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Analysis of polar organic micropollutants in water with ion chromatography–electrospray mass spectrometry

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Abstract

The coupling of ion chromatography (IC) with electrospray mass spectrometry (ES-MS) opens new ways for the determination of polar organic micropollutants in water samples. The technique of conductivity suppression has been found to reduce the background signal in the range of about two-orders of magnitude leading to a significant increase in sensitivity. In addition, the formation of salt adducts has been avoided. The usefulness of this method was proven on several polar and environmentally relevant micropollutants such as the herbicide glyphosate and its metabolite aminomethylphosphonic acid (AMPA), the chelating agent ethylenediamine tetraacetate (EDTA) and diacetonketogulonic acid (DAG). This present study has shown that IC–ES-MS is a simple, sensitive and quick method for the determination of these polar organic traces in water samples after separation on an anion-exchange column without any derivatization. In this work, several possibilities of applications of IC–ES-MS (with varying conditions) are presented. Analysis of glyphosate, AMPA, DAG and EDTA in ground and surface waters has been achieved by IC–ES-MS without additional sample preparation at a concentration level of 1 μg/l.

Keywords: Water analysis; Mass spectrometry; Polar organic micropollutants; Glycophosphate; Aminoethylphosphonic acid; Ethylenediamintetraacetate

1. Introduction

Electrospray (ES) coupled to liquid chromatography (LC)–mass spectrometry (MS) is used more and more for the determination of organic micropollutants, especially in aqueous matrices. This is manifested by recent publications dealing with its applications on compounds such as pesticides, surfactants and phenols [1–5]. However when it comes to the analysis of the extremely polar and water soluble environmentally relevant compounds, there is still a barrier for their determination by LC–MS. Well known examples of such compounds are the widely used pesticide glyphosate [*N*-(phosphonomethyl)glycine], the chelating agent ethylenediaminetetraacetate (EDTA) and structurally similar pollutants.

Glyphosate and its degradation product aminomethylphosphonic acid (AMPA) for example, are usually analyzed by high-performance liquid chromatography (HPLC)–fluorescence detection with post-column derivatization with *o*-phthalaldehyde/mercaptoethanol [6] or after derivatization, by gas chromatography (GC)–MS or LC–MS-MS. With the

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usual LC–MS method glyphosate is inadequately separated and isolated without derivatization. A good determination of the compounds was successful only after derivatization with 9-fluorenyl methoxycarbonyl chloride (F-moc-Cl) [7]. The F-moc derivatives of glyphosate and AMPA were well separated on a reversed-phase (RP) C_{18} column and detected very sensitively by LC–MS-MS.

Due to the widespread use of EDTA, it is ubiquitously present and environmentally relevant at concentrations of up to 50 μg/l in surface waters [8], it has become a typical example of a compound relevant for drinking water quality. It is extremely soluble in water and poorly biodegradable with resulting concentrations in drinking water almost comparable to the concentration of the surface water used. The analysis of EDTA is still performed after enrichment on either anion-exchange material (SAX) or vaporization, derivatization to the tetra-isopropylester and GC–MS analysis [9]. Problems are often encountered in both the enrichment step and the derivatization part which is quite often incomplete. The determination of EDTA–Fe utilizing HPLC with diode array detection (DAD)–UV detection lacks sensitivity for the analysis of drinking waters [10].

In a few areas of Germany di-isopropylidene-α-L-xylo-2-hexulofuranosonic acid (diacetonketogulonic acid, DAG), another polar organic micropollutant, can be found even in drinking water. DAG is introduced into surface water as intermediate of the vitamin C synthesis [12]. A problem is the simultaneous determination of the intermediates, which can be done either through the insensitive analysis with HPLC–refractive index (RI) detection [11] or utilizing GC–MS after derivatization with diazomethane [12]. The only limitation of applying this technique in general is the given risk to human safety due to the use of carcinogenic alkylating agents.

The development of a method to analyze polar compounds, such as organic acids directly, may well solve the problem of incomplete recoveries in both enrichment and derivatization steps. Because of the ionic nature of the polar organic acids LC–ES-MS would be the method of choice, due to it's specificity and sensitivity. In order to obtain satisfactory HPLC separations the use of saline eluents or buffer solutions is necessary. This is a problem in LC–MS coupling, because the use of such eluents causes a high background in the MS chromatogram. Likewise, cluster ions are measured and strong incrustations at the vacuum interface could be observed. LC–ES-MS appears to be a good tool for this application if problems due to high amounts of salts can be solved.

This paper aims to overcome these high background and incrustation problems by using a suppressor between LC and MS resulting in a cation-exchange of the effluent as well as from the sample against H^+ [13]. In the recent literature the application of electrospray ion chromatography (IC)–MS-MS for the analysis of oxyhalides has already been described, also showing the usefulness of this new method for the determination of inorganic compounds [14]. Anion-exchange columns could be utilized for the chromatographic separation of the target analytes resulting in a coupling of IC and MS. This has been described for determination of organic ammonium and sulfate compounds [15]. The new MS interfaces allow higher flow-rates of up to 0.5 ml/min into the mass spectrometer compared with the 0.02 ml/min as previously reported, making the analysis more sensitive. Many separations have already been reported using buffer solutions as mobile phase but not with high salt concentration solutions as presented in this paper.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical grade. Glyphosate and diacetonketogulonic acid were obtained from Ehrenstorfer, AMPA from Sigma and ethylendiaminetetraacetate-disodium salt, sulfuric acid, sodium carbonate and sodium hydrogencarbonate from Merck, Darmstadt. Milli-Q water was used in all the experiments.

2.2. Apparatus

The HPLC–MS system consisted of a LC 200 binary pump (Perkin-Elmer) and a PE Sciex API 150 single quadrupole mass spectrometer equipped with an atmospheric pressure ionization (API) source, via a turbo ionspray interface. The instrument was run in

the negative ion mode at an ionization voltage of −3600 V, an orifice voltage of −32 V and a ring voltage of −140 V. To assure a flow of 0.25 ml/min into the electrospray ionization (ESI) interface the LC effluent flow (0.5 ml/min) was split (1:1) by means of a zero dead volume T-piece. The interface temperature was held at 450°C (the recommended temperature for daily use is 400°C). As Turbo ion spray and curtain gas in the API source 5.0 purity nitrogen at a flow-rate of 1.25 l/min, and oxygen as nebulizing gas, at a flow-rate of 1.48 l/min, was used.

Optimization of the ES-MS interface was performed in order to obtain the most abundant ions for identification and quantification. These were in case of AMPA (m/z=110) and DAG (m/z=273) the single negatively charged molecular ions $[M–H]^-$. No fragmentation was obtained for these compounds by varying the orifice voltage from −10 to −90 V. At the optimum voltage of −32 V for EDTA, besides the $[M–H]^-$ ion (m/z=291), a much more intense ion resulting from the doubly negatively charged molecular ion (m/z=145 $[M–H]^{2-}$) was obtained (Table 1). This was also found to be the optimum voltage for glyphosate, leading beside m/z=168 $[M–H]^-$ to additional fragment ions at m/z=150 $[M–H_2O\text{-}H]^-$ and 124 $[M–COOH]^-$.

A Metrohm suppressor module 753 consisting of three small ion exchanger columns was switched between the column and the T-piece of the ES-MS interface. While the first suppressor is integrated into the effluent flow for cation-exchange against H^+, a second column is regenerated with 25 mmol/l sulfuric acid containing 10% (v/v) acetone and the third micro cation exchanger is rinsed with ultra pure water (Milli-Q). The used suppressor module has a high resistance to pressure, no dead volume and is inert to the use of organic solvents. To prevent an overload of the micro cation-exchange columns a fresh regenerated unit was switched into the effluent flow after every run, at least after 60 min. For further uses, 50 mmol/l ammonium sulfate solution instead of sulfuric acid was used for regeneration. The assembly of IC–MS apparatus is shown in Fig. 1.

2.3. Chromatographic conditions

The sample (100 μl) was injected on a Metrohm Dual 2 anion-exchange column which was held at 35°C. Preliminary investigations with AMPA and glyphosate were done under isocratic conditions using disodium carbonate (1.3 mmol/l) and sodium hydrogencarbonate (2.0 mmol/l) as mobile phase (eluent A, pH 10.30). Better results for the determination of AMPA and glyphosate were obtained under gradient conditions. Disodium carbonate (13 mmol/l) and sodium hydrogencarbonate (20 mmol/l) were used as eluent B (pH 10.08). The initial conditions of the gradient program were 95% A and 5% B, held for 10 min. In the next 20 min eluent A was reduced to 50% and after 5 min the eluent was adapted again to the start conditions and the stationary phase equilibrated for 5 min before the next run. At the beginning of the equilibration time, the suppressor module was switched to the next position.

Table 1
Comparison of most abundant ions of EDTA and their relative abundance by LC–ES-MS measurement without and with suppressor

m/z	Ions	Relative abundance (%)	
		Without suppressor[a]	With suppressor[b]
145	$[M–2H]^{2-}$	–[c]	100
291	$[M–H]^-$	12	15
313	$[M–2H+Na]^-$	33	n.d.[d]
335	$[M–3H+2Na]^-$	60	n.d.
357	$[M–4H+3Na]^-$	100	n.d.

[a] Mass range m/z=200–450.
[b] Mass range m/z=100–450.
[c] Below mass range.
[d] n.d.=Not detected.

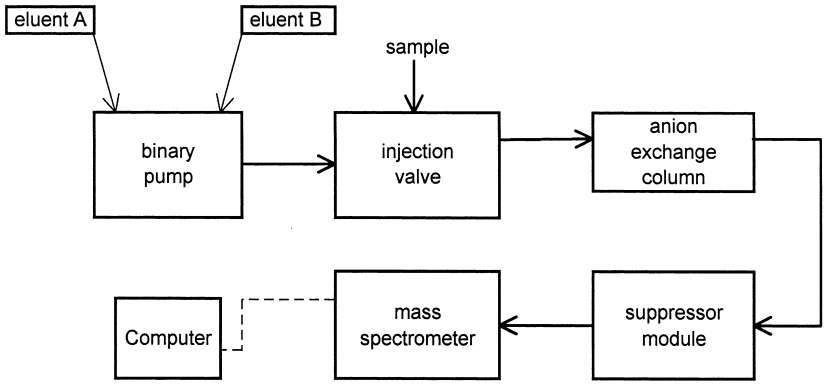


Fig. 1. Assembly scheme of the used IC–MS coupling.

2.4. Sample preparation

The samples were injected into the IC–MS system in general without any further sample treatment except filtration.

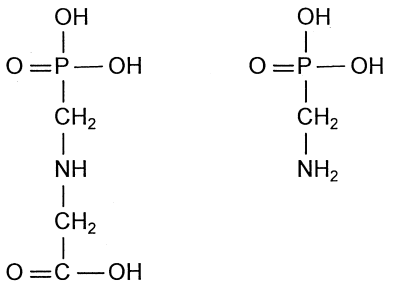
3. Results and discussion

3.1. Standards

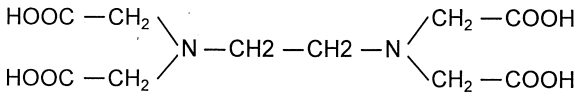
Several polar organic acids, such as glyphosate, AMPA, EDTA and Dikegulac (DAG) were chosen as model compounds (Fig. 2).

Glyphosate and AMPA spiked into Milli-Q water at concentrations of 50 μg/100 ml each (100 μl injected), can be separated on a RP C_{18} column without derivatization utilizing 90% ammonium dihydrogenphosphate buffer at pH 6.9 and 10% methanol. Selecting the quantifying ions for AMPA and glyphosate as described in Section 2.3 can distinguish glyphosate as a sharp peak eluting at a retention time (t_R) of 7 min whereas AMPA can only be separated as a broad bump eluting between 10 and 14 min from the column. However, it was not possible to separate these compounds in spiked real water samples, even in ground water after enrichment through lyophilization by a factor of 100. Both compounds were coeluting with the solvent front and were masked in the high salt peak (t_R between 4 and 10 min). A separation from the solvent front was only possible through derivatization of the analytes prior to or after lyophilization with F-moc or perfluorated aliphatic acid anhydrides such as trifluoroacetic acid anhydride, pentafluoropropionic acid anhydride or heptafluorobutanoic acid anhydride. During all of the tested derivatization steps various new problems occurred leading to irreproducible recoveries. In order to overcome all these problems there was a need for a new simple technique to enhance the separation of the underivatized analytes throughout reduction of the salt peak.

This problem can be overcome by the use of a suppressor module which is switched into the eluent flow between the separation column and the mass spectrometer. Suppressor modules are necessary for increase in sensitivity in ion chromatography due to the exchange of interfering cations against H^+. This will also be the case if anion-exchange columns are used for the separation of strongly polar organic substances (IC) combined with their determination by MS. Together with the conductivity detector established IC applications, several organic acids and other polar micropollutants could be suitably analyzed under these conditions with high sensitivity using MS. Also no incrustation at the vacuum interface can be observed. To prevent corrosion in the mass spectrometer only aqueous solutions of salts from weak acids like acetate, carbonate or hydrogencarbonate should be used. The use of highly diluted hydroxide solution is also possible. Cation-exchange in the suppressor module produces acetic acid, carbon dioxide–carbonic acid and water which compared to their salts create no difficulties in the mass spectrometer. Only low background signals are measured and a better signal-to-noise ratio can be



Glyphosate (mw 169) AMPA (mw 111)



EDTA (mw 292)

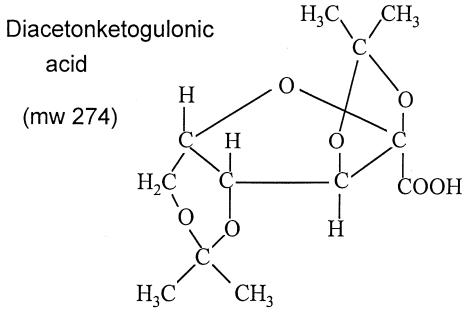


Fig. 2. Chemical structures of the investigated organic acids.

observed resulting in lower detection limits. The sensitivity can be further increased and thereby the measurement enhanced by the addition of acetonitrile or methanol to the mobile phase throughout a better ionization in the spray.

Glyphosate and AMPA were used first as model compounds to test the utility of the IC–MS method. The chromatogram obtained under isocratic conditions with a simple disodium carbonate–sodium hydrogencarbonate eluent (eluent A) is shown in Fig. 3a). It has already been reported that it is possible to separate the analytes without derivatization under isocratic standard conditions quite well using this technique [16]. Both the sodium ions of the eluent and the cations of the sample were exchanged for H^+ by the intervening suppressor leading to a reduction of the baseline total ion current (TIC) from 10^6 cps to 10^4 cps. Thus, the sensitivity of the method has been increased considerably well but both analytes eluted in very broad peaks, AMPA at 14.6 min and glyphosate at 78.8 min. A change in the chromatographic conditions from isocratic to gradient essentially corrected the shape of the glyphosate peak (Fig. 3b) with AMPA eluting now at 11.2 min, still with a broad peak. Glyphosate appears in the chromatogram at 27.5 min in a very sharp peak in contrast to the peak obtained under isocratic conditions. The sensitivity of the method for glyphosate also increased under the chosen gradient conditions. The addition of a ten-fold more concentrated sodium bicarbonate–sodium hydrogencarbonate solution led to an increase in the background signal but also to an increase in sensitivity, which compensated for the analysis of glyphosate. The detection limit for glyphosate in spiked surface waters was improved to below 1 μg/l without any sample treatment during application of IC–MS under the above-mentioned conditions.

In addition to the signals of AMPA and glyphosate, a negative peak of the background signal was recognized (as shown in Fig. 3b). This was the result of advancing the suppressor module at ca. 30 min. A fresh, regenerated and washed cation cartridge was switched into the eluent flow at this time. The peak from the washing water led to a slump in the background signal in the MS system.

The reason for a broad peak for AMPA is traced back with high probability to the employed suppressor. In this suppressor module, the amino group of the AMPA presumably becomes protonated. Consequently, AMPA becomes a cation which interacts with the cation exchanger of the suppressor module. Further studies of these observed effects should enhance the knowledge about a possible retardation of the analytes on the micro cation exchanger of the suppressor module.

Contrary to glyphosate and AMPA discussed earlier, the complexing agent EDTA can be measured with ES-MS only with diluted sulfuric acid as solvent spray. Thereby not only the $[M–H]^-$ ion is detected but also and even in a higher yield the

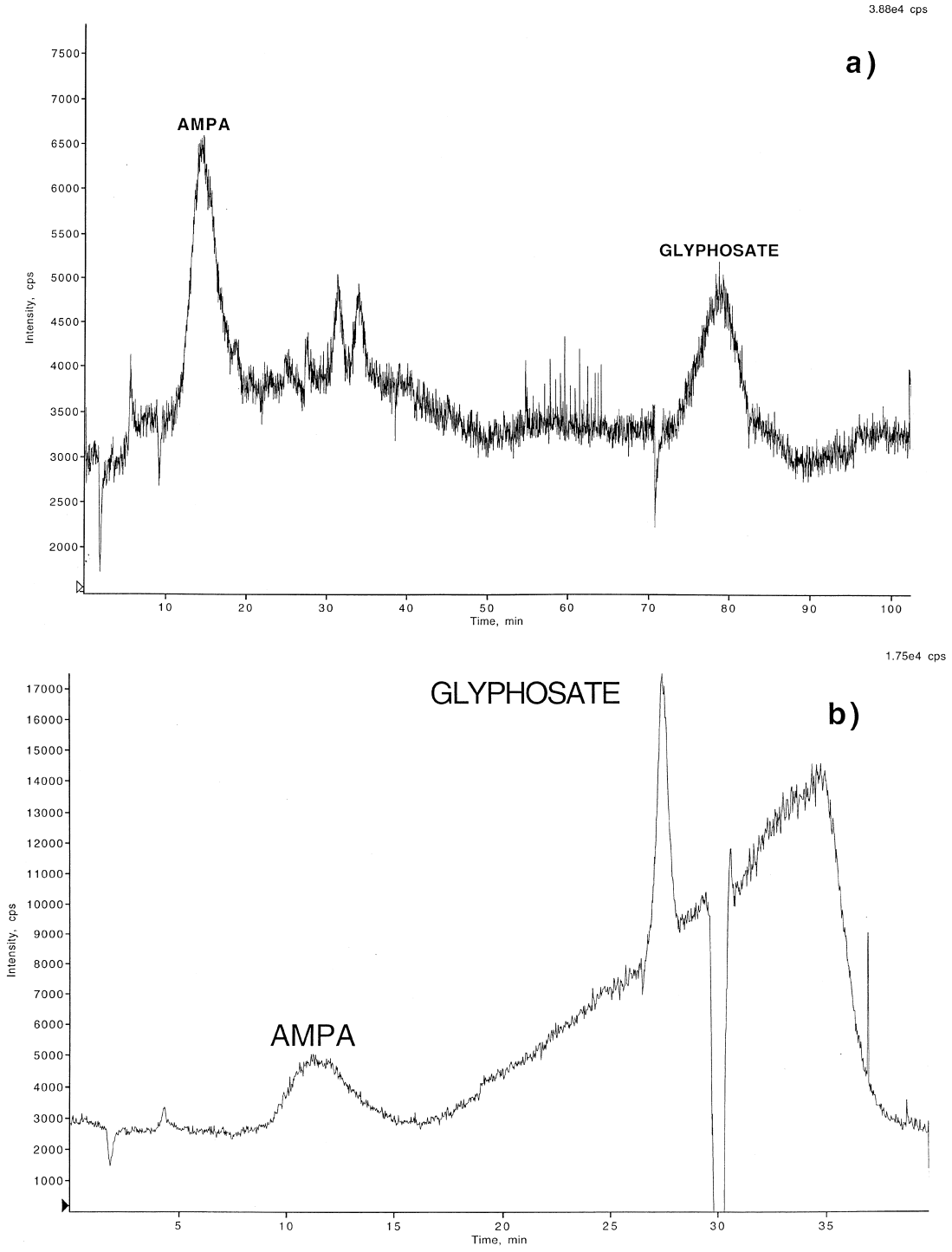


Fig. 3. IC–MS chromatogram of 8 μg/l AMPA and 7.1 μg/l glyphosate spiked into river Rhine water under (a) isocratic conditions (eluent: 1.3 mmol/l disodium carbonate and 2.0 mmol/l sodium hydrogencarbonate) and (b) gradient conditions (eluent A: 1.3 mmol/l disodium carbonate; eluent B: 12 mmol/l disodium carbonate and 20 mmol/l sodium hydrogencarbonate). Flow-rate, 0.5 ml/min; injection volume, 100 μl.

mono-, di- and trisodium adducts (Table 1). A fragmentation pattern as well as doubly charged ions cannot be seen in spectrum due to an abundant chemical noise in the mass range below $m/z=250$.

EDTA could also be determined by IC–MS in a very simple way under the same conditions as shown for glyphosate and AMPA. While the mass spectrum of EDTA without suppressor is characterized by several sodium adducts, the mass spectrum of EDTA by application of the suppressor technique has no sodium adducts (Table 1). The highest signal of $m/z=145$ belongs to $[(HOOC)_2\text{-}CH_2\text{-}H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2\text{-}CH_2\text{-}(COO)_2]^{2-}$ while the signal 291.0 can be assigned to $[(HOOC)_2\text{-}CH_2\text{-}H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2\text{-}CH_2\text{-}(COOH)(COO)]^-$ (Fig. 4). The further obtained fragments are assigned in the caption to Fig. 4.

EDTA was spiked into Milli-Q water in concentrations from 1 to 100 μg/l. Monitoring the ions at $m/z=145$ and 291 a calibration curve being linear from 2 (limit of detection, LOD) to 100 μg/l was obtained. With this calibration curve EDTA could be quantified in river Rhine samples (see Section 3.2).

DAG, spiked into Milli-Q water at a concentration of 5 μg/l, gave only one signal at $m/z=273$ and eluted at a retention time of 5.6 min.

3.2. Real samples

Real water samples were measured easily with IC–MS. In all of the presented experiments, with the exception of membrane filtration, no further sample pretreatments (preconcentration or derivatization) were carried out.

The chromatogram of a membrane-filtered sample of river Rhine water is presented in Fig. 5. No indigenous AMPA or glyphosate were detected in the samples and thus these analytes were added to the water samples at 8 μg/l and 7.1 μg/l, respectively. The signal for AMPA ($m/z=110$) appeared in the

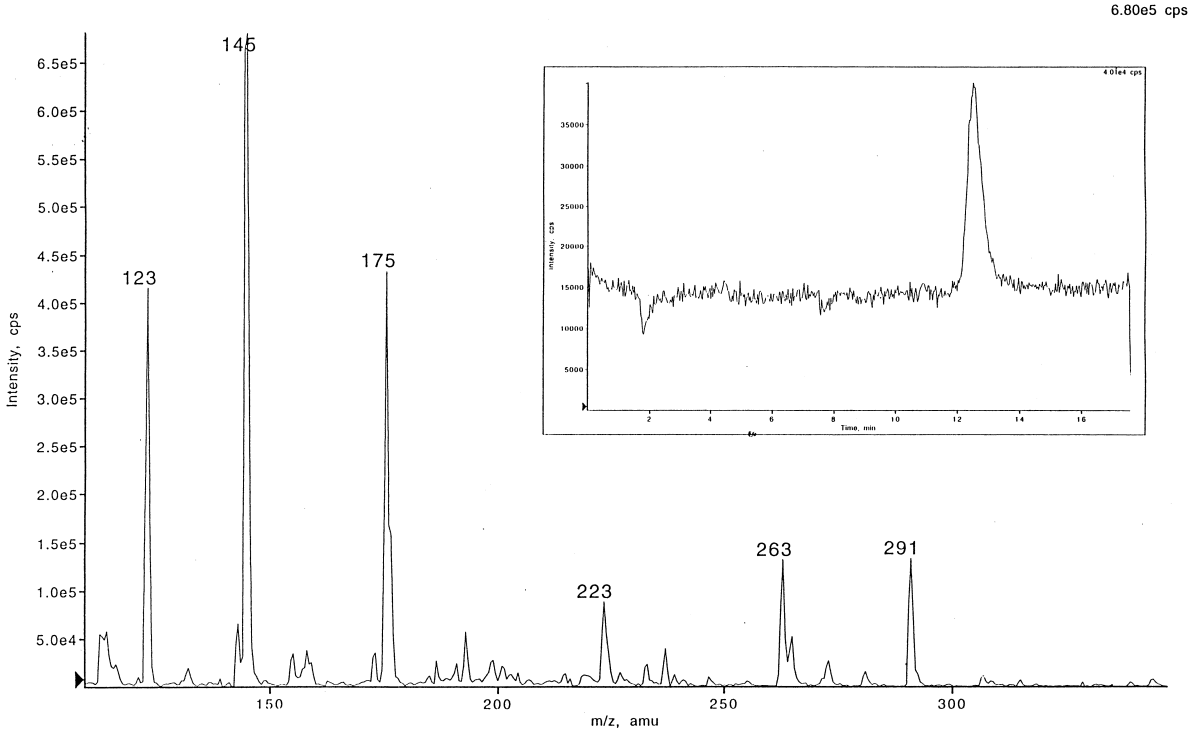


Fig. 4. IC–MS chromatogram and ES-MS spectrum of 20 μg/l EDTA spiked into Milli-Q water. Assignment of fragment ions (m/z): 291 $[M–H]^-$, 263 $[M–COH]^-$, 223 $[M–CH_2COOH]^-$, 175 $[M–H\text{-}2(CH_2COO)]^-$, 145 $[M–2H]^{2-}$, 123 $[M–H\text{-}COOH]^{2-}$. Gradient conditions. Flow-rate, 0.5 ml/min; injection volume, 100 μl.

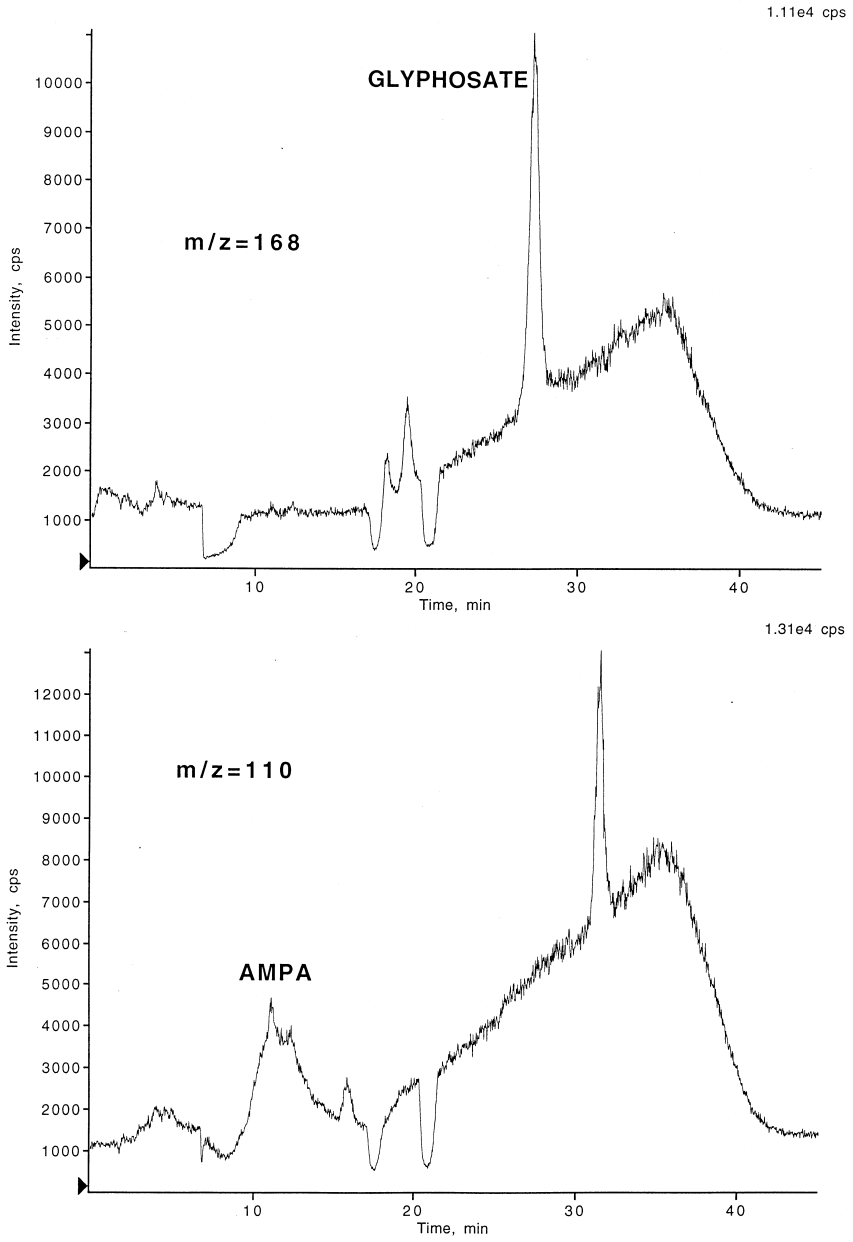


Fig. 5. IC–MS chromatogram (XIC) of glyphosate and 8 μg/l AMPA spiked into river Rhine water without further sample treatment. Gradient conditions. Flow-rate, 0.5 ml/min; injection volume, 100 μl.

chromatogram at 11.1 min as broad as the peak in the standard presented in Fig. 3b. This signal was overlaid by signals from several other peaks, possibly indicating a wide range of still unknown compounds in the surface water. Glyphosate (m/z= 168), spiked into the matrix Rhine water appeared in the chromatogram as a sharp and undisturbed signal. In addition to the ''positive still unknown peaks'' negative signals likewise occurred at ca. 8, 18 and 21 min. These are caused by the indigenous anions

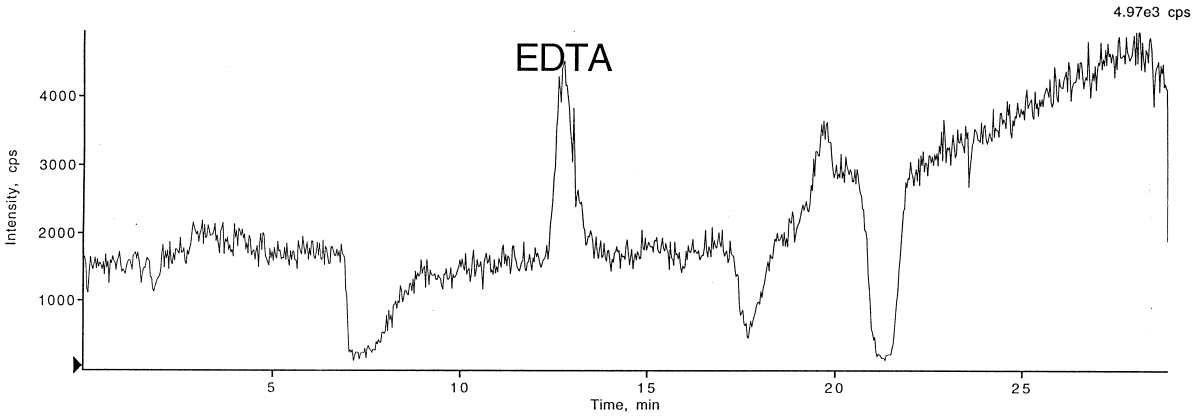


Fig. 6. IC–MS chromatogram of river Rhine water. XIC of EDTA (m/z=291). Gradient conditions. Flow-rate, 0.5 ml/min; injection volume, 100 μl.

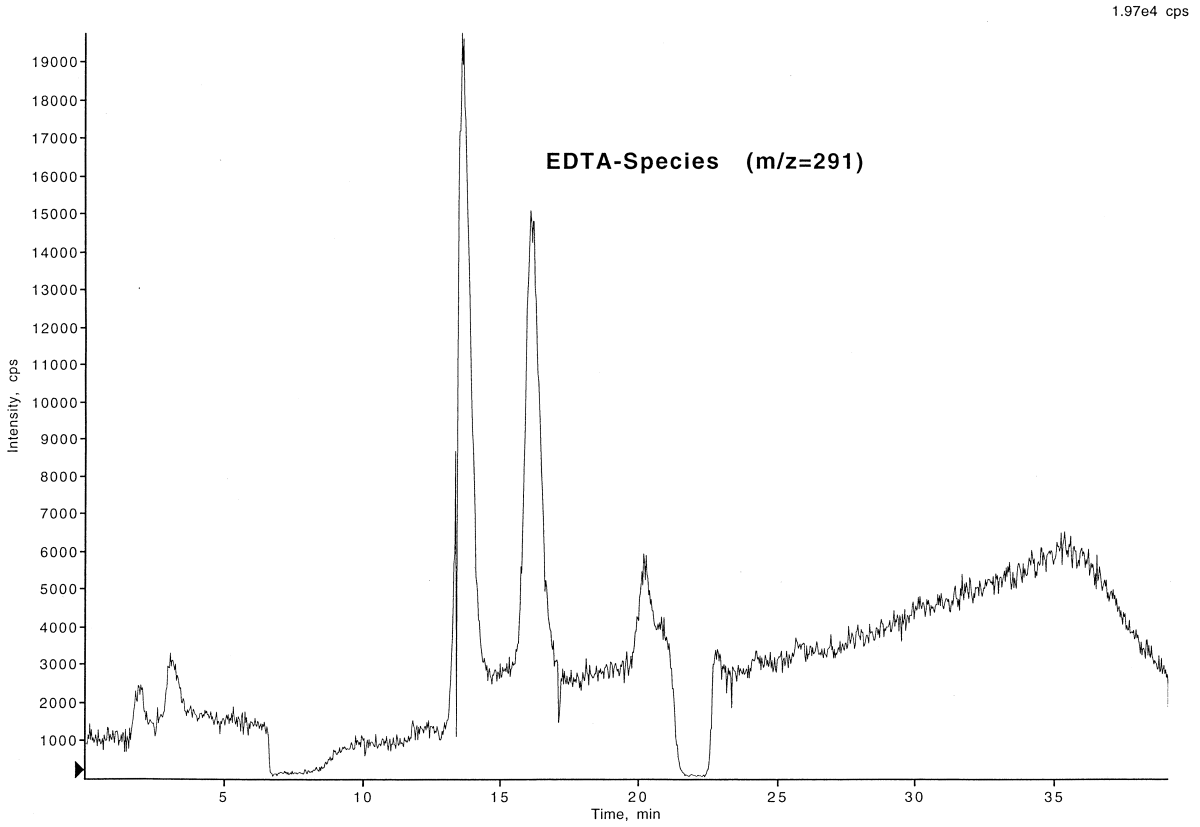


Fig. 7. IC–MS chromatogram of a groundwater sample. XIC of EDTA (m/z=291). Gradient conditions. Flow-rate, 0.5 ml/min; injection volume, 100 μl.

(chloride, nitrate and sulfate) present in the sample. These anions, which are in large excess compared to the analytes disturb the analysis through ionization interferences in the mass spectrometer resulting in a collapse of the baseline (Fig. 5) and probably a loss of sensitivity. In case of the various unknowns present in the spectra, those samples should be further investigated by running the MS in the full-scan mode under variation of the orifice voltage. Alternatively MS-MS experiments could be done.

Another IC–MS chromatogram (m/z 291) of a Rhine water sample is shown in Fig. 6. A clear peak was detected at a retention time of 13 min and was identified as EDTA at a concentration of 5 μg/l. The IC–MS chromatogram of a groundwater sample of the Hessian Ried reported earlier [17] is shown in

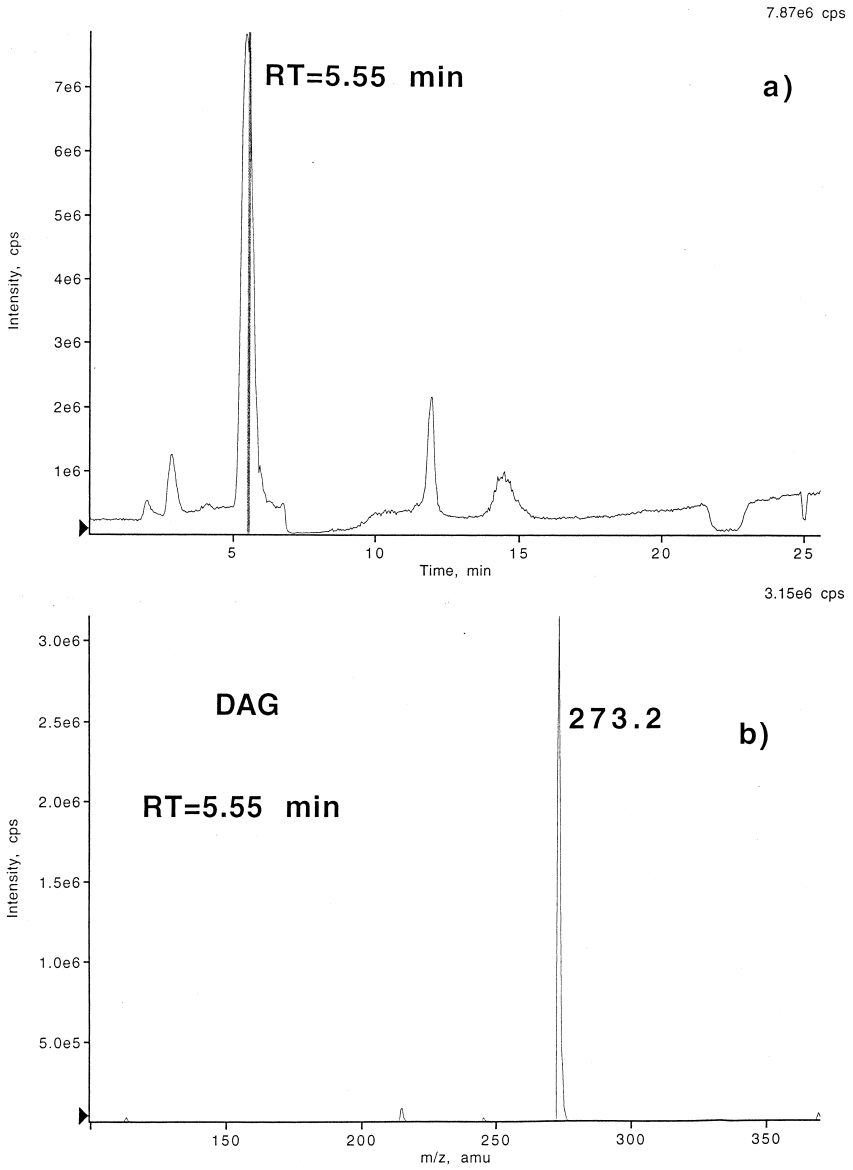


Fig. 8. Full scan (m/z=200–370) IC–MS chromatogram of a groundwater sample. Gradient conditions. Flow-rate, 0.5 ml/min; injection volume, 100 μl.

Fig. 7. At $m/z=291$ two EDTA signals at 13.6 and 16.1 min were clearly recognized. The shift in the retention time due to the presence of two different EDTA species was confirmed by different experiments with spiked samples of Ca^{2+}– and Fe^{2+}–EDTA complexes to the original ground water sample. Under the chosen conditions the Ca^{2+}–EDTA complex is eluting at $t_R=13.6$ min, while the Fe^{2+}–EDTA complex is retained longer on the column ($t_R=16.2$ min). A third, much smaller signal showing up at a t_R of 20 min could not be assigned to a further EDTA complex utilizing IC–MS. The identification of this possible EDTA complex will be done with inductively coupled plasma (ICP)-MS.

Comparing the IC–MS chromatograms obtained from Rhine water and reducing groundwater (Fig. 6 and 7), no negative peak at ca 17 min was observed in the groundwater sample because such strong reduction in the background does not take place if the sample is free of nitrate.

An IC–MS chromatogram (mass scan from $m/z=200$ to $m/z=370$) of a different groundwater sample of the Hessian Ried close to Darmstadt in Germany is presented in Fig. 8. In addition to three unidentified peaks, the signal at a retention time of 5.55 min can clearly been assigned to DAG ($[M-H]^-=273$), which has infiltrated into the subsoil and consequently was accounted in the groundwater (standard not shown) [11,12]. In establishing the mass spectra in the scan mode from $m/z=100$ to $m/z=370$ in addition to DAG, several other polar and still unknown organic substances were obtained. For these and other still unknown organic micropollutants IC–MS could be the method of choice for their further evaluation.

4. Conclusions

With the integration of a suppressor module into a LC–MS system, new measurement conditions are possible, opening the door for analysis of polar micropollutants through LC–MS even further. Polar organic traces which have an acid group in the molecule were well separated and quantified with the use of an anion-exchange column. IC–MS allowed the determination of compounds, such as glyphosate, EDTA and DAG in a very quick and simple way. Presumably a great number of polar organic analytes such as carboxylic acids, sulfonic acids, sulfonates, sulfone amides, polyamino carboxylic acids, amino acids, phosphonic acids and sugars could also be determined by relatively simple analysis and with high sensitivity by suppressor IC–MS(–MS).

By detachment of the cations it was possible to reduce the background signal of the mass spectrometer which led to a higher sensitivity diminishing also the need of further concentration or derivatization steps. In comparison with the other determination methods, the IC–MS allowed a considerable advantage in terms of time. And because there is no derivatization step necessary the analytical error is likewise reduced.

Although the use of suppressor modules in LC–MS(–MS) or IC–MS(–MS) enabled new ways in the determination of polar organic trace in water samples, more work is still to be done in order to develop methods suitable for routine analysis.

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