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Comparison of on-line coupling of ion-chromatography with atmospheric pressure ionization mass spectrometry and with inductively coupled plasma mass spectrometry as tools for the ultra-trace analysis of bromate in surface water samples

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Abstract

Ion chromatography in combination with atmospheric pressure ionization mass spectrometry (API-MS) as well as with inductively coupled plasma mass spectrometry (ICP-MS) had been compared for trace analysis of bromate. The results indicate that both techniques yield comparable results, which are in excellent agreement with standard methods for bromate determination. Furthermore, both techniques showed almost equal absolute detection limits (approximately 50 pg bromate injected). Contrary to IC–API-MS, IC–ICP-MS can tolerate a higher salt concentration in the mobile phase. This allows the use of high-capacity columns combined with large sample volumes. This lowered the concentration based detection limits by one order of magnitude for IC–ICP-MS compared to IC–API-MS (0.06 μg/l vs. 0.5 μg/l). On the other hand, IC–API-MS is able to allow a positive identification of bromate even in cases when IC does not fully separate bromate from other bromine-containing species. The performance data of both IC–MS techniques have been established by participation in an international round robin test.

Keywords: Water analysis; Environmental analysis; Mass spectrometry; Bromate; Inorganic anions

1. Introduction

Bromate is formed during the disinfection process of drinking water utilizing ozone. Source is the ubiquitous bromide anion [1], which is oxidized at medium to high pH-values. Bromate is recognized as potential kidney carcinogen to rats and mice at mg/l levels [2]. Newer toxicological studies [3] have led the International Agency for Research on Cancer (IARC) to classify bromate as a group 2B carcinogen to humans with renal tumor risks at concentrations above 0.05 μg/l. Recently discussed maximum concentration levels for bromate in drinking water are between 10 and 25 μg/l [4–6].

The determination of bromate in water samples at the low μg/l level is still difficult. The methods generally applied to this problem include ion chromatography with various detectors [7,8], ion pairing chromatography [9], isotope dilution mass spectrometry [10,11], photometry [12], gas chromatography [13], flow injection analysis [14], fluorimetry [15] and polarography [16]. The favourite method for the separation of bromate from interfering com-

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pounds is ion chromatography. The methods of detection vary from conductivity [7,8], photometry [17], inductively coupled plasma mass spectrometry (ICP-MS) [10,11,18–21] to mass spectrometry (LC-MS) [22–26].

With regard to the required limit of detection of less than 1 μg/l of bromate, only a very few methods remain. Various mass spectrometric techniques are powerful enough to obtain detection limits below 1 μg/l. At least two techniques were directly applicable to aqueous samples, ICP-MS and API-MS.

Both methods are able to determine bromate at very low levels, but a critical comparison of advantages or disadvantages of both techniques is still missing. Based on an interlaboratory trial organized for the characterization of a new ISO-standard for the determination of bromate in potable water (ISO/DIS 15061), the two mass spectrometric methods were compared for a variety of samples ranging from aqueous standard solutions to untreated river water.

The chromatography modules were optimized for each detection device separately because of completely different precautions for the composition of an ''ideal'' mobile phase for coupling purposes. As direct consequence, the composition of the mobile phase rules the column properties for IC–ICP-MS and IC–API-MS.

2. Experimental

2.1. IC–ICP-MS

2.1.1. Ion chromatography

All chromatographic equipment was delivered by Metrohm, Herisau, Switzerland. The chromatographic system consisted of the IC pump 709 equipped with a membrane pulse dampener for lowest pressure pulsation. A six-port stainless steel valve of the IC Separation Center 733 (Rheodyne) was used for sample injection. All columns, tubing and fittings were made of polyether ether ketone (PEEK).

The elution system was based on 75 m*M* nitric acid, which was prepared from doubly subboiled distilled suprapure concentrated nitric acid (Riedel de Haën, Seelze, Germany). The eluent pH was adjusted to pH 6 with suprapure ammonia (25%, w/w) (Riedel-de Haën). Eluent flow-rate was set to 1.0 ml/min and an injection volume of 585 μl was used. Other conditions are as noted in the figure captions.

The separation column P150497 MN DEMA was filled with a homemade anion exchanger based on a polystyrene–divinylbenzene (PS–DVB) copolymer. The functional group was a quaternized diethanol-methyl amine. The exchange capacity of a standard bore column (120×4 mm I.D.) as determined for chloride was 600 μmol or 450 μmol/ml bed volume.

2.1.2. ICP-MS

A Fisons/VG PlasmaQuad Turbo 2+ (Fisons, Winsford, UK) in standard configuration was used for mass spectrometric detection of bromate. A V-groove-nebulizer was utilized for nebulization of the eluent. Data were collected using the DOS software of VG. All further data treatment was done by a self written software package. Statistical calculations were carried out by a spreadsheet program.

The ICP-MS operating conditions are given in Table 1. The ^{79}Br isotope was selected for detection because the plasma species $^{40}Ar_2H^+$ did interfere with the isotope ^{81}Br. Data were collected using single ion monitoring to ensure maximum sensitivity for bromine. An internal standard of 20 μg/l Sr was used and were added to the eluent. By switching to m/z 88 at the beginning and the end of each analysis the intensity of the ^{88}Sr isotope was measured in order to correct for instrumental drift during analysis. We simply used the average of both values as internal standardization.

2.2. IC–API-MS

2.2.1. Ion chromatography

IC was performed on a HP 1100 HPLC system equipped with a vacuum degasser, quaternary pump and a HP 1050 autosampler (all Hewlett-Packard, Palo Alto, CA, USA). Eluent suppression was done by a Metrohm suppressor module 753 using 20 m*M* sulfuric acid as the regenerant.

The eluent for IC–API-MS consisted of 5 m*M* sodium carbonate containing 10% (v/v) acetonitrile at pH 11.3 without any pH adjustment. The separation column (100×2 mm I.D.) was homepacked with the stationary phase of a Waters IC-Pak Anion

Table 1
Experimental conditions of the chromatography modules

	IC–API-MS	IC–ICP-MS
Column	IC-Pak Anion HR (Waters) Methacrylate based	Selfmade PS/DVB type DEMA functionality Q=600 μmol/column
Dimension	100×2 mm I.D.	120×4 mm I.D.
Eluent	5 m*M* Na_2CO_3 10%(v/v) acetonitrile	75 m*M* NH_4NO_3
Injection volume	100 μl	585 μl
Flow rate	150 μl/min	1 ml/min
Suppressor	Metrohm MSM 753	None

HR column based on methacrylate with quaternary ammonium as the functional group. Additional IC operating parameters are given in Table 1.

2.2.2. API-MS

API-MS measurements were done on a quadrupole system HP 5989B using an atmospheric pressure ionization interface HP 59987A (Hewlett-Packard) equipped with a radiofrequency (RF) only hexapole (Analytica of Branford, Branford, CT, USA). The interface was operated in the pneumatically assisted electrospray mode using nitrogen 5.0 as both the spraying gas (5 bar) and the drying gas (7 L/min, 300°C). Data acquisiton was performed in the selected ion monitoring mode at the m/z values of the two bromate isotopes (126.9 and 128.9).

2.3. Sample description

The samples used for comparison are taken from an international round robin test for the ISO/DIS proposal 15061 for the ion chromatographic determination of bromate utilizing conductivity detection (IC–CD). The performance of both methods was investigated for a set of six samples, which are described in detail in Table 2. The simplest sample was a 10 mg/l bromate standard solution (not included in Table 2), followed by a 5.7 μg/l bromate standard (sample 1), a hard water spiked with 2.7 μg/l bromate (Sample 2, Figs. 1 and 2), a soft water containing 8.6 μg/l bromate (Sample 3, Figs. 3 and 4), an ozone treated water sample containing approximately 8.2 μg/l bromate (sample 4) and a river water sample spiked with 4 μg/l bromate (sample 5).

2.4. Sample pretreatment and analysis

The samples supplied for the trial were all filtered through a 0.45 μm membrane filter.

Table 2
Characteristics of the samples used for comparison of IC–ICP-MS and IC–API-MS; (all values in mg/l unless otherwise stated)

	Sample no.				
	1	2	3	4	5
Bromate	0.0057	0.0027	0.0086	0.0087	0.004
Conductivity (μS/cm)	<10	567	197	347	202
Total hardness ($CaCO_3$)	<5	283	70	155	97.5
Total organic carbon	<0.3	0.3	2.14	2.2	0.95
Alkalinity (HCO_3^-)	<10	267	26	79	110
Chloride (Cl^-)	<10	41	14	21	6.1
Nitrate (NO_3^-)	<1	7.2	2.9	15.6	<1
Sulfate (SO_4^{2-})	<10	44	44	72	4.3
Bromide (Br^-)	<0.010	0.042	0.019	0.036	0.015
Description	Standard	Hard water	Soft water, spiked	Ozonylated soft water	River water

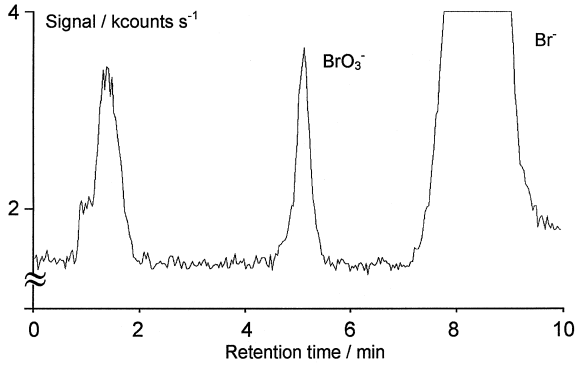

Fig. 1. IC–ICP-MS chromatogram obtained for sample 2, a hard water treated with ozone containing 2.7 μg/l bromate. The sample was used for the bromate interlaboratory trial using the IC-CD method.

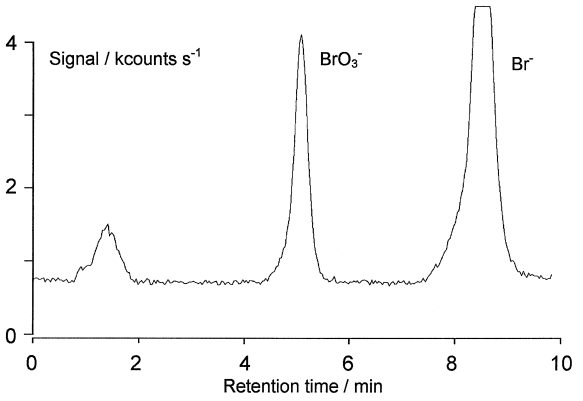

Fig. 3. IC–ICP-MS chromatogram obtained for sample 3, a soft water spiked 8.6 μg/l bromate. The sample was used for the bromate interlaboratory trial using the IC-CD method.

For IC–API-MS measurements, the samples were pretreated with an SCX cartridge in the Ag^+ form for chloride removal prior to injection. A calibration curve was established every day of analysis. The IC–API-MS measurements were carried out on five different days with one sample analysis per day. The samples were then quantified by first injecting an appropriate standard solution twice followed by two injections of the first sample, followed by another standard injection (twice) and the second sample and so on. Standard addition was only used once to ensure the absence of suppressing effects. For IC–ICP-MS the samples were analyzed as supplied without any further pretreatment. The measurements are carried on two different days (at least two days are required for the ISO round robin test) with five samples a day. The measurements started and ended with the measurement of five calibration standards (4,8,12,16 and 20 μg/l bromate) for external calibration. Data for Figs. 5 and 6 were obtained by

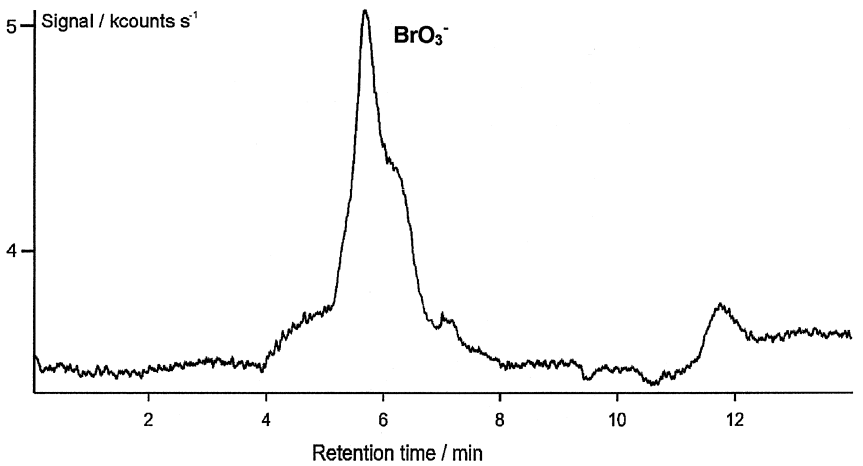

Fig. 2. IC–API-MS chromatogram of the same sample as used for Fig. 1.

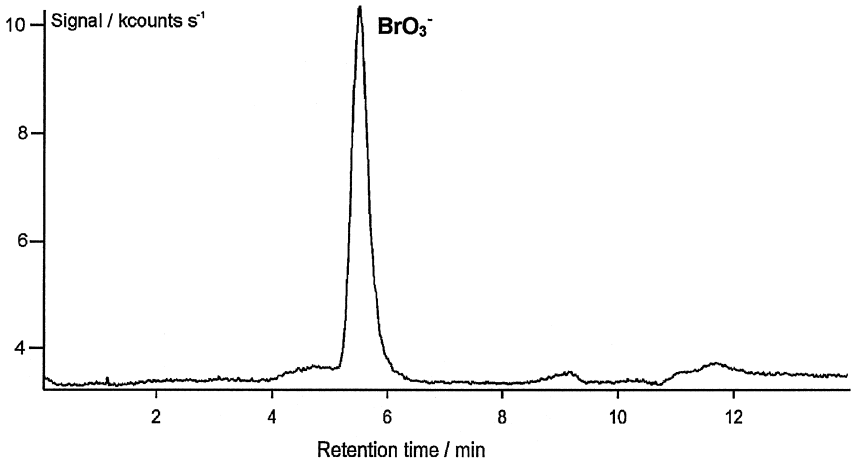

Fig. 4. IC–API-MS chromatogram of the same sample as used for Fig. 3.

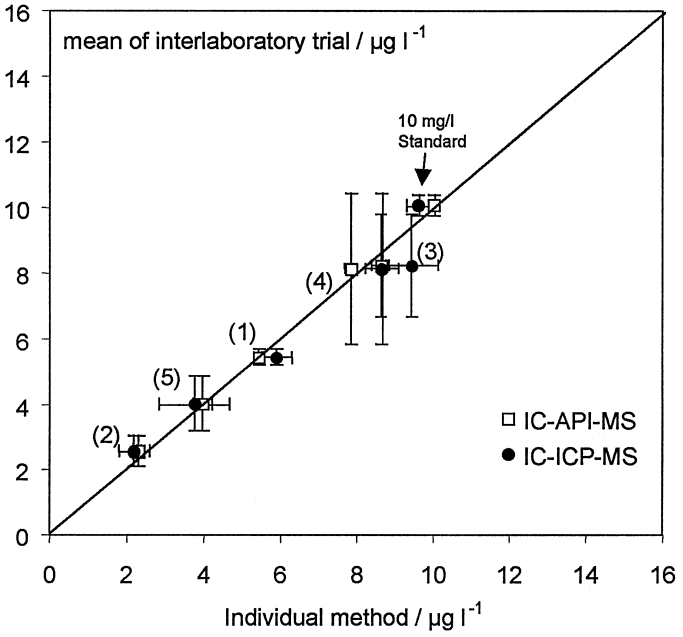

Fig. 5. Comparison of IC–API-MS and IC–ICP-MS results with the mean of an interlaboratory trial organized for the standardization of the ISO/DIS 15061. The standard deviations of all methods are displayed as horizontal or vertical error bars and were calculated from five independent measurements throughout the entire procedure.

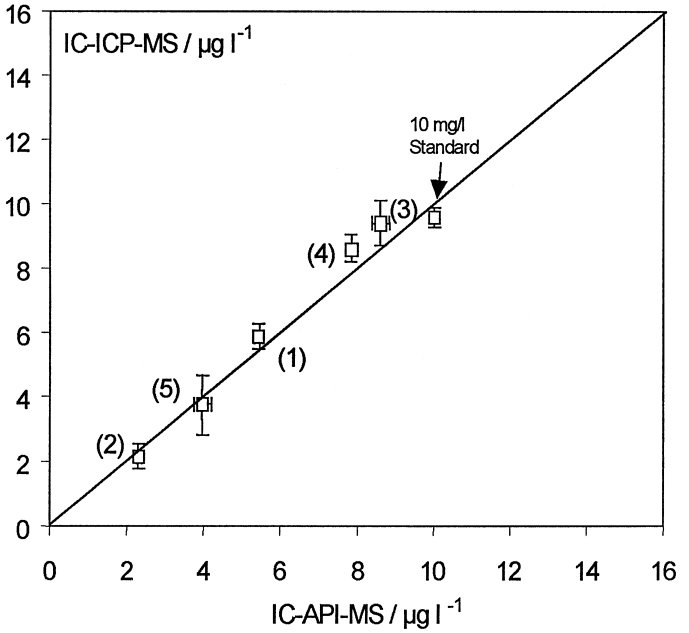

Fig. 6. Direct comparison of IC–API-MS and IC–ICP-MS results for the samples as described in Table 2. The standard deviation of five replicates is displayed as error bar.

external calibration without standard addition. Each sample was analyzed five times throughout the entire procedure.

3. Results and discussion

3.1. Determination of bromate using IC–ICP-MS

On-line-coupling of anion chromatography with ICP-MS represent a sensitive tool for the determination of bromate in all kinds of water samples. In combination with ion chromatography the ICP-MS allows a specific detection of Br-containing species. The IC–ICP-MS operating at m/z 79 detects bromine and other molecular ions with similar masses, such as $^{39}K^{40}Ar^{+}$. Furthermore the high background count rate of 100 to 1000 counts per second (depending on operating conditions) is caused by the molecular ion $^{38}Ar^{40}Ar^{1}H^{+}$ and by the strong nearby signal of $^{40}Ar_2^{+}$.

The ICP-MS tolerates strong eluents such as nitrate or perchlorate solutions. This ruggedness allows the use of high-capacity anion exchangers. The selection of ammonia nitrate as eluent was based on the high elution power of the nitrate anion. The invisibility of ammonia nitrate in the ICP-MS makes the sometimes within IC–ICP-MS applications used suppressor obsolete. Additionally, the medium pH value of the eluent avoids the precipitation of $CaCO_3$ or $Mg(OH)_2$ on the column and removes the H^{+}-cartridge pretreatment commonly used for water samples in IC.

Major benefits are the analysis of water samples using large sample volumes even in case of high ionic strength samples and the absence of any sample pretreatment. Furthermore, the total analysis time can be reduced to under 10 min. Examples of IC–ICP-MS chromatograms show the measurement of a hard water containing 2.7 µg/l bromate (sample 2, Fig. 1) and as much easier matrix the spiked soft water containing 8.6 µg/l bromate (sample 3, Fig. 3). The chromatograms are measured at two different days with a different sensitivity of the ICP-MS. The signal at 0.8 to 1.8 min is caused by the elution of

unretained compounds in the dead volume, mainly the cations including ^{39}K, the source of $^{39}K^{40}Ar^{+}$.

3.2. Determination of bromate using IC–API-MS

Because API-MS is a soft ionization technique, the determination of unfragmented bromate is possible resulting in a highly selective detection with little background noise. Contrary to the IC–ICP-MS method, the use of strong inorganic eluents such as nitrate or perchlorate is not recommended for API-MS; therefore, suppressed IC using carbonate as the eluting species was chosen offering both short retention times (comparable to the IC–ICP-MS method) and high sensitivity due to the absence of electrolytes entering the API interface.

In order to remove chloride in the water samples, which would interfere with the MS detection of bromate due to signal suppression, a sample pretreatment by passing the sample through an Ag^{+} cartridge is inevitable. Without this pretreatment the signal intensity is suppressed by about 40%.

For samples with a moderate ionic strength such as sample 3, this pretreatment step is sufficient to obtain a symmetric peak shape without peak distortions (see Fig. 4). For hard water showing high alkalinity which is the case for sample 2, the removal of chloride is not enough for a symmetric bromate peak (Fig. 2). In this case the additional removal of hydrogen carbonate by passing the sample through an SCX cartridge in the H^{+} form would improve the peak shape. Nevertheless, as standard addition experiments showed, the peak area was not affected and so the determination of bromate in hard water was also possible with sufficient accuracy; therefore sample pretreatment was limited to the removal of chloride in order to avoid time consuming pretreatment procedures.

3.3. Comparison of IC–API-MS and IC–ICP-MS

The following comparison is based on the criteria (1) chromatographic requirements, (2) accuracy and precision and (3) limit of detection. The sample chromatograms shown in Figs. 1–4 depict different properties of both techniques.

3.3.1. Chromatographic requirements

A short comparison of the chromatographic systems used for both techniques is given in Table 1. Major differences are the column geometry and the packing material. The API-MS prefers low flow-rates of a water/solvent mixtures without ionic compounds. Therefore a microbore column packed with a low capacity resin using a carbonate eluent was chosen. The carbonate is suppressed using a micro-column suppressor (MSM, Metrohm), which allows an almost complete removal of carbonate ions. The distorted peak shape of the BrO_3^- peak in Fig. 2 indicate the maximum matrix level which can be handled by the chromatographic part of the IC–API-MS system. The simplicity of the IC–API-MS chromatograms as shown in Figs. 2 and 4 show the high selectivity of API-MS, which is truly molecule selective. The background is extremely low.

The IC–ICP-MS method use the ICP-MS device for a more rugged chromatographic part. A high capacity column, which is not compatible to suppressable eluents, is used with ammonia nitrate eluent. The decomposition products of this eluent are despite non-ionic species only N- and O-containing molecular ions, which are not interfering with the ^{79}Br detection. The ionic strength of the eluent prevent from peak distortion caused by high concentrations of matrix ions as present for IC–API-MS (Fig. 1).

3.3.2. Accuracy and precision

Fig. 5 shows the comparison of IC–API-MS and IC–ICP-MS with the proposed method of ISO/DIS 15061.

The agreement is excellent and the S.D. values for the critical samples (3), (4) and (5) are far better due to the element or molecule specific detection. The good agreement with IC based on conductivity detection is mainly caused by the extensive sample pretreatment used for IC–CD. It includes a Cl^-, SO_4^{2-} and CO_3^{2-} elimination step. Furthermore, the IC–CD method requires a preconcentration step for the determination of low levels of bromate. IC–API-MS and IC–ICP-MS are much faster techniques with reduced or without sample pretreatment. The high selectivity of MS-detectors allows faster and less selective chromatographic procedures.

The direct comparison of both MS techniques

Table 3
Feature comparison of IC–API-MS and IC–ICP-MS for bromate analysis

	IC–API-MS	IC–ICP-MS
Limit of detection (conc.)	0.5 μg/l	0.06 μg/l
Limit of detection (mass)	50 pg	35 pg
Speed of analysis (8 h, 2 replicates)	8 samples/day	16 samples/day
MS mode	Selected ion monitoring at m/z 126.9 and 128.9 (negative ion)	Single ion monitoring at m/z 79 and 88 (Sr)
Dwell time	300 ms	2 s
Internal standard	No	^{88}Sr

(Fig. 6) shows a tendency for higher values obtained by IC–ICP-MS, but the agreement is still good. The agreement is independent from sample composition and bromate concentration. The S.D. values for IC–API-MS are far better than for IC–ICP-MS, presumably caused by the plasma as the major source of noise in ICP-MS.

3.3.3. Limits of detection

The limits of detection as shown in Table 3 are calculated using the three-fold S.D. of the background signal at the expected retention time of bromate. No smoothing or other data manipulation were performed prior to S.D. determination. For a comparison without dominating influence of the chromatographic part we used the absolute detection limit for bromate. The values for IC–ICP-MS and IC–API-MS are equal within the precision observed for both methods. Assuming an almost equal performance of the MS units of ICP-MS and API-MS the sample transfer efficiency of both interfaces (ICP and API) are comparable.

The concentration based detection limits clarify the superior performance of IC–ICP-MS due to the optimized chromatographic part. It is not possible to operate IC–API-MS under similar conditions. A possible way to enhance the performance of IC–API-MS is the use of very hydrophilic high capacity columns based on quaternized triethanolamine functional groups. Those columns operate with pure hydroxide eluents.

4. Conclusions

Both methods are well suited for fast determination of low levels of BrO_3^- in water samples. The IC–ICP-MS method is more powerful when extremely low detection limits are required. Furthermore, the IC part must be adjusted to each individual method and that is a major limiting factor with respect to concentration based detection limits.

The strength of IC–ICP-MS is the absence of any sample pretreatment and the truly element specific detection. The main advantage of IC–API-MS is the truly molecule selective detection. Differences between both techniques are traceable to the ruggedness of the interface. While the API transfers complete molecules into the MS, the Plasma of the ICP destroys every chemical bond and therefore leads to a rugged, almost matrix independent technique. In contrast, the API process of negative ionization is subject to severe interferences. Almost every electron capturing anion suppresses the ion beam to almost zero. Therefore the IC–API-MS method requires completely suppressible eluents and a chloride elimination step. The chromatographic conditions reflect this behavior.

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