Germanium dioxide as internal standard for simplified trace determination of bromate, bromide, iodate and iodide by on-line coupling ion chromatography-inductively coupled plasma mass spectrometry

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Abstract

The use of elemental mass spectrometry as detection for ion chromatography allows sensitive determination of several bromine and iodine species at a reasonable time scale. Lowest concentrations observable are $66\,ng\,L^{-1}$ for bromate, $45\,ng\,L^{-1}$ for iodate, $74\,ng\,L^{-1}$ for bromide and $151\,ng\,L^{-1}$ for iodide. A major drawback of previous IC–ICP–MS applications is the high consumption of time and thus the running costs. The use of GeO_2 as internal standard not only allows improved external calibration, but also semiquantitative determination of bromate, bromide, iodate and iodide without any calibration procedure. Furthermore, GeO_2 can be used for all known types of anion exchange columns regardless of their construction principles. It is shown, that the analyte-to-GeO_2 ratio of four bromine and iodine species was nearly constant over 4 months and almost independent from the ICP–MS instrumental settings. The quantification by means of the analyte-to-GeO_2 ratio for samples taken from a bromate round robin test shows that the values obtained are in excellent agreement with calibration curve and isotope dilution results.

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1. Introduction

Internal standards (IS) are commonly used in inductively coupled plasma–mass spectrometry (ICP–MS) to correct variations in sensitivity. They can improve both precision and accuracy. If ICP–MS is used as an on-line coupled detector for ion chromatography (IC), the ideal IS needs to fulfil special requirements for these two techniques: It is required to be water-soluble but uncharged in order to give a constant signal if used together with different kinds of modern anion exchange materials. The isotope of the IS element should match the mass of the analyte elements as closely as possible but must not overlap. Germanium exhibits these properties perfectly, especially in comparison with bromine.

Applications of IS in various discrete sample introduction methologies have been studied recently by Stefanova et al. [1]. A dynamic IS correction, based on the every sweep analyte-to-internal standard ratio, results in low R.S.D.s and allows the analysis of difficult samples. In another approach for internal standardization, Al-Ammar uses a new mathematical function to improve the analysis of geological ICP–MS samples [2]. The correction of drift and matrix effects for all analytes irrespective of their difference in mass and ionization potential is achieved with only two internal reference elements. Hieftje and coworkers emphasize the capability of virtually simultaneous multi-element detection with ICP-time-of-flight-MS [3]. They use novel flow injection strategies and determine element ratios to study matrix interferences. Also a possible concentration calculation using analyte/analyte ratios is indicated.

Analyzing oxyhalides and their precursors in waters has attracted a lot of attention over the last few years in the context of water disinfection with ozone. If the oxidizing agent chlorine is replaced by ozone, the formation of harmful chloric disinfection by-products is inhibited. However, ozone is capable of generating bromate as a by-product in waters containing the precursor bromide. Bromate has been classified as a group 2B probable human carcinogen by the International Agency for Research on Cancer [4]. A

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potential 10^{-4} risk of cancer after a lifetime exposure in drinking water at $5.0 \mu g L^{-1}$ was assessed and a potential 10^{-5} risk at $0.5 \mu g L^{-1}$ [5]. The European Council defines a maximum allowed concentration of $10 \mu g L^{-1}$ bromate in drinking water in the "Directive 98/83 on the quality of water intended for human consumption" [6]. It is stated that member states should strive for a lower value where possible without compromising disinfection. Thus, it is necessary to develop and improve methods for the ultra trace determination of bromate. Techniques with bromate detection limits of $2.5 \mu g L^{-1}$ or less are required for satisfactory results.

Recently, the US Environmental Protection Agency's (EPA) official methods 300.0, 300.1 and 317.0 for the determination of inorganic anions and inorganic oxyhalide disinfection by-products in water have been reviewed [7]. Also a new method 326.0 for the analysis of bromate has been published [8]. In these methods ion chromatography, either with conductivity detection or with absorbance detection after post column derivatization, is applied. The associated limits of detection (LOD) are $1.44 \mu g L^{-1}$ for Br^- and BrO_3^- with conductivity detection and $0.17 \mu g L^{-1}$ BrO_3^- with absorbance detection. In the alternative EPA method 321.8 ion chromatography is combined with an ICP–MS as detector and a LOD of $0.30 \mu g L^{-1}$ BrO_3^- is achieved [9]. LODs in the range of $0.050–0.065 \mu g L^{-1}$ can be reached with IC–ICP–MS using microbore column technique in combination with a self-made high-capacity and high-performance anion exchanger [10]. Isotope dilution analysis is well suited for the analysis of bromate [11,12]. It is known to be a fast quantification method with very accurate and precise results.

An European Commission project tried to identify causes of interference in ion chromatography with conductivity detection usually applied for the analysis of bromate in drinking water. An attempt was made to find automated sample pretreatment and interference removal steps which led to the development of several alternative laboratory and field-based methods [13]. These methods included spectrophotometry, fluorescence and ICP–MS detection. For example, a novel flow injection separation with ICP–MS detection yielded an LOD for bromate of $0.13 \mu g L^{-1}$ [14]. Recently, solid-phase extraction cartridges containing silver were used to selectively remove bromide in waters prior to ICP–MS determination [15].

The presence of the anion iodide in drinking water can lead to a slightly metallic taste if trace concentrations of elemental iodine are formed [16]. Producers of mineral water try to circumvent this problem by oxidizing iodide to the tasteless iodate, for example with the help of ozone. Iodide is a very polarizable anion with a relatively high lipophilic character. On modern ion chromatography stationary phases, iodide is strongly retained on the PS/DVB support material due to secondary, non-ionic interactions with π-electrons. This causes peak tailing. The iodide signal can even disappear at concentrations in the low $\mu g L^{-1}$ range due to this predominant adsorption effect. These problems can be reduced by the use of a latex anion exchanger with lipophobic quaternary am-

monium functions. These columns together with the element-selectivity of ICP–MS enable the analysis of the four anions iodate, bromate, bromide and iodide in one chromatographic run of only 15 min, which is very uncommon in IC with conductivity detection. The element-specific detector allows the analysis of the four analytes even if the peaks are not completely chromatographically resolved.

2. Experimental

2.1. Reagents

High purity water (Millipore, $18.2 M\Omega$) was used for all standard preparations, sample dilutions and eluents. Sodium bromate, potassium iodate (Fluka, Buchs, Switzerland), sodium bromide, sodium iodide (Merck, Darmstadt, Germany), and germanium dioxide (99.99%, Heraeus, Karlsruhe, Germany) were of analytical grade. Nitric acid (69%, Selectipur, Merck) and ammonium hydroxide in water (>25%, Traceselect, Fluka) were used to prepare the eluents.

2.2. Instrumentation

A schematic picture of the on-line coupling is shown in Fig. 1. The ion chromatography equipment consisted of a HPLC pump 709 (Metrohm, Herisau, Switzerland), a 6-port/3 way electric injection valve (VICI AG, Schenkon, Switzerland), polyetheretherketone (PEEK) tubing and several self-made columns. Column type 1 (100 mm × 4 mm) was filled with a self-made PS/DVB-type anion exchanger which was agglomerated with latex particles having diethanol-methyl-amine-funtionality (DEMA) with an ion exchange capacity of 60 μeq/column. Column type 2 (250 mm × 4 mm) contained an anion exchanger from PS/DVB-type which was surface-functionalized with dimethyl-ethanol-amine (DMEA) and had a capacity of 910 μeq/column. The sample loop was filled by drawing up the sample with the help of a syringe. The injection volumes varied between 0.153 and 0.585 mL. The eluent flow rate was set to $1 mL min^{-1}$. The eluent for column 1 was 25 mM HNO_3 adjusted to pH 4–6 with NH_3 and with an IS concentration of $15 \mu g L^{-1}$ Ge. pH-values were measured with a pH-meter 744 using a glass electrode 6.0202.000 (Metrohm, Herisau, Switzerland). The eluent for column 2 was made up of 120 mM HNO_3, 1 mM $HClO_4$ and $15 \mu g L^{-1}$ Ge and adjusted to pH 4–6 with NH_3. Prior to use, all eluents were
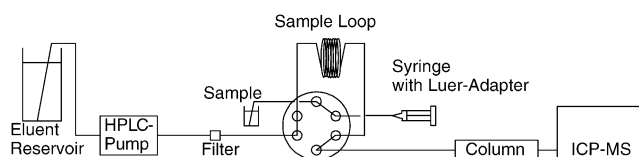

Fig. 1. Schematic diagram of the IC–ICP–MS system (valve in "inject" position).

Table 1
Optimized ICP–MS operating parameters

Parameter	Optimized operating conditions
Power (W)	1350
Cool gas (L min^{-1})	13
Aux gas (L min^{-1})	0.5–1.5
Neb gas (L min^{-1})	0.83–0.93 (V-groove nebulizer)
Spraychamber (°C)	−4 (double pass quartz, Scott-type)
Sample and skimmer cone	Nickel (orifice diameters: ∼1 mm, ∼0.7 mm)
Detector mode	Pulse
Operating pressure (mbar)	$1.2 \cdot 10^{-6}$
Software	OS/2 PQ-Vision 4.30 TRA-Mode
Integration times	Peak jump, one point per peak, time slice = 0.89 s dwell time: ^{52}Cr and ^{127}I = 200 ms, ^{79}Br = 400 ms, ^{74}Ge = 40 ms

degassed under vacuum for 10 min. For this purpose a Falcon 7111 bottle top filter with vacuum adapter (Becton Dickinson Labware, New Jersey, USA) was sealed using a round slice of polyethylene and placed on a 2 L glass bottle (Schott Duran, Mainz, Germany).

The ICP–MS used was a VG Elemental PQ2+ turbo equipped with S-Option and STE-Controller (Thermo, Winsford, UK). The ICP–MS was coupled to IC by simply connecting the outlet of the column to the inlet of the nebulizer via a piece of tubing. The typical operating parameters are given in Table 1.

The transient data was exported to ASCII files and converted via a self-written Microsoft Excel macro to the correct format for the import to IC-Net 2.3 software (Metrohm, Herisau, Switzerland), which was used for data smoothing and integration (smoothing parameters: spikes = yes, slit gaussian = 1 and slit median = 1). IC-Net is capable of multi-channel (multi-mass) visualization but only one channel (the analyte mass) can actually be integrated. A second channel was used to monitor and read off the germanium signal only.
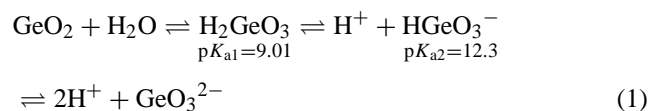
3. Results and discussion

3.1. Selection criteria for IS in on-line coupling applications

From an ion chromatographic point of view it is desirable to find an IS which does not interact with anion exchange columns. By simply adding the standard to the eluent a constant signal is produced allowing to read off the current sensitivity at any time in the chromatogram. This is ideal for IS correction, for real time calibration and for monitoring the system performance. Furthermore, IS which show no retention on the columns do not take part in the dynamic process of ion exchange. They can neither be influenced by high ion concentrations nor do they block exchange sites. The selection of a proper IS is complified by the diversity of modern anion exchange materials.

Stationary phases with high separation efficiency mostly consist of sulfonated poly(styrene-divinylbenzene) spheres as substrates to which small aminated latex particles are attached [17]. Due to the coexistence of $-NR_3^+$ and $-SO_3^-$ groups, the materials exhibit not only anion but also cation exchange capacity. Anions and cations interact with these zwitterionic phases. Thus, an IS needs to be water-soluble but neutral at the same time. Some requirements for ICP–MS have also to be fulfilled. Most importantly, the IS element has to be similar to the analytes by means of mass and physical properties, e.g. first ionization energy. Furthermore the IS must have at least one interference-free mass and it must be a rare element because corrections would be wrong if it is present in samples in a detectable concentration.

3.2. Investigation of H_3BO_3, GeO_2 and dissolved tellurium as IS

Three IS candidates were investigated: boric acid (pK_a 9.25), germanium dioxide and tellurium solution. These were expected to be neutral in ammonium nitrate eluents with pH values from 4 to 6. The conjugated acids H_2GeO_3 (pK_{a1} 9.01) and H_2TeO_3 (pK_{a1} 2.48) are formed in small equilibrium concentrations and could be deprotonated. Therefore, the neutrality of the species had to be tested. Uncharged molecules elute within the dead volume in ion chromatography, so 50 μg L^{-1} solutions of the three substances were injected on an anion exchange column type 1 with an ammonium nitrate eluent at pH 5.8. As can be seen in Fig. 2, an ionic tellurium species, probably $HTeO_3^-$, interacting with the anion exchanger was present. This excludes Te from the possible IS. GeO_2 and boric acid are well suited since they do not show any retention on the column. However, boric acid also has an immense drawback, which is the low mass of boron (11 amu). It was found to behave quite differently from mid-mass analytes like bromine and iodine in a mass spectrometer. Therefore boric acid cannot correct sufficiently for sensitivity variations and was rejected. The best IS substance from this experiment proved to be GeO_2. Its aqueous chemistry is described in Eq. (1). At pH values from 4 to 6 mainly the neutral species germanium dioxide and germanic acid exist.

$$GeO_2 + H_2O \rightleftharpoons \underset{pK_{a1}=9.01}{H_2GeO_3} \rightleftharpoons H^+ + \underset{pK_{a2}=12.3}{HGeO_3^-}$$

$$\rightleftharpoons 2H^+ + GeO_3^{2-} \tag{1}$$

Finding germanium in real samples is quite unusual since it is a rare element in the outer earth's crust (0.00056%). The isotope with the highest abundance is ^{74}Ge with 36.5%. An eye must be kept on possible interferences (Table 2), but their influence is rather low, if the IS concentration is high enough (e.g. 15–30 μg L^{-1} Ge according to 5.5–11 μg L^{-1} of the isotope ^{74}Ge). The interfering ^{36}Ar^{38}Ar-dimer consists only of very rare isotopes and a ^{37}Cl$_2$-signal was not found to be of significance even in samples with high chloride matrix (e.g. mineral water). A good alternative isotope is ^{73}Ge, which has less interferences but is also less abundant.
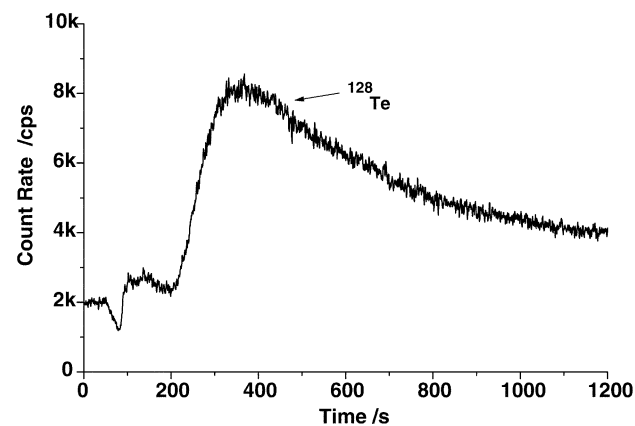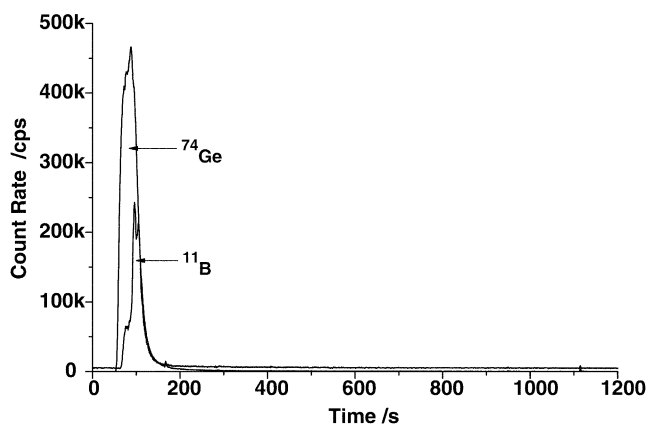
Fig. 2. Neutrality test: column type 1, eluent 50 mM NH_4NO_3 pH 5.8, injection of 585 μL 50 μg L^{-1} B or Ge or Te. The B- and Ge-species elute with the dead volume whereas the Te-species is retained.

3.3. Advantages of GeO_2 as IS

An ideal IS in ICP–MS can correct instrument instability, signal drift and also matrix effects, including signal suppression/enhancement or differences in the nebulization efficiency. For this correction it is assumed that these variations in sensitivity affect the IS element in the same way as the analyte. As already mentioned, it is most important for IS to have similar mass to the analytes. Also analogue physical properties enhance the correction. One of these parameters is the first ionization energy which differs not too much between germanium (7.89 eV), bromine (11.85 eV) and iodine (10.46 eV).
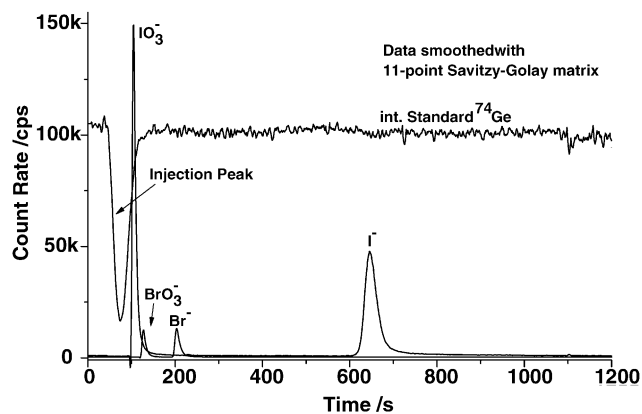

Fig. 3. Typical chromatogram for column 1. Concentration of all analytes 10 μg L^{-1} with a sample loop of 585 μL, eluent 30 mM NH_4NO_3 pH 7.1, IS Ge 15 μg L^{-1}.

Several introduction modes for IS can be distinguished: pulsed or continuous and pre-column or post-column mode. The continuous pre-column introduction mode exhibits several benefits compared to post-column internal standardization: in the post-column mode the IS is added via a T-piece or another mixing device. A second pump, usually a peristaltic pump is needed. Special care must be taken to provide an absolutely constant pumping and mixing rate in order to receive a stable signal. For example, degradation of the tubing is a possible source of error. Furthermore, every mixing step of liquids generates additional mixing noise. In contrast no expensive equipment is needed for the pre-column IS addition. The neutral IS GeO_2 can be added directly to the eluent in a concentration high enough to give a signal level with good precision. The IS experiences the same conditions as the analytes in the whole analytical system but results in a constant signal. Only in the pre-column mode variations of sensitivity resulting from the HPLC-pump can be monitored and corrected. The continuous introduction allows the (quasi) real time analyte-to-IS ratioing.

3.4. GeO_2 as monitoring tool for instrument failures and for non-spectroscopic interferences

The advantages of GeO_2 as IS for the operator of IC–ICP–MS system during the measurements can be summarized as follows: If the measurement is normal (Fig. 3) a constant signal is produced except for the injection peak

Table 2
Possible ICP–MS interferences for germanium (in parentheses: abundance or product of abundances; formation rates not included)

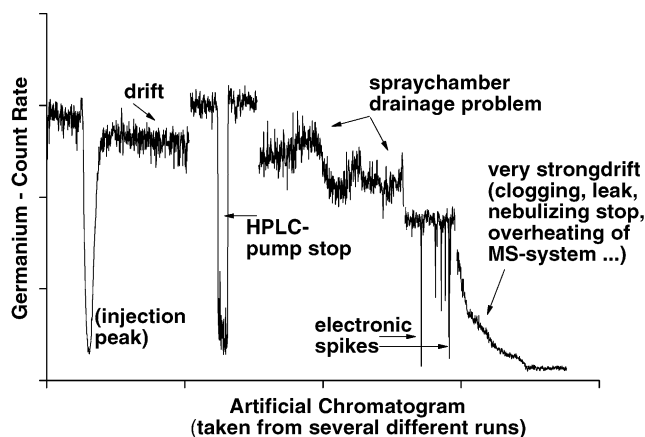| Isotope (%)	Possible interferences
^{70}Ge (20.5)	$[^{40}ArNO]^+$ (99.0%), $[^{35}Cl_2]^+$ (57.4%), $^{70}Zn^+$ (0.6%), $[^{54}CrO]^+$ (2.36%), $[^{54}FeO]^+$ (5.79%), (La, Ce, Pr)$^{2+}$
^{72}Ge (27.4)	$[^{36}Ar_2]^+$ (0.0011%), $[^{35}Cl^{37}Cl]^+$ (18.4%), $[^{56}FeO]^+$ (91.5%), $[^{55}MnOH]^+$ (99.7%), (Nd, Sm)$^{2+}$
^{73}Ge (7.8)	$[^{36}Ar_2H]^+$ (1.1 × 10^{-3}%), $[^{40}Ar^{32}SH]^+$ (94.6%), $[^{57}FeO]^+$ (2.19%), $[^{56}FeOH]^+$ (91.5%), (Nd, Sm)$^{2+}$
^{74}Ge (36.5)	$[^{36}Ar^{38}Ar]^+$ (2.1 × 10^{-4}%), $^{74}Se^+$ (0.9%), $[^{37}Cl_2]^+$ (5.87%), $[^{58}NiO]^+$ (68.1%), $[^{58}FeO]^+$ (0.28%), (Sm, Nd)$^{2+}$
^{76}Ge (7.8)	$[^{38}Ar_2]^+$ (4.0 × 10^{-5}%), $^{76}Se^+$ (9.0%), $[^{75}AsH]^+$ (99.99%), $[^{60}NiO]^+$ (26.0%), (Eu, Sm, Gd)$^{2+}$

Fig. 4. Examples of system faults easy recognizable with IS Ge m/z 74 (data not smoothed).

(dead time marker). The current system sensitivity and noise overall level can be observed instantly from the Ge-signal. Matrix influence and instrumental failures like drift, transport problems, different nebulization due to changes in viscosity or surface tension, clogging or leaks in the way to the plasma, warm up, HPLC pump failures or disruptions, electronic spikes and more are visually detectable (Fig. 4).

3.5. GeO_2 as a tool for semiqantitative analysis in on-line coupling applications

The properties of GeO_2 for semiquantitave quantification and simultaneous IS correction were evaluated in 64 bromate-, 110 bromide-, 107 iodate- and 81 iodide-measurements with IC–ICP–MS over 4 months. Analysis of BrO_3^-, Br^-, IO_3^- and I^- in fortified reagent water solutions and different ozone-treated and non-treated mineral waters were performed. It was observed that, although the columns, eluents and tuning conditions were changed, the ratio R of the analyte peak area-to-the germanium dioxide signal height remained relatively stable over this long period of time. For the evaluation of the value of R different sample loop sizes were normalized to $100\,\mu L$ (Eq. (2)). For a better comparison, the ratios were additionally normalized (R_{norm}) to a concentration of $10\,\mu g\,L^{-1}$ (Eq. (3)). The relative standard deviations for R_{norm}. for BrO_3^-, Br^-, IO_3^- and I^- measured over 4 months ranged from only 20 to 30%. The dataset is statistically difficult to evaluate because of quite different concentration ranges and the fact that low $\mu g\,L^{-1}$-samples contribute much higher relative standard deviations. The real world samples naturally differed significantly in concentration range and number of results. Sample concentrations typically found were 0–$3\,\mu g\,L^{-1}$ for BrO_3^-, 100–$500\,\mu g\,L^{-1}$ for Br^-, 1–$400\,\mu g\,L^{-1}$ for IO_3^- and 1–$20\,\mu g\,L^{-1}$ for I^-. The
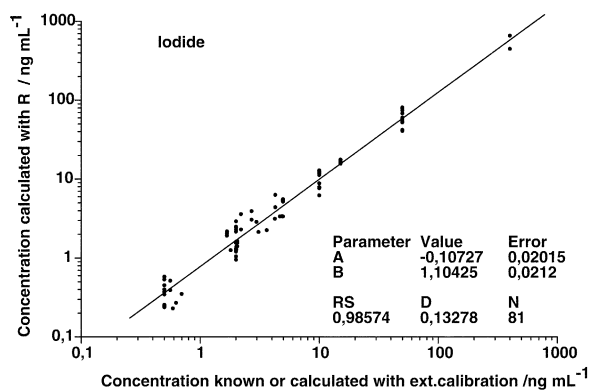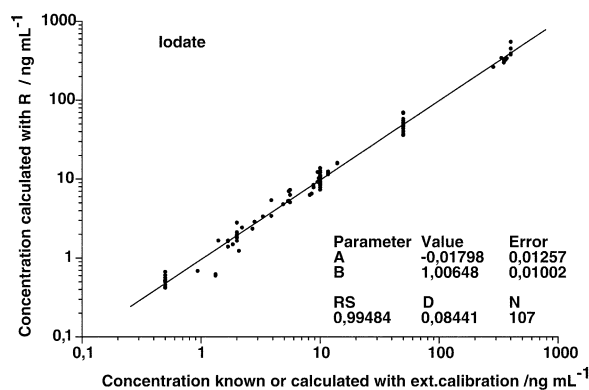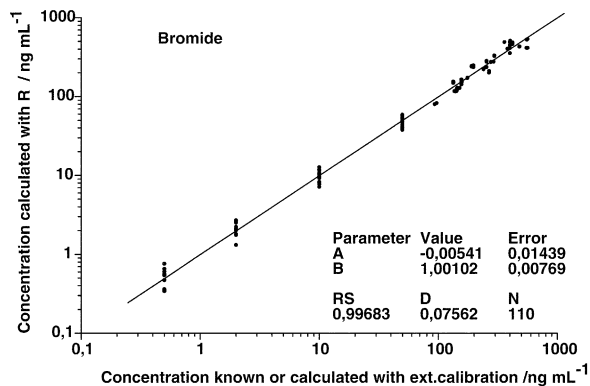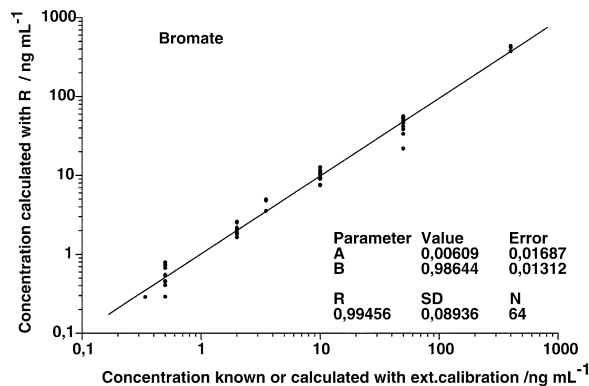

Fig. 5. Correlation between sample concentrations determined with the analyte-to-GeO_2 ratio and either concentrations determined with common external calibration or known concentration (if it was a measurement of a standard).

Table 3
Limits of detection of IC–ICP–MS with or without GeO$_2$ for IS correction

	Confidence level (%)	Correction with IS GeO$_2$	Limits of detection (μg L^{-1})			
			Iodate	Bromate	Bromide	Iodide
Method 1[a]: calibration curve method	95	No	0.064	0.088	0.129	Not determined
		Yes	0.049	0.066	0.074	Not determined
Method 2[b]: EPA method	99	No	0.084	0.069	0.124	0.182
		Yes	0.045	0.071	0.104	0.151

[a] DIN32645 [18], 10 equidistant calibration points from 0.1 to 1.0 μg L^{-1}, sample loop 585 μL, column type 1, outliers eliminated.
[b] 3.14-fold standard deviation of seven replicates, fortified concentration 0.5 μg L^{-1} in reagent water, sample loop 585 μL, column type 1.

Table 4
Analysis of samples from a round robin test for the EPA Method 317.0

Sample name[a]	Bromate concentration (μg L^{-1})				
	Reference value	Quantification method			
		External calibration	External calibration + IS correction	Isotope dilution [12]	Analyte-to-GeO$_2$ ratio + IS correction
BWB	1.79	1.99	2.06	1.52 ± 0.18	2.00
BW-1	3.29	3.34	3.60	3.21 ± 0.06	3.48
BW-2	3.96	4.03	4.45	3.74 ± 0.11	4.29
BW-4	7.27	7.60	7.84	6.58 ± 0.12	7.55
TWB	<LOD	<LOD	0.24	0.18 ± 0.07	0.24
TW-1	1.74	1.87	1.92	1.83 ± 0.10	1.86
TW-2	2.38	2.51	2.65	2.63 ± 0.05	2.56
TW-4	5.16	6.08	6.38	5.31 ± 0.05	6.07

[a] BW: bottled water, TW: tap water, B: blind value.

concentration range for all standards was 0.5–400 μg L^{-1}. A relative standard deviation of 30% is often tolerable in ultra trace analysis. Hence, the ratio R of analyte peak area-to-GeO$_2$ signal can be used to perform fast semiquantitative analysis.

$$R = \frac{\text{peak area}_{\text{analyte}}}{\text{signal height}_{\text{germanium}}} \frac{100\,\mu\text{L}}{\text{volume}_{\text{sample loop}}}$$

$$(\text{analyte} : \text{BrO}_3{}^-, \ \text{Br}^-, \text{IO}_3{}^- \text{ or } \text{I}^-) \tag{2}$$

$$R_{\text{norm}} = R \frac{10\,\mu\text{g L}^{-1}}{\text{concentration}_{\text{known}}} \tag{3}$$

$$\text{concentration}_{\text{sample}} = R \frac{10\,\mu\text{g L}^{-1}}{R_{\text{norm,known}}} \tag{4}$$

Since R_{norm} was found to be stable for weeks it is designated $R_{\text{norm,known}}$. The value of $R_{\text{norm,known}}$ has to be determined for BrO$_3{}^-$, Br$^-$, IO$_3{}^-$ and I$^-$ only once from previous measurements or by one daily measurement of a standard. Eq. (3) can then be transformed to Eq. (4) for concentration calculations.

In case of the regular measurement of the anions, the routine process can be simplified and measurement times shortened, since it is not necessary to record a time-consuming calibration series on a daily basis. The analyte-to-germanium dioxide quanification method corresponds to a 1-point-1-mass-calibration, but it has the great advantage to perform

not only calibration but also IS correction almost without a time lag between sample and standard measurement (real time).

A comparison of the accuracy of the two quantification strategies–daily linear calibration and concentration determination via the signal ratio of analyte-to-germanium dioxide, was made. Excellent correlation was found for all analytes as can be seen in Fig. 5.

The limits of detection for iodate, bromate, bromide, and iodide determined by IC–ICP–MS with GeO$_2$ added as IS are provided in Table 3. The LODs calculated with several quantification methods lie in the typical range of 0.05–3.5 μg L^{-1} reported in literature for ion chromatography with ICP–MS detection [15].

The accuracy of quantification methods with GeO$_2$ as IS was tested for bromate by analyzing bottled water and tap water samples of a round robin test for the EPA Method 317.0. The results obtained by simple external calibration, by external calibration with IS correction, by isotope dilution analysis and by using the analyte-to-GeO$_2$ ratio were compared to the reference values (Table 4) and good agreement was found.

4. Conclusion

The on-line coupling of IC and ICP–MS has been widely described in literature. Different kinds of columns, eluents and calibration strategies were investigated. However, the

practical acceptance of this coupling technique is still low due to economic deficits. The overall analysis time is typically governed by the calibration procedure, the accuracy and reproducability by the instrument stability. A way to speed up analysis and to improve the analytical results is the use of isotope dilution or of an IS as a calibration and/or a normalization tool. Isotope dilution analysis requires a specific sample preparation and also an approximately known value of the expected analyte concentration for proper operation. An IS is typically used for the correction of instrumental drift and other non-spectroscopic interferences only but not for calibration. However, the real time analyte-to-germanium dioxide signal ratio has been found to be very useful for simplified quantification.

If the exact mass response of an ICP–MS is known, it is capable of determining the concentrations of different elements with only one element standard. The ratio of analyte peak area-to-germanium signal for normalized concentrations turned out to be very stable over a long time and almost independent of ICP–MS instrumental settings. Hence, changes in the mass response and ionization efficiency of Br, I and Ge are correlating. This stability allows to omit the classical calibration procedure and to perform a semiquantitive calibration simply by using the ratio of analyte peak area and GeO_2 count rate. It is sufficient to determine the value of the ratio once a day with one calibration standard or if possible by calculating the mean value of previous measurements. Subsequently, the real time analyte-to-germanium dioxide signal ratio can be exploited for fast and simple concentration determination of bromine and iodine species. The GeO_2-ratioing method combines advantages of continuous internal standardization and isotope dilution calibration.

The IS in coupling applications must be compatible to the chromatographic system, which means that the chemical form of the element used as IS is not retained on the column. The new IS GeO_2 fulfils all requirements and is also able to visualize instrumental drift and instrument failures as well as showing good performance in internal standardization. The comparison with samples used for the setup of EPA method 317.0 showed the similarity of the results obtained by the round robin test, by simple external calibration, by external calibration with internal standardization, by isotope dilution analysis and by semiquantitative calculation using the analyte-to-GeO_2 ratio.

Acknowledgements

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