Challenge
Matrix effects, sample digestion, interferences, calibration, and low concentration

Solution
Meticulous sample preparation using boric acid to redissolve fluoride precipitates during microwave-assisted digestion following ISO 14869-3:2017 and employing matrix-matched standards, advanced interference management using optimized iCRC parameters

Intended audience
Environmental consultants, agricultural industry, mining companies, soil testing labs, research institutions

Determination of 60 Elements in Geological Samples Using Microwave-assisted Digestion Followed by ICP-MS Analysis

Introduction

Accurate determination of elements in soil analysis presents a challenge due to the complex nature of soil matrices. This application note focuses on addressing this challenge by utilizing microwave digestion and ICP-MS. The objective is to achieve reliable and accurate quantification of 60 elements in soil, ore, and sediment samples. These types of samples require careful preparation due to their heterogeneity and potential interferences. Key analytical parameters include sensitivity, detection limits, and the elimination of matrix effects to ensure accurate quantification. Overcoming these challenges is crucial to obtain reliable and high-quality data from a wide range of geological and environmental samples.[1]

To address the analytical challenges, the methodology employs PlasmaQuant MS, a state-of-the-art ICP-MS system and Speedwave XPERT, a microwave system for sample preparation. PlasmaQuant MS offers exceptional sensitivity, dynamic range, and interference management required for multielement analysis. The system utilizes integrated collision/reaction cell technology (iCRC) to mitigate plasma- and matrix-based polyatomic interferences, ensuring accurate quantification of REEs and other elements. Speedwave XPERT's advanced microwave capabilities enable rapid and efficient sample preparation, optimizing recovery and minimizing contamination risks. The combination of these instruments streamlines the analytical workflow, enhancing productivity, and ensuring confidence in the obtained data.

The innovative aspect of this methodology lies in its novel approach to sample preparation. Addressing the paramount challenge of stabilizing all 60 elements simultaneously, this method introduces the use of boric acid. The addition of boric acid in the sample preparation process plays a pivotal role in redissolving potential fluoride precipitates, thereby ensuring the comprehensive stabilization of all elements throughout the analysis.

This groundbreaking step significantly contributes to the reliability and accuracy of the quantification process, marking a significant highlight in this work's approach to achieve a comprehensive and stable analysis of elements in soil, ore, and sediment samples.
By employing this solution, users can achieve reliable and accurate multielement analysis including REE in soils, ores, and sediments. The unique benefits of PlasmaQuant MS and Speedwave XPERT lie in their advanced capabilities, including sensitivity, robustness, interference management, and microwave-assisted sample preparation. This comprehensive approach ensures data integrity, providing valuable insights for geological exploration, environmental monitoring, and mining operations.

Materials and Methods

Samples and reagents

For digestion purposes the following high purity reagents were used:

- Deionized water (>18.2 MΩ/cm, Millipore MilliQ)
- Nitric acid Supra-quality 69 % (ROTIPURAN® Supra)
- Hydrochloric acid Supra quality 35 % (ROTIPURAN® Supra)
- Hydrofluoric acid Supra quality 48 % (ROTIPURAN® Supra)
- Boric acid 99.9999 % (Supelco Suprapur®)
- NIST 1646a estuarine sediment (National Institute of Standards & Technology, Gaithersburg, MD 20899, USA)
- NIST 2711a Montana II soil (National Institute of Standards & Technology, Gaithersburg, MD 20899, USA)
- NCS DC 73319a soil (China National Analysis Center for Iron and Steel, Beijing, China)
- NCS DC 73325 stream sediment (China National Analysis Center for Iron and Steel, Beijing, China)

Sample preparation

In total, four Certified Reference Materials of soil and sediments were prepared in triplicate for method validation purposes. Each solid sample was weighed into the pre-cleaned SpeedWave XPERT digestion system vessel and mixed with the reagent(s) according to the settings specified in Table 2.
The solutions were made up to 50 mL with 0.5 mol/L HNO_3 following the two-step digestion. They were then diluted twofold with DI H_2O before undergoing ICP-MS analysis. The final acid concentrations were as follows: 8 % (v/v) HNO_3, 4 % (v/v) HCl, 1 % (v/v) H_2O_2, and 0.4 % (w/v) H_3BO_3. The 2 % (v/v) HF included in the digestion mix was masked by the addition of H_3BO_3. The concentration of total dissolved solids (TDS) in the final digests analyzed was approximately 0.17 % (1700 ppm), which included sediment matrix (~0.1 %) and boron (0.07 %). It's worth noting that samples containing up to 0.3 % TDS are easily within the limit that the PlasmaQuant MS can handle routinely, without requiring further aerosol dilution.

Each soil/sediment CRM was also spiked after the two-step microwave digestion procedure. The final concentration of each spiked element ranged from 0.25 up to 250 ppb depending to the expected concentration of each element.

Table 1: Parameters for microwave-assisted digestion using SpeedWave XPERT

Parameter	Specification
Sample weight	0.1 g, dried and sieved
Volume of H_2O	Few drops
Volume of HCl	4 mL
Volume of HNO_3	8 mL
Volume of HF	1 mL
Volume of H_2O_2	1 mL
Vessel	PM60
Temp. / Ramp / Hold	200 °C / 15 min / 20 min at 1200 W
Cooling / Time	Room / 30 min
Volume of Boric acid	10 mL of 4 % (w/v)
Temp. / Ramp / Hold	170 °C / 25 min / 20 min at 1000 W
Cooling / Time	Room / 30 min
Final volume	Fill up to 50 mL with 0.5 mol/L HNO_3
Centrifuged	3500 rpm / 5 min
Dilution for ICP-MS analysis	1:2 with 1 % (v/v) HNO_3

Calibration

Standard solutions for external calibration were matrix-matched using 8 % (v/v) HNO_3, 4 % (v/v) HCl and 0.4 % (w/v) H_3BO_3 by appropriate dilution in 50 mL VWR® Metal-Free Centrifuge Tubes. No HF was added to the standard solutions. Standard multielemental solution containing Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Sr, Ag, Cd, In, Te, Cs, Ba, Tl, Pb and Bi (10 mg/L, 10 % HNO_3, traces of HF, Periodic table mix 1 for ICP, 33 elements, TraceCERT®, Supelco®), single element solutions (CertiPUR® 1000 mg/L, in 2-3 % HNO_3) for Ge, Zr, Nb, Mo, Sn, Sb, Hf, Ta, W, Re, Au, Hg, Th and U, single element solutions (CertiPUR® 10 000 mg/L, in 2-3 % HNO_3) for Na, Mg, Al, P, K, Ca, Ti and Fe, and a Rare Earth element mix for ICP (TraceCERT®, 16 elements, 50 mg/L in 2-3 % HNO_3) were used to prepare five-point concentration curves as follow:

- 0.01 up to 2.5 µg/L for Re and Hg
- 0.1 up to 25 µg/L for Sc, Y, and REE
- 0.1 up to 50 µg/L for Ag
- 0.05 up to 12.5 µg/L for Ge and U
- 0.5 up to 125 µg/L for Mo
- 0.1 up to 250 µg/L for Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Cd, In, Te, Cs, Ba, Hf, Ta, W, Tl, Pb, Bi, and Th
- 1 up to 250 µg/L for Nb, Sn, and Sb
- 2 up to 450 µg/L for Al, Ti, and Zr
- 10 up to 1250 µg/L for Na, Mg, and P
- 20 up to 2250 µg/L for K, Ca, and Fe

Excellent linearity was achieved for major elements and trace elements, as indicated by the four representative calibration curves shown in Figure 1. In all cases, the correlation coefficient was greater than 0.9998.

Instrument settings

All analytical work was performed using the PlasmaQuant MS featuring the integrated collision/reaction cell (iCRC) technology to remove polyatomic ions formed in the plasma improving the precision and accuracy of an analysis. The ICP-MS system was coupled to a CETAC ASX-560 autosampler and a CETAC ASXPress Plus injection valve. A Scott type spray chamber with Peltier chiller and a SeaSpray™ nebulizer were used for the quantification of 60 elements in four Certified Reference Materials of soil and sediments. The use of boric acid (H_3BO_3) for masking the HF during the digestion meant that an "inert" (HF resistant) sample introduction kit was not required, and the standard glass/quartz sample introduction system was used instead.
The digestion of the soil samples was carried out by closed-vessel microwave-assisted SpeedWave XPERT system, and the content of the selected metals and metalloids in the prepared solutions was determined by ICP-MS.
All experiments were carried out in a routine analytical laboratory, not under 'clean room' conditions. Instrument operating conditions are summarized in Table 1, including iCRC modes using helium and hydrogen gases to remove problematic spectral interferences on the first-row transition metals.

Table 2: Instrument settings – PlasmaQuant MS

Parameter	Specification	
Plasma Gas Flow	9.0 L/min	
Auxiliary Gas Flow	1.50 L/min	
Sheath Gas Flow	0.00 L/min	
Nebulizer Gas Flow	1.07 L/min	
Sampling Depth	6.0 mm	
Plasma RF Power	1.40 kW	
Rump Rate	20 rpm – black/black PVC pump tubing (<1 mL/min)	
Stabilization Delay	10 s	
iCRC Gas Setting	He 120 mL/min	^{31}P, ^{49}Ti, ^{71}Ga, ^{74}Ge, and REE
	He 150 mL/min	^{27}Al, ^{44}Ca, ^{45}Sc, ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, and ^{125}Te
	No Gas	^{7}Li, ^{9}Be, ^{23}Na, ^{24}Mg, ^{39}K, ^{85}Rb, ^{86}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{133}Cs, ^{137}Ba, ^{178}Hf, ^{181}Ta, ^{182}W, ^{185}Re, ^{201}Hg, ^{205}Tl, $^{206+207+208}Pb$, ^{209}Bi, ^{232}Th, and ^{238}U
	H_2 150 mL/min	^{57}Fe, ^{75}As, and ^{78}Se

Parameter	Specification
Dwell Time	10 ms (No Gas) and 30 ms (iCRC)
Scans per Replicate	20 (peak hopping, 1 pt/peak)
No. of Replicates	3
Sample Uptake Time	0 s – ASXPress Plus sample introduction system used
Internal Standards	^{103}Rh and ^{193}Ir at 25 µg/L, interpolate correction

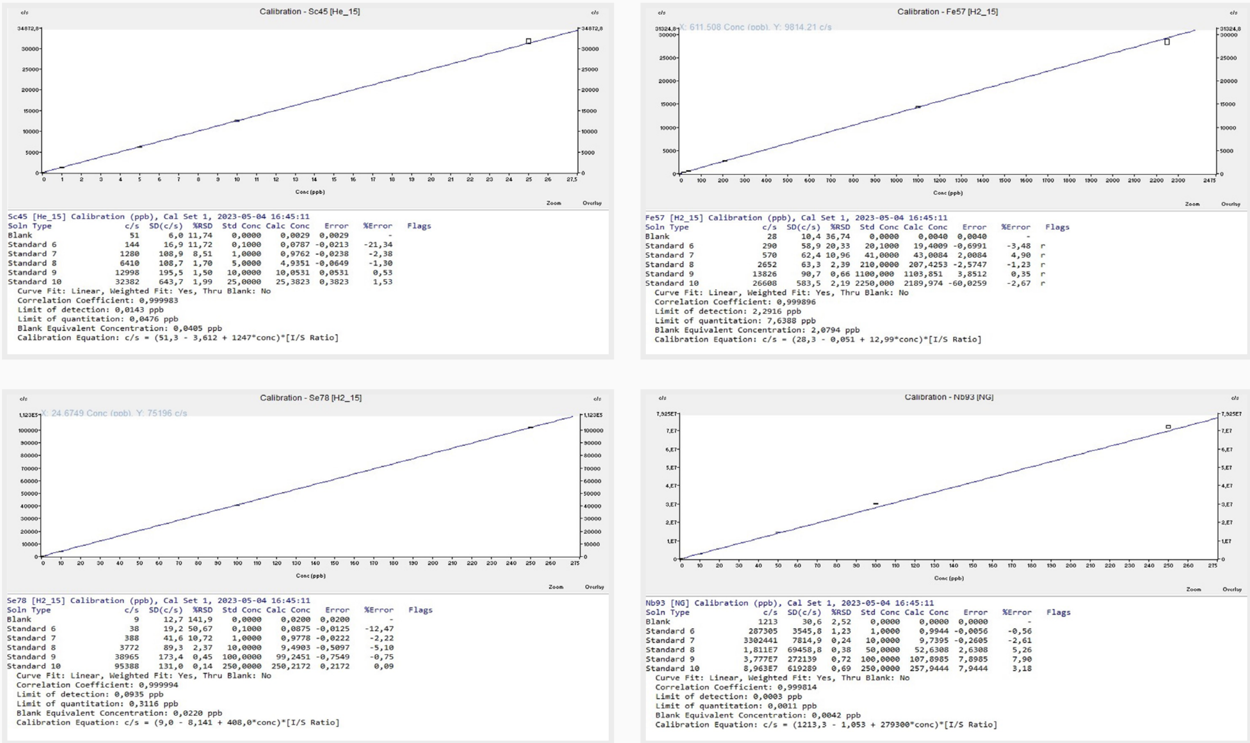

Figure 1: Calibration graphs for some investigated major and minor elements

Results and Discussion

Digested blank solutions and method detection limits

Digested blank solutions were prepared in the same way as sample solutions: equal volumes of acid mixture and the same microwave-assisted digestion program as applied for the soil samples digestion. The concentrations measured of the elements in the procedural blank were subtracted from the concentration values measured in the soil CRM solutions.

The method detection limits (MDL) shown in Table 3 were determined by running a full calibration and were calculated as three standard deviations (3σ) of the calibration blank intensity measured, divided by the slope and multiplied by the dilution factor (1000).

The method detection limits (MDLs) achieved using the demonstrated approach, ranging from an exceptional 0.00001 mg/kg for trace elements to 50 mg/kg for major elements, stand notably lower than the typical concentrations found in soils. This difference enables precise quantification of major elements, heavy metals, and rare earth elements (REEs) in soils, ores, and sediments. With the ability to effectively cover 60 crucial elements pertinent to geology, geochemistry, mining, and environmental monitoring applications, this approach offers unparalleled sensitivity and accuracy in detecting and quantifying trace elements within soil samples.

Table 3: Method detection limits (MDL) of metals in soil samples obtained by using PlasmaQuant MS after microwave-assisted digestion of samples in closed vessels

Element	MDL (mg/kg)	Element	MDL (mg/kg)	Element	MDL (mg/kg)	Element	MDL (mg/kg)	Element	MDL (mg/kg)
Li	0.05	Mn	0.09	Y	0.001	La	0.001	Yb	0.00001
Be	0.003	Fe	11.3	Zr	0.003	Ce	0.001	Lu	0.004
Na	25	Co	0.003	Nb	0.001	Pr	0.0002	Hf	0.001
Mg	0.01	Ni	0.06	Mo	0.002	Nd	0.00001	Ta	0.0001
Al	0.37	Cu	0.03	Ag	0.006	Sm	0.001	W	0.010
P	46.2	Zn	0.12	Cd	0.001	Eu	0.0003	Re	0.001
K	10.8	Ga	0.006	In	0.04	Gd	0.001	Hg	0.004
Ca	5.2	Ge	0.007	Sn	0.003	Tb	0.00001	Tl	0.001
Sc	0.09	As	0.20	Sb	0.01	Dy	0.0003	Pb	0.002
Ti	0.83	Se	0.04	Te	0.10	Ho	0.00001	Bi	0.003
V	0.09	Rb	0.003	Cs	0.001	Er	0.00001	Th	0.0003
Cr	0.04	Sr	0.16	Ba	0.007	Tm	0.00001	U	0.00001

Spike recoveries, CRM recoveries, and precision

Tables 4a, 4b, 4c, and 4d show the results of 60 major and trace elements determined in the four Certified Reference Materials tested, including information of spike recoveries, mean recoveries compared to the certified values, and the precision. The spike level in some elements/CRM (e.g., major elements such as, Al, Ti, Na, K, Mg and Fe) were insignificant compared to the concentration in the original samples and are not shown. The overall spike recoveries were within 76 % to 122 %. The mean concentration values of three digested replicates were in good agreement compared to the certified ones with overall recoveries ranging from 76 % to 135 % and RSD < 5 % for most of the results. However, some quantified elements exceeded 5 % of relative standard deviation (RSD) which can arise from various sources. These include the presence of elements lacking certification or those with target concentrations in parts per trillion (ppt), the heterogeneous nature of soil matrices impacting measurement consistency, the inherent challenge of accurately quantifying elements at extremely low concentrations, and the potential for cross-contamination during sample handling and preparation. Each of these factors can individually or collectively contribute to the observed variability, making achieving tighter precision in the quantification of elements a complex endeavor in soil analysis. Refractory elements, such as Zr and Hf, mainly in the samples NIST 2711a and NCS DC 73319 can also lead to poor precision.

Table 4a: Metals and semi-metals concentration, recoveries, precision, and spike recoveries achieved in the NIST 1646a (sediment) after microwave-assisted digestion (n=3)

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike recovery (%)
Li	18*	22	122	6.9	105
Be	<1*	0.79	-	2.5	100
Na	7410 ± 170	7616	103	1.4	111
Mg	3880 ± 90	4006	103	1.7	120
Al	22970 ± 180	22506	98	3.3	-

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike recovery (%)
P	270 ± 10	302	112	5.7	105
K	8640 ± 160	8939	103	0.8	96
Ca	5190 ± 200	4986	96	3.5	100
Sc	5*	5.1	102	3.1	101
Ti	4560 ± 210	4138	91	2.2	-
V	44.8 ± 0.8	44	97	2.4	101
Cr	40.9 ± 1.9	34	84	8.7	100
Mn	234.5 ± 2.8	237	101	3.2	103
Fe	20080 ± 390	21028	105	4.0	117
Co	5*	5.0	99	11.0	99
Ni	23*	27	115	9.4	99
Cu	10 ± 0.3	11.7	117	7.3	99
Zn	48.9 ± 1.6	55	113	3.6	99
Ga	5*	6.3	126	3.8	99
Ge	-	1.16	-	3.6	98
As	6.2 ± 0.2	6.54	105	0.9	97
Se	0.19 ± 0.03	0.19	101	12.7	99
Rb	38*	33.0	87	2.9	100
Sr	68*	69	101	4.6	95
Y	-	8.3	-	4.3	96
Zr	-	50	-	4.3	102
Nb	-	8.6	-	4.2	103
Mo	1.8*	1.974	110	0.2	94
Ag	<0.3*	0.20	-	9.1	102
Cd	0.15 ± 0.01	0.16	104	3.7	100
In	-	0.025	-	10.9	105
Sn	1*	1.3	128	4.4	99
Sb	0.3*	0.32	105	5.2	95
Te	-	0.10	-	4.1	86
Cs	-	1.23	-	3.9	104
Ba	210*	195	93	7.2	98
La	17*	18.3	108	1.2	93
Ce	34*	38.7	114	1.1	90
Pr	-	4.53	-	1.2	102

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike recovery (%)
Nd	15*	17.3	115	1.5	109
Sm	-	3.25	-	2.4	99
Eu	-	0.57	-	3.0	100
Gd	-	2.54	-	2.7	100
Tb	-	0.34	-	5.4	104
Dy	-	1.79	-	2.3	100
Ho	-	0.33	-	6.6	100
Er	-	0.88	-	5.1	102
Tm	-	0.14	-	7.5	102
Yb	-	0.87	-	1.5	101
Lu	-	0.13	-	9.3	100
Hf	-	1.58	-	5.0	98
Ta	-	0.60	-	9.7	98
W	-	0.589	-	0.7	102
Re	-	0.0023	-	9.1	99
Hg	0.04*	0.049	123	12.5	102
Tl	<0.5*	0.207	-	2.7	107
Pb	11.7 ± 1.2	11.0	94	4.8	99
Bi	-	0.080	-	2.5	104
Th	5.8*	4.94	85	1.4	101
U	2*	1.60	80	1.1	103

* Informative values, not certified

Table 4b: Metals and semi-metals concentration, recoveries, precision, and spike recoveries achieved in NIST 2711a (Montana II Soil) after microwave-assisted digestion (n=3)

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Li	-	32.0	-	2.1	104
Be	-	3.0	-	11.0	102
Na	12000 ± 100	12478	104	1.1	-
Mg	10700 ± 600	12574	118	0.7	122
Al	67200 ± 600	68643	102	8.9	-
P	842 ± 11	867	103	8.0	96
K	25300 ± 1000	26051	103	0.8	-
Ca	24200 ± 600	22593	93	7.5	100

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Sc	8.5 ± 0.1	9.4	110	6.4	102
Ti	3170 ± 80	2782	88	1.9	97
V	81 ± 6	82	101	9.1	101
Cr	52 ± 3	47	90	4.3	100
Mn	675 ± 18	691	102	5.7	105
Fe	28200 ± 400	30969	110	5.5	84
Co	9.9 ± 0.2	11	109	9.5	100
Ni	22 ± 1	22.1	100	0.5	101
Cu	140 ± 2	139	100	4.2	98
Zn	414 ± 11	422	102	3.6	92
Ga	-	17.7	-	4.3	97
Ge	-	1.9	-	5.3	96
As	107 ± 5	106.4	99	2.8	98
Se	2*	2.02	101	3.2	102
Rb	120 ± 3	123	103	2.4	102
Sr	242 ± 10	233	96	2.8	104
Y	-	25.3	-	2.7	98
Zr	-	74	-	2.1	100
Nb	-	16.0	-	3.9	105
Mo	-	2.025	-	0.04	95
Ag	6*	5.5	92	4.8	102
Cd	54 ± 1	53.2	99	1.2	100
In	1*	1.16	116	1.9	103
Sn	-	4.38	-	0.1	100
Sb	24 ± 1	21.4	89	2.6	95
Te	1*	1.58	-	7.3	91
Cs	6.7 ± 0.2	6.6	98	3.4	102
Ba	730 ± 15	744	102	1.5	105
La	38 ± 1	39	101	3.1	101
Ce	70*	76	108	3.1	98
Pr	-	8.8	-	3.0	100
Nd	29 ± 2	33	113	3.2	98
Sm	5.9 ± 0.3	6.4	108	3.9	98
Eu	1.1 ± 0.2	1.11	101	5.6	101
Gd	-	5.3	-	4.0	101
Tb	-	0.82	-	6.8	102
Dy	5*	4.6	92	5.3	101

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Ho	-	0.91	-	5.8	98
Er	-	2.45	-	2.9	98
Tm	-	0.40	-	5.1	100
Yb	3*	2.6	86	7.5	101
Lu	1*	0.42	-	8.2	99
Hf	9.2 ± 0.2	2.6[a]	-	13.7	100
Ta	1*	1.21	121	3.3	99
W	-	3.52	-	2.2	99
Re	-	0.0031	-	9.5	100
Hg	7.4 ± 0.2	7.13	96	0.6	101
Tl	3*	2.70	90	3.0	107
Pb	1400 ± 10	1440	103	5.1	99
Bi	-	2.8	-	3.8	102
Th	15 ± 1	14.2	95	4.0	99
U	3 ± 0.1	2.8	92	4.2	100

* Informative values, not certified
[a] Refractory element/matrix

Table 4c: Metals and semi-metals concentration, recoveries, precision, and spike recoveries achieved in the NCS DC 73319a (Soil) after microwave-assisted digestion (n=3)

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Li	28 ± 2	37.9	135	10.2	104
Be	3.3 ± 0.3	3.74	113	1.7	105
Na	12240 ± 519	12675	104	1.8	106
Mg	7056 ± 241	7564	107	8.7	-
Al	68378 ± 1111	67157	98	3.0	-
P	2300 ± 200	2226	97	8.0	80
K	23659 ± 664	24428	103	1.4	76
Ca	19868 ± 786	18780	95	7.1	-
Sc	8.3 ± 0.3	8.5	102	5.3	102
Ti	3260 ± 90	3228	99	1.6	-
V	61 ± 4	62.3	102	0.4	99
Cr	44 ± 3	43.0	98	0.5	99
Mn	1310 ± 60	1324	101	3.4	78
Fe	30846 ± 1399	31200	101	4.5	-
Co	10.3 ± 0.6	10	101	10.0	100

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Ni	16.9 ± 1.5	18.2	108	3.4	98
Cu	42 ± 5	51	122	4.2	95
Zn	475 ± 30	496	104	5.2	118
Ga	18.1 ± 1.4	18.6	103	2.3	100
Ge	1.3 ± 0.2	1.6	122	7.9	95
As	33 ± 3	36.0	109	2.7	100
Se	0.22*	0.27	123	16.6	102
Rb	137 ± 9	141	103	2.7	99
Sr	192 ± 9	191	99	3.9	91
Y	38 ± 3	33.7	89	1.1	89
Zr	218 ± 10	104a	-	1.7	105
Nb	15.3 ± 1.4	13.0	85	2.6	100
Mo	2 ± 0.2	2.34	117	2.0	94
Ag	0.81 ± 0.04	1.37***	-	3.3	102
Cd	2.5 ± 0.2	2.61	104	2.1	99
In	0.12 ± 0.02	0.112	94	1.0	101
Sn	9.8 ± 1.1	9.5	96	2.8	99
Sb	2.4 ± 0.3	2.79	116	1.0	95
Te	0.06*	0.07	109	-	83
Cs	7.2 ± 0.5	6.7	94	2.8	105
Ba	700 ± 40	679	97	2.3	96
La	39 ± 2	38	97	3.3	86
Ce	71 ± 5	70	99	3.5	84
Pr	8.5 ± 0.7	8.1	96	3.1	91
Nd	30.8 ± 1.3	29	93	3.6	82
Sm	5.9 ± 0.4	5.6	95	1.8	95
Eu	0.89 ± 0.08	0.79	88	2.1	95
Gd	5.5 ± 0.4	5.03	91	1.4	91
Tb	0.98 ± 0.09	0.84	86	7.0	97
Dy	6 ± 0.5	5.39	90	1.3	91
Ho	1.3 ± 0.2	1.1	85	8.7	95
Er	3.8 ± 0.4	3.23	85	2.8	94
Tm	0.61 ± 0.06	0.47	78	3.2	94
Yb	3.8 ± 0.4	3.11	82	1.7	92

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Lu	0.57 ± 0.06	0.45	80	1.5	96
Hf	6.5 ± 0.5	3.17a	-	2.1	106
Ta	1.3 ± 0.1	1.02**	78	1.5	97
W	3.5 ± 0.5	3.8	108	9.7	98
Re	-	0.0017	-	20.7	100
Hg	0.31 ± 0.03	0.39	126	3.5	103
Tl	1.2 ± 0.1	1.14	95	3.6	102
Pb	339 ± 12	348	103	2.3	102
Bi	1.4 ± 0.2	1.35	97	1.9	101
Th	13.1 ± 0.9	12.3	94	1.1	101
U	6 ± 0.06	6.2	103	3.0	100

* Informative values, not certified
*** Contaminated
[a] Refractory element/matrix

Table 4d: Metals and semi-metals concentration, recoveries, precision, and spike recoveries achieved in the NCS DC 73325 (Soil) after microwave-assisted digestion (n=3)

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Li	19.5 ± 0.9	21.9	112	3.6	95
Be	2.8 ± 0.6	2.5	91	4.2	100
Na	593.5 ± 148	468	79	0.3	91
Mg	1568 ± 181	1341	86	3.0	98
Al	154896 ± 1800	138428	89	5.0	-
P	1150 ± 39	1153	100	11.3	97
K	1660 ± 166	1423	86	1.2	88
Ca	1144 ± 143	988	86	7.4	97
Sc	28 ± 2	26.9	96	3.0	94
Ti	20200 ± 500	20164	100	3.5	-
V	245 ± 21	244	99	3.5	97
Cr	410 ± 23	408	99	2.7	101
Mn	1780 ± 113	1811	102	2.2	105
Fe	131216 ± 2308	127990	98	1.8	114
Co	97 ± 6	99	102	3.7	96
Ni	276 ± 15	281	102	1.8	99
Cu	97 ± 6	97	100	2.9	95

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Zn	142 ± 11	147	104	3.4	95
Ga	39 ± 5	40.0	102	4.9	98
Ge	1.6 ± 0.3	1.88	118	2.0	100
As	4.8 ± 1.3	7.02***	-	0.6	99
Se	0.32 ± 0.05	0.35	108	8.1	100
Rb	16 ± 03	15.3	96	6.2	101
Sr	26 ± 4	27.3	105	5.5	94
Y	27 ± 4	24.4	90	3.0	97
Zr	318 ± 37	311	98	1.0	100
Nb	64 ± 7	67.9	106	3.4	105
Mo	2.9 ± 0.3	3.15	109	2.1	93
Ag	0.057 ± 0.011	0.96***	-	9.5	101
Cd	0.08 ± 0.02	0.138***	-	1.5	100
In	0.1 ± 0.03	0.116	116	6.8	104
Sn	3.6 ± 0.7	3.7	103	4.4	99
Sb	0.42 ± 0.09	0.47	112	7.3	96
Te	0.047*	0.043	92	0.0	90
Cs	2.7 ± 0.8	2.40	89	2.8	105
Ba	180 ± 27	173	96	5.1	92
La	46 ± 5	45	98	2.4	99
Ce	98 ± 11	106	108	2.3	102
Pr	11 ± 1	11.1	101	2.0	101
Nd	45 ± 2	46	103	3.0	99
Sm	10.3 ± 0.4	10.5	102	1.6	104
Eu	3.4 ± 0.2	3.3	98	2.9	97
Gd	9.6 ± 0.9	9.0	94	1.8	97
Tb	1.3 ± 0.2	1.26	97	5.8	98
Dy	6.6 ± 0.6	6.2	93	2.1	99
Ho	1.1 ± 0.2	1.03	93	6.8	99
Er	2.7 ± 0.5	2.4	90	6.2	97
Tm	0.42 ± 0.05	0.32	77	5.6	101
Yb	2.4 ± 0.4	1.89	79	3.6	99
Lu	0.35 ± 0.06	0.29	82	5.3	104
Hf	7.7 ± 0.5	7.19	93	0.6	103

Isotope	Certified value (mg/kg)	Conc. Found (mg/kg)	Recovery (%)	RSD (%)	Spike (%)
Ta	3.9 ± 0.6	3.78	97	2.1	99
W	1.2 ± 0.2	0.95	79	9.8	90
Re	-	0.0022	-	9.5	103
Hg	0.061 ± 0.006	0.095***	-	5.8	97
Tl	0.21 ± 0.06	0.187	89	2.8	97
Pb	14 ± 3	12.99	93	0.1	91
Bi	0.2 ± 0.04	0.191	95	2.8	104
Th	9.1 ± 0.7	8.42	92	1.1	99
U	2.2 ± 0.4	2.08	95	2.1	100

* Informative values, not certified
*** Contaminated

Figure 2 presents the accuracy (recoveries) and precision of the four certified reference materials (CRMs) tested, providing valuable insights into the overall performance achieved. The majority of recoveries fall within the range of 80 % to 120 %, indicating good accuracy. However, certain elements exhibit higher uncertainties in the reference values, leading to some recoveries falling outside this range. The overall relative standard deviations (RSD) are below 5 %. Nevertheless, due to some elements' concentrations being near the method detection limit (MDL), specific RSDs fall within the range of 5 % to 15 %. It is noteworthy that all measurements demonstrated excellent precision and accuracy across the ppb to % concentration range, showcasing the effectiveness of the applied methodology.

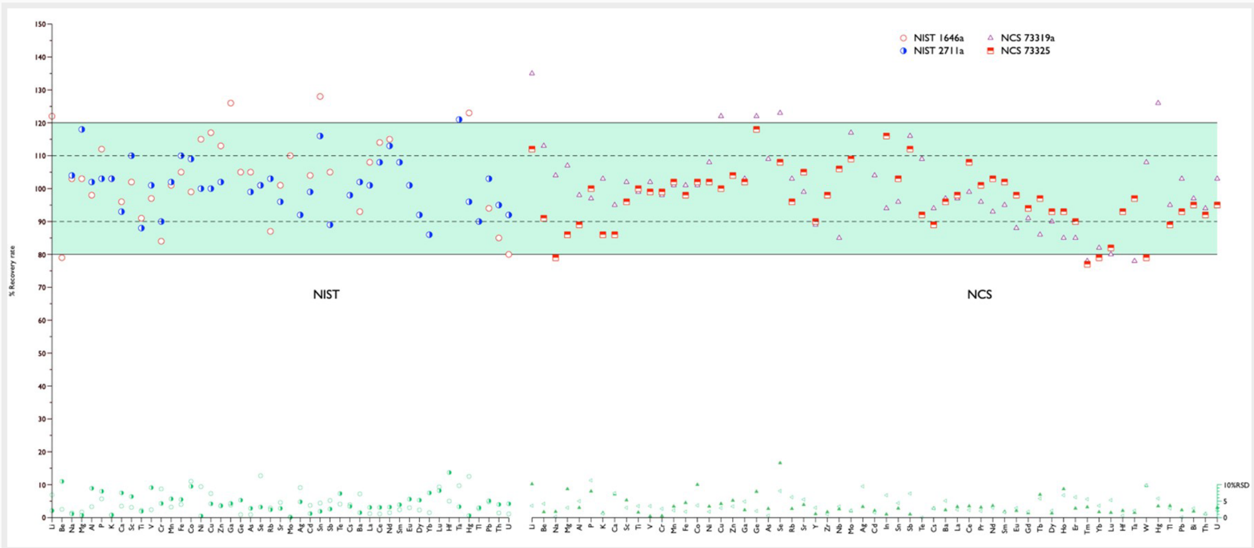

Figure 2: Recovery (%) and precision (%RSD) of four CRMs

Digested blank solutions and method detection limits

For this study, a total of 145 solutions were analyzed within 7 hours and 30 minutes. The isotopes ^{103}Rh and ^{193}Ir were selected as internal standards, and the recovery measurements of all internal standards (ISTDs), as depicted in Figure 3, exhibited excellent performance within ±30 %. Notably, the majority of ISTD recoveries were within ±20 %, demonstrating the high matrix tolerance of the PlasmaQuant MS for soils, sediments, and ores samples. This matrix tolerance resulted in minimal variability in the ISTD signals from sample to sample throughout the run, and it effectively prevented significant matrix deposition on the interface throughout the sequence.

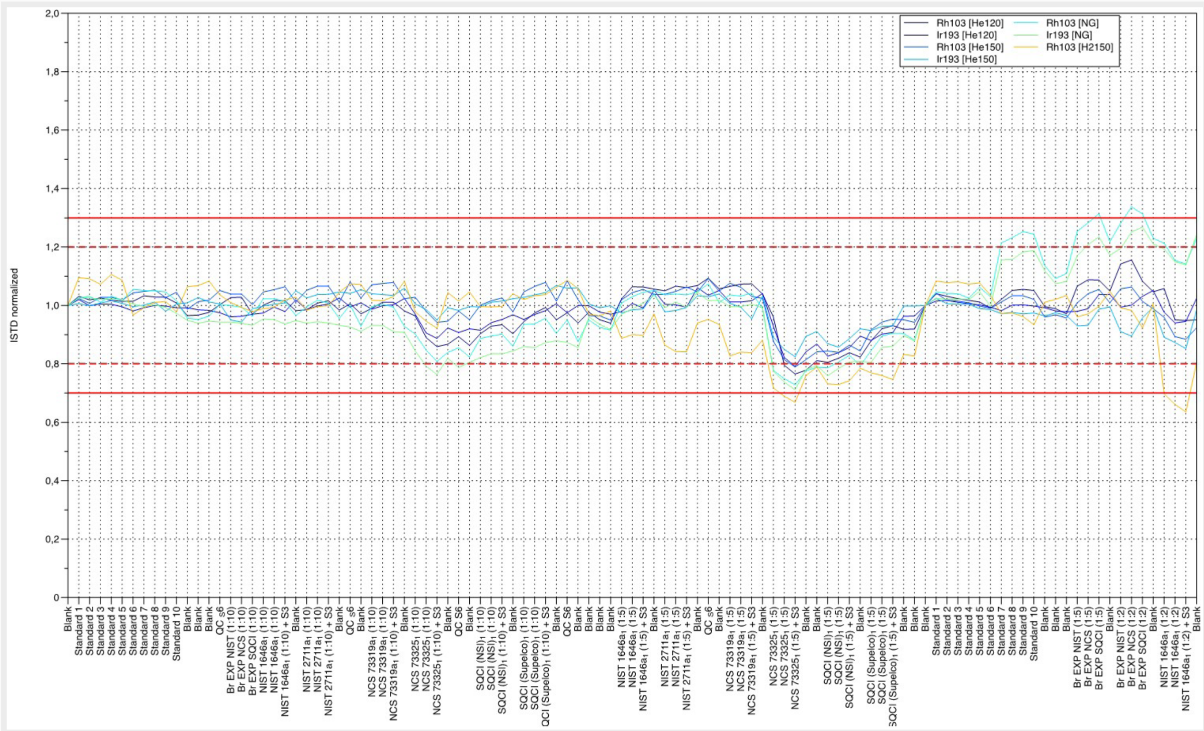

Figure 3: Internal standards stability during the analysis of a total of 145 solutions measured over a 7.5 h run (ISTD for all samples have been normalized to the calibration blank)

Summary

The developed method for determining major elements, heavy metals, and rare earth elements in soils, sediments, and ores covering a total of 60 elements has been demonstrated with great success. The analysis yielded accurate and precise data, as evidenced by the excellent performance observed for the four certified reference materials used.
The methodology's versatility allows for its broad application in various fields, including geology, geochemistry, mining, and environmental monitoring. These findings underscore the method's potential to contribute significantly to research, exploration, and monitoring efforts in these domains.
It is important to note that certain refractory elements, such as Hf and Zr, may still present challenges in terms of digestion or dissolution in tough matrices. Alternative sample preparation approaches, specifically tailored for these elements, can be explored to overcome these difficulties. By investigating and implementing alternative approaches, it is possible to enhance the analysis of refractory elements in challenging matrices and further expand the capabilities of the developed methodology.
The PlasmaQuant MS has proven to be invaluable in providing comprehensive information on a range of 60 elements, covering a wide concentration range from parts per billion (ppb) up to percentage levels, all within the same sample solution. This capability allows for efficient and accurate analysis across diverse samples, enabling researchers to gain a deeper understanding of element distribution and concentration in various matrices.

Figure 4: PlasmaQuant MS

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant MS Elite S - The sensitive ICP-MS for demanding samples requiring best signal-to-noise performance	818-08020-2	Compact, bench top ICP-MS system for applications requiring best sensitivity and signal-to-noise ratio such as Ultra-trace REE detection in geochemical analyis
Speedwave XPERT	819-5005000-2	Universally applicable microwave digestion system for the preparation of organic and inorganic sample materials that impresses with its reliability, safety, and economy
Teledyne-Cetac ASX-560 autosampler for ICP-OES and ICP-MS	810-88015-0	Autosampler designed to simplify analysis and save time
Cetac ASXPress Plus for PQMS	810-88017-0	The ASXPress Plus Rapid Sample Introduction System reduces time required for autosampler movement, sample uptake, stabilization, and rinse operations, thereby reducing sample run times significantly

References

[1] Falciani, R.; Novaro, E.; Marchesini, M. and Gucciardi, M.; MULTI-ELEMENT ANALYSIS OF SOIL AND SEDIMENT BY ICP-MS AFTER A MICROWAVE ASSISTED DIGESTION METHOD. J. Anal. At. Spectrom. 2000, 15/5, pages 561-565

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