

Fast, Accurate Analysis of 28 Elements in Water using ISO Method 17294-2 for ICP-MS

Agilent 7850 ICP-MS controls polyatomic and doubly charged interferences to deliver long-term accuracy and reproducibility in diverse water samples



Authors

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Introduction

The international standard method ISO 17294 outlines the analysis of elements in water samples using ICP-MS (1, 2). Part 1 (2004) provides general directions for the use of the ICP-MS technique. And part 2 (2016) describes the determination of trace and major elements in samples such as drinking waters, surface waters, ground waters, and wastewaters. The list of more than 60 elements specified in ISO 17294-2:2016 includes many novel contaminants, such as rare earth elements (REEs). REEs are increasingly being used in new industrial processes and products, leading to increasing interest in their distribution and fate in the environment. Potential sources of REE contamination include pollution from mining activities, oil refining, disposal of electronic devices, transport, agriculture, and hospital waste. As a result, surface and groundwater and other environmental samples may contain elevated levels of the REEs.

The REEs have low second ionization potentials, meaning that it is relatively easy for them to form doubly charged (M^{2+}) ions in the plasma. In quadrupole ICP-MS, ions are separated based on their mass to charge ratio (m/z), so REE^{2+} ions appear at half their true mass, where they can cause spectral overlaps on As and Se (3).

In addition to developing methods to meet new regulations and ensure data quality in variable sample types, environmental testing laboratories also face the challenge of managing the sample-testing workflow. Commercial laboratories often analyze hundreds of samples every day for a range of potential contaminants, so maintaining a high level of productivity and data quality is vital to the success of the lab. Labs can benefit from reducing the time required for key steps of the analytical workflow – from preparing calibration standards and samples, developing methods, performing daily checks, reviewing data, and reporting results.

The Agilent 7850 ICP-MS meets these requirements with easy to use, standardized methodology that delivers fast, accurate, and reproducible results for major and trace analytes in a variety of environmental samples. The 7850's Octopole Reaction System (ORS⁴) cell technology uses an optimized helium (He) collision mode to remove the polyatomic ion interferences that affect many analytes in typical, routine applications. The ICP-MS MassHunter instrument control software includes an easy to use, automated Method Wizard that sets the acquisition and data analysis parameters needed for the correction of doubly charged ion interferences. M^{2+} correction ensures that unknown samples—even samples that contain REEs—can be analyzed successfully without needing a reactive cell gas to resolve M^{2+} overlaps, simplifying the method and improving productivity.

In this study, the 7850 ICP-MS was used to analyze 28 elements in various natural water, mineral water, and tap water samples according to ISO 17294-2. Two natural water certified reference materials (CRMs) were spiked with REEs to evaluate the M^{2+} correction feature of ICP-MS MassHunter for accurate analysis of As and Se.

Experimental

Instrumentation

An Agilent 7850 ICP-MS equipped with the standard Ultra High Matrix Introduction (UHMI) system and ORS⁴ cell was used for the analysis. Automated sampling was performed using an Agilent SPS 4 autosampler. The standard MicroMist nebulizer, Scott-type spray chamber, and one-piece quartz torch with 2.5 mm id injector were used. The interface consisted of a nickel-plated copper sampling cone and a nickel skimmer cone.

The ORS⁴ uses a small cell volume and octopole ion guide for optimum performance in He collision mode. ORS⁴ He mode reduces the transmission of all polyatomic ions, minimizing errors due to common matrix-based polyatomic interferences. An enhanced He mode is also available to deal with overlaps from high intensity background species, such as Ar_2 on Se at m/z 78, N_2 on ^{28}Si , and NO/NOH on ^{31}P , without the need to use a potentially hazardous reactive cell gas such as O_2 , H_2 , or NH_3 (4). Avoiding reactive cell gases not only simplifies operation but also ensures that no new molecular interferences are formed in the cell, improving data quality, particularly for multi-element methods and unknown sample matrices.

In this work, most elements were measured in He mode, while Se was measured in enhanced He mode. For optimum detection limits, Li, Be, and B were measured in no gas mode. If analytical speed is a higher priority than achieving the lowest detection limits, these elements can also be measured successfully in He mode.

To create an analytical method quickly and easily, analysts can use the ICP-MS MassHunter Method Wizard. The Method Wizard guides users through a series of questions to select analytes and internal standard elements (often using predefined lists). For this application a "General Purpose" preset method was selected, which includes robust plasma conditions (low CeO^+/Ce^+ ratio). Selecting " M^{2+} Correction" in the Method Wizard automatically sets all the parameters needed for the correction, making it fast to set up and easy to use. The parameters include which masses to measure, peak resolution (narrow peak mode), and correction equations. In this method, M^{2+} correction was applied to the measurement of As and Se to correct the contribution from REE^{2+} ions.

The parameters in the shaded rows in Table 1 were predefined in the preset method, and lens voltages were autotuned.

Table 1. 7850 ICP-MS operating conditions.

ICP-MS Parameter	No Gas Mode	Helium Mode
Plasma Mode	General purpose	
RF Power (W)	1550	
Spray Chamber Temp (°C)	2	
Sampling Depth (mm)	10	
Nebulizer Gas Flow (L/min)	1.09	
Dilution Gas Flow (L/min)	0.0	
Lens Tune	Autotune	
Cell Gas Flow (mL/min)	0.0	4.3 (10*)
Energy Discrimination (V)	5.0	5.0 (7.0*)
Number of Elements	3 analytes, 1 ISTD	25 analytes, 5 ISTDs

The shaded parameters are defined automatically by the preset plasma conditions.

**Enhanced He mode settings used for Se.*

Standard and sample preparation

The calibration standards and samples were prepared in an acid matrix of 1% HNO₃ and 0.5% HCl. The inclusion of HCl ensures the long-term stability of elements such as Hg, Ag, Sn, Sb, and Mo. Calibration standards for most elements were prepared using the Agilent Environmental Calibration Standard (part number 5183-4688) multi-element stock solution. Single element standards were used for Li, B, and Hg (Kanto Chemicals, Japan) and P (SPEX CertiPrep, Metuchen, NJ, USA). Six-point calibrations including calibration blank were prepared at the following concentrations ranges: 0.1 to 100 ppb for trace elements; 10 to 10,000 ppb for Na, Mg, K, Ca, and Fe; 1 to 1,000 ppb for P; 0.01 to 2 ppb for Hg.

The diluent, 1% HNO₃ and 0.5% HCl, was used as the continuing calibration blank (CCB) sample. A mid-concentration calibration standard was used as the quality control (QC) sample with trace elements at 50 ppb, mineral elements at 5000 ppb, P at 500 ppb, and Hg at 1 ppb. The CCB and QC check were repeated periodically throughout the sample sequence.

The internal standard (ISTD) solution containing 1 ppm Sc, Ge, Rh, In, Ir, and Bi was added automatically using the standard ISTD mixing connector. The ISTD flow rate was approximately 15 times less than the sample flow rate, due to the use of different internal diameter pump tubing.

The CRMs used in the analysis were NIST 1640a Natural Water (NIST, Gaithersburg MD) and SLRS-6 River Water CRM for Trace Metals and other Constituents (National Research Council of Canada, Ottawa, Canada). Each CRM was prepared undiluted and 2x diluted.

The spike recovery test was performed according to the ISO 17294-2 method. Matrix spike samples were prepared by spiking the two 2x diluted CRMs with trace elements at 10 ppb, mineral elements at 1000 ppb, P at 100 ppb, and Hg at 0.2 ppb. To test the M²⁺ correction function in ICP-MS MassHunter, the undiluted SRM 1640a sample was spiked with 100 ppb Nd and Sm, and 10 ppb Gd and Dy.

Two brands of bottled water (sample A and sample B) and a tap water (sample C) were also analyzed in this study. The samples were analyzed repeatedly with periodic insertion of a QC and CCB standard after every 10 samples.

Results and discussion

Method detection limits

All analytes were measured using the 7850 ICP-MS acquisition parameters listed in Table 1. Three sigma method detection limits (MDLs) and 10 sigma Limit of Quantitation (LOQs) were calculated from 10 measurements of the blank (Table 2). The LOQs obtained for the critical trace analytes were significantly below the specifications in ISO 17294-2, confirming the high sensitivity and good control of polyatomic overlaps of the 7850 ICP-MS. The LOQ of K was a little higher than specified in ISO 17294-2, due to contamination of the blank.

Table 1. 10 sigma method LOQs compared to the requirements specified in ISO 17294-2.

Element and Mass Number	Gas Mode	LOQ (ppb)	ISO Method Specs (ppb)
7 Li	No gas	0.004	1
9 Be	No gas	0.003	0.1
11 B	No gas	0.088	1
23 Na	He	1.47	10
24 Mg	He	0.290	1
27 Al	He	0.313	1
31 P	He	0.573	5
39 K	He	7.335	5
44 Ca	He	8.972	50
51 V	He	0.028	0.1
52 Cr	He	0.030	0.1
55 Mn	He	0.035	0.1
56 Fe	He	0.103	5
59 Co	He	0.010	0.2
60 Ni	He	0.056	0.1
63 Cu	He	0.028	0.1
66 Zn	He	0.205	1
75 As	He	0.018	0.1
78 Se	He*	0.055	0.1
95 Mo	He	0.004	0.5
107 Ag	He	0.007	0.5
111 Cd	He	0.002	0.1
121 Sb	He	0.043	0.2
137 Ba	He	0.060	3
202 Hg	He	0.004	0.05
205 Tl	He	0.026	0.1
Pb**	He	0.007	0.1
238 U	He	0.0004	0.1

* Enhanced He mode. **Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208.

Correcting M²⁺ interferences on As and Se

The M²⁺ ions of the REEs such as neodymium (Nd), samarium (Sm), gadolinium (Gd), and dysprosium (Dy) appear between *m/z* 65 and 82 where they can overlap the singly charged ions of As and Se. For example, ¹⁵⁰Nd²⁺ and ¹⁵⁰Sm²⁺ would overlap ⁷⁵As⁺, and ¹⁵⁶Gd²⁺ and ¹⁵⁶Dy²⁺ would overlap ⁷⁸Se⁺. If the analyst is not aware of the presence of REEs in a sample, the M²⁺ interferences could lead to false positive results being reported for As and Se (3).

As and Se were measured in He mode, with M²⁺ correction applied and the calibration curves, prepared in 1% HNO₃ and 0.5% HCl, are shown in Figure 1. The calibrations confirm the linearity, good precision, and effective control of Cl-based polyatomic interferences (low BEC) for As and Se using this method.

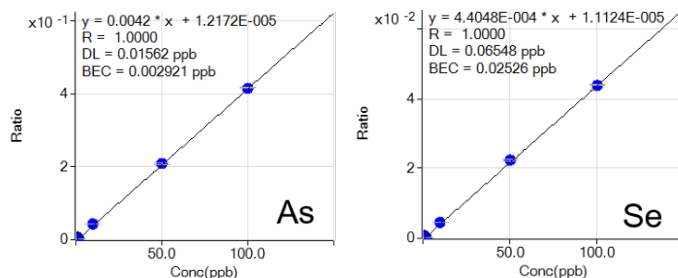


Figure 1. Calibration curves of As and Se acquired under M²⁺ correction conditions.

The 7850 ICP-MS—with and without M²⁺ correction—was used to measure As and Se in NIST SRM 1640a water spiked with REEs. The darker shading for Nd, Sm, Gd, and Dy in the IntelliQuant “heat map” display for the spiked sample, shown in Figure 2, clearly indicates the presence of REEs.

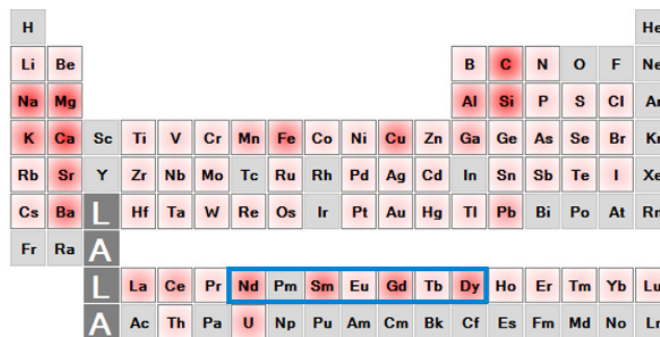


Figure 2. IntelliQuant heat map confirming the presence of Nd, Sm, Gd, Dy in REE spiked SRM 1640a.

Recoveries of the certified values for As in the presence of 100 ppb Nd and Sm and for Se in the presence of 10 ppb Gd and Dy are shown in Figure 3. Without M²⁺ correction, the contribution of the REE²⁺ overlaps led to high recoveries for As and Se. However, by applying automated M²⁺ correction, the accuracy for both elements was improved significantly – with recoveries within ±3% of the certified values.

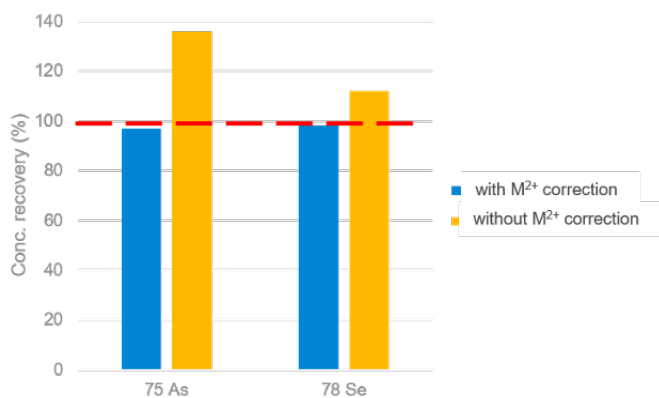


Figure 3. Recovery of ⁷⁵As and ⁷⁸Se in SRM 1640a spiked with REEs, with M²⁺ correction (blue bars) and without M²⁺ correction (yellow bars).

ISTD recovery (%)

As a long-term stability test, two bottled water samples and one tap water were repeatedly measured during a sequence lasting eight hours. All the ISTD recoveries were within $\pm 20\%$ throughout the sequence, demonstrating the robustness and stability of the method (Figure 4). The ISTD stability shows that the 7850 ICP-MS method continued to produce reliable data with no retuning or recalibration over a typical 8-hour shift. Agilent ICP-MS MassHunter software includes a function to run a post run performance check at the end of the analytical sequence. This check enables the analyst to confirm the status of the instrument before starting work the next morning. Based on the minimal loss of ISTD sensitivity, it is likely that the post run tune check would indicate that no maintenance would be required before starting the next day's analysis.

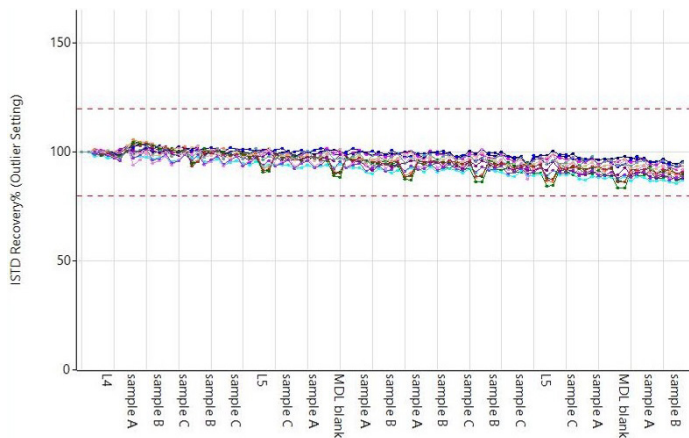


Figure 4. Stability of ISTD signals over eight hours analysis of varied water samples. The ISTD recoveries have been normalized to the calibration blank for all samples. Not all sample names are shown due to limited space.

QC recovery (%)

The continuing QC sample was analyzed after every 10 samples and, as specified in the ISO method, the recovery limits were set to $\pm 10\%$. If the measured concentration falls outside the limit, recalibration is needed. All the elements measured in the QC samples met the method criteria, with no QC failures, as shown in Figure 5.

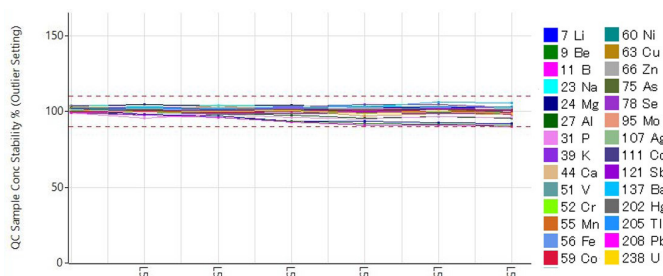


Figure 5. QC recoveries over the course of the 8-hour analytical sequence.

Accurate analysis in undiluted and spiked CRMs

The CRMs SLRS-6, 1640a, and 1640a spiked with REEs were analyzed undiluted. Each sample was measured six times over the sequence and the mean concentrations and recoveries were calculated for each analyte (Table 3). Not all reference materials are certified for all analytes, and blank cells indicate the absence of a certified value. Excellent recoveries of between 89 and 108% of the certified values were obtained for all analytes in this analysis, except for Cd in SLRS-6. The certified concentration of Cd in this sample (at 6.3 ± 1.4 ppt) is below the LOQ required in ISO 17294-2. The good recoveries of all elements in the 1640a sample spiked with the REEs confirm that M²⁺ correction did not affect the accuracy of analysis of any of the elements.

Matrix spike recoveries in 2x diluted water CRMs

Table 4 shows that the matrix spike recoveries in the two CRMs were between 91 and 105% for all elements – including Cd, which was below the method LOQ in the unspiked sample. The results show the high accuracy of the method.

Table 3. Mean measured values and mean recoveries for certified elements in three undiluted CRM samples.

Element	SLRS-6			1640a			1640a + REEs	
	Mean Measured Concentration (ppb)	Certified Value (ppb)	Recovery (%)	Mean Measured Concentration (ppb)	Certified Value (ppb)	Recovery (%)	Mean Measured Concentration (ppb)	Recovery (%)
7 Li	0.481	-	-	0.399	0.4034 ± 0.0092	99	0.383	95
9 Be	0.006	0.0066 ± 0.0022	98	2.84	3.002 ± 0.027	95	2.82	94
11 B	6.07	-	-	278	300.7 ± 3.1	92	276	91
23 Na	2620	2770 ± 220	95	3040	3112 ± 31	98	2970	95
24 Mg	2060	2137 ± 58	97	1010	1050.2 ± 3.4	96	990	94
27 Al	31.0	33.8 ± 2.2	92	52.0	52.6 ± 1.8	98	50.4	95
31 P	2.23	-	-	4.38	-	-	4.57	-
39 K	607	651 ± 54	93	569	575.3 ± 2	99	555	96
44 Ca	8180	8770 ± 200	93	5840	5570 ± 16	105	5730	103
51 V	0.335	0.352 ± 0.006	95	14.1	14.93 ± 0.21	95	13.7	92
52 Cr	0.232	0.252 ± 0.012	92	38.0	40.22 ± 0.28	94	37.2	92
55 Mn	2.06	2.12 ± 0.1	97	38.9	40.07 ± 0.35	97	38.1	95
56 Fe	80.3	84.5 ± 3.6	95	36.6	36.5 ± 1.7	100	35.7	98
59 Co	0.057	0.053 ± 0.012	108	19.1	20.08 ± 0.24	95	18.6	93
60 Ni	0.551	0.617 ± 0.022	90	23.6	25.12 ± 0.12	94	23.1	92
63 Cu	24.3	24 ± 1.8	102	81.8	85.07 ± 0.48	96	79.8	94
66 Zn	1.71	1.76 ± 0.12	97	53.2	55.2 ± 0.32	96	52.1	94
75 As	0.536	0.57 ± 0.08	94	7.66	8.01 ± 0.067	96	7.78	97
78 Se	0.087	-	-	19.9	19.97 ± 0.16	100	19.4	97
95 Mo	0.192	0.215 ± 0.018	89	41.9	45.24 ± 0.59	93	41.6	92
107 Ag	<0.007	-	-	7.38	8.017 ± 0.042	92	7.29	91
111 Cd	0.008	0.0063 ± 0.0014	129	3.66	3.961 ± 0.072	92	3.62	91
121 Sb	0.316	0.3377 ± 0.0058	94	4.69	5.064 ± 0.045	93	4.62	91
137 Ba	13.3	14.3 ± 0.48	93	143	150.6 ± 0.74	95	142	94
202 Hg	<0.004	-	-	0.004	-	-	0.002	-
205 Tl	<0.026	-	-	1.58	1.606 ± 0.015	98	1.56	97
Pb**	0.164	0.17 ± 0.026	97	11.9	12.005 ± 0.04	99	11.8	98
238 U	0.065	0.0699 ± 0.0034	93	22.8	25.15 ± 0.26	90	22.5	89

The shaded rows indicate that As and Se data were determined using M^{2+} correction. ** Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208.

Table 4. Matrix spike (MS) recoveries for 2x diluted SLRS-6 and 1640a.

Element	SLRS-6			1640a		
	Mean Concentration (ppb)	Mean Concentration Spike (ppb)	Recovery (%)	Mean Concentration (ppb)	Mean Concentration Spike (ppb)	Recovery (%)
7 Li	0.275	10.5	102	0.19	10.1	99
9 Be	0.004	9.96	100	1.43	11.0	96
11 B	3.67	13.1	95	142	151	93
23 Na	1370	2400	103	1560	2530	97
24 Mg	1050	2060	101	504	1480	97
27 Al	16.4	26.2	98	25.4	34.6	92
31 P	0.539	9.87	93	2.42	11.7	93
39 K	309	1330	102	285	1260	97
44 Ca	4260	5280	102	2880	3850	97
51 V	0.166	10.2	100	7.04	16.4	94
52 Cr	0.118	10.2	100	19.0	28.3	94
55 Mn	1.04	11.1	100	19.2	28.9	97
56 Fe	41.9	1070	103	18.2	985	97
59 Co	0.033	10.2	101	9.58	19.0	95
60 Ni	0.186	10.4	101	11.8	21.1	93
63 Cu	12.8	23.0	102	41.0	50.1	91
66 Zn	0.765	11.1	103	26.6	35.9	93
75 As	0.288	10.4	101	3.73	13.4	97
78 Se	0.05	10.3	102	9.92	20.1	102
95 Mo	0.113	10.1	100	21.3	30.7	95
107 Ag	0.004	10.2	102	3.75	12.9	91
111 Cd	0.005	10.2	102	1.85	11.3	94
121 Sb	0.156	10.4	102	2.36	11.9	95
137 Ba	6.72	16.9	102	71.1	80.7	96
202 Hg	0.005	0.201	98	0.001	0.194	96
205 Tl	0.006	10.5	105	0.770	10.8	100
Pb**	0.089	10.6	105	5.86	15.7	98
238 U	0.035	10.4	103	11.3	20.7	94

The shaded rows indicate that As and Se data were determined using M^{2+} correction. **Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208.

Conclusion

The Agilent 7850 ICP-MS was used to measure 28 elements in environmental waters, bottled water, and tap water, easily meeting the detection limit and QC requirements defined in ISO 17294-2.

The 7850 removes many of the common time-consuming and unproductive activities in the analytical workflow. The Method Wizard and autotuning—included in the ICP-MS MassHunter software—were used to simplify and speed up instrument setup and development of the method. The robust plasma (low CeO/Ce ratio) ensured that variable water sample matrices could be analyzed reproducibly over a long sample sequence, without requiring matrix matching of the calibrations. The robust operating conditions also ensured that stable analysis was maintained throughout the working day, with no retuning or recalibration required during the eight-hour sequence. For busy routine laboratories, the post run performance check feature helps with scheduling essential maintenance, ensuring that high performance is maintained while avoiding unnecessary downtime during the working week.

The consistent ORS⁴ He collision mode provided reliable and effective removal of common polyatomic overlaps, ensuring that all analytes were measured accurately, free from interferences. M²⁺ correction automatically applied all method acquisition parameters and data analysis settings required to correct for REE doubly charged ion overlaps. The combination of He mode and M²⁺ correction provides reliable analysis using standard conditions, without requiring extensive, time-consuming, sample-specific method setup or the use of reactive cell gases. M²⁺ correction reduced setup time and improved the accuracy of As and Se in the presence of REE²⁺ interferences, with no adverse effect on the measurement of the other elements.

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