

Application Note # CA-270108

The Analysis of Environmental Waters using the Bruker 820-MS

Introduction

Drinking water quality has been directly associated with a variety of health risks. Consequently many countries have developed standards for water quality establishing maximum levels for contaminants. In the United States drinking water quality standards are established by the section 1412 of the Public Health Service Act and the Safe Drinking Water Act (Pub. L. 93–523). In support of this legislation the United States Environmental Protection Agency (EPA) has developed analysis procedures for determination of trace elements in waters using inductively coupled plasma mass spectrometry. Method 200.8 provides analysis procedures for 21 elements in ground waters, surface waters and drinking waters. The purpose of this study is to explore the additional performance capabilities for water analysis provided by a new solution for interference management, the Collision Reaction Interface (CRI) [1].

Instrumentation

All sample analyses were performed on the 820-MS equipped with the standard sample introduction system, and SPS-3 autosampler fitted with an autosampler cover to prevent contamination of the samples from laboratory dust during the course of the analysis. Bruker's patented 90 degree ion mirror ion optics [2] provides unsurpassed efficiency of transfer of ions from the interface to the mass analyzer [3], which enables the 810-MS and 820-MS to achieve more than 1000 million c/s/mg/L sensitivity while maintaining oxides (CeO^+/Ce^+) below 3%. The 820-MS includes Bruker's unique and patented interference management system [4], the Collision Reaction Interface (CRI). This interface reduces interferences on elements such as As, Se, Cr, V and Fe, permitting lower detection limits under normal, hot plasma conditions. Unlike other interference management systems, the CRI does not use a pressurized multipole prior to the mass analyzer to reduce interferences. Instead, reaction and collision gases are injected into the tips of the interface cones, as shown in Fig.1.

Due to highly efficient pumping within the interface region, switching between gases is very rapid, enabling multiple condition sets to be run on a single solution. The simplicity of the CRI is complimented by the flexibility to inject gases into the tip of either the skimmer or sampler cone, or both at once, as seen in the Figure 1. The gas type can also be varied, providing ultimate flexibility in the control of interferences. This simple approach avoids the complexity of using a pressurized multipole ion guide in the high vacuum region of the mass spectrometer, thus permitting rapid determinations.

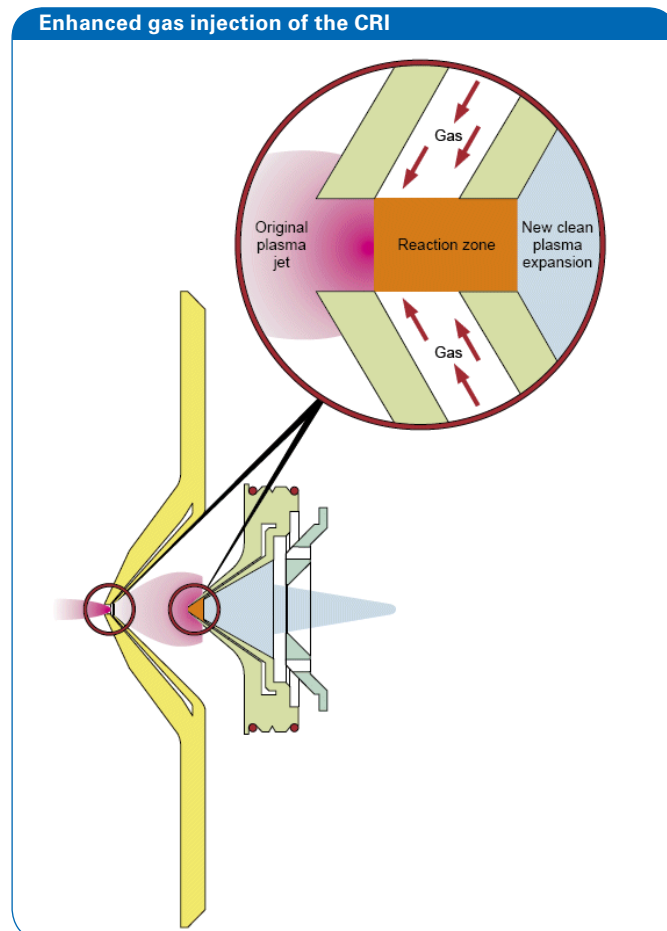


Figure 1: Schematic diagram of the CRI system

Materials and Reagents

High-purity nitric acid (Ultrapur[®] HNO₃ 60%, Merck, Kilsyth, Victoria, Australia) and deionized water (18 MΩ cm, Millipore Milli-Q, Billerica, MA, USA) were used for the solution preparations. Prior to use, all labware was thoroughly cleaned using a combination of acid washing and rinsing. The calibration standards were prepared by diluting multi-element stock standards (Var-Cal-1, Var-Cal-2 and Var-Major-1, Inorganic Ventures, Inc., Lakewood, NJ, USA) with 1% v/v HNO₃, and working standards of below 10 µg/L were prepared immediately before the measurement. Table 1 lists the elements contained in the multi-element stocks and their concentrations. All samples were analysed directly without further dilution with the exception of NIST 1640 which was also analysed following a 10-fold dilution.

Table 1: Multielement stock standards used for standard preparation

Solution	Concentration (mg/L)	Elements
Var-Cal-1	100	Sb, Mo, Sn, Ti
Var-Cal-2	100	Al, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, Th, U, V, Zn
Var-Major-1	500	Ca, Fe, Mg, K, Na

The internal standard stock solution (Var-IS-1) containing ⁶Li, Sc, In, Y, Tb and Bi was obtained from Inorganic Ventures, Inc. (Lakewood, NJ, USA). Reference waters were obtained from several sources. Standard Reference Materials SRM 1640 (Trace Elements in Natural Water), and SRM 1643e (Trace Elements in Water) were obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA). Japanese certified reference materials JSAC 0301-1 and JSAC 0302 (The Japan Society for Analytical Chemistry) were obtained from Seishin Trading Co., Ltd. (2-1, Sannomiya-Cho, 1-Chome, Chuo-Ku, Kobe, 650-0021 Japan). SLRS-4 (River Water Reference Material for Trace Metals) was purchased from the National Research Council of Canada (Institute for National Measurement Standards, M-12 Montreal Road Ottawa, Ontario, Canada K1A 0R6).

Standards Preparation

Calibration standards were prepared as summarized in table 2. All samples and standard reference materials were spiked with an internal standard solution, containing ⁶Li, Sc, In, Y, Tb and Bi at a concentration of 100 µg/L.

Conditions

The analysis conditions are summarized in Table 3.

Discussion

Environmental water samples (including drinking water) can vary widely in elemental and matrix composition. As

Table 2: Calibration Standard Preparation

Elements	Calibration Std. Conc. in µg/L
Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Ti, Tl, U, V, Zn	0.1, 1, 10, 100, 500
Ca, Fe, K, Mg, Na	100, 500, 1000, 10000, 50000
Fe	10, 100, 500, 1000, 10000, 50000

Table 3: ICP-MS Analysis Conditions

	Parameters	Settings
Gas flow (L/min)	Plasma flow	16.5
	Auxiliary flow	1.65
	Nebulizer flow	0.90
	Sheath flow	0.20
CRI Gases (mL/min)	Skimmer (with He)	160
	Skimmer (with H ₂)	100
RF	RF Power (kW)	1.28
Sample Introduction	Sampling depth (mm)	6.5
	Pump rate (rpm)	5
	Stabilization time (s)	60
	Spray chamber (°C)	3
Ion Optics (volts)	1st Extraction lens	-1
	2nd Extraction lens	-85
	3rd Extraction lens	-175
	Corner lens	-197
	Mirror lens left	25
	Mirror lens right	22
	Mirror lens bottom	25
	Entrance lens	0
	Entrance plate	-10
	Fringe bias	-1
Pole bias	0	
Quadrupole scan	Scan mode	Peak hopping
	Dwell time (ms)	20
	Points per peak	1
	Scans/Replicate	50
	Replicates/Sample	3

is well known, ICP-MS analyses are subject to a number of interferences from matrix elements. For this reason laboratories may choose to pre-screen samples prior to analysis by ICP-MS. Pre-screening is helpful in determining potential problematic matrix content, but can limit efficiency and productivity.

Laboratory efficiency and productivity can be enhanced through the processing of varying and unknown sample

matrices, within the same analytical sample run, without prescreening. This can be done through the use of CRI mode for elements subject to polyatomic overlaps. Data from reference standards indicates the viability of established conditions for aqueous analysis. Use of the CRI mode provides the assurance to run samples without having to predetermine the presence or concentration of potential interfering elements in varying sample matrix. Analytical results for the five standard reference waters are summarized in tables 4 to 6.

Iron is an interesting example as it has multiple possible interferents. Low level detection of iron can be important as certain regions of the world are required to meet very stringent regulations. One interferent is ArO⁺ which interferes with the most abundant isotope of iron (⁵⁶Fe). The use of the CRI with hydrogen effectively attenuates the ArO⁺, interference observed at mass 56. This is demonstrated in the results for the JSAC 0301-1 standard and NIST 1640 (10-fold dilution) where the impact of the ArO⁺ background is negligible even when measuring trace levels of Iron.

Table 4: Analysis results for JSAC 0301-0 and JSAC 0302

Analyte	JSAC 0301-1 (µg/L)			JSAC 0302 (µg/L)		
	Certified	Measured	% Recovery	Certified	Measured	% Recovery
⁹ Be		0.03		0.99	1.070	108
²³ Na	4400	4710	107	4330	4600	106
²⁴ Mg	2850	3020	106	2830	2940	104
²⁷ Al	19	20.2	106	67	66.9	99.9
³⁹ K	570	600	105	570	588	103
⁴⁴ Ca	12000	12100#	101	12200	12400#	102
⁵² Cr	0.15	0.16#	107	10.1	10.2#	100
⁵⁵ Mn	0.125	0.15@	119	5	5.25@	105
⁵⁶ Fe	4.7	5.42@	115	56	62.1@	111
⁶⁰ Ni		0.21		9.9	9.66	97.5
⁶⁵ Cu	0.57	0.68#	119.	10.3	10.5#	102
⁶⁸ Zn	0.19	0.51@*	269	10.2	11.1@	109
⁷⁵ As	0.24	0.29#	120	5.3	5.31#	100
⁷⁸ Se	0.13	0.12@	95.3	5	5.22@	105
⁹⁸ Mo	0.38	0.40#	106	0.38	0.37#	98.1
¹¹¹ Cd	0.0023	0.006*	278	1.01	1.06	105
¹³⁸ Ba	0.6	0.649	108	0.6	0.64	107
^{206,7,8} Pb	0.005	0.0091@	182.0	10.1	10.1@	100
²³⁸ U	0.0029	0.0032@	110	0.0029	0.0036@	126

Values displayed in **bold** were measured in CRI mode # with He and @ with H₂
*Suspected contamination

Table 5: Analysis results for NIST 1640

Analyte	NIST 1640 (µg/L)			1:10		1:1	
	Certified	Measured	% Recovery	Measured	% Recovery	Measured	% Recovery
⁹ Be	34.9	3.37	96.5	36.8	105		
²³ Na	29350	3170	108	32000	109		
²⁴ Mg	5819	610	105	6240	107		
²⁷ Al	52.0	5.4	107	50.0	96.2		
³⁹ K	994	91.2	91.7	964	96.9		
⁴⁴ Ca	7045	833#	119	7950#	113		
⁵¹ V	12.99	1.22#	93.6	12.4#	96.1		
⁵² Cr	38.6	3.63#	94.0	37.1#	96.0		
⁵⁵ Mn	121.5	12.9@	106	121@	99.9		
⁵⁶ Fe	34.3	4.36@	127	36.1@	105.		
⁵⁹ Co	20.28	2.09	103	20.4	101		
⁶⁰ Ni	27.4	2.72	99.1	26.4	96.2		
⁶⁵ Cu	85.2	7.93#	93.1	83.1#	97.6		
⁶⁸ Zn	53.2	5.35@	101	55.7@	105		
⁷⁵ As	26.67	2.64@	98.9	29.1@	109		
⁷⁸ Se	21.96	1.87@	85.2	23.4@	107		
⁹⁸ Mo	46.75	4.87#	104	45.2#	96.7		
¹⁰⁷ Ag	7.62	0.79	103	7.89	104		
¹¹¹ Cd	22.79	2.18	95.6	23.3	102		
¹²¹ Sb	13.79	1.38	100	15.0	109		
¹²³ Sb	13.79	1.39	101	15.1	110		
¹³⁸ Ba	148.0	15.4	104	153	103		
^{206,7,8} Pb	27.89	2.97	106.0	29.6	106		

Table 6: Analysis results for NIST 1643e and NRC SLRS-4

Analyte	NIST 1643e (µg/L)			NRC SLRS-4 (µg/L)		
	Certified	Measured	% Recovery	Certified	Measured	% Recovery
⁹ Be	13.98	13.2	94.4	0.007	0.027	386
²³ Na	20700	22060	106	2400	2407	100.
²⁴ Mg	8037	8530	106	1600	1660	103.
²⁷ Al	141.8	144	102	54	54.6	101
³⁹ K	2034	2120	104	680	676	99.5
⁴⁴ Ca	32300	33200#	103	6200	6420#	104
⁵¹ V	37.89	38.0#	100	0.32	0.351#	110
⁵² Cr	20.4	20.0	98.1	0.33	0.307#	93.0
⁵⁵ Mn	38.97	40.6@	104	3.37	3.44@	102
⁵⁶ Fe	98.1	117@	119	103	117@	114
⁵⁹ Co	27.06	26.8	98.9	0.033	0.043	131
⁶⁰ Ni	62.41	58.3	93.5	0.67	0.741	111
⁶⁵ Cu	22.76	21.0#	92.2	1.81	1.83#	101
⁶⁶ Zn	78.5	73.3@	93.4	0.93	0.995@	107
⁷⁵ As	60.45	62.2@	103	0.68	0.747@	110
⁷⁸ Se	11.97	11.9@	99.3	-		
⁹⁸ Mo	121.4	120#	99.2	0.21	1.08**	514
¹⁰⁷ Ag	1.062	1.02	95.9	-		
¹¹¹ Cd	6.568	6.23	95.6	0.012	0.015	122
¹²¹ Sb	58.3	58.6	100	0.23	0.289	126.
¹³⁸ Ba	544.2	534.0	98.0	12.2	13.8	113
²⁰⁵ Tl	7.445	7.62	102	-	0.007	
^{206,7,8} Pb	19.63	20.1	103	0.086	0.091	106
²³⁸ U	-	0.002		0.05	0.051	103

Another potential interferent on ^{56}Fe is calcium, present as CaO^+ . Calcium levels can vary significantly based on the type/source of water samples. The use of CRI can also effectively reduce the CaO^+ interference on ^{56}Fe to insignificant levels interference on ^{56}Fe . Fig.2 shows the recovery of $1\mu\text{g/L}$ Fe in various calcium concentration levels.

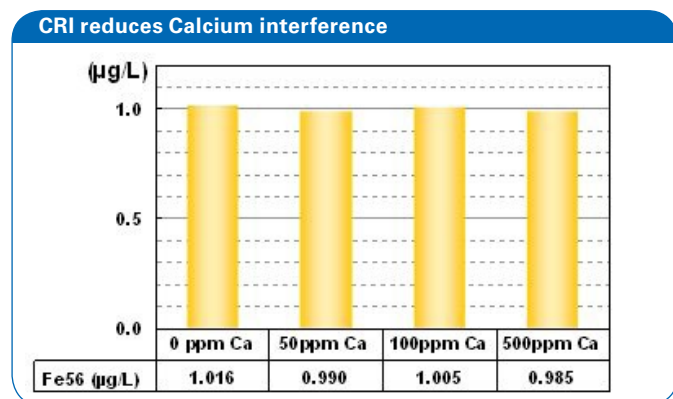


Figure 2: Recovery of $1\mu\text{g/L}$ Fe in various Ca concentrations

Conclusion

This work shows that the 820-MS excels at providing a simple and effective solution for the successful analysis of waters in widely varying matrices.

The lowest detection limits can be achieved while assuring no polyatomic overlap contribution on analyte signal in "real world" samples which often have unknown elemental matrix constituents.

Detection limits are significantly improved for As, Se and Fe using the CRI option. Finally use of the CRI gases for low mass analytes provides a means of attenuating polyatomic interferences allowing accurate analyses of widely varying environmental waters.

References

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Keywords

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Instrumentation & Software

Bruker 820-MS
SPS3 autosampler
ICP-MS Expert Software

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