Routine soil analysis using an Agilent 8800 ICP-QQQ

Application note

Environmental

Authors

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Introduction

Quadrupole ICP-MS (ICP-QMS) is one of the most widely used analytical techniques in inorganic testing laboratories, due to its performance characteristics of high sensitivity, low detection limits, wide dynamic range, and high speed multi-element analysis.

Recent advances have seen a dramatic improvement in matrix tolerance: Agilent's High Matrix Introduction (HMI) technology uses aerosol dilution to reduce the sample matrix load on the plasma, ensuring that much higher matrix levels—up to % levels of total dissolved solids (TDS)—can be analyzed routinely.

Control of interferences has also been improved significantly, with Agilent's octopole-based collision/reaction cell (CRC) operating in helium (He) collision mode to eliminate a wide range of matrix based polyatomic interferences using one set of cell conditions [1]. Reliable and accurate quantitation of all required elements at the regulated levels in a wide variety of sample matrices is now possible using ICP-QMS. However, some

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applications require greater sensitivity for some specific elements, while some complex sample matrices may cause spectral interferences that remain a challenge.

Improved interference removal with ICP-QQQ
The Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) is a new type of ICP-MS that was first commercialized in 2012. With its unique tandem MS configuration, comprising two scanning quadrupole mass analyzers either side of an octopole-based collision reaction cell, the Agilent 8800 is able to use MS/MS mode to resolve difficult spectral interferences [2]. The improved control of reaction cell chemistry offered by MS/MS mode has meant that the instrument has found widespread acceptance in industry and research labs in fields such as semiconductor device and high purity chemical/material manufacturing, life-science, geoscience, radio-nuclides and many others [3-5].

MS/MS mode can also be beneficial for the more difficult elements and problematic interferences sometimes encountered in routine applications such as the analysis of soils, waste water, groundwater, and food samples. The Agilent 8800 ICP-QQQ has matrix tolerance and robustness comparable to Agilent quadrupole ICP-MS systems, so the instrument can be used to analyze high-matrix samples such as soil, ground water and food digests routinely.

Solving problems associated with As and Se analysis
Many countries regulate the permitted concentrations of arsenic (As) and selenium (Se) in drinking water, surface water, soils, and foodstuffs. Arsenic is a well-known toxic element which is also carcinogenic to humans. Se is known to be an essential element for humans, but can be toxic in excess. The preferred isotopes of both As and Se can suffer spectral interferences from polyatomic ions including $ArCl^+$, $CaCl^+$, $ArAr^+$, GeH^+, and BrH^+. These interferences can be reduced using ICP-QMS operating in He mode, allowing the accurate and precise measurement of As and Se at the concentration levels required to meet typical regulatory demands.

Removal of doubly charged REE interferences
He mode can be considered a universal cell gas for reducing polyatomic interferences using kinetic energy discrimination (KED), but KED is not effective against doubly-charged ion overlaps. A quadrupole mass analyzer separates ions based on their mass to charge ratio (*m/z*), so a doubly-charged ion appears at half its true mass. The isotopes normally used for the determination of As (at *m/z* 75) and Se (at *m/z* 78 or 80) can therefore suffer overlap from the doubly charged ions of rare earth elements (REE) with isotopes at *m/z* 150, 156 and 160 (^{150}Nd, ^{150}Sm, ^{156}Gd, ^{156}Dy, ^{160}Gd, and ^{160}Dy). The presence of these REEs in the sample can therefore lead to errors in As and Se determination, especially when the levels of As and Se are low relative to the REE content. One example is the determination of Se in soil, as illustrated by the analysis of the certified reference material (CRM) National Institute of Standards and Technology (NIST) 1646a, shown in Figure 1. The result obtained for Se in He mode was about 3x the certified value of 0.193 ppm (in the original solid material). A semi-quantitative analysis revealed that the digested CRM sample contained a significant concentration of gadolinium (Gd); the doubly-charged ions ($^{154}Gd^{++}$), $^{156}Gd^{++}$ and $^{160}Gd^{++}$ overlap ($^{77}Se^+$), $^{78}Se^+$ and $^{80}Se^+$ respectively, causing false positive errors.

Arsenic (monoisotopic at *m/z* 75) also suffers doubly-charged interference from REEs $^{150}Sm^{++}$ and $^{150}Nd^{++}$. To avoid the REE^{++} overlaps, an alternative mode can be used to measure As and Se using oxygen (O_2) cell gas. Using MS/MS and mass shift mode, the reaction product ions formed in the cell (AsO^+ at *m/z* 91 and SeO^+ at *m/z* 94 or 96) are measured, free from REE^{++} overlaps. MS/MS is required for accurate results in this mode, as the first quadrupole (Q1) must operate as a mass filter to remove any existing ions that might overlap the newly-formed product ions (e.g. $^{91}Zr^+$ on $^{75}As^{16}O^+$, and $^{94}Mo^+$ on $^{78}Se^{16}O^+$).

As can be seen in Figure 1, MS/MS mode using mass shift with O_2 reaction gas successfully avoided the doubly-charged interferences allowing consistent, low-level determination of Se measured as $^{78}SeO^+$ and $^{80}SeO^+$ at *m/z* 94 and 96 respectively. The recoveries in O_2 mode are a little lower that the certified value due to the fact that an acid extraction was used, rather than a total digestion with hydrofluoric acid (HF).
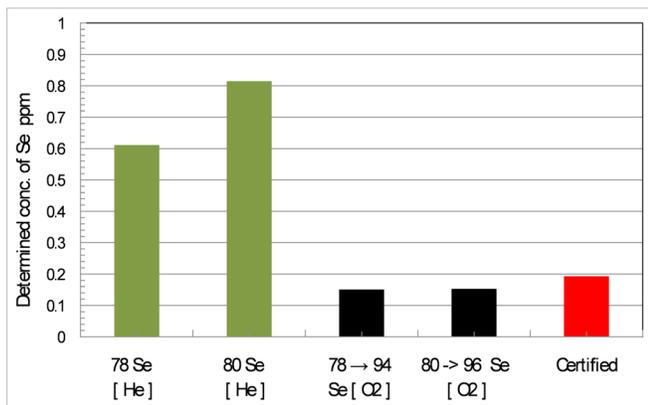
Figure 1. Measured concentration of Se in NIST 1646a. He mode (green bars), O_2 mass shift mode (black bars) and certified value (red bar). These results were obtained without using HF in the digestion procedure.

A similar mass-shift approach using O_2 cell gas and MS/MS mode on the 8800 ICP-QQQ was used to determine As and Se in NIST 1547 Peach Leaves and NIST 1515 Apple Leaves, which contain low µg/kg levels of As and Se in the presence of mg/kg levels of REEs [6].

Typically, the REE content of environmental samples is low, but the use of MS/MS mode with O_2 reaction cell gas for the determination of As and Se avoids the potential risk of overestimating the concentration of these two important elements in the case of an unexpectedly high level of REEs.

In this study, the Agilent 8800 ICP-QQQ was evaluated as a the routine tool for the analysis of 28 elements, including As and Se, in soil and sediment digests.

Experimental

Instrumentation

A standard Agilent 8800 ICP-QQQ equipped with a quartz spray chamber, glass concentric nebulizer, on-line internal standard (ISTD) addition kit, and Ni interface cones was used. HMI technology is standard on the Agilent 8800, allowing %-level matrix samples such as undiluted seawater to be analyzed [7]. The plasma conditions were selected according to the sample type and expected matrix level using the "Preset plasma" function of ICP-MS MassHunter software. Preset plasma condition HMI-4, where the number 4 represents the approximate aerosol dilution factor, was used for this analysis.

Acquisition conditions

For the multi-element analysis of the soil samples, a multi-tune method was used so all elements could be acquired in the optimum cell gas mode. He mode was used for all elements apart from S, Se and As, which were determined in O_2 mode. The method was based on the standard preset method for soil samples ("EPA6020"), which was modified to include O_2 cell gas mode. Preset plasma condition "HMI-4" was selected, to provide robust plasma conditions with a Ce oxide ratio of 0.4-0.5%, suitable for the analysis of soil digests and ground waters. The HMI setting automatically applies the predefined and calibrated parameters for RF power, sampling depth, carrier gas flow rate and dilution gas flow rate, giving precise and consistent plasma conditions for the target sample types. The lens voltages were auto-tuned for maximum sensitivity. Table 1 summarizes the instrument operating parameters.

Table 1. Agilent 8800 ICP-QQQ operating conditions

Parameter	Setting	
	He mode	O_2 mode
Plasma conditions	HMI-4	
RF power (W)	1600	
Sampling depth (mm)	10	
Carrier gas flow rate (L/min)	0.57	
Dilution gas flow rate (L/min)	0.34	
Extract 1 (V)	0	
Extract 2 (V)	-200	
Omega lens (V)	8.0	
Omega bias (V)	-115	
Cell gas flow (mL/min)	5.0	0.3 (30% of full scale)
KED (V)	5	-7

Shaded parameters were predefined by selecting preset plasma condition HMI-4.

Reagents
Certified Reference Materials

Five soil and sediment CRMs purchased from High-Purity Standards Inc. (Charleston, SC, USA) were analyzed in this study. These included CRM River Sediment A, CRM River Sediment B, CRM Estuarine Sediment, CRM Soil A and CRM Soil B.

Standards

Calibration standards were prepared from an Agilent multi-element environmental calibration standard (p/n 5183-4688) which contains 1000 ppm each of Fe, K, Ca, Na, Mg, and 10 ppm each of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, and Zn. The mercury calibration was prepared from an Atomic Absorption grade single element Hg standard purchased from Kanto Chemicals (Tokyo, Japan). Sulfur and phosphorus calibrations were prepared from Spex single element S and P standards (SPEX CertiPrep, NJ, USA). The ISTD solution was prepared from an Agilent internal standard stock solution for ICP-MS systems (p/n 5188-6525), which was diluted 250 fold and added to the sample via the on-line ISTD kit. All solutions were prepared in 1% HNO_3 and 0.5% HCl using electronics (EL) grade acids from Kanto Chemicals.

The calibration range was 0 to 100 ppb for most elements, 0 to 2 ppb for Hg and 0 to 10 ppm for Na, Mg, Al, P, S, K, Ca and Fe.

Sample analysis and quality control protocol

The sequence consisted of an initial multi-level calibration, covering the typical range for the target analytes, followed by a QC block containing an Initial Calibration Blank (ICB) check, Low Level Initial Calibration Verification (LLICV) solution and Initial Calibration Verification (ICV) solution. After calibration and initial QC check, thirteen sample blocks were analyzed per the flow chart shown in Figure 2; each block consisted of 10 samples (2 each of Soil A, Soil B, Estuarine Sediment, River Sediment A, River Sediment B). A Periodic Block consisting of Continuing Calibration Blank (CCB) and Continuing Calibration Verification (CCV) samples was automatically inserted into the sequence after each set of 10 real samples.
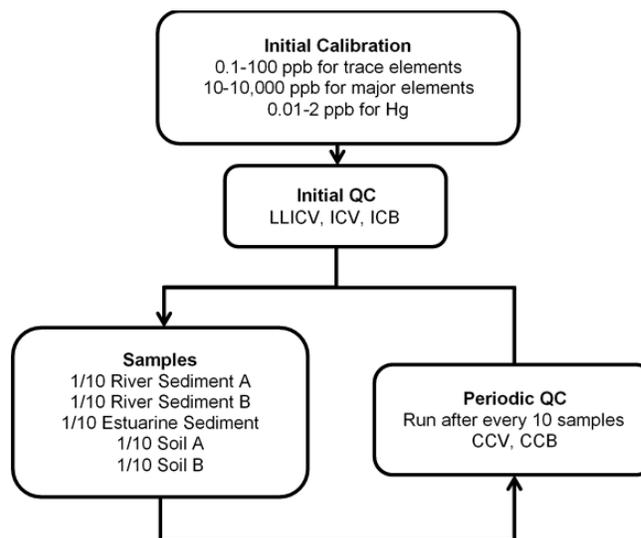
Figure 2. Sequence of calibrants, samples, and QC solutions analyzed in a single 12 hour sequence. Sample Block was repeated continuously with automatic insertion of Periodic QC Block after every 10 sample runs.

The total number of analyses of calibration standards, QC samples and soil samples was 177 over ~12 hours. The sample-to-sample run time was about 4 minutes which included a 15 s probe rinse and 50 s sample introduction system rinse.

Table 2 details the selected isotopes, integration times, ISTD reference elements, and method performance figures for all of the analytes measured.

Table 2. Details of elements analyzed

Analyte	Isotope	Cell mode	Integration time (sec)	ISTD	LLICV (ppb)	LLICV recovery (%)	MDL (ppb)	PQL (ppb)
Be	9	He	3	6 Li	0.5	94	0.06	0.18
Na	23	He	0.1	45 Sc	10	103	0.98	2.9
Mg	24	He	0.1	45 Sc	10	106	0.73	2.2
Al	27	He	0.1	45 Sc	10	99	1.00	3.0
P	31	He	1	45 Sc	20	93	3.20	9.6
K	39	He	0.1	45 Sc	50	123	7.50	22.5
S	32	O_2 (32 $\rightarrow$ 48)	0.1	74 $\rightarrow$ 90 Ge	20	104	4.10	12
Ca	44	He	0.1	45 Sc	100	87	2.70	8.1
V	51	He	0.3	74 Ge	0.2	118	0.021	0.063
Cr	52	He	0.3	74 Ge	0.5	128	0.040	0.12
Mn	55	He	0.3	74 Ge	0.5	97	0.062	0.19
Fe	56	He	0.1	74 Ge	10	115	0.45	1.4
Co	59	He	0.3	74 Ge	0.1	104	0.017	0.051
Ni	60	He	0.3	74 Ge	0.2	115	0.049	0.15
Cu	63	He	0.3	74 Ge	0.1	91	0.021	0.063
Zn	66	He	0.3	74 Ge	0.2	80	0.063	0.19
As	75	O_2 (75 $\rightarrow$ 91)	1	74 $\rightarrow$ 90 Ge	0.2	123	0.024	0.072
Se	78	O_2 (78 $\rightarrow$ 94)	3	74 $\rightarrow$ 90 Ge	0.2	120	0.049	0.15
Mo	95	He	0.3	115 In	0.1	105	0.022	0.066
Ag	107	He	0.3	115 In	0.1	111	0.015	0.045
Cd	111	He	3	115 In	0.1	104	0.012	0.036
Sb	121	He	0.3	115 In	0.1	107	0.011	0.033
Ba	135	He	0.3	115 In	0.2	95	0.055	0.17
Hg	201	He	1	193 Ir	0.01	92	0.003	0.009
Tl	205	He	0.3	175 Lu	0.1	107	0.008	0.024
Pb	208	He	0.3	175 Lu	0.1	94	0.009	0.027
Th	232	He	0.3	175 Lu	0.1	97	0.007	0.021
U	238	He	0.3	175 Lu	0.1	102	0.009	0.027

Results and discussion

Method detection limits (MDL), practical quantitation limits (PQL) and LLICV recovery

The MDL for each element was calculated as 3 times the standard deviation of 10 replicates of the low level standard (trace elements: 0.1 ppb, mineral elements: 10 ppb, Hg: 0.01 ppb). PQLs were calculated as 3x the MDL. The results are summarized in Table 2. The method provided excellent sensitivity (PQLs for most elements were in the ppt range), under operating conditions that also provided high matrix tolerance. The LLICV check results are also given in Table 2, demonstrating that recoveries for all elements were within the ±30% required by EPA 6020A.

ISTD and CCV stability

Figure 3 shows the ISTD signal stability for 130 soil and sediment samples analysis over 12 hours. The ISTD recoveries for all samples were well within the EPA6020 requirements of between 30% and 120% of the value in the initial calibration standard. These ISTD recoveries are comparable to the results obtained routinely using ICP-QMS, demonstrating the equivalent robustness of ICP-QQQ to ICP-QMS.
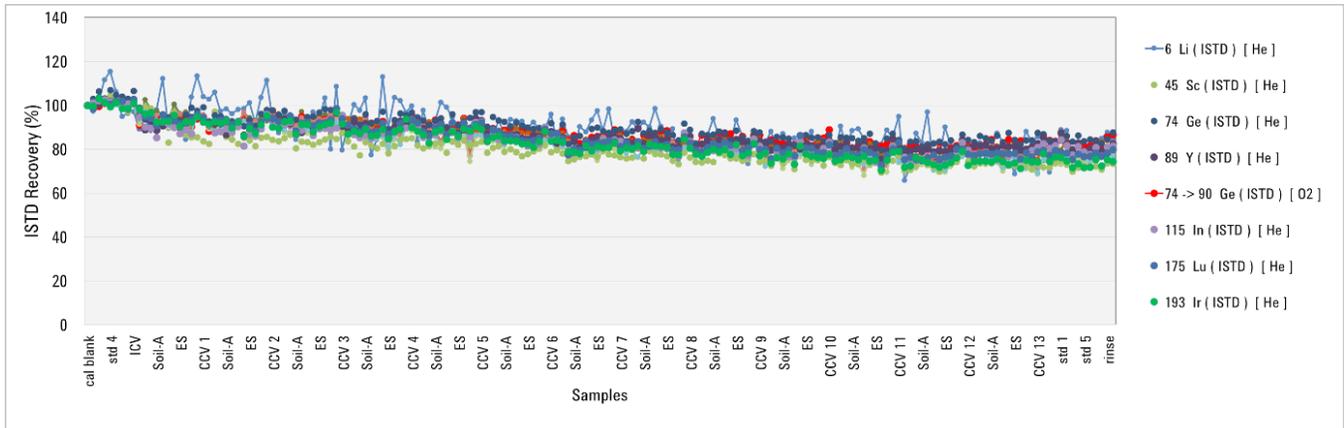
Figure 3. ISTD signal stability for 130 soil/sediment samples (plus calibration standards and QC samples) over 12 hours
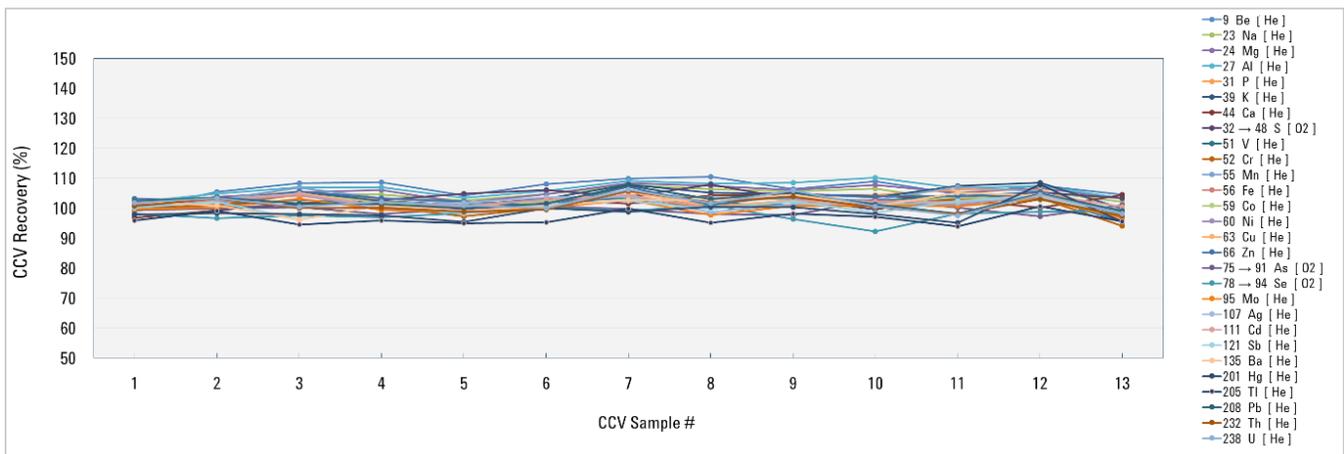
Figure 4. CCV recovery for all elements over the 12 hour analysis period

The midpoint of the calibration was used as the CCV solution. CCV recovery over the 12 hours analysis was within ±10% for all elements, as shown in Figure 4. The CCV recovery test results over the 12 hour analytical cycle met the criteria of EPA 6020A, again demonstrating that the Agilent 8800 has the high matrix tolerance required for routine soil/sediment analysis.

CRM recovery
The accuracy of the method was evaluated by analyzing the five soil and sediment CRMs as unknown samples. Each CRM was measured 26 times in the batch. The mean concentrations and relative standard deviation (%RSD) were calculated and compared to the certified value, as shown in Table 3. The mean concentration for all elements was in good agreement with the certified value, with most RSDs being well below 5% over the 12 hour analysis.

Table 3. Mean measured values, %RSDs, and mean recoveries for all certified elements in the five CRMs analyzed. Blank cells indicate no certified value.

	River Sediment A (1/10, n=26)				River Sediment B (1/10, n=26)				Estuarine Sediment (1/10, n=26)			
	Mean conc. (ppb)	RSD (%)	Certified, (ppb)	Mean Recovery (%)	Mean conc., (ppb)	RSD (%)	Certified, (ppb)	Mean Recovery (%)	Mean conc. (ppb)	RSD (%)	Certified (ppb)	Mean Recovery (%)
[9]Be	ND				ND				2.1	5.5	2.0	106
[23]Na	5191	2.6	5000	104	5019	3.3	5000	100	20862	2.4	20000	104
[24]Mg	7292	2.6	7000	104	12036	3.2	12000	100	10553	2.7	10000	106
[27]Al	25862	2.4	25000	103	58736	3.1	60000	98	70884	2.7	70000	101
[31]P	ND				995	3.4	1000	99	520	2.4	500	104
[32]S	ND				ND				ND			
[39]K	15623	2.2	15000	104	19868	3.3	20000	99	15568	2.7	15000	104
[44]Ca	28860	2.1	30000	96	28663	1.6	30000	96	7760	3.2	8000	97
[51]V	26	2.6	25	105	97	3.6	100	97	103	2.9	100	103
[52]Cr	29792	2.7	30000	99	1381	4.1	1500	92	83	3.0	80	104
[55]Mn	809	2.2	800	101	571	3.4	600	95	399	2.9	400	100
[56]Fe	120085	2.7	120000	100	38968	3.0	40000	97	35335	3.3	35000	101
[59]Co	11	2.9	10	106	15.2	3.1	15	101	10.8	2.8	10	108
[60]Ni	52	2.8	50	103	49.4	3.0	50	99	30.7	3.2	30	102
[63]Cu	102	2.9	100	102	97.6	3.1	100	98	20.2	3.1	20	101
[66]Zn	1499	2.5	1500	100	480	2.9	500	96	151	2.9	150	101
[75]As	60	3.6	60	100	19.7	3.8	20	99	10.5	3.6	10	105
[78]Se	2.0	3.6	2.0	101	1.0	7.1	1.0	96	4.9	3.0	5.0	99
[95]Mo	0.19	10.5			0.27	9.9			ND			
[107]Ag	0.15	9.0			0.17	7.3			0.015	16.4		
[111]Cd	10.3	2.0	10	103	3.1	2.3	3.0	103	0.11	4.5		
[121]Sb	50.8	2.1	50	102	4.2	3.3	4.0	104	0.58	4.4		
[135]Ba	50.9	2.1	50	102	397	2.8	400	99	1.5	5.4		
[201]Hg	ND				ND				ND			
[205]Tl	0.97	2.0	1.0	97	1.15	1.8	1.0	115	ND			
[208]Pb	719	2.1	700	103	197	3.1	200	99	30.7	2.6	30	102
[232]Th	2.1	3.1	2.0	106	10	3.4	10	99	10.4	2.5	10	104
[238]U	1.0	2.4	1.0	104	2.9	3.3	3.0	98	ND			

Table 3 continues on next page.

Table 3. continued... Mean measured values, %RSDs, and mean recoveries for all certified elements in the five CRMs analyzed. Blank cells indicate no certified value.

	Soil A (1/10, n=26)				Soil B (1/10, n=26)			
	Mean conc. (ppb)	RSD (%)	Certified (ppb)	Mean Recovery (%)	Mean conc. (ppb)	RSD (%)	Certified (ppb)	Mean Recovery (%)
^{9}Be	ND				ND			
^{23}Na	7292	2.6	7000	104	10449	2.1	10000	104
^{24}Mg	7341	2.6	7000	105	8444	2.2	8000	106
^{27}Al	51034	2.5	50000	102	71051	2.6	70000	102
^{31}P	1042	2.0	1000	104	1034	2.5	1000	103
^{32}S	ND				ND			
^{39}K	20678	2.3	20000	103	21678	2.2	21000	103
^{44}Ca	33670	1.8	35000	96	12209	3.2	12500	98
^{51}V	10.4	3.4	10	104	82	2.4	80	103
^{52}Cr	ND				41	2.5	40	102
^{55}Mn	10.9	3.0	10	109	9650	2.7	10000	97
^{56}Fe	20215	2.2	20000	101	35350	2.5	35000	101
^{59}Co	0.33	3.1			11	2.2	10	107
^{60}Ni	30.2	2.6	30	101	21	2.5	20	104
^{63}Cu	30.2	2.4	30	101	307	2.3	300	102
^{66}Zn	101	2.3	100	101	6767	2.4	7000	97
^{75}As	20.4	3.0	20	102	614	5.5	600	102
^{78}Se	1.0	6.2	1.0	99	ND			
^{95}Mo	ND				0.21	12.6		
^{107}Ag	0.038	17.3			0.075	12.7		
^{111}Cd	0.37	2.9	0.30	125*	21	2.1	20	103
^{121}Sb	3.2	3.5	3.0	106	41	1.9	40	104
^{135}Ba	513	2.6	500	103	724	1.7	700	103
^{201}Hg	0.018				ND			
^{205}Tl	ND				0.15	3.4		
^{208}Pb	41	2.4	40	101	6080	1.7	6000	101
^{232}Th	10	2.2	10	103	10	1.9	10	102
^{238}U	1.0	2.5	1.0	102	25	1.9	25	102

ND: less than detection limit
*A previous study [8] also showed high Cd recovery for Soil A, possibly indicating a bias in the reference value. The high Cd result was not due to interference from MoO, as He mode successfully removes MoO, and the Mo concentration in this sample is low (<DL).

Conclusions

The Agilent 8800 ICP-QQQ with HMI offers the robustness and matrix tolerance required for the routine analysis of the widest range of trace and major elements in high matrix samples such as soil and sediments. Doubly-charged REE interferences that can affect arsenic and selenium measurement at trace levels were avoided using O_2 cell gas and MS/MS mass-shift mode. Most other elements were measured in He mode, proven to remove common matrix-based polyatomic interferences in complex and variable matrices.

While not all soils, sediments and food products contain significant concentrations of REEs, the presence of REEs can lead to false positive results for As and Se when such samples are analyzed using conventional quadrupole ICP-MS. The use of the ICP-QQQ with MS/MS improves confidence in the results for these two important elements, in the analysis of environmental and food samples that often contain complex, variable, high TDS matrices. Furthermore, method development is simplified with the use of pre-set methods and auto tuning, ensuring reproducible performance from day to day and irrespective of operator experience.

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