Anal Bioanal Chem (2004) 379 : 512–518
DOI 10.1007/s00216-004-2618-x

ORIGINAL PAPER

Z. Cheng · Y. Zheng · R. Mortlock · A. van Geen

Rapid multi-element analysis of groundwater by high-resolution inductively coupled plasma mass spectrometry

Received: 27 January 2004 / Revised: 17 March 2004 / Accepted: 21 March 2004 / Published online: 20 April 2004

Abstract A rapid and sensitive method was developed to determine, with a single dilution, the concentration of 33 major and trace elements (Na, Mg, Si, K, Ca, Li, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, In, Sn, Sb, Cs, Ba, Re, Hg, Pb, Bi, U) in groundwater. The method relies on high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS) and works across nine orders of magnitude of concentrations. For most elements, detection limits for this method are considerably lower than methods based on quadrupole ICP-MS. Precision was within or close to ±3% (1σ) for all elements analyzed, with the exception of Se (±10%) and Al (±6%). The usefulness of the method is demonstrated with a set of 629 groundwater samples collected from tube wells in Bangladesh (Northeast Araiharzar). The results show that a majority of tube well samples in this area exceed the WHO guideline for As of $10\,\mu g\,L^{-1}$, and that those As-safe wells frequently do not meet the guideline for Mn of $500\,\mu g\,L^{-1}$ and U of $2\,\mu g\,L^{-1}$.

Keywords HR ICP-MS · Groundwater · Multi-element analyses · Bangladesh

Introduction

Rarely is the measurement of a single parameter sufficient to properly address a question in environmental research or monitoring. Consequently, there is a considerable interest in developing rapid, yet accurate analytical methods that measure a wide suite of parameters. Analysis of multiple constituents of aqueous samples that range over several orders of magnitude of concentrations often have to rely on several different instruments and sample preparations (e.g., colorimetry, titration, and atomic absorption/emission spectrometry). There are some widely used methods for multi-element quantification that are based on inductively coupled plasma optical emission spectrometry (ICP-OES), or quadrupole ICP mass spectrometry (ICP-MS), such as US EPA method 200.8 [1], but these often require considerable correction for spectral interferences in emission or mass from other elements and polyatomic molecules. With HR ICP-MS, which relies on a magnetic sector to separate ions with greater discrimination according to their mass/charge ratio, many of these interferences can be eliminated. A growing number of multi-element methods that rely on HR ICP-MS have therefore been developed in recent years, but they typically involve a limited array of elements and a well-defined sample matrix (e.g., high-purity metals [2], sediments [3], marine particulate material [4], coastal seawater [5], Mn–Fe nodules [6], and fresh surface water [7]).

In this paper, we describe a rapid and sensitive analytical method based on HR ICP-MS for the precise quantification of 33 elements in groundwater that requires only a single dilution step. The analytes include all major cations present in groundwater (Na, K, Ca, Si, Mg) and most minor, trace, and ultra-trace elements that are of common environmental interest (Li, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, In, Sn, Sb, Cs, Ba, Re, Hg, Pb, Bi, U). The list includes 13 of the 19 inorganic constituents for which health concerns have led the World Health Organization (WHO) to set guideline values [8, 9] We also show that the developed method can be applied to the analysis of wastewaters. We conclude with a demonstration of the method with a set of 629 groundwater samples collected from tube wells in Bangladesh.

Z. Cheng (✉) · Y. Zheng · R. Mortlock · A. van Geen
Lamont Doherty Earth Observatory of Columbia University,
Palisades, NY 10964, USA
Tel.: +1-845 365 8649, Fax: +1-845 365 8154,
e-mail: czhongqi@ldeo.columbia.edu

Y. Zheng
School of Earth and Environmental Sciences, Queens College,
CUNY, Flushing, NY, 11367, USA

Experimental

Reagents

High-purity water (denoted as MQ hereafter) with a resistivity >18 MΩ was obtained from a Millipore MQ ion-exchange system fed with deionized water (US filter). Nitric acid (1%) was prepared from high-purity concentrated (16 M) HNO_3 (Optima, Seastar Chemical). A diluent containing 200 µg L^{-1} Sc, 50 µg L^{-1} of Ge, and 1 µg L^{-1} Tl internal standard spikes in 1% HNO_3 was prepared and used throughout for sample and standard dilutions for drift correction. Hydrochloric acid (Optima, SeaStar Chemical) was diluted to 6 M and then used to acidify all groundwater samples to 1% HCl in the field.

Major and trace element standards were prepared as two separate primary stock solutions each in 5% HNO_3. This is required to prevent the precipitation of some insoluble salts (e.g., $Ca_3 (PO_4)_2$) and because the solids used to make major ion standards could contain appreciable amounts of trace elements. The major element stock solution was prepared by dissolving $CaCO_3$ (Puratronic, Alfa Aesar), KNO_3, and $NaNO_3$ solids (Fisher brand), and mixing with Mg and Si single standards (SpecPure, Alfa Aesar). A trace element stock solution was prepared first by mixing single element standards (for Mn, Fe, Al, Ti, Zn, As, Ba, Sr, Cs, and Pb, SpecPure, Alfa Aesar) and an existing mixed metal solution in the lab containing 1 mg L^{-1} of most metals (SpecPure, Alfa Aesar); small amounts of KH_2PO_4 and $K_2S_2O_8$ solids (Fisher brand) were added later to obtain the desired concentrations of P and S. The mixed multi-element standards were then calibrated against single element standards to determine the exact concentrations. The major element stock contained 100 mg L^{-1} Na, Mg, Si, 200 mg L^{-1} K, and 400 mg L^{-1} Ca. The trace element stock had 50 mg L^{-1} Fe, 25 mg L^{-1} Mn, 20 mg L^{-1} S, 10 mg L^{-1} P and Ba, 5 mg L^{-1} As, Sn, and Sr, 1 mg L^{-1} Al, Zn, Se, Pb, and 0.5 mg L^{-1} Ti, Cr, Co, Ni, Cu, Cd, In, Hg, Li, V, Mo, Sb, Cs, Re, Bi, and U.

Samples and stock standards were diluted with the diluent in 6-mL Omni* polyethylene vials (Wheaton) that fit a Gilson Model 221–222 autosampler. Early tests found that unwashed vials gave low blanks and they were therefore used as purchased. A leaching with acid would be preferable, especially for some ultra-trace metals. Analysis takes about 10 min per sample and requires a total volume of 1–1.5 mL of diluted sample. For both major and trace elements, standard series were prepared by diluting 0.5, 1.0, and 2.0 mL of primary stock solution with 20 mL of diluent. For trace elements, standard series were prepared by diluting 100, 200, and 400 µL of stock solution with 20 mL diluent. For unknowns, 0.5 mL of sample was diluted 10-fold with diluent directly in the vials.

Instrumental settings

We used an Axiom Single Collector HR ICP-MS (Thermo Elemental, Germany) which combines a double-focusing, magnetic sector mass spectrometer with an optimized ICP ion source. This specific model is no longer produced, but it is not fundamentally different from other HR ICP-MS instruments on the market. The VG Axiom features a range of resolution settings, with a maximum resolving power (RP) of 16,000 that is sufficient to eliminate virtually all potential spectral interferences for groundwater analysis. The detector system combines an on-axis Faraday cup and a fast switching electron multiplier, and provides nine orders of magnitude of working dynamic range. For sample introduction, we used a PFA-100 micro-nebulizer (Elemental Scientific, Inc.) at an actual flow rate of about 150 µL min^{-1}.

Instrument settings and operating conditions that were routinely employed for groundwater analysis are listed in Table 1. Isotopes ^{23}Na, ^{39}K, and ^{45}Sc were acquired in Faraday cups, while all other isotopes (^{7}Li, ^{26}Mg, ^{27}Al, ^{30}Si, ^{31}P, ^{32}S, ^{43}Ca, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{74}Ge, ^{75}As, ^{78}Se, ^{88}Sr, ^{98}Mo, ^{111}Cd, ^{115}In, ^{120}Sn, ^{121}Sb, ^{133}Cs, ^{137}Ba, ^{187}Re, ^{202}Hg, ^{203}Tl, ^{207}Pb, ^{209}Bi, and ^{238}U) were acquired using the multiplier. To limit the time required to reset the slits, only three resolution settings with RPs of about 400, 4,000, and 12,000 were used. These are referred to hereafter as low-, medium-, and high-resolution settings, respectively. Although high resolution was mainly employed to resolve interferences (^{32}S, ^{55}Mn, ^{57}Fe, ^{75}As, ^{78}Se, and ^{88}Sr), we also use high resolving power to reduce sensitivity and avoid saturation of the multiplier for high concentration elements S, Mn, Fe, and Sr. Isotope ^{74}Ge was also acquired at the same setting for drift correction. Medium resolution was used for ^{23}Na, ^{26}Mg, ^{27}Al, ^{30}Si, ^{31}P, ^{39}K, ^{43}Ca, ^{47}Ti, ^{51}V, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{74}Ge, ^{121}Sb, and ^{137}Ba. Low resolution was used for all other isotopes. The interfering masses and remaining unresolved interfering molecules are listed in Table 2. Typical peak width was set at 2.5, and for isotopes measured at low-resolution settings it was limited to 0.1 to expedite data acquisition. Dwell time was set to 40 ms for most isotopes, but for isotopes acquired at high resolution it was increased to 70 ms to improve counting statistics and compensate for the significantly lower sensitivity (reduced to approximately 2% that of low resolution).

Table 1 Instrument settings and measurement conditions

Nebulizer	Microconcentric, pneumatic
Spray chamber	Temperature-controlled impact bead type, quartz
RF power (W)	1,350
Magnet settling time (s)	0.5
Gas flow rates (L min^{-1})	
Nebulizer	0.6–0.8
Auxiliary	1.5–2.0
Cooling	≈14
Sample uptake rate (µL min^{-1})	150
Sample uptake time (s)	60
Wash time (s)	60
Bench temperature (°C)	32–34

Each analysis for one sample consisted of three replicate measurements (i.e., three sweeps) and each measurement scans over all isotopes. For isotopes acquired with a narrower window (0.1 peak width), the number of scans per measurement was increased to 3 to improve precision.

Analytical procedure

Prior to analysis of samples, the instrument settings are first optimized with a 1 µg L^{-1} mixed-metal (Be, Mg, Co, Y, In, Pb, Bi, and U) solution by adjusting the torch position and nebulizer and auxiliary gas flow rates. A 1 µg L^{-1} mixed-metal solution typically gives 1 million counts s^{-1} for ^{115}In at 400 RP; obtaining a steady and low-noise beam at this point is critical for the quality of subsequent analyses. The tuning procedure is then followed by a mass calibration performed at medium resolution.

Following acquisition, the data were transferred to a spreadsheet for drift correction based on counts obtained for ^{45}Sc, ^{203}Tl, and ^{74}Ge. Sensitivity drift for isotopes acquired with the Faraday collector (^{23}Na and ^{39}K) at medium resolution were corrected with ^{45}Sc counts acquired at the same resolution. All isotopes acquired at high resolution were corrected with ^{74}Ge counts obtained at high resolution. High mass isotopes (^{187}Re, ^{202}Hg, ^{207}Pb, ^{209}Bi, and ^{238}U) were corrected with ^{203}Tl counts acquired at low resolution. All other isotopes were corrected with ^{74}Ge counts acquired at medium resolution. Since the Axiom software does not permit the scanning of an isotope at more than one resolving power, ^{74}Ge was fictitiously identified as ArS at medium resolution.

Quality control samples and natural groundwater samples analyzed

In addition to blanks determined for 1% HNO_3, 1% HCl, and the diluent used for drift correction, an artificial groundwater sample

Table 2 Interference molecules for isotopes used for acquisition. The equivalent interfered-element concentration was determined with 0.1% HCl–1% HNO_3 solutions containing internal standard elements and possible levels of remaining interfering elements in groundwater

	Resolved Interferences	Remaining interferences[a]	Equivalent interfered-element conc. (µg L^{-1})[b]
Isotopes acquired at low resolution (400)			
^{98}Mo		Ar-Fe(10,047), Ar-Ni(12,755), Br-OH, Br-O (9,776)	0.45
^{111}Cd		Ar-As(7,372), Br-S(8,051), MoO(32,343)	0.08
^{133}Cs		BaH(17,879),SnO(17,567)	0.02
^{115}In		ArAs(5,775), Br-S(6,223)	0.1
Isotopes acquired at medium resolution (≈4 K)			
^{23}Na	Ti++, Li-O		
^{26}Mg	Cr++, C-N, C-C, B-O, BeO		
^{27}Al	Cr++, Fe++, C-N, B-O, C-N, Be-O		
^{30}Si	Ni++, N-O, C-O, N-N-H		
^{31}P	Ni++, N-O, N-O-H		
^{39}K	Na-O	ArH(5,690)	80
^{43}Ca	Al-O, Ar-Li, Mg-O, Mg-O-H	Sr++(10,391)	53
^{47}Ti	P-O, S-N, P-O, Ar-Li, P-O, N-O-O	Mo++(60,335)	0.2
^{51}V	Cl-O, Cl-N, S-O-H, Ar-B, Ar-N-H, S-O-H		
^{52}Cr	Ar-C, Ar-O, Ar-N, Cl-N, Cl-O, Cl-O-H		
^{59}Co	Sn++, Ca-O, Ar-Na, Ar-F, K-O, Ar-O-H		
^{60}Ni	Ca-O, Sn++, Ar-Mg, Na-Cl		
^{63}Cu	Ti-O,Ar-Al, Ar-Na, Sc-O, Ti-O-H, P-O-O		
^{66}Zn	S-S, Ar-Mg, Ti-O, Ti-O-H, Ba++, V-O, S-O-O	Ar-Si(4,839), Ti-O(4,418), Cr-O(4,111)	0.11
^{121}Sb		Ar-Br(4,806)	0.06
^{137}Ba		Sb-O(19,341), Sn-O(40,915), BaH(20,855)	0.5
Isotopes acquired at high resolution (≈12 K)			
^{74}Ge	ArS, Ni-O, Ar-Ar, Cl-Cl, K-Cl, Fe-O, Ca-O-O, Sm++, Nd++	Fe-O(12,936)	0.002
^{32}S	Zn++, S-H, O-O, O-O-H, N-O-H		
^{55}Mn	Cd++, Sn++, Ar-O, Ca-O, K-O, Ar-N-H, Cl-O-H		
^{57}Fe	Sn++, Cd++, K-O, Ar-F, Ar-O, Ca-O, K-O, Ar-O-H		
^{75}As	Co-O, Ar-Cl, Ar-K, Ni-O, Ca-O-O, Sm++, Nd++		
^{78}Se	Ar-Ar, Ar-Ca, K-Cl, Ni-O	Ni-O(13,081)	0.2
^{88}Sr	Ar-Ca, Ge-O	Ar-Cr(36,175), Ar-Ti(18,684)	0.03

[a] Numbers in parentheses are minimum resolving power needed for that specific molecule

[b] Concentrations for interfering elements are 10 µg L^{-1} for Cr, Ti, Ni, Sn, Sb, and Mo, 500 µg L^{-1} for Ba and Sr, 1,000 µg L^{-1} for As, 2 mg L^{-1} for Fe, 40 mg L^{-1} for Br. All solutions were in 0.1% HCl–1%HNO_3 diluent solution

(LDEOGW) with all elements of interest served as a lab consistency standard and was analyzed with each batch of groundwater samples. A natural water standard (SRM 1640, Trace elements in natural water) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD) was used for external quality control. An array of standard addition experiments were also conducted for additional quality control, particularly for the accuracy of a few elements not referenced in SRM 1640, and to examine potential matrix and interference effects. The samples used for standard addition experiments included two groundwater samples from Bangladesh, one sample of tap water, a bottled commercial drinking water, and two wastewater samples (sample Waste-1 is the gas condensate from a landfill and sample Waste-2 is from a cooling tower where pressure-treated wood was used). Finally, 629 groundwater samples collected from tube wells, a subset of samples collected from 6,000 wells within a 25-km^2 area of Bangladesh [10], were analyzed by HR ICP-MS.

Results and Discussion

Blanks and detection limits

Blank levels were measured for two solutions: the diluent solution containing internal standard elements and 1% HNO_3, and a 0.1% HCl in diluent solution mimicking "real" diluted groundwater sample (Table 3). Overall, the level of blanks and their variations are insignificant compared to mean concentrations of most elements reported for groundwater [11, 12]. There are some small but noticeable differences between solutions and among elements, and in many cases the blank variations were larger than the blank

Table 3 Blanks, detection limits of the HR ICP-MS method. The WHO guideline values and US EPA maximum contaminant levels (MCL), maximum contaminant level (MCLG) are given for comparison

	Blanks		Detection limits		Regulations		
	0.1% HCl +diluent	Diluent	This method	US EPA (200.8)	WHO	EPA MCL	EPA MCLG
Major elements (mg L^{-1})							
Na	0.06	0.07	0.01				
Mg	0.002	0.007	0.001				
Si	0.009	0.004	0.007				
K	0.1	0.1	0.01				
Ca	0.09	0.06	0.06				
Trace elements (μg L^{-1})							
P	0.7	0.9	0.04				
S	3.6	3.9	0.5				
Mn	0.08	0.13	0.05	0.1	500		
Fe	2.5	1.7	0.4				
Al	0.5	0.3	0.04	0.05			
Ti	0.08	0.07	0.1				
Cr	0.08	0.05	0.03	0.07	50	100	100
Co	0.008	0.05	0.005	0.03			
Ni	0.11	0.09	0.09	0.2	20		
Cu	0.09	0.06	0.02	0.03	2,000	1,300	1,300
Zn	0.3	0.2	0.2	0.2			
As	0.08	0.08	0.07	0.9	10	50	0
Se	0.15	0.17	0.15	7.9	10		
Cd	0.01	0.02	0.03	0.1	3	5	5
In	0.04	0.02	0.06				
Ba	0.15	0.03	0.3	0.5	700	2,000	2,000
Hg	0.06	0.07	0.15		1	2	2
Li	0.01	0.01	0.002				
V	0.05	0.006	0.02	20			
Sr	0.02	0.01	0.01				
Mo	0.06	0.07	0.03	0.1	70		
Sn	0.01	0.01	0.01				
Sb	0.007	0.004	0.06	0.1	5	6	6
Cs	0.0004	0.0006	0.02				
Re	0.001	0.0002	0.001				
Pb	0.1	0.06	0.05	0.1	10		
Bi	0.005	0.001	0.002				
U	0.001	0.0006	0.00007	0.02	2		30

level itself. This suggests that in these cases the major contributors to the blank were not the water or reagents, but the test tubes and pipettor tips used for dilution, the sample introduction, and instrument systems (i.e., rinse blank), or perhaps minor spectral interferences.

It is possible that for some elements the blank levels are dominated by isobaric interferences. The magnitude of potentially significant interferences are expressed as equivalent interfered-element concentrations and given in Table 2. Interferences are insignificant (e.g., <1% that of sample concentrations) for normal groundwater samples and therefore do not require correction. However for some samples with abnormally high Fe, S (reducing groundwater), Br (brines), Ni, Cr, Ti, As, Mo, Sn, Sb, and Ba (wastewater) concentrations, the interferences cannot be ignored.

Table 3 also lists typical detection limits, calculated as 3σ standard deviations of 10 measurements for the 0.1% HCl in diluent solution for isotopes with no unresolved interferences. Residual interferences for some isotopes (^{98}Mo, ^{111}Cd, ^{133}Cs, ^{115}In, ^{43}Ca, ^{47}Ti, ^{66}Zn, ^{121}Sb, ^{137}Ba, ^{78}Se, ^{88}Sr) were determined with 0.1% HCl–1% HNO_3 solutions containing internal standard elements and possible levels of interfering elements in diluted groundwater (Table 2). The detection limits for individual real samples may be somewhat higher, probably closer to those listed in Table 2, due to sample-to-sample concentration variations for interfering elements and other matrix effects that are often difficult to evaluate.

The high sensitivity and resolving power of the instrument result in detection limits of the order of μg L^{-1} for major elements and sub-μg L^{-1} to sub-ng L^{-1} level for trace elements. In comparison, the detection limits of the method for many elements (U, As, Co, V, Se) are several orders of magnitude lower than for US EPA method 200.8. Other

Table 4 Summary of measurement results for a laboratory control sample (LDEOGW) and a certified standard (NIST 1640)

	LDEOGW				NIST 1640				
	LDEOGW	In-run[a] (uncorr)	In-run[a] (corr)	Long-term (n=26)	Ref Values	±	HR ICP-MS (n=26)	±	%
Major elements (mg L^{-1})									
Na	20.8	10.7	3.4	1.8	29.35	0.31	29.0	0.6	1.9
Mg	18.3	10.3	3.1	3.5	5.819	0.056	5.79	0.12	2.1
Si	25.3	8.9	1.8	2.6	4.73	0.12	4.80	0.15	3.1
K	19.8	8.3	1.1	2.2	994	27	1002	44	4.4
Ca	71.3	6.7	0.5	1.9	7.045	0.089	7.15	0.11	1.5
Trace elements ($\mu\text{g L}^{-1}$)									
P	1,380	7.4	2.1	0.9					
S	1,980	4.8	0.8	1.4					
Mn	1,896	4.6	0.4	0.9	121.5	1.1	120.5	1.7	1.4
Fe	1,947	5.4	3.0	1.0	34.3	1.6	33.4	1.5	4.5
Al	2,204	7.9	1.3	5.5	52.0	1.5	52.3	0.5	1.0
Ti	3.8	6.7	3.7	4.5					
Cr	7.8	6.4	1.6	3.5	38.6	1.6	37.7	1.4	3.7
Co	5.8	5.5	2.9	2.1	20.28	0.31	20.16	0.33	1.6
Ni	26.9	4.2	5.2	3.8	27.4	0.8	26.8	1.4	5.2
Cu	10.6	6.7	1.3	3.3	85.2	1.2	84.9	2.0	2.4
Zn	45.6	6.7	2.6	1.6	53.2	1.1	53.9	0.9	1.7
As	320	6.0	4.8	2.0	26.67	0.41	26.3	0.5	1.9
Se	5.2	9.0	8.2	10.0	21.96	0.51	20.9	1.8	8.6
Cd	2.50	2.9	4.0	3.5	22.79	0.96	21.4	1.1	5.1
In	10.1	1.6	1.5	1.2					
Ba	465	5.5	3.2	3.2	148.0	2.2	149.0	3.1	2.1
Hg	3.4	4.6	3.5	3.0					
Li	10.0	1.8	3.8	2.2	50.7	1.4	50.9	1.4	2.8
V	5.6	9.5	1.5	1.8	12.99	0.37	13.10	0.20	1.5
Sr	191	3.0	2.4	2.3	124.2	0.7	123.4	2.5	2.0
Mo	4.82	2.7	1.9	1.5	46.75	0.26	46.8	0.9	1.9
Sn	10.5	9.0	6.8	4.3					
Sb	0.97	7.2	3.4	1.7	13.79	0.42	13.3	0.5	3.4
Cs	1.20	3.1	7.6	2.5					
Re	1.50	5.5	2.7	2.0					
Pb	3.57	4.1	2.2	3.5	27.89	0.14	27.60	0.30	1.1
Bi	1.50	8.0	4.2	3.0					
U	2.60	4.6	3.2	2.9					

[a] 1σ relative standard deviation (%) of three measurements for a sample. "Uncorr" is without internal standard drift correction, while "corr" is with internal standard drift correction

detection limits are considerably lower (Ba, Mo, Sb, Ni, Cd, Pb, and Mn) or at least comparable (Al, Zn, Cr, and Ba). The detection limits of the method for elements of health concern are also several orders of magnitude lower than WHO guideline values, EPA maximum contaminant level (MCL), or even the EPA maximum contaminant level goal (MCLG).

Precision

Typical drift in instrument sensitivity over a 6-hour period is of the order of 10–15% for ^{45}Sc, 15–25% for ^{74}Ge, 5–10% for ArS and ^{203}Tl. Superimposed on this gradual drift are sample-to-sample variations of up to 5% due to fluctuations in the sample aspiration rate. Three internal standards spanning the mass range were monitored at different resolutions because the drift typically increases with resolution.

The effectiveness of drift correction using internal standards to improve precision is demonstrated by results from repeated analysis of LDEOGW every 30–40 samples. In-run precision as 1σ standard deviations of 7 replicate analyses of LDEOGW during a run (Table 4) shows that correction based on internal standards improves the in-run precision to generally better than 3%. Comparable precision was observed for repeated analysis of LDEOGW over a 3-month period, with the exception of Al (≈5%)

and Se (10%). The slightly higher variability in Al is probably due to a more variable Al blank in the system. Our analyses of groundwater samples suggested that Al content could vary by 4 orders of magnitude, which sometimes generates memory effects that are difficult to eliminate. The precision of Se measurements is limited by the low count rate (because of lower ionization efficiency of Se, high-resolution acquisitions, and low concentrations of Se in analyzed groundwater) and some residual interference from the very large Ar–Ar peak.

Accuracy

The accuracy of the measurements was determined by repeated analysis of external standard SRM 1640. This standard solution is rather different in composition from that of typical drinking water (e.g., Pb, Se, Cd, Cr exceed EPA MCL) or groundwater but is probably the closest that is available. Twenty-six replicates of SRM 1640 were analyzed during a 3-month period. For all 24 elements our results within uncertainty are in excellent agreement with certified or reference values, which were determined with 11 different methods excluding HR ICP-MS (Table 4). The largest differences occur for Cd (6%), Se (5%), and Sb (4%); all other elements agree within 3%. The accuracy of all elements (in particular the 9 elements not referenced in SRM 1640) is also demonstrated by results of the standard addition recovery experiment. Most recoveries of the standard additions are close to 100%, and typically within 3% (Fig. 1). This clearly suggests that despite signal suppression from groundwater matrix, the matrix effect can be sufficiently corrected by internal standard isotopes in the same sample solution. In general, groundwater, tap water, and drinking water samples show more consistent recoveries than the two wastewater samples. This is probably due to a larger matrix effect and higher concentrations of interfering elements in the wastewater samples.

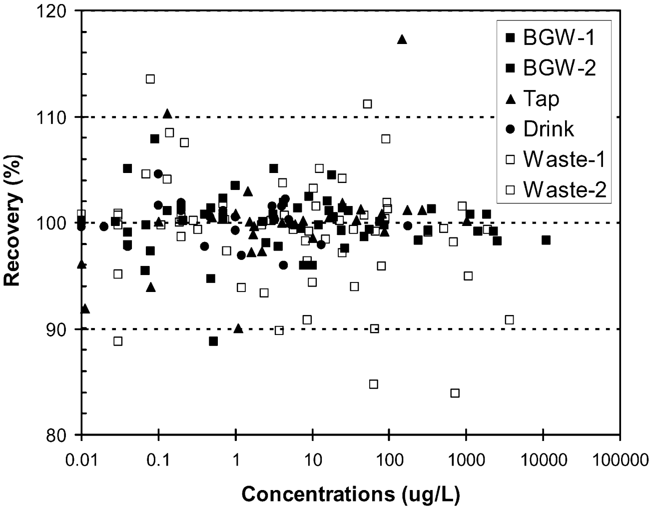

Fig. 1 Recovery of standard additions into real groundwater (*BGW-1* and *BGW-2*), tap water (*Tap*), commercial drinking water (*Drink*), and two waste water samples (*Waste-1* and *Waste-2*). Note that the data points are for all 33 elements in 6 samples

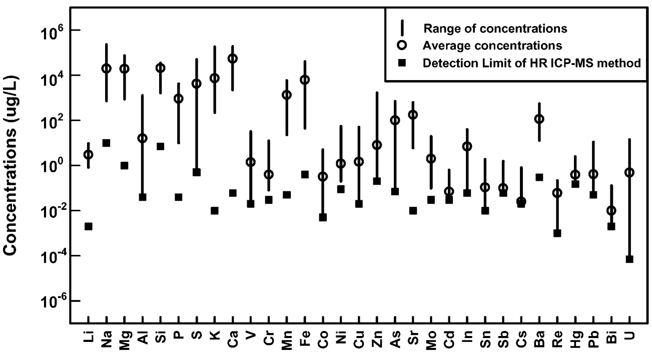

Fig. 2 Summary of concentrations of 31 elements in 629 groundwater samples from Bangladesh

Applications to the analysis of Bangladesh groundwater

Groundwater is increasingly used without treatment as a source of potable water, particularly in developing countries where surface water is frequently contaminated with microorganisms. The rapid acquisition of data for many elements by HR ICP-MS greatly facilitates groundwater studies, monitoring, and remediation efforts. Soon after the development of the method, a batch of 629 tube well samples from Araihazar upazila, Bangladesh, was analyzed for 31 elements (Se and Ti was not targeted initially for these samples). The analytical work was completed within about one week. A summary of the concentrations is presented in Fig. 2. The concentration of each analyte varies by at least one, and frequently by several, orders of magnitude. In the case of As, Al, S, V, Cr, Co, Ni, Cu, Zn, Mo, Cd, In, Sn, Sb, Cs, Re, Hg, Pb, Bi, and U, minimum concentrations are the same as the detection limit of even this sensitive method. Our results also show that in addition to As, a large number of tube wells that tap into shallow aquifers of Araihazar, Bangladesh, do not meet WHO guidelines for drinking water [8, 9]. In the case of Mn and U, 84% and 5% of the 629 groundwater samples that were analyzed did not meet the WHO guideline values of 500 and 2 μg L^{-1}, respectively. On the other hand, the concentrations of 10 other elements (Cr, Ni, Cu, Se, Cd, Ba, Hg, Mo, Sb, and Pb) measured for the same set of samples were well below their respective WHO guideline values. Our observations based on this regional study are generally consistent with recent nationwide surveys [12, 13]. The fractions of wells that meet the As and Mn guidelines set by WHO guidelines in Araihazar are significantly lower than the equivalent statistic for the entire country (Table 5). Only 25 (4%) of the 629 tube wells that were tested simultaneously meet the WHO guideline limits for As, Mn, and U.

Table 5 Percentage of wells that meet the WHO guideline limits ($\mu g\,L^{-1}$) for As, Mn, and U in this study (Northeast Araihazar) and in 3 other datasets for Bangladesh nationwide survey

Analytical Method	This study	BGS survey[a]	BWDB[a]	Frisbie et al.[b]
	HR ICP-MS	HG-AFS, HG-ICP-AES, ICP-AES	ICP-AES, ICP-MS	ICP-MS
Total samples analyzed	629	3,534	101	112
% of samples As<10	11	58	69	51
% of samples Mn<500	16	65	68	50
% of samples U<2	95	–	88	–
% of samples As<10 and Mn<500 and U<2	4	–	44	–

[a] BGS report (2001), Phase 2. "BGS Survey" is national hydrochemical survey data, and "BWDB" is Bangladesh Water Quality Monitoring Network data (only samples with complete As-Mn-U data were used

[b] Ref. [13]

Conclusions

This HR ICP-MS method provides a convenient means of routinely measuring the concentrations of many elements in aqueous samples with good precision and accuracy. The analysis needed only a single dilution, and fast data collection takes less than 10 min per sample. The method has lower detection limit and better precision than quadrupole ICP-MS methods, especially for some elements of health significance, such as As and Se. The lower detection limits are important for studying the subsurface behavior of many metals and metalloids whose environmental levels can be very low. Through careful selection of resolution, isotopes, and collectors, the method covers all major and most trace elements of health significance or geochemical interest. This is an improvement from existing HR ICP-MS methods that only target a small number of elements whose concentrations usually do not vary by many orders of magnitude [1, 2, 3, 4, 5, 6, 7].

Although developed primarily for groundwater analysis, the method can also be applied to a wide range of matrices such as drinking water, surface water, and even some wastewater. The good recovery rates from the standard addition experiments suggested that sensitivity loss due to matrix effect can be corrected with internal standards. In addition, the list of analytes could be expanded for a few other elements of potential health concern, such as Be, Ag, and Th; however, we have not done so because their concentrations in groundwater are generally too low to be of sufficient interest.

The method does not provide the best detection limit and precision for some elements, however, compared to the capability of the instrument when a single element is targeted. A much lower detection can be reached for As and Se, for instance, by combining HR ICP-MS with hydride generation [14]. But the method reported here gives approximately 10% precision with a detection limit at $0.2\,\mu g\,L^{-1}$ for Se and approximately 5% precision with a detection limit of $0.10\,\mu g\,L^{-1}$ for As, both of which are sufficient for environmental analysis under the current WHO and US EPA MCL standards. Mercury (Hg) is an element that is typically analyzed with cold vapor methods approved by US EPA. Our standard addition experiments with fresh prepared Hg solution and analyzed by HR ICP-MS also show excellent recovery rates, suggesting that Hg analysis with HR ICP-MS at detection limits lower than $0.2\,\mu g\,L^{-1}$ may be possible, baring memory effects which have been noted by many researchers. The accuracy of such Hg analysis by HR ICP-MS needs to be verified with other methods, however.

Acknowledgments The development of this method was supported by the US NIEHS/Superfund Basic Research Program (Grant P42ES10349). NSF grant OCE 9977429 contributed to the purchase of the VG Axiom. We thank Xiaoguang Meng (Stevens Institute of Technology, Hoboken, NJ) for providing the two wastewater samples. This is Lamont Doherty Earth Observatory contribution number 6600.

References

1. US EPA (1992) Methods for the determination of metals in environmental samples. US Environmental Protection Agency, Cincinnati, Ohio
2. Matschat R, Czerwensky M, Hamester M, Pattberg S (1997) Fresenius J Anal Chem 359:418–423
3. Schnetger B (1997) Fresenius J Anal Chem 359:468–472
4. Cullen JT, Field P, Sherrel M (2001) J Anal Atom Spectrom 16:1307–1312
5. Field PM, Cullen JT, Sherrell RM (1999) J Anal Atom Spectrom 14(9):1425–1432
6. Axelsson MD, Rodushkin I, Ingri J, Ohlander, N (2002) Analyst 127:76–82
7. Field PM, Sherrell RM (2003) J Anal Atom Spectrom 18(3): 254–259
8. WHO (1996) Guidelines for drinking-water quality, 2nd edn, vol 2, health criteria and other supporting information. World Health Organization, Geneva, p 940
9. WHO (1998) Guidelines for drinking-water quality, 2nd edn, addendum to vol 2. World Health Organization, Geneva, p 281
10. Van Geen A, Zheng Y, Versteeg R (2003) Water Resour Res 39(6):1140–1153
11. Allard B (1995) Groundwater. In: Salbu B, Steinnes E (eds) Trace elements in natural waters. CRC, Boca Raton, p 151
12. BGS/DPHE (2001) Arsenic contamination of groundwater in Bangladesh, Final Report. British Geological Survey, Keyworth, UK
13. Frisbie SH, Ortega R, Maynard DM, Sarkar B (2002) Environ Health Persp 110:1147–1153
14. Klaue B, Blum JD (1999) Anal Chem 71(7):1408–1414