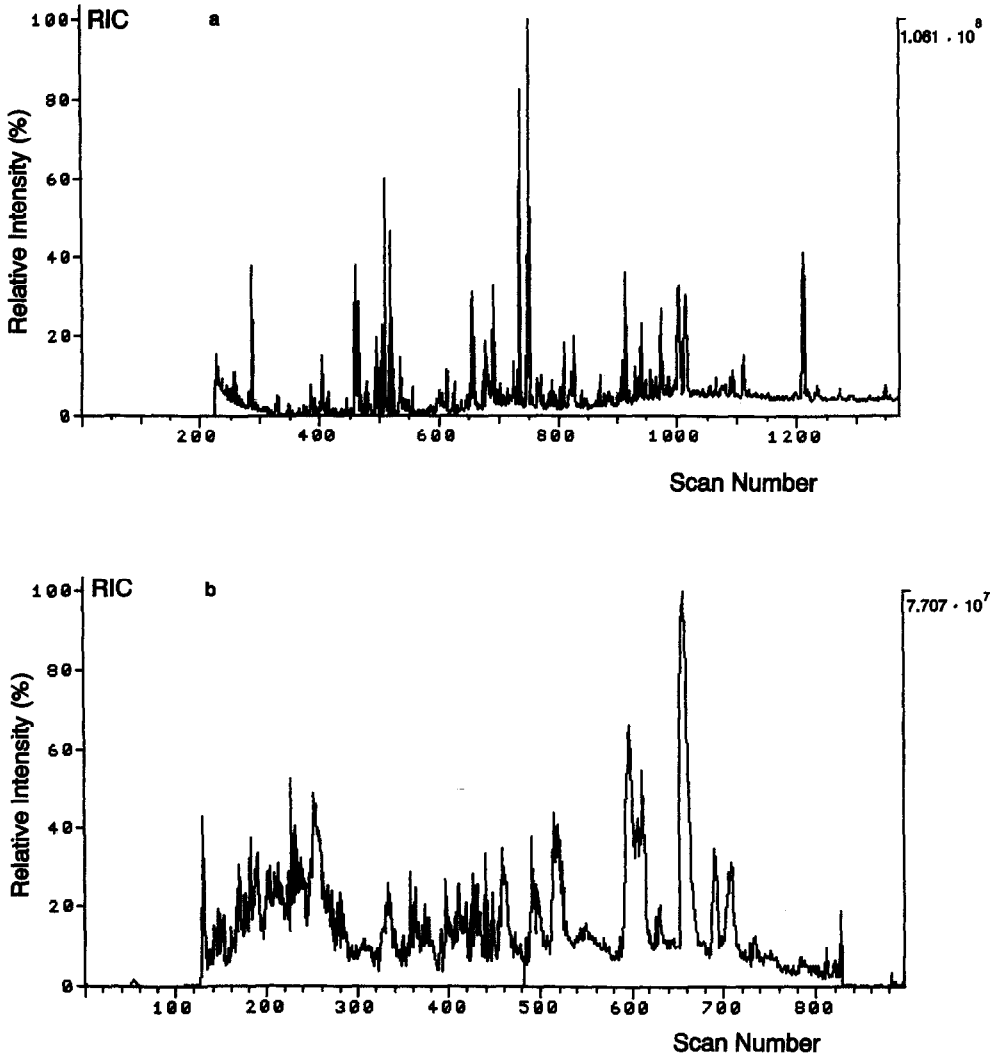

Fig. 14. (a) GC–MS total ion current trace of a waste water treatment plant effluent from a chemical company. Liquid–liquid extract, solvent hexane. (b) LC–TSP–MS total ion current trace of waste water in (a); C_{18} solid-phase extract, eluent methanol; C_{18} column, chromatographic conditions as in Fig. 2a.

ic eluent and TSP interface with discharge ionization is limited because the ionization process by the discharge electrode generates carbon by pyrolysis of hexane and 2-propanol which is deposited in the ion source, inducing a considerable decrease in sensitivity of the mass spectrometer.

The clean-up procedure after application of organic solvents as eluents is very time consuming and limits the use of this ionization technique much more than aqueous eluents.

CONCLUSIONS

Extracts of drinking water and effluents from sewage treatment plants contain a wide variety of pollutants. HPLC separations are time consuming

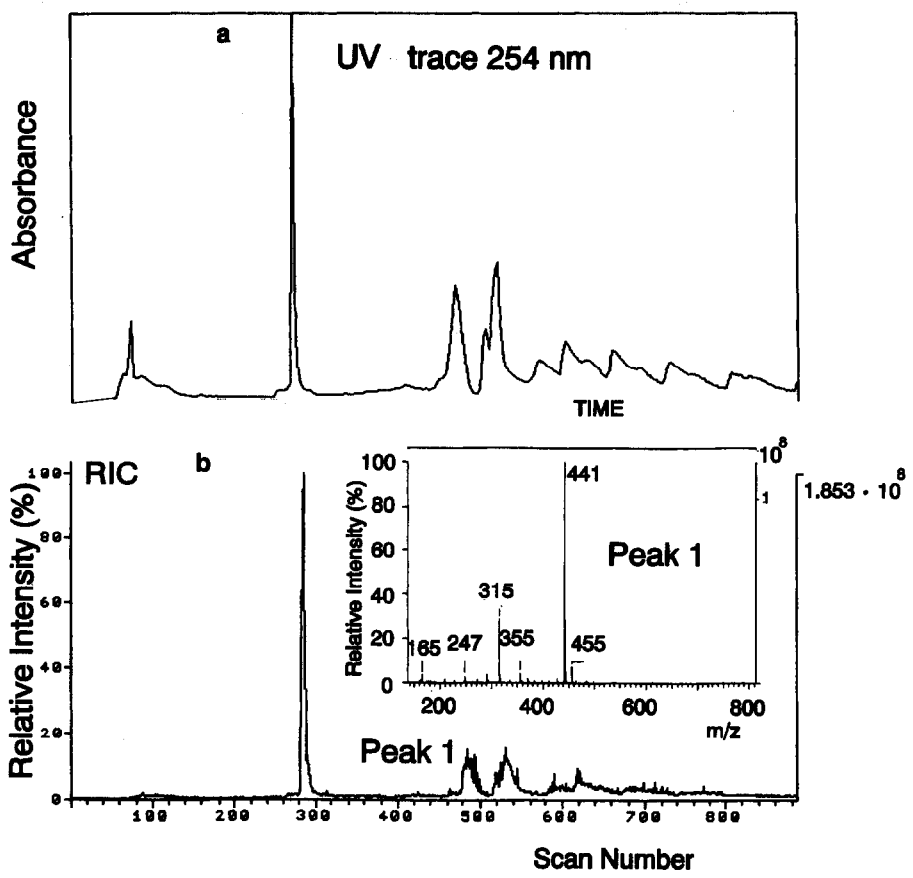

Fig. 15. (a) UV trace (254 nm) of waste water extract in Fig. 14b containing nonylphenol ethoxylates. C_{18} solid-phase extract, eluent methanol; amino-bonded normal-phase column, mobile phase hexane–2-propanol, gradient from 100% hexane to 70% 2-propanol in 60 min, flow-rate 1.5 ml/min. (b) LC–MS total ion current trace of waste water extract in (a) and LC mass spectrum of peak 1; LC conditions as in (a); discharge ionization, discharge voltage 700 V.

and not always satisfactory. Surface-active compounds in these extracts interfere and influence the elution behaviour, which makes an identification by retention time comparison impossible.

The detection and characterization of these compounds will fail if only unspecific detection systems such as UV or fluorescence detectors are used. On the one hand, many of these polar pollutants do not possess any chromophore for optical detection and on the other, it cannot be excluded that several compounds may be hidden under the signal registered by these detection systems. Soft ionization techniques such as TSP ionization in combination with MS–MS allow a definite characterization after time-consuming HPLC separation or time-saving mixture analysis using FIA. Hence polar pollutants such as non-ionic detergents of the alkanol polyethylene and propylene glycol ether types, fatty acid diethanolamides or nonylphenol ethoxylates and their possible metabolites can be detected by LC–MS and characterized by LC–MS–MS in drinking and waste waters. Many compounds of this type can be detected and identified only in this way.

Target analysis for nonlyphenol ethoxylates in waste water is more efficient using normal-phase chromatography combined with discharge ionization instead of reversed-phase chromatography and TSP ionization.

UV detection additionally performed in parallel to HPLC–TSP-MS investigations seems to be very

helpful in obtaining information about non-TSP-active compounds.

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