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Studies on the combination of ion chromatography–particle-beam mass spectrometry with capillary columns

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Abstract

A particle beam interface was investigated for coupling ion chromatography with mass spectrometric detection. Several prerequisites must be fulfilled, including mobile phases containing volatile buffers and high amounts of organic solvents at low flow-rates. Microcolumns with inner diameters between 130 and 1000 μm (packed with a silica-based anion-exchange material) in combination with a microflow aerosol generator meet these requirements. Organic solvents in the mobile phase lead to considerable changes in separation selectivity, so that the retention order can be partly reversed in comparison with aqueous mobile phases. The performance of the interface and the mass spectrometric detection has been studied for a series of inorganic anions as well as for aminopolycarboxylic acids and their metal complexes. The detection limits are between 10 and 100 ng injected and are significantly poorer than those for conductivity detection. On the other hand, the possibility of operating the detector at pre-selected masses greatly improves the selectivity of the analysis and helps to confirm peaks from a non-selective conductivity detector. On-line and off-line preconcentration techniques allow the detection of anions in drinking water at ppb levels.

Keywords: Interfaces; Detection, LC; Inorganic anions; Aminopolycarboxylic acids; Metal complexes

1. Introduction

Ion chromatography (IC) is a well established technique for the analysis of low-molecular-mass inorganic and organic ionic species. Among the various detection modes available for IC, conductivity detection is the most commonly used method. However, the use of non-selective conductivity detectors can be unsuccessful for the analysis of complex samples, and it does not yield any structural information about unknown sample components. Mass spectrometric (MS) detectors can overcome such disadvantages and, thus, they are becoming increasingly important in combination with liquid chromatography. The most commonly used interfaces are particle beam [1], thermospray [2], continuous-flow fast atom bombardment (FAB) [3], atmospheric pressure chemical ionization [4] and electrospray [5]. The commercial availability of these interfaces has led to a wide range of different applications. Contrary to this trend, there are not yet many investigations on the combination of MS with IC. One of the major problems that can arise upon coupling IC to MS is the possible incompatibility of the electrolyte of the mobile phase with the interface and the ion source of the MS. To circumvent this problem, a micromembrane suppressor, identical to that for conductivity suppression, can be incorporated into the system between the IC column outlet and the mass spectrometer. In this way, ion-exchange chromatography has successfully been coupled to MS by various interfaces, such as a thermospray

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interface for the analysis of carbohydrates [6], an electrospray interface for the analysis of organic ammonium and sulfate compounds [7] as well as inorganic anions [8] and a particle beam interface for the analysis of aromatic sulfonic acids [9,10]. Some ion-exchange separations have been reported that worked without a membrane suppressor but used volatile buffers (such as in the analysis of aromatic sulfonic acids with a particle beam interface [9]) or introduced just a small portion of the column effluent into the mass spectrometer, as has been described for the analysis of cationic organoarsenic species [11] and for bromate in drinking water with an electrospray interface [12]. Ion-exclusion chromatography with HCl as the mobile phase can also be used without a membrane suppressor for the analysis of organic acids, in combination with a thermospray [13] or particle beam interface [14].

It seems that possible improvements for the combination of IC with MS are not yet fully explored. Our interest has been focused mainly on techniques that would not depend on the use of a membrane suppressor so that the selection of mobile phases would not be restricted to the commonly used carbonate buffers or to sodium hydroxide. In this case, the development of microcolumns for the IC system seems advisable, as the corresponding low flow-rates might be more compatible with the mass spectrometer. Throughout this work, the term microcolumn refers to a packed IC column with an inner diameter of between 130 and 1000 μm. A particle beam interface was chosen for the work presented in this paper. This type of interface does not necessarily yield the best performance for all the possible applications in IC. Nevertheless, it has some advantages over other types of interfaces in so far as the process of volatilization of the column's effluent is independent of the ionization process in the mass spectrometer. This separation of the two processes allows the use of different ionization techniques, such as electron impact or chemical ionization, with various reagent gases to maximize the information obtainable from the mass spectrum. For these reasons, fundamental studies on the behavior of a particle beam interface for coupling microcolumn IC with MS were carried out. Inorganic anions as well as aminopolycarboxylic acids and their metal complexes were used as model compounds in this work.

2. Experimental

2.1. Instrumentation

The binary gradient system used for IC consisted of two 510 HPLC pumps (Waters, Milford, MA, USA), a micro injection valve (Vici, Schenkon, Switzerland) with a 60-nl or a 200-nl loop or a 7010 injector (Rheodyne, Cotati, CA, USA) with a 1-μl loop or a 15-μl packed loop for on-line preconcentration, laboratory-packed columns (see below) and a Maxima 820 Chromatography Data Workstation (Waters). For flow-rates of less than 100 μl/min a laboratory-made T-splitter was placed between the pumps and the injection valve.

The interface was a 59980B particle beam unit (Hewlett-Packard, Palo Alto, CA, USA) coupled with a 5989A quadrupole mass spectrometer (Hewlett-Packard). The aerosol generator of the particle beam unit was replaced by a laboratory-made microflow aerosol generator, the design of which was similar to that reported in the literature [15,16]; it was machined from brass and plated with gold to withstand corrosion. The effluent of the IC column was fed to the point of nebulization by means of a fused-silica capillary (25 or 50 μm I.D.). Helium 4.6 purity grade was used as the nebulizer gas. The temperature of the desolvation chamber of the interface was 65°C and the temperature of the mass spectrometric ion source was 200°C. The quadrupole was kept at 100°C.

Alternatively, the IC column was coupled to an M486 variable-wavelength UV detector (Waters) or to a fixed-wavelength UV detector, which was obtained from a Quanta 4000 capillary electrophoresis instrument (Waters).

2.2. Preparation of microcolumns

The columns were prepared from stainless steel tubing (1000 μm I.D.), polyether ether ketone (PEEK) tubing (750, 500, 250 or 130 μm I.D.) or deactivated fused-silica capillaries (700 μm O.D.× 530 μm I.D.) obtained from J&W Scientific (Folsom, CA, USA) that were inserted into PEEK tubing (750 μm I.D.). The outer diameter of all the stainless steel and PEEK tubing was 1/16 in. and the length was between 150 and 250 mm (1 in.=2.54 cm). HPLC

unions were fitted with 3 μm stainless steel frits and were used as end fittings for the columns.

The packing material was a 5-μm LiChrospher C_{18} modified silica (Merck, Darmstadt, Germany) used as a 2% aqueous suspension in 1% sodium dodecylsulfate or a 5-μm Bakerbond quaternary amine silica (Baker, Deventer, Netherlands) used as a 2% suspension in 25 m*M* ammonium formate, prepared in water–acetonitrile–methanol (50:30:20, v/v/v). Immediately before using the suspension for column packing, it was treated in an ultrasonic bath for 20 min.

In the packing process, an end fitting was placed onto one end of the column, while the other end was connected to a reservoir (stainless steel tubing; 15 cm×4 mm I.D.). The reservoir was filled with a suspension of the packing material and connected to an HPLC pump. The flow-rate for packing was between 100 μl/min for columns with 130 μm I.D. and 600 μl/min for columns with 1000 μm I.D. Once all the suspension had been pumped into the column (indicated by no further increase in the back-pressure), the flow was stopped, the reservoir was refilled with the suspension and the packing process was continued until a back-pressure of 3500 p.s.i. was reached for PEEK columns or 4500 p.s.i. for all other columns (1 p.s.i.=6894.76 Pa). After putting the second end-fitting onto the column, those packed with C_{18} silica were flushed with water–acetonitrile (25:75, v/v) for 15 h, whereas columns packed with anion-exchange material were flushed with aqueous 50 m*M* ammonium formate for 10 h.

3. Results and discussion

3.1. Efficiency and selectivity of micro IC columns

In this work, two types of packing materials were used for the preparation of micro IC columns, namely a silica-based anion-exchanger and a C_{18}-modified silica. The latter material can be used as an anion-exchanger if it is permanently coated with a hydrophobic quaternary ammonium salt. The quality of the packing procedure for the silica-based anion-exchanger was tested by injection of chloride (mobile phase, acetonitrile–1.5 m*M* ammonium formate, pH 5, 85:15, v/v) and for the C_{18}-modified silica by injection of pyrene (mobile phase, acetonitrile–water, 80:20, v/v). The number of theoretical plates per meter was approximately 18 000 for the anion-exchange material and 50 000 for the C_{18} silica. The performance was virtually independent of the inner diameter of the column, provided that the linear velocity of the mobile phase was kept constant. The results of these experiments indicate that the packing procedure described above is adequate for the preparation of microcolumns with reasonable efficiency.

Mass spectrometric detection without membrane suppressors requires a volatile electrolyte in the mobile phase. Ammonium acetate has been suggested for this purpose [9]. In this work, we used ammonium formate, which should give fewer interferences in the mass spectrum due to its lower molecular mass. Furthermore, it is well known that the performance of the particle beam interface increases when the amount of organic solvent in the mobile phase is increased. Ion-exchange chromatographic separations are generally carried out with totally aqueous mobile phases. The use of organic solvents has received little attention, although they can be a valuable tool for optimization of separation selectivity. Some aspects of mobile phases containing organic solvents have been discussed recently for anion-exchange chromatography [17] as well as for cation-exchange chromatography [18,19] using resin-based stationary phases. Unfortunately, even highly cross-linked polymer particles can still exhibit some swelling or shrinking when switching between totally aqueous mobile phases and mobile phases containing various organic solvents. For this reason, a silica-based anion-exchange material was used throughout this work.

The dependence of separation selectivity upon the content of acetonitrile is shown in Fig. 1 for a series of inorganic anions (UV detection at 210 nm). There are two regions of suitable mobile phase compositions, namely below 20% and above 60% acetonitrile. Whereas the former yields the ordinary retention order of inorganic anions, the latter results in an almost complete reversal of the retention order. Ionic solvation may play a major role in the changes in separation selectivity [19], although this is still, to some degree, a speculation and there might be several competing effects that have not yet been investigated in detail. All further investigations on

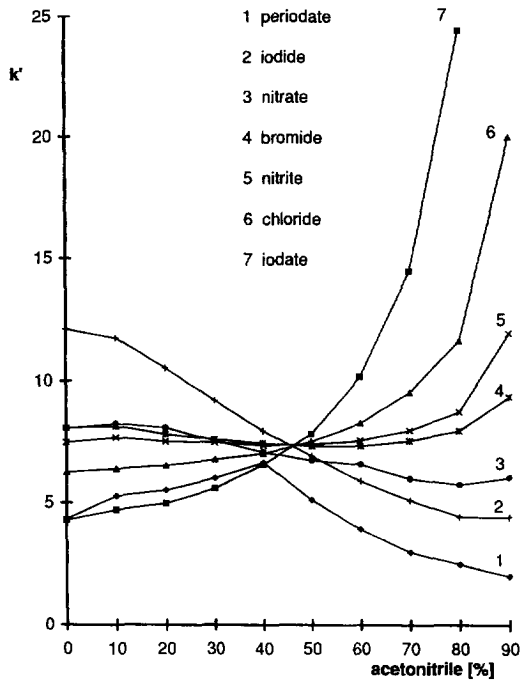

Fig. 1. Dependence of the capacity factors (k') of inorganic anions upon the percentage of acetonitrile in the mobile phase (10 m*M* ammonium acetate, pH 4.95, mixed with varying amounts of acetonitrile).

inorganic anions were done with mobile phases containing more than 70% organic solvent to ensure a reasonable performance of the particle beam interface. In this case, the retention order for the whole range of inorganic anions studied in this work was periodate, perchlorate, iodide, chlorate, nitrate, bromide, nitrite and bromate, chloride, thiocyanate, iodate, thiosulfate, sulfite, sulfate. During gradients runs with mobile phases with very high acetonitrile concentrations and an increasing ionic strength of the formate buffer, care must be taken to avoid precipitation of analyte ions like bromate, iodate, perchlorate and periodate.

Aminopolycarboxylic acids and their metal salts are commonly separated by ion-interaction chromatography [20–24] or anion-exchange chromatography [25–27]. Ion-interaction reagents in the mobile phase are virtually incompatible with mass spectrometric detection because they yield a series of strongly interfering peaks in the mass spectrum. Therefore, in this work, the ion-exchange mode was preferred, using the same silica-based anion-exchanger as was used for the separation of inorganic anions. Alternatively, a C_{18}-modified silica that was permanently coated with a hydrophobic quaternary ammonium salt was employed. The coating was accomplished by pumping 3 m*M* cetyltrimethylammonium bromide in water–methanol (50:50, v/v) through the column. Unfortunately, even with mobile phases containing only 7% of organic solvents, some bleeding of the coating was observed, therefore, fixed-site ion-exchangers proved to be the better stationary phase if mass spectrometric detection is applied. The silica-based anion-exchanger mentioned above and mobile phases containing a formate buffer at pH 4.2 and more than 80% acetonitrile led to the retention order 1,2-diaminocyclohexanetetraacetic acid (CDTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA), which differs considerably from the retention order described for totally aqueous mobile phases [28]. Dependencies of retention on the percentage of organic modifier have not been fully investigated in this work, because UV detection of aminopolycarboxylic acids was not possible in mobile phases containing a formate buffer and MS detection did not work at low percentages of organic modifier. The separation of metal–EDTA complexes could be optimized by using varying amounts of acetonitrile or methanol in the mobile phase, as can be seen from Fig. 2 (UV detection at 254 nm).

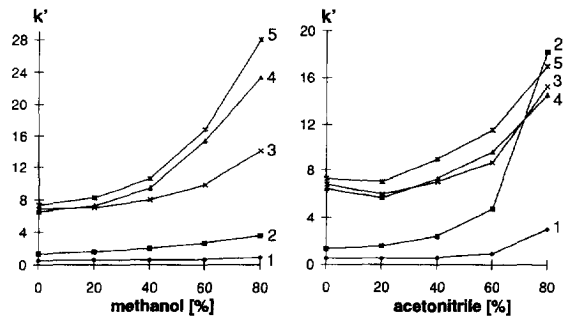

Fig. 2. Dependence of the capacity factors (k') of metal–EDTA complexes upon the percentage of organic modifier in the mobile phase. 1=Bi-EDTA; 2=Fe(III)–EDTA; 3=Pb–EDTA; 4=Ni–EDTA; 5=Cu–EDTA. Mobile phase: 30 m*M* ammonium acetate containing 0.4% formic acid and varying amounts of methanol or acetonitrile.

3.2. Mass spectrometric detection

The formate buffer of the mobile phase used in this work resulted in various mass spectrometric signals in a range up to m/z 46 (formic acid). Therefore, in the scan mode, data were acquired starting at m/z 47. In some cases, signals for m/z lower than 47 could be measured in the selected-ion monitoring (SIM) mode.

Table 1 summarizes the signals obtained for inorganic anions in the positive electron impact (EI) mode or in the positive chemical ionization (CI) mode. For interpretation of these spectra, one has to take into account chemical reactions of the analytes in the particle beam interface as well as reactions in the ion source of the mass spectrometer, such as fragmentation during EI ionization or hydrogen transfer during chemical ionization. Although it was not possible to relate the results unequivocally to one of these processes, the anions can be grouped in the following way, according to their behavior in the EI mode: chloride, bromide, iodide and thiocyanate yield a base signal that corresponds to the formation of hydrogen chloride, hydrogen bromide, and so on; sulfite, sulfate, thiosulfate and nitrate did not yield molecular ion peaks, but did yield base signals corresponding to sulfur dioxide or nitrogen dioxide; chlorate, bromate, iodate, perchlorate and periodate showed signals for the corresponding hydrogen halogenides as well as the corresponding oxides (with hydrogen attached), although molecular ion peaks could not be observed; ions like iodate, periodate and bromate yielded additional signals at m/z 254 and 160, respectively, corresponding to the dimer of the halogen. Fig. 3 gives examples of mass spectra for selected anions.

Detection of inorganic anions with positive chemical ionization using methane as the reagent gas yielded mass spectra that were similar to those of electron impact ionization. In accordance with generally known characteristics of CI, there was a tendency for species to be formed that contained one hydrogen more than found in species obtained with EI. Otherwise, positive chemical ionization did not produce significantly more information than EI and was not further investigated. Negative chemical ionization, which can be used successfully in organic mass spectrometry, did not yield any peaks for inorganic anions.

Since the analytes separated by IC already carried a negative charge, several experiments were carried out to see if some of these analytes might pass the particle beam interface in the form of anions, so that mass spectrometric detection in the negative mode without an ionization source would be sufficient. The results showed that no signals at all could be obtained in the negative mode when the current of the glowing filament in the EI source was turned off. This would indicate that only neutral adducts enter the mass spectrometric ion source or that collisions

Table 1
Main mass spectrometric signals obtained for inorganic anions in the positive detection mode with electron impact (EI) or chemical ionization (CI)

Ion	m/z (EI)	m/z (CI)
Iodide	128, 127	
Iodate	127, 128, 254	
Periodate	254, 127, 128	
Bromide	80, 82, 79, 81	81, 83
Bromate	80, 82, 96, 81, 79, 98, 57, 55, 160	
Chloride	36, 38, 35, 37	37, 39
Chlorate	67, 51, 69, 52, 53, 36	
Perchlorate	67, 69, 73, 48, 83, 100, 36	
Nitrate	46, 47	47, 48, 64
Sulfate	64, 48, 80, 66	65, 49, 64, 48, 81
Sulfite	64, 48	
Thiosulfate	64, 48, 66, 96	65, 49, 48
Thiocyanate	59, 58	

Data for the signals are given in decreasing order of intensity.

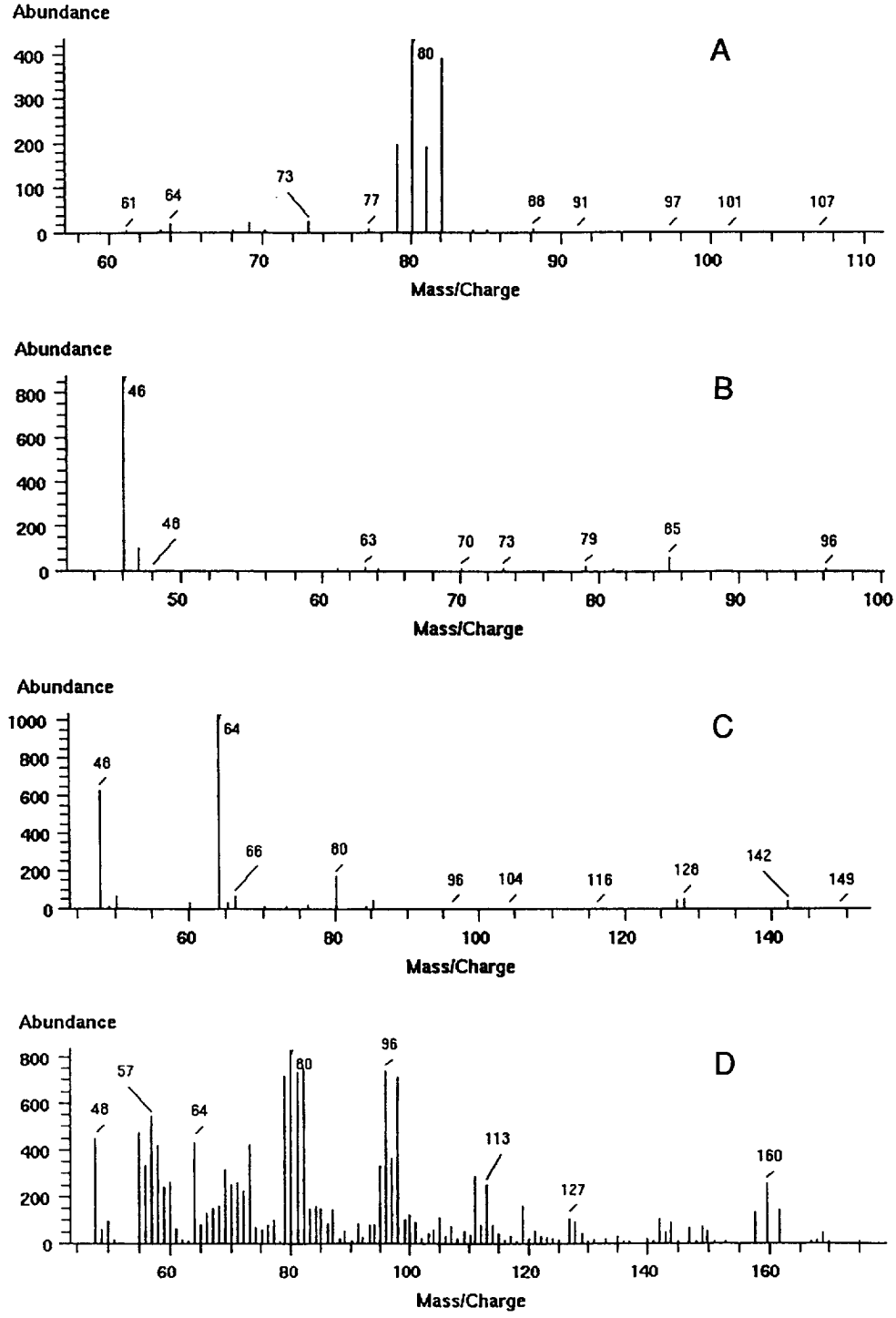

Fig. 3. Examples of EI mass spectra (background-subtracted) of inorganic anions separated by ion-exchange chromatography. A=bromide; B=nitrate; C=sulfate and D=bromate.

with the hot source walls might induce changes that could produce neutral species. On the other hand, the formation of positively charged adducts cannot be ruled out at the particle beam interface. In this case, a detection in the positive mode should be possible without EI ionization. However, no signals could be observed in a series of corresponding experiments.

In organic mass spectrometry, the EI source is commonly used at an electron energy of 70 eV. For the inorganic anions, it turned out that the signals of some masses increased considerably when the ionization energy was decreased. This is shown in Fig. 4 for the anions chloride, bromide, iodide and nitrate. Decreasing the ionization energy to 10 eV results in an almost twenty-fold increase in sensitivity for the base peak of iodide at m/z 128 (corresponding to hydrogen iodide), whereas the iodide peak at m/z 127 is virtually unaffected. For practical work, an ionization energy of 40 eV was chosen, because lower energies decreased the life time of the filament considerably.

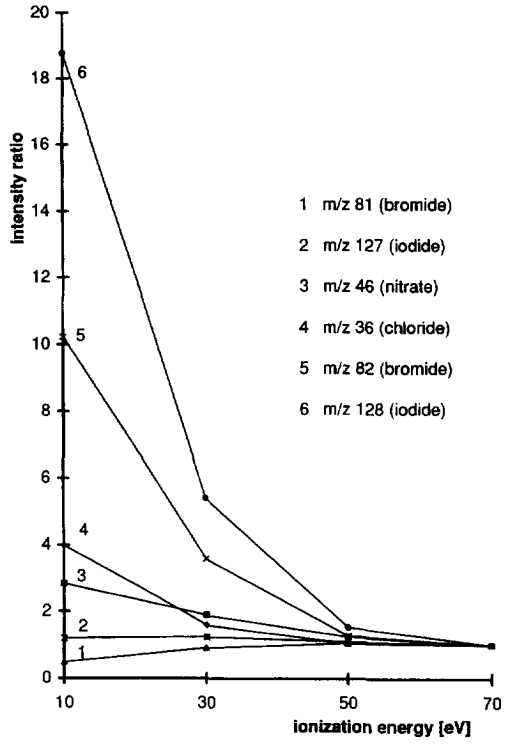

Fig. 4. Dependence of mass spectrometric peak intensity upon the electron energy of the EI source. Peak areas normalized to the peak area at 70 eV are plotted on the y-axis.

An interesting phenomenon was observed when a column had been used for the separation of iodine species for a prolonged time. When chlorate, bromate or iodate were injected onto such a column, the mass spectra of these anions were quite different to those obtained with a "normal" column. For all three anions, the base peak was at m/z 254. The only explanation that can be given at the moment might be a contamination of some part of the system by iodine species that react selectively with the injected chlorate, bromate or iodate to form elemental iodine (m/z 254). Further work is in progress to elucidate this phenomenon with respect to practical applications, because this mode allows improved detectability (of course at the expense of positive identification of the analytes) for chlorate, bromate and iodate (and maybe other oxidizing species not yet investigated), especially when a reduced electron energy is used in the EI source.

Mass spectra of NTA and EDTA are shown in Fig. 5. Aminopolycarboxylic acids with higher molecular masses, like DTPA, gave spectra similar to that of EDTA. Table 2 summarizes the mass spectrometric signals for different aminopolycarboxylic acids. No molecular mass peaks could be observed. Fig. 6 shows the fragment ions that most probably account for the signals in the mass spectrum of EDTA. Metal–EDTA complexes yielded the same base peak as EDTA, but no molecular mass peak. Therefore, mass spectrometric detection did not allow a differentiation of metal–EDTA complexes that were not fully separated by chromatography.

Separations of inorganic anions and aminopolycarboxylic acids with mass spectrometric detection are shown in Figs. 7 and 8. Table 3 summarizes the detection limits (thiocyanate is not included because, for reasons not yet known, it yielded a very poor peak shape). The anions, carbonate, nitrite fluoride and cyanide, could not be detected due to losses in the interface and/or interferences in the mass spectrum by the mobile phase.

Obviously, the detection limits for the amounts injected are poorer than those for conductivity detection. Applications to real samples require suitable preconcentration procedures. To this end, the loop of the microinjector was replaced by a packed

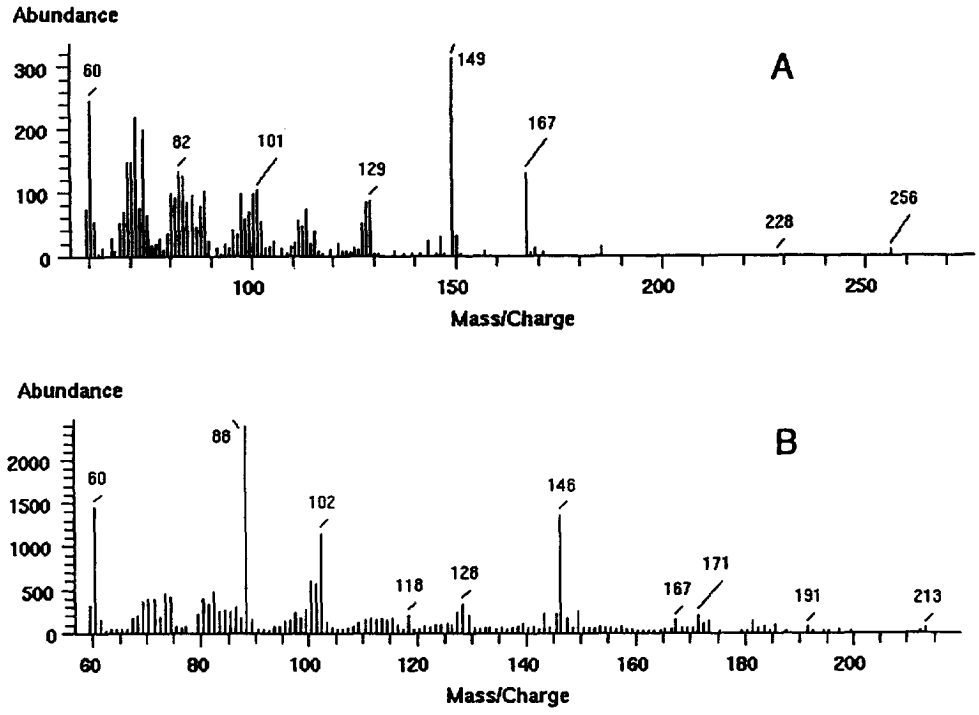

Fig. 5. EI mass spectra (background-subtracted) of EDTA and NTA separated by ion-exchange chromatography. A=EDTA and B=NTA.

loop containing the same anion-exchange material as that of the column. This arrangement allowed the injection of volumes up to 250 μl for samples of low-to-medium ionic strength, such as drinking water. The detection limits for the concentration could be lowered to the ppb range.

4. Conclusions

Ion chromatography can be successfully coupled to mass spectrometry by means of a particle beam interface, if microcolumns with flow-rates in the μl/min range of mobile phases with a high content of organic modifiers are used. The low flow-rates are

Table 2
Main mass spectrometric signals obtained for aminopolycarboxylic acids in the positive detection mode with electron impact (EI) ionization

Ion	*m/z*
NTA	88, 60, 146, 102
EDTA	149, 60, 71, 73, 167
DTPA	149, 71, 167, 70, 60
CDTA	84, 71, 97, 110, 149, 167

Data for the signals are given in decreasing order of intensity.

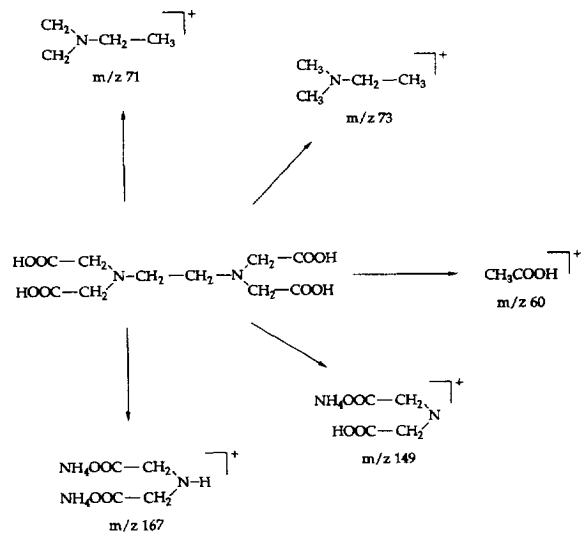

Fig. 6. Suggestions for electron impact fragmentation of EDTA separated by ion-exchange chromatography.

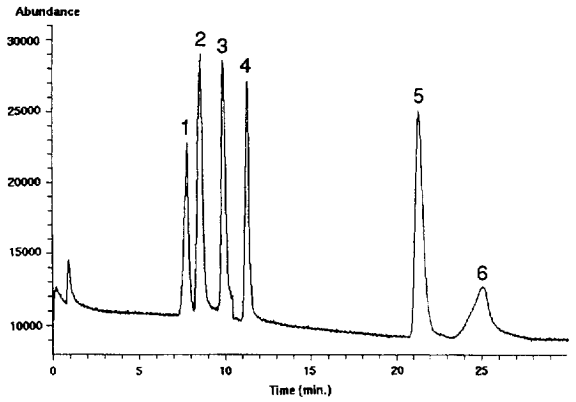

Fig. 7. Gradient separation of inorganic anions with EI mass spectrometric detection. Column: stainless steel, 200×1 mm I.D., packed with 5 μm silica-based anion-exchange particles. Eluent A: 1.5 m*M* ammonium formate in acetonitrile–water (85:15, v/v); eluent B: 95 m*M* ammonium formate in acetonitrile–methanol–water (72:18:10, v/v/v), pH 5.6. Gradient: 100% A from 0–6 min, followed by an increase of B from 0 to 100% over 15 min. Flow-rate: 100 μl/min. Peaks: 1=iodide; 2=nitrate; 3=bromide; 4=chloride; 5=thiosulfate and 6=sulfate. Amounts injected: 450–750 ng of each.

fully compatible with the mass spectrometric detection, so that there is no need to split the effluent of the column and to sacrifice sensitivity. While the

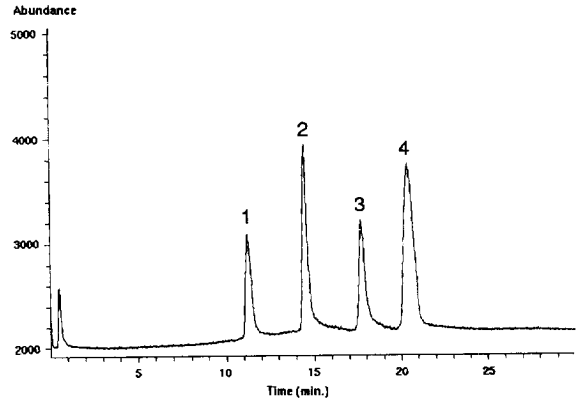

Fig. 8. Gradient separation of aminopolycarboxylic acids with EI mass spectrometric detection. Column: PEEK, 200×0.75 mm I.D., packed with 5 μm silica-based anion-exchange particles. Eluent A: 1.5 m*M* ammonium formate in acetonitrile–water (86:14, v/v); eluent B: 95 m*M* ammonium formate in acetonitrile–methanol–water (68:26:6, v/v/v), pH 4.2. Gradient: 95% A and 5% B from 0–5 min, followed by an increase of B from 5 to 100% over 12 min. Flow-rate: 100 μl/min. Peaks: 1=CDTA; 2=EDTA; 3=DTPA and 4=NTA. Amounts injected: 770–880 ng of each.

Table 3
Detection limits (signal-to-noise ratio of 3) for mass spectrometric detection of anions after IC separation

Ion	EI (40 eV) (ng injected)	positive CI
Iodide	30	
Chlorate	65 (40)	
Nitrate	65	70
Bromide	45	80
Bromate	45 (20)	
Chloride	50	60
Iodate	40 (40)	
Thiosulfate	20	
Sulfate	80	200
EDTA	30	
NTA	30	
DTPA	30	
CDTA	50	

SIM mode was used for the mass spectrometric base peak of each analyte. Data in brackets refer to the measurement of *m/z* 254 in an iodine-contaminated system (details see text).

work presented in this paper had been carried out, the electrospray interface has grown in significance as an alternative tool for coupling liquid chromatography with mass spectrometry. In fact, the most recent papers on IC–MS with an electrospray interface [8,12] indicate that this interface should be able to lower the detection limits considerably. Nevertheless, even this new type of interface will display its whole potential only in combination with capillary IC columns. One should also keep in mind that the particle beam interface will still remain one of the most versatile interfaces with specific advantages (not all of them being relevant for the applications described in this paper), such as the fact that the ionization process is independent of the desolvation process and yields EI or CI spectra that are little influenced by the chromatographic mobile phase.

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