



## A Single Analysis of Elements in Groundwater (ng L<sup>-1</sup> to g L<sup>-1</sup>) by DRC ICP-MS Using Extended Dynamic Range Techniques

JIANGYI ZHANG<sup>1</sup>, WEI GUO<sup>2,\*</sup> and GUOMIN LI<sup>1</sup>

<sup>1</sup>Key Laboratory of Shale Gas and Geoenvironment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, P.R. China

<sup>2</sup>State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, P.R. China

\*Corresponding author: Fax: +86 27 67848602; Tel: +86 27 67883456; E-mail: Wei.Guo@cug.edu.cn

Received: 11 June 2014;

Accepted: 30 September 2014;

Published online: 27 April 2015;

AJC-17165

Simultaneous determination of elements in groundwater (ng L<sup>-1</sup> to g L<sup>-1</sup>) in single analysis by DRC ICP-MS was developed. The technique of extended dynamic range based on DRC could be able to detune the signal response of selective elements to enable incorporation of high concentration elements (outside of the ion detector' dynamic range to 1e<sup>9</sup> cps) into a single analysis without affecting signal response of other trace elements. The signal sensitivity of high concentration element (*i.e.*, K, Na, Ca, Mg and Fe) was suppressed easily by adjusting the voltage parameters of DRC quadrupole (RPa) and the groundwater samples could be online diluted any multiples (*i.e.*, from one time to million times) according to the actual need. In order to eliminate mass spectral interferences (*i.e.*, <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>, <sup>40</sup>Ar<sup>40</sup>Ar<sup>+</sup>, <sup>12</sup>C<sup>40</sup>Ar<sup>+</sup>, <sup>44</sup>Ca<sup>16</sup>O<sup>+</sup>, <sup>23</sup>Na<sup>40</sup>Ar<sup>+</sup>, <sup>25</sup>Mg<sup>38</sup>Ar<sup>+</sup> and <sup>26</sup>Mg<sup>40</sup>Ar<sup>+</sup>), the operational conditions of the DRC, working with CH<sub>4</sub> as reaction gas, were optimized for <sup>75</sup>As, <sup>80</sup>Se, <sup>52</sup>Cr, <sup>60</sup>Ni, <sup>63</sup>Cu and <sup>66</sup>Zn. The analytical results of a reference material CASS-5 were in good agreement with the certified values. Reliability of the data was also tested by comparing the results for 29 groundwater samples with those determined by ICP-OES and good agreement was obtained for the high concentration elements. As the routine method in our laboratory, the satisfactory results indicate that it has great potential for the determination of low and high concentration level elements by one single analysis in various samples.

**Keywords:** Extended dynamic range techniques, ng L<sup>-1</sup> to g L<sup>-1</sup> level, DRC ICP-MS, Groundwater.

### INTRODUCTION

Groundwater element analysis is very important to understand the change in water quality due to rock water interaction or any type of anthropogenic influence<sup>1-3</sup>. The key monitoring elements are K, Na, Ca, Mg, Fe, As, Se, Cd, Cr, Ba, Cu, Zn, Hg, Pb, rare earth elements, *etc.* The most widely used method is ICP-MS, which mainly based on the US EPA method<sup>4</sup>. However, in the real analysis of groundwater samples, the concentration of some elements (*i.e.*, K, Na, Ca, Mg, Fe, *etc.*) are up to g L<sup>-1</sup> level, which too high to be directly analyzed, because these high concentration elements could saturate the ion detector of ICP-MS (the highest response of detector is 10<sup>9</sup>cps, which equivalent to 10 mg L<sup>-1</sup>).

Physical dilution of the sample is usually employed to overcome this problem, which operated prior to analysis by manual or auto-sampler with aqueous solution (*i.e.*, 2% HNO<sub>3</sub>) and aerosol dilution (so-called high matrix introduction) with argon<sup>5,6</sup>, respectively. However, one problem encountered that further dilution of the sample is not always possible since elements already present at trace concentrations may be rendered too low to be measured. That is required establishing

two independent calibration curves and analyzing samples two times for the macro-level and micro-level elements, respectively. Therefore, in order to improve the speed of analysis, reduce costs, while avoid the risk of sample contamination and possibility of dilution error, it is necessary to develop a new analytical method for measuring both low and high level of elements in a single analysis.

It is well-known that the quadrupole has the capability of filtering the selective mass and often as the mass analyzer in many different types of mass spectrometer<sup>7</sup>. In this work, a double quadrupole ICP-MS (DRC-ICP-MS) was used to achieve the signal reduction of the high concentration elements without affecting high concentration elements without affecting signal response of other trace elements. This is accomplished by adjusting the bandpass parameters (the voltage parameters of the first quadrupole DRC) with no gas in the cell. In addition, the DRC technique was applied to remove the polyatomic ion interferences. The optimization of this method and its analytical performance, as well as its applications to the determination of low and high level elements in seawater reference material CASS-5 and groundwater sample are discussed in this work.

## EXPERIMENTAL

A Perkin Elmer SCIEX ELAN DRC-e (Dynamic Reaction Cell) ICP-MS instrument was described in detail elsewhere<sup>8,9</sup>. The typical operating parameters of DRC-ICP-MS used for this work are summarized in Table-1. In our method, the elements were grouped into three modes: standard mode, extended dynamic range (EDR) mode and DRC mode using CH<sub>4</sub> (99.999 %) as a reaction gas. The extended dynamic range and DRC conditions listed in Table-2.

ICP-MS instrument	Perkin-Elmer Sciex Elan DRC-e
Sample introduction	PFA-400 Micro flow nebulizer
Spray chamber	Cyclonic spray chamber
Injector tube	1.0 mm id Quartz
Interface cones	Ni (Sampler 1.1mm id, Skimmer 0.9 mm id)
RF power	1300W
Plasma gas flow	16 L min <sup>-1</sup>
Auxiliary gas flow	1.00 L min <sup>-1</sup>
Nebulizer gas flow	0.75 L min <sup>-1</sup>
Autolens	On
Dwell time	50 ms
Sweeps	20
Readings	1
Replicate	3

Mode	Isotope	DRC quadrupole parameters			
		DRC Gas	Gas flow, (mL min <sup>-1</sup> )	RPa	RPq
Standard	<sup>7</sup> Li, <sup>47</sup> Tl, <sup>89</sup> Y, <sup>98</sup> Mo, <sup>111</sup> Cd, <sup>139</sup> La, <sup>140</sup> Ce, <sup>141</sup> Pr, <sup>142</sup> Nd, <sup>152</sup> Sm, <sup>153</sup> Eu, <sup>158</sup> Gd, <sup>159</sup> Tb, <sup>164</sup> Dy, <sup>165</sup> Ho, <sup>166</sup> Er, <sup>169</sup> Tm, <sup>174</sup> Yb, <sup>175</sup> Lu, <sup>202</sup> Hg, <sup>208</sup> Pb	No	0	0	0.25
Extended dynamic range	<sup>43</sup> Ca			0.013	
	<sup>55</sup> Mn, <sup>57</sup> Fe			0.014	
DRC	<sup>88</sup> Sr, <sup>138</sup> Ba	No	0	0.016	0.25
	<sup>23</sup> Na, <sup>27</sup> Al			0.017	
	<sup>24</sup> Mg, <sup>39</sup> K			0.018	
DRC	<sup>75</sup> As		0.3		0.50
	<sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn, <sup>80</sup> Se	CH <sub>4</sub>	0.8	0	0.60
	<sup>52</sup> Cr		1.2		0.75

High purity water (18.2 M cm<sup>-1</sup>) used for the preparation of all blank, standards and sample solutions was obtained from a Millipore water purification system (Millipore, France). The multi-element standard solutions (Perkin Elmer, USA) and single element stock solutions (NCATSM, China) were used to prepare the calibration solutions. A seawater RM CASS-5 was used to assess the accuracy of this method. 29 groundwater samples were collected from the province of Xinjiang and Yunnan in China. The samples were filtered through a membrane filter (0.45 μm), then transferred to the pre-cleaned polyethylene bottles, finally acidified with ultra-pure HNO<sub>3</sub> (99.999 %) to pH = 1.5.

## RESULTS AND DISCUSSION

**High signals selective attenuation by extended dynamic range techniques:** ICP-MS is usually used to analysis the

concentrations ranged from ng L<sup>-1</sup> to mg L<sup>-1</sup> level of elements<sup>10</sup>. However, the high concentration of some interested elements high up to hundreds or even thousands mg L<sup>-1</sup> in the real ground-water samples. Therefore, extending the dynamic range from mg L<sup>-1</sup> to g L<sup>-1</sup> is required. In this work, it is accomplished by adjusting the voltage parameters of DRC quadrupole (RPa) with no gas in the cell. Fig. 1 shows the effect of RPa on the signals of 2 mg L<sup>-1</sup> multi-element mixed standard solutions and the blank solution. As shown in Fig. 1a, the signal intensities of selected elements were decreased with the RPa increasing. When the RPa value is high enough, no ions through the DRC quadrupole, the signal intensity of elements will be low. Fig. 1b shows that the background signal in the blank solution has a similar trend. In other words, the signal to background (S/B) is independent of the RPa. Fig. 2 shows the effect of RPa value on the dilution factor of these elements. Because the bandpass parameters (RPa) of DRC quadrupole can be adjusted on a per-mass basis, sensitivity can be reduced on selected isotopes without affecting other elements in one

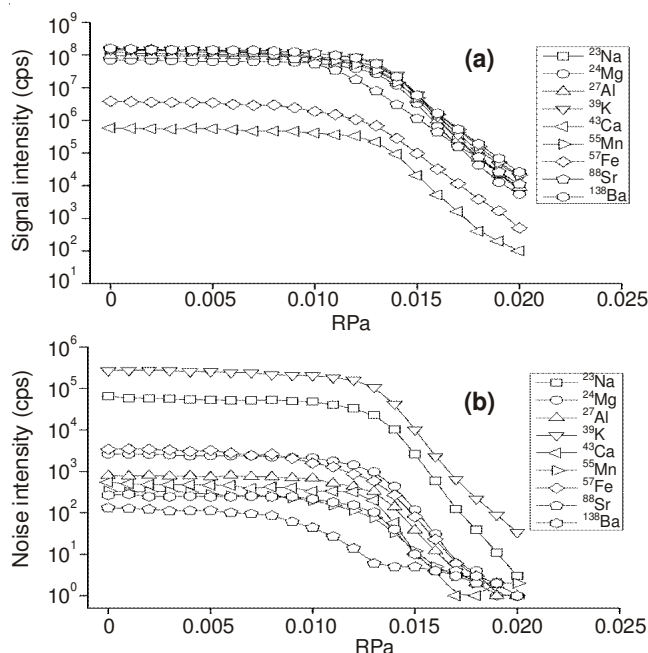


Fig. 1. Effect of RPa on the signals of (a) 2 mg L<sup>-1</sup> multi-element mixed standard solutions and (b) blank solution

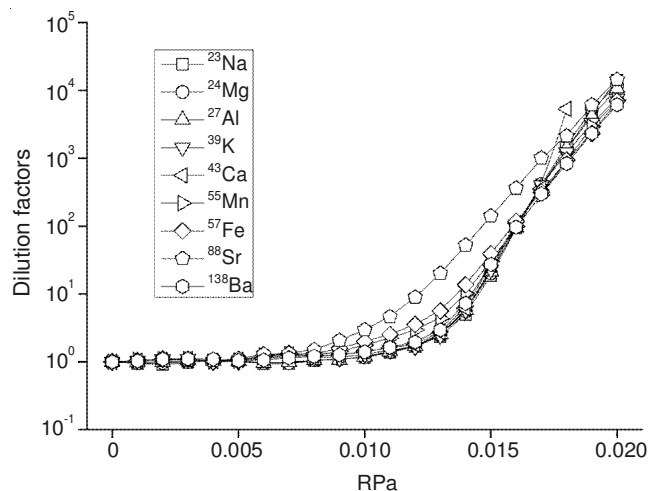


Fig. 2. Effect of RPa value on the dilution factors of the selected element

method. Therefore, the analyzed solution could be online diluted any multiples (*i.e.*, from one time to million times) according to the actual requirement. This advantage is seen when analyzing samples for both low and high level elements. The optimized RPq value of every isotope for the real groundwater samples was listed in Table-2.

#### Elimination of mass spectral interference by DRC:

Mass spectral interferences caused by atomic or molecular ions which have the same mass-to-charge as analytes of interest are existed in groundwater samples analysis by ICP-MS<sup>11,12</sup>. To eliminate the mass spectral interferences (*i.e.*, <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>, <sup>40</sup>Ar<sup>40</sup>Ar<sup>+</sup>, <sup>12</sup>C<sup>40</sup>Ar<sup>+</sup>, <sup>44</sup>Ca<sup>16</sup>O<sup>+</sup>, <sup>23</sup>Na<sup>40</sup>Ar<sup>+</sup>, <sup>25</sup>Mg<sup>38</sup>Ar<sup>+</sup> and <sup>26</sup>Mg<sup>40</sup>Ar<sup>+</sup>) on <sup>75</sup>As, <sup>80</sup>Se, <sup>52</sup>Cr, <sup>60</sup>Ni, <sup>63</sup>Cu and <sup>66</sup>Zn, the DRC with CH<sub>4</sub> as the reaction gas was used, in combination with the appropriate DRC rejection parameter q (Rpq). A mixed solution contained 200 mg L<sup>-1</sup> of K, Na, Ca, Mg, Fe, Al and 1 % HCl and 1 % HNO<sub>3</sub> was treated as the matrix blank to simulate the interfering ions on As, Se, Cr, Ni, Zn, Cu determination. As shown in Fig. 3a, b, the signal profile indicates that polyatomic interferences at 75, 80 could be eliminated and the interfered ions were reduced by up 100, 10000 times for As, Se, respectively. This well documented effect of reaction gas flow on interference reduction is attributed to molecular reactions between CH<sub>4</sub> and interfering species, forming neutral species and/or polyatomic ions with different *m/z*<sup>13,14</sup>. The RPq values are important to filter out unwanted precursors of interfering species from the ion beam to eliminate interference created in the cell by reaction gas<sup>15</sup>. The optimized RPq values (Fig. 3c,d) were selected at 0.6, 0.55 for As, Se. Similar process were used to eliminate the interferences of <sup>12</sup>C<sup>40</sup>Ar<sup>+</sup>, <sup>44</sup>Ca<sup>16</sup>O<sup>+</sup>, <sup>23</sup>Na<sup>40</sup>Ar<sup>+</sup>, <sup>25</sup>Mg<sup>38</sup>Ar<sup>+</sup>, <sup>26</sup>Mg<sup>40</sup>Ar<sup>+</sup> on <sup>52</sup>Cr, <sup>60</sup>Ni, <sup>66</sup>Zn, <sup>63</sup>Cu determination, the optimized conditions of the CH<sub>4</sub> flow rate and the RPq value were showed in Table-2. The interfered ions were reduced by up to 400, 40, 20 and 20 times for Cr, Ni, Cu, Zn (Table-3). The analytical performances listed in Table-4.

Analytes	Interfered ions	Reduced times
<sup>52</sup> Cr	<sup>12</sup> C <sup>40</sup> Ar <sup>+</sup>	400
<sup>60</sup> Ni	<sup>44</sup> Ca <sup>16</sup> O <sup>+</sup>	40
<sup>63</sup> Cu	<sup>23</sup> Na <sup>40</sup> Ar <sup>+</sup> , <sup>25</sup> Mg <sup>38</sup> Ar <sup>+</sup>	20
<sup>66</sup> Zn	<sup>26</sup> Mg <sup>40</sup> Ar <sup>+</sup>	20
<sup>75</sup> As	<sup>35</sup> Cl <sup>40</sup> Ar <sup>+</sup>	100
<sup>80</sup> Se	<sup>40</sup> Ar <sup>40</sup> Ar <sup>+</sup>	10000

Elements	Working curve (μg L <sup>-1</sup> )	Correlation coefficient	LOQ (μg L <sup>-1</sup> )
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb	0.1-100	0.99999	0.01-0.03
As, Cr, Cu, Li, Ni, Pb, Se, Zn	0.1-200	0.99998	0.01-0.06
Hg, Tl, Cd	0.1-20	0.99998	0.009-0.01
K, Na, Ca, Mg with extended dynamic range mode	100-500 000	0.99997	5-9
Fe, Al, Ba, Sr, Mn with Standard mode	0.1-200	0.99998	0.01-0.06
Fe, Al, Ba, Sr, Mn with extended dynamic range mode	100-200 000	0.99996	5-10

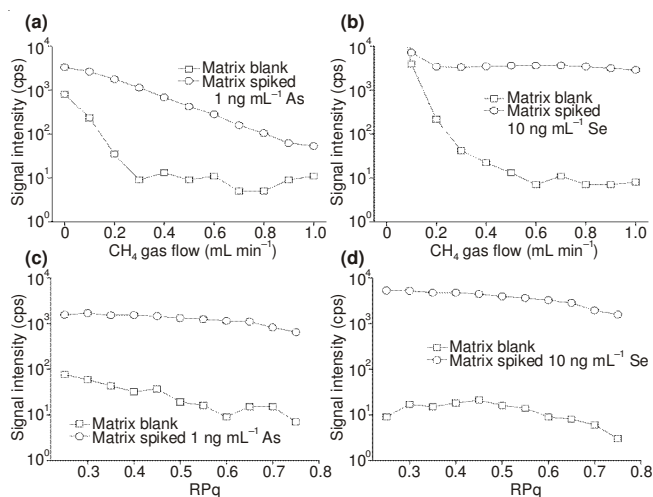


Fig. 3. (a) Effect of the CH<sub>4</sub> gas flow and (c) RPq value on the signal of <sup>75</sup>As in matrix blank and matrix spiked 1 ng mL<sup>-1</sup> As; (b) The effect of the CH<sub>4</sub> gas flow and (d) RPq value on the signal of <sup>80</sup>Se in matrix blank and matrix spiked 10 ng mL<sup>-1</sup> <sup>80</sup>Se. A solution of 200 mg L<sup>-1</sup> of K, Na, Ca, Mg, Fe, Al and 1 % HCl and 1 % HNO<sub>3</sub> was treated as the matrix blank

#### Seawater RM (CASS-5) and groundwater samples analysis:

To investigate the accuracy and precision of the proposed method, one similar matrix CASS-5 seawater reference material was analyzed. As shown in Table-5, the analytical results of CASS-5 were in good agreement with the certified values for the trace elements, meanwhile results of the high concentration elements (*i.e.*, K, Na, Ca, Mg, Ba, Sr and Al) are agreed with that of ICP-OES. It was confirmed that the new method could measure both the low and high levels of elements in a single run. As our laboratory method, it was used to analyze the 29 groundwater samples (collected from the province of Xinjiang and Yunnan, China). The results of high concentration elements were listed in Tables 6 and 7. For comparison, EDR-ICP-MS (extended dynamic range mode), SM-ICP-MS (standard mode) and ICP-OES were used to analyze the samples, respectively. Fig. 4 showed the results of

Elements	This method	Certified Values	ICP-AES	Units
As	1.180	1.24 ± 0.09	/b	μg L <sup>-1</sup>
Cd	0.020	0.0215 ± 0.0018	/	μg L <sup>-1</sup>
Cr	0.113	0.106 ± 0.013	/	μg L <sup>-1</sup>
Cu	0.400	0.380 ± 0.028	/	μg L <sup>-1</sup>
Fe	1.520	1.44 ± 0.11	/	μg L <sup>-1</sup>
Pb	0.011	0.011 ± 0.002	/	μg L <sup>-1</sup>
Mn	2.710	2.62 ± 0.20	/	μg L <sup>-1</sup>
Ni	0.340	0.330 ± 0.023	/	μg L <sup>-1</sup>
Zn	0.782	0.719 ± 0.068	/	μg L <sup>-1</sup>
Mo	9.8	(9.8)	/	μg L <sup>-1</sup>
K	153.0	/a	163.6	mg L <sup>-1</sup>
Na	9620.0	/	9459.8	mg L <sup>-1</sup>
Ca	442.0	/	403.3	mg L <sup>-1</sup>
Mg	1210.1	/	1195.0	mg L <sup>-1</sup>
Ba	0.009	/	0.009	mg L <sup>-1</sup>
Sr	7.17	/	7.02	mg L <sup>-1</sup>
Al	0.05	/	0.045	mg L <sup>-1</sup>

<sup>a</sup>Not available; <sup>b</sup>No detection

TABLE-6  
RESULTS OF HIGH LEVEL ELEMENTS IN GROUNDWATER BY ICP-MS AND ICP-AES (mg L<sup>-1</sup>)

Sample	Na		K		Mg		Ca		Al		Mn		Fe		Sr		Ba						
	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-MS*	ICP-AES	ICP-MS	ICP-MS*	ICP-AES	ICP-MS	ICP-MS*	ICP-AES	ICP-MS	ICP-MS*	ICP-AES			
CP-01	1.21	1.13	2.45	2.38	3.79	3.96	5.33	5.13	0.205	199.8	0.199	0.027	20.8	0.022	0.243	233.0	0.244	0.014	12.9	0.013	0.062	58.2	0.064
CP-17	2.76	2.42	0.60	0.58	36.00	34.26	57.40	55.45	1.090	S	1.052	0.041	47.5	0.047	1.090	1030.0	0.973	0.033	31.8	0.030	0.087	86.6	0.086
CP-11	35.90	34.88	4.60	4.72	35.30	34.78	85.70	81.86	0.086	83.4	0.082	0.560	653.0	0.497	0.428	405.0	0.430	0.277	264.0	0.253	0.140	125.0	0.125
CP-13	8.07	7.83	5.01	4.68	19.60	20.28	35.70	34.65	0.145	141.0	0.148	<0.010	9.8	0.010	0.246	234.0	0.249	0.053	49.6	0.051	0.106	98.8	0.097
CP-05	17.10	16.91	7.64	7.50	8.84	9.42	28.70	29.83	3.960	S	4.032	0.620	S	0.675	2.920	S	3.082	0.026	24.7	0.027	0.050	49.8	0.053
JING5	26.40	25.56	3.16	2.94	2.91	2.91	4.94	4.49	0.428	419.0	0.398	0.176	182.0	0.182	0.015	14.1	0.016	0.032	28.0	0.028	0.138	137.0	0.142
JING4	140.00	129.84	8.96	8.87	29.10	28.95	36.00	34.90	0.022	18.7	0.020	<0.010	0.1	<0.001	0.080	63.6	0.073	0.280	268.3	0.269	0.590	569.0	0.566
XJ-28	138.00	127.73	2.55	2.37	16.40	15.89	10.90	8.00	0.450	418.0	0.439	<0.010	1.1	0.001	0.051	49.9	0.058	2.440	S	2.469	<0.010	3.8	0.0040
XJ-30	105.00	96.15	2.10	1.94	15.00	14.59	12.30	9.43	0.260	202.0	0.235	<0.010	0.6	<0.001	0.048	44.8	0.043	2.480	S	2.431	<0.010	2.7	0.0035
XJ-31	113.00	103.05	2.04	1.89	14.30	13.99	10.80	8.09	0.026	27.8	0.021	<0.010	0.6	<0.001	0.037	35.9	0.033	2.440	S	2.336	<0.010	2.2	0.0024
XJ-32	102.00	94.46	2.01	1.92	15.50	14.93	13.40	10.63	0.035	30.8	0.031	<0.010	0.4	<0.001	0.045	39.1	0.045	2.460	S	2.335	<0.010	2.3	0.0022
XJ-34	106.00	97.25	2.04	1.94	13.20	13.21	10.80	8.83	0.046	39.9	0.042	<0.010	0.2	<0.001	0.031	29.3	0.032	1.880	S	1.795	<0.010	2.2	0.0026
XJ-35	105.00	92.68	1.91	1.84	13.10	12.97	10.20	8.06	0.059	55.1	0.057	<0.010	0.7	<0.001	0.071	67.6	0.065	2.050	S	1.986	<0.010	3.9	0.0034
XJ-99	139.00	125.79	1.80	1.58	31.70	31.26	34.60	30.33	0.035	34.5	0.037	<0.010	0.4	<0.001	0.095	89.4	0.095	1.070	S	0.980	<0.010	1.6	0.0016
XJ-100	129.00	118.91	2.64	2.46	40.90	40.98	41.30	36.10	0.117	98.7	0.106	<0.010	0.2	<0.001	0.080	74.1	0.073	1.290	S	1.247	<0.010	1.6	0.0015
XJ-102	119.00	107.01	3.05	2.86	29.00	30.32	17.10	15.60	0.043	44.8	0.048	<0.010	0.6	<0.001	0.037	37.1	0.037	1.020	S	0.990	<0.010	1.6	0.0014
XJ-105	113.00	111.62	1.65	1.58	35.20	36.95	44.10	40.89	0.106	98.4	0.099	<0.010	0.3	<0.001	0.111	99.1	0.012	1.310	S	1.242	<0.010	1.7	0.0017
1-D1	156.00	159.37	1.51	1.53	49.90	51.62	197.00	213.30	0.311	284.0	0.305	0.078	68.2	0.073	1.000	956.0	0.996	1.410	S	1.450	0.034	30.1	0.036
1-D4	108.00	114.37	1.69	1.77	31.50	32.61	84.80	97.04	3.270	S	3.285	1.550	S	1.492	20.700	S	21.399	0.558	S	0.595	0.025	24.4	0.026
1-D8	154.00	159.57	1.52	1.53	39.70	41.35	162.00	176.61	0.170	159.0	0.166	0.146	130.0	0.148	1.110	1020.0	1.084	1.100	S	1.156	0.027	26.8	0.030
1-D9	142.00	148.49	2.02	2.18	58.50	60.92	194.00	215.99	2.110	S	2.225	0.127	115.0	0.129	3.240	S	3.341	1.840	S	1.676	0.040	36.0	0.042
1-D10	147.00	147.10	1.37	1.36	39.10	41.32	141.00	154.84	0.653	591.0	0.637	0.127	121.0	0.132	1.240	1180.0	1.239	1.040	S	0.986	0.046	38.5	0.045
1-D11	145.00	149.02	1.97	1.98	50.10	51.19	204.00	217.05	1.590	S	1.662	0.334	256.0	0.318	2.120	S	2.109	1.660	S	1.564	0.048	42.0	0.048
1-D12	125.00	120.36	1.94	1.95	39.80	41.08	117.00	122.10	0.157	147.0	0.146	<0.01	1.6	0.002	0.292	248.0	0.298	1.270	S	1.161	0.028	23.8	0.027
1-D13	236.00	229.64	1.61	1.63	42.90	43.55	155.00	165.47	1.200	S	1.277	0.590	63.4	0.064	1.020	1030.0	0.996	1.190	S	1.090	0.028	24.2	0.027
1-D14	72.50	69.37	2.04	1.99	11.50	12.31	70.10	71.94	8.100	S	7.995	0.195	188.0	0.206	7.620	S	7.476	0.345	365.0	0.345	0.107	99.1	0.109
XJ-912	115.00	120.29	2.52	2.70	73.30	75.58	137.00	145.16	10.500	S	10.788	1.420	S	1.566	98.900	S	94.393	1.170	S	1.075	0.031	29.1	0.033
XJ-913	110.00	110.76	3.93	3.96	59.00	62.97	138.00	142.80	8.030	S	8.423	1.540	S	1.674	106.000	S	97.452	1.050	S	0.991	0.044	41.0	0.044
3-M1	125.00	127.99	4.85	4.89	83.30	85.80	161.00	175.91	19.400	S	20.039	3.900	S	3.708	102.000	S	98.533	1.220	S	1.177	0.027	22.4	0.022

ICP-MS: extended dynamic range mode; ICP-MS\*: Standard mode,  $\mu\text{g L}^{-1}$  S: Ion detector saturated

TABLE-7  
RESULTS OF TRACE LEVEL ELEMENTS IN GROUNDWATER BY ICP-MS ( $\mu\text{g L}^{-1}$ )

Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Mo	Li	Cr	Ni	Cu	Zn	Tl	Pb	As	Se	Cd	Hg
CP-01	0.18	0.55	0.23	0.02	0.12	0.04	0.02	0.02	<0.01	0.02	<0.01	0.02	0.02	<0.01	<0.01	<0.03	1.57	2.89	3.53	20.60	31.20	1.47	1.37	0.87	2.12	<0.01	<0.009
CP-17	4.51	1.73	3.82	0.95	4.84	1.51	0.32	1.60	0.19	1.23	0.20	0.57	0.11	0.19	<0.01	0.66	1.63	2.12	5.83	17.00	38.30	4.80	4.96	0.45	3.73	<0.01	<0.009
CP-11	0.07	0.09	0.13	<0.01	0.06	0.04	0.02	0.02	<0.01	0.03	<0.01	<0.01	0.03	<0.01	<0.01	1.15	1.64	0.51	3.28	13.40	8.83	0.66	0.87	5.32	<0.1	<0.01	<0.009
CP-13	0.44	0.11	0.20	0.03	0.16	0.07	0.03	0.07	<0.01	0.06	0.02	<0.01	0.02	<0.01	0.15	1.12	1.69	0.71	4.28	5.99	10.40	1.20	1.14	0.95	<0.1	<0.01	<0.009
CP-05	5.87	2.89	4.31	0.66	2.71	0.66	0.15	0.84	0.12	0.57	0.13	0.38	0.06	0.38	<0.01	4.72	1.65	3.40	6.72	24.70	40.40	2.83	29.60	10.50	9.58	<0.01	<0.009
JING5	3.86	9.62	74.00	2.25	7.91	1.77	0.36	2.25	0.20	0.97	0.20	0.56	0.10	0.58	0.05	<0.03	0.89	0.33	0.69	0.67	10.60	2.60	26.30	0.27	<0.1	<0.01	<0.009
JING4	6.03	7.67	0.02	0.88	3.16	0.66	0.20	0.68	0.09	0.67	0.12	0.30	0.06	0.10	0.05	0.08	0.96	0.49	1.10	3.97	24.40	1.32	1.35	1.10	1.10	<0.01	<0.009
XJ-28	0.09	0.05	0.09	<0.01	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02	<0.01	<0.01	9.73	10.30	2.28	2.28	4.07	38.50	2.36	2.34	1.00	6.24	<0.01	<0.009
XJ-30	0.05	0.03	0.06	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.10	6.60	8.72	0.62	1.24	2.66	43.70	1.85	1.64	0.67	2.73	<0.01	<0.009
XJ-31	<0.03	0.02	0.04	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	6.77	8.96	3.51	1.08	1.25	5.08	0.91	1.08	0.69	<0.1	<0.01	<0.009
XJ-32	<0.03	0.02	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	4.97	9.10	0.42	2.03	0.50	33.30	3.33	3.20	0.46	0.41	<0.01	<0.009
XJ-34	<0.03	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	6.04	8.66	0.43	1.56	0.58	17.30	2.70	2.70	0.49	<0.1	<0.01	<0.009
XJ-35	<0.03	0.02	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	5.99	7.88	0.60	1.97	3.73	24.60	1.67	1.75	0.45	<0.1	<0.01	<0.009
XJ-99	<0.03	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02	<0.01	<0.01	2.32	6.75	0.47	1.51	1.49	14.60	2.26	2.35	0.49	<0.1	<0.01	<0.009
XJ-100	<0.03	0.02	0.03	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	3.44	9.20	1.18	0.57	0.82	19.00	0.97	1.03	0.52	1.29	<0.01	<0.009
XJ-102	<0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	3.06	10.30	0.46	1.01	0.51	9.31	1.71	1.76	0.38	0.28	<0.01	<0.009
XJ-106	<0.03	0.02	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.05	1.72	7.87	0.57	0.92	0.86	16.70	1.28	1.34	0.51	0.98	<0.01	<0.009
1-D1	0.23	0.13	0.31	0.03	0.11	0.04	<0.01	0.04	<0.01	0.03	<0.01	0.05	<0.01	<0.01	<0.01	3.82	11.40	20.10	4.87	2.20	8.36	6.15	5.72	0.76	1.36	<0.01	<0.009
1-D4	12.40	14.70	28.40	2.87	10.00	2.09	0.47	2.94	0.35	2.08	0.42	1.11	0.12	0.48	0.30	2.19	36.60	21.50	35.80	0.91	166.00	6.49	7.00	49.40	31.70	<0.01	<0.009
1-D8	0.13	0.10	0.21	0.02	0.09	0.02	<0.01	0.02	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	0.15	4.26	11.10	20.00	4.32	5.18	13.30	6.31	6.62	0.62	0.61	<0.01	<0.009
1-D9	1.32	1.55	3.48	0.40	1.63	0.35	0.07	0.31	0.05	0.17	0.05	0.14	0.02	<0.01	<0.01	2.03	14.80	22.60	8.66	3.32	19.50	7.38	7.17	0.80	3.42	<0.01	<0.009
1-D10	0.32	0.32	0.70	0.08	0.31	0.08	0.02	0.07	<0.01	0.08	<0.01	0.02	0.01	0.10	<0.01	4.51	11.00	16.20	2.51	1.32	12.20	4.98	4.97	1.24	0.40	<0.01	<0.009
1-D11	0.67	0.86	2.01	0.24	0.88	0.20	0.04	0.21	0.03	0.17	0.03	0.13	0.04	<0.01	0.10	4.08	14.70	18.60	3.33	2.19	20.00	5.03	5.14	0.81	2.02	<0.01	<0.009
1-D12	0.07	0.11	0.23	0.03	0.11	0.03	<0.01	0.03	<0.01	0.02	<0.01	0.02	0.02	<0.01	0.05	4.43	13.30	0.51	1.68	1.12	5.22	0.62	0.70	0.60	<0.1	<0.01	<0.009
1-D13	0.59	0.69	1.63	0.19	0.71	0.18	0.04	0.19	0.03	0.15	0.03	0.07	0.05	<0.01	<0.01	14.10	12.90	15.10	21.90	2.10	11.00	5.90	5.79	17.20	0.94	<0.01	<0.009
1-D14	2.99	4.29	9.83	1.16	4.37	0.99	0.23	1.05	0.15	0.76	0.13	0.30	0.03	0.29	0.05	3.25	11.00	32.70	17.20	12.10	52.10	12.80	13.30	23.10	11.40	<0.01	<0.009
XJ-912	78.50	49.70	97.90	10.70	44.20	10.20	2.61	14.90	2.00	12.80	2.54	6.75	0.86	4.40	1.15	1.18	66.10	36.60	132.00	3.91	488.00	11.90	12.10	38.60	77.30	<0.01	<0.009
XJ-913	126.00	48.10	102.00	29.60	179.00	21.10	4.79	29.80	3.97	22.50	4.35	12.10	1.72	7.47	1.54	0.72	136.00	43.40	238.00	6.03	933.00	37.70	35.90	18.90	113.00	<0.01	<0.009
3-M1	83.70	121.00	316.00	89.60	120.00	73.40	16.30	89.30	11.80	63.20	11.80	34.20	4.74	25.10	4.98	1.56	147.00	159.00	572.00	42.40	382.00	23.60	142.00	13.40	151.00	<0.01	<0.009



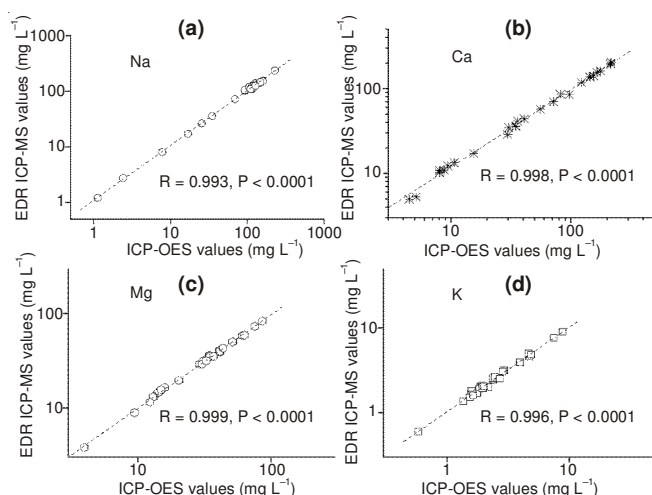


Fig. 4. Comparison of the results of high level elements (a) Na, (b) Ca, (c) Mg and (d) K with extended dynamic range ICP-MS method and ICP-OES in the 29 real groundwater samples

K, Na, Ca and Mg (1-250 mg L<sup>-1</sup>) by extended dynamic range ICP-MS were agreed with that of ICP-OES and their relationship ( $R > 0.98$ ) between two methods further demonstrated the extended dynamic range techniques could effectively measure the high concentration level elements. For some elements (*i.e.*, Fe, Al, Mn, Sr and Ba), the concentrations have a far wider range (from 0.0001 to 100 mg L<sup>-1</sup>). When the analyte concentration is low (< 1 mg L<sup>-1</sup>), it can be detected by SM ICP-MS (standard mode) as well as the other trace elements. If the concentration of analyte is high (>1 mg L<sup>-1</sup>), the calibration curve of extended dynamic range ICP-MS can be used. Because there are two sets of standard curves in one method (Table-4), the different concentration levels of elements in groundwater all can be measured in a single run.

### Conclusion

This work has demonstrated that the micro-level and macro-level elements in groundwater can be simultaneous measured in one single analysis by DRC ICP-MS without additional dilution step. The technique of extended dynamic

range could be able to detune the signal response of selective elements to enable incorporation of high concentration elements into a single analysis without affecting signal response of other trace elements. The advantages of this method are of high throughput, low costs and less risk of sample contamination.

### ACKNOWLEDGEMENTS

Financially supported by the National Basic Research Program of China (No. 2010CB428801) and the National Nature Science Foundation of China (No. 21175120) and the National Key Scientific Instrument and Equipment Development Projects of China (No. 2011YQ06010008), and the Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan) (No. CUGL140411) are gratefully acknowledged.

### REFERENCES

1. J.M. McArthur, P.K. Sikdar, B. Nath, N. Grassineau, J.D. Marshall and D.M. Banerjee, *Environ. Sci. Technol.*, **46**, 669 (2012).
2. B. Zhang, X.F. Song, Y.H. Zhang, D.M. Han, C.Y. Tang, Y.L. Yu and Y. Ma, *Water Res.*, **46**, 2737 (2012).
3. L. Belkhir, L. Mouni and A. Tiri, *Environ. Geochem. Health*, **34**, 1 (2012).
4. Methods for the Determination of Metals in Environmental, US Environmental Protection Agency, Cincinnati, Ohio (1994).
5. V. Celo, E. Dabek-Zlotorzynska, J.J. Zhao, I. Okonskaia and D. Bowman, *Anal. Chim. Acta*, **706**, 89 (2011).
6. Bruker Technical Note # CA-275622, Advantages of Aerosol Dilution on the Bruker Aurora M90.2011.
7. R.S. Houk, V.A. Fassel, G.D. Flesch, H.J. Svec, A.L. Gray and C.E. Taylor, *Anal. Chem.*, **52**, 2283 (1980).
8. W. Guo, S.H. Hu, Y.X. Wang, L.Y. Zhang, Z.C. Hu and J.Y. Zhang, *Microchem. J.*, **108**, 106 (2013).
9. W. Guo, S.H. Hu, J. Zhao, S.S. Jin, W.J. Liu and H.F. Zhang, *Microchem. J.*, **97**, 154 (2011).
10. R.S. Houk, *Anal. Chem.*, **58**, 97A (1986).
11. T.W. Way and R.H. Wiedmeyer, *At. Spectrosc.*, **19**, 150 (1998).
12. V.N. Epov, D. Lariviere, E.N. Epova and R.D. Evans, *Geostand. Geoanal. Res.*, **28**, 213 (2004).
13. J.W. Olesik and D.R. Jones, *J. Anal. At. Spectrom.*, **21**, 141 (2006).
14. D. Pick, M. Leiterer and J.W. Einax, *Microchem. J.*, **95**, 315 (2010).
15. S.D. Tanner, V.I. Baranov and D.R. Bandura, *Spectrochim. Acta B*, **57**, 1361 (2002).