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Comparison of NTIMS and ICP-OES methods for the determination of boron concentrations in natural fresh and saline waters

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Abstract Determination of B concentrations in natural fresh and saline waters by ICP-OES may be strongly affected by matrix effects resulting in a deviation (shift to apparently lower values) in the order of 10 to 20% (if working without matrix-matched standard solutions), at variance with the NTIMS (Negative Thermal Ionization Mass Spectrometry) isotope dilution technique which is virtually unaffected by such effects. NTIMS isotope dilution is a highly sensitive, precise and effective technique which requires only trace amounts of boron (1–10 ng B) and allows boron concentrations in natural waters to be analyzed with an analytical uncertainty of $\pm 2\%$ (2σ).

Introduction

Boron isotope geochemistry is an innovative tracer in earth and environmental sciences with a great potential for discerning distinct sources and modeling geochemical processes in natural aquatic systems since (a) boron is highly soluble in aqueous solutions and, hence, an ubiquitous minor or trace constituent in nearly all water types, and (b) the relatively large mass difference between the two stable isotopes of boron, ^{10}B and ^{11}B , leads to a wide range of boron isotope variations in nature [1]. The utilization of boron isotope systematics for tracing sources of anthropogenic contamination in groundwater systems that are characterized by a distinct background signature [e.g. 2–4] is of great general interest.

Several analytical techniques have been developed over the last ten years for analysis of boron isotopic compositions and concentrations (see [5] for a comprehensive review). Boron analysis in natural waters that may have B concentrations as low as in the ng/g range, however, still suffers from analytical difficulties which account for the sparse data base available for natural surface waters. The NTIMS (Negative Thermal Ionization Mass Spectrometry) technique is characterized by high analytical sensitivity and, hence, this is the preferred technique for precise analysis of waters with low B concentrations. This study is the first which reports a direct comparison of boron

concentration data measured by distinct analytical techniques, NTIMS isotope dilution and ICP-OES (inductively coupled plasma-optical emission spectrometry), for a series of natural fresh and saline surface waters from a riverine to marine transition zone. In combination with additional salinity and Na concentration data, these data will give an impression to which extent B concentration measurements by ICP-OES (if performed without matrix-matched standard solutions) can be affected by matrix effects.

Experimental

The chemically untreated water samples were spiked with the NIST SRM-952 standard (^{10}B -enriched boric acid) and loaded onto rhenium filaments (1–10 ng B) with addition of 1 μL B-free seawater and 1 μL 1 mol/L HCl as loading reagents (analytical procedure as outlined by [6]). The $^{11}\text{B}/^{10}\text{B}$ isotopic ratios ($^{11}\text{BO}_2^-$ and $^{10}\text{BO}_2^-$ ions at masses 43 and 42, respectively) of the water samples have been measured by NTIMS using an NBS-design 15 cm radius-of-curvature 60° sector solid-source mass spectrometer at the State University of New York at Stony Brook (USA).

It is demonstrated here that B concentrations of natural waters can be measured by NTIMS isotope dilution with an analytical uncertainty of $\pm 2\%$ (2σ) (see caption to Table 1). This

Table 1 B and Na concentrations and salinity data of natural fresh and saline waters

No.	B ^{a,*} (mg/L)	B ^b (mg/L)	Na ^b (g/L)	Salinity ^{c,*} (‰)
1	0.25	0.22	0.39	< 0.50
2	0.64	0.55	1.35	3.10
3	0.60	0.54	1.24	3.92
4	0.76	0.68	1.66	4.50
5	1.3	1.1	2.61	8.81
6	1.5	1.3	3.57	10.81
7	1.9	1.6	4.35	13.53
8	2.3	1.9	5.45	17.04
9	3.1	2.5	7.17	20.50
10	2.9	2.3	6.70	21.41
11	3.4	2.8	8.27	24.46
12	3.9	3.1	9.34	26.90
13	4.5	3.6	10.8	32.50
14	4.8	3.7	11.0	33.70
15	4.7	3.8	11.2	34.70

^a B concentrations of natural waters from a riverine to marine transition zone (Elbe Estuary and North Sea) determined by NTIMS isotope dilution with an analytical uncertainty (2σ) of $\pm 2\%$ (four replicate $^{11}\text{B}/^{10}\text{B}$ measurements performed on sample No. 15 yielded B concentrations of 4.70 mg/L, 4.68 mg/L, 4.62 mg/L, and 4.72 mg/L)

^b ICP-OES measurements of Na and B concentrations (analytical uncertainty (2σ) of $\pm 5\%$), without using matrix-matched standard solutions

^c Salinity determined by salinometer with an analytical uncertainty of $\pm 0.01\%$

* Data given in Barth (in prep.)

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is in agreement with the results obtained on a variety of groundwater samples indicating an analytical uncertainty of $\pm 1\text{--}2\%$ (2σ) for B concentration analysis by NTIMS isotope dilution (Barth, in prep.). As indicated by the excellent analytical precisions of $\pm 0.3\%$ and $\pm 0.7\%$ determined for isotopic compositions by replicate analysis of (unspiked) natural waters and the NIST SRM-951 boric acid standard ($2\sigma_{\text{mean}}$, corresponding to $2\sigma/n^{0.5}$, where $n = 3$ to 8 replicate analyses; Barth, in prep.), respectively, the NTIMS measurements were not (or at least not significantly) affected by isobaric interferences resulting from cyanogene (CNO^-).

Results and discussion

B and Na concentrations and salinity data of the fresh and saline natural waters analyzed in the present study are given in Table 1. The water samples comprise a large range in salinity from <0.50 to 34.70‰, accompanied by variations in Na con-

centration from 0.39 to 11.2 g/L. B concentrations determined by NTIMS isotope dilution and ICP-OES on the same samples vary from 0.25 to 4.8 mg/L and 0.22 to 3.8 mg/L, respectively.

Comparison of the B concentration values, determined by these distinct analytical techniques, shows fairly good correspondence for samples in the low concentration range, exemplified for instance by B concentrations of 0.25 mg/L (NTIMS isotope dilution) and 0.22 mg/L (ICP-OES) measured for sample No. 1 (Table 1). However, for samples in the higher concentration range a marked shift towards apparently lower B concentration values determined by ICP-OES as compared to NTIMS isotope dilution is observed. This is evident from B concentration measurements on sample No. 15 (seawater representative of the North Sea), which yielded values of 4.7 mg/L and 3.8 mg/L determined by NTIMS isotope dilution and ICP-OES, respectively (Table 1). A similar discrepancy is observed for two other seawater samples (Pacific Ocean, salinity of 34.69; not listed in Table 1) which yielded a mean B concentration of 3.7 mg/L determined by ICP-OES, significantly lower than the mean B concentration of 4.7 mg/L determined by NTIMS isotope dilution. In view of the world-wide constant B concentration of seawater of 4.6 mg/L [7], the ICP-OES values obtained on the seawater samples appear to be too low by about 20%.

In order to investigate whether the observed discrepancy between the applied analytical techniques may be due to matrix effects on the ICP-OES measurements, salinity and Na concentrations were analyzed on the same samples. As shown in Fig. 1, the deviation in B concentration values determined by NTIMS isotope dilution and ICP-OES increases systematically with increasing salinity (Fig. 1a) and Na concentration (Fig. 1b). These positive correlations indicate that B concentration analysis of natural water samples by ICP-OES is strongly affected by matrix effects which may result in a deviation (shift to apparently lower values) in the order of 10 to 20% (if working without matrix-matched standard solutions). At variance, B concentration analysis by NTIMS isotope dilution is virtually unaffected by such effects.

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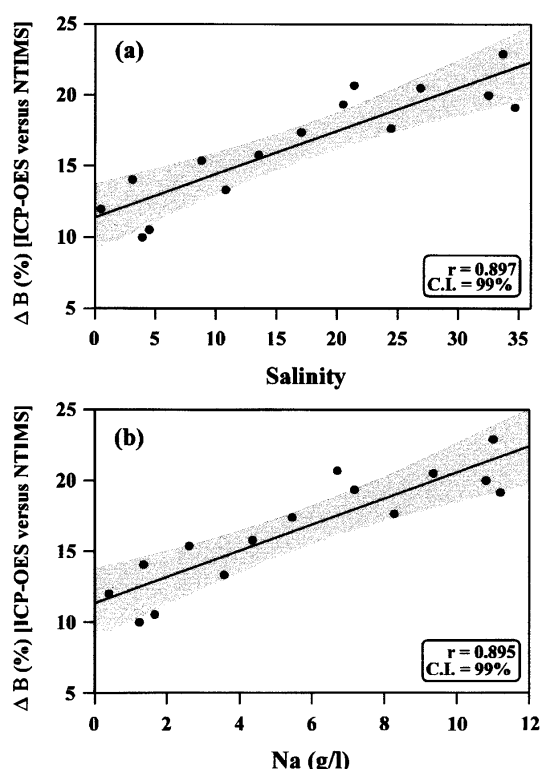


Fig. 1 a, b ΔB (%) [ICP-OES versus NTIMS] versus (a) salinity and (b) Na concentration diagrams (data from Table 1). The deviation in the B concentration, determined on the same water samples by applying different analytical techniques (NTIMS isotope dilution and ICP-OES), is calculated according to: $[(B_{\text{NTIMS}} - B_{\text{ICP-OES}}) / B_{\text{NTIMS}}] \times 100$. The offset increases systematically with increasing salinity ($y = 0.30x + 11.41$; correlation coefficient $r = 0.90$) and Na concentration ($y = 0.92x + 11.34$; $r = 0.90$) of the samples (99% confidence intervals correspond to the shadowed fields). This is related to increasing matrix effects which have a strong influence on ICP-OES measurements but leave the NTIMS analyses virtually unaffected

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