

# Multi-element testing of soil and sediment samples using ICP-MS

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## Keywords:

Soil Testing, trace elements; water sediments; simultaneous determination; Inductively coupled plasma mass spectrometry;

## Goal

To demonstrate the applicability of the Thermo Scientific™ iCAP™ RQ ICP-MS for simultaneous determination of trace elements in soil and water sediment samples with high throughput analysis in complex environmental samples.

## Application Image (Shutterstock 1195825864):

### Introduction:

Over the past few decades, numerous concerns have been raised in China over the issue of environmental sustainability. Consequently, the Chinese government started several environmental monitoring initiatives focusing on pollution in air, water and soil. A series of such initiatives is the “Ten-provision” preparation work associated with the Action Plan for Air Pollution Prevention and Control, the Action Plan for Water Pollution Prevention and Control and the Action Plan for Soil Pollution Prevention and Control.

Specifically, in June 2016, the Ministry of Ecology and Environment (MEE) of the People’s Republic of China released the standard HJ 803 on Soil and Sediment-Determination of Aqua Regia Extracts of Metal Elements-Inductively Coupled Plasma Mass Spectrometry. It was the first national method that established Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in testing multiple metals simultaneously in soil and sediment samples. In 2018, MEE and



State Administration for Market Regulation jointly released updated GB15618 on Soil environmental quality: Risk control standard for soil contamination of agricultural land, and GB36600 on Soil environmental quality: Risk control standard for soil contamination of development land. These two standards are foundational technical regulations involved in national soil contamination survey of agricultural and development lands that are to be completed by 2020. In both GB standards, HJ 803 was referenced as a major standard to test basic item of arsenic and additional items such as antimony,

cobalt and vanadium. Compared with other metal-testing technologies, ICP-MS is the technique of choice for rapid and sensitive multi-elemental analysis.

The use of ICP-MS for the determination of trace elements in soils offers the advantages of simple and straightforward operation in routine laboratories, and the ability to perform a full screening of a variety of elements in a short time, essentially allowing high throughput analysis.

In a typical laboratory performing the analysis of soils for trace elements, more than 500 samples could be analyzed in a day, with figures 1 & 2 showing the typically arriving samples.



**Figure 1 and 2. Large number of soil samples require high throughput and low cost of analysis**

At the same time, modern single quadrupole ICP-MS systems are able to remove the majority of potentially occurring interferences, achieve high detection sensitivity (translating into lower detection limits) and allow to analyze samples with wide concentration ranges. All of the above-mentioned characteristics are important for routine screening for trace elements in soils according to Chinese National Standard Method HJ803-2016.

In this application note, analysis of trace elements in soil using the Thermo Scientific™ iCAP™ RQ ICP-MS is assessed. Analytical pa-

rameters such as sensitivity, limits of detection, and robustness in routine analysis are investigated for the simultaneous determination of 25 prevalent trace elements in soil and sediments samples.

A simplified sample preparation using acid digestion was employed, avoiding the high salinity introduced by methods such as alkali fusion, as well as interferences typically caused through the introduction of salt rich matrices. The sample preparation method has been verified with the recommended reference standard substances GBW07304a and GBW07308a (stream sediment standard materials), as well as GBW07402 and GBW07408 (soil composition analysis standards materials).

## Instrument Configuration

All measurements were performed using the iCAP RQ ICP-MS. The sample introduction system used included a PFA concentric nebulizer and spray chamber, as well as a demountable sapphire torch with a 2.0 mm i.d. injector tube. A standard interface using sample and skimmer cones were used. In order to improve robustness of the system, a robust skimmer cone insert was used in order to reduce matrix effects causing suppression and potential drift of the internal standard, but also to enable a larger analytical range of the method. The instrument uses pure helium as the collision gas and can be operated routinely in a kinetic energy discrimination (KED) collision cell mode. The typical operating parameters of the ICP-MS instrument are detailed in Table 1.

Table 1. ICP-MS Working Parameters

Instrument Parameter	Set Value
Nebulizer	PFA concentric nebulizer 400 $\mu\text{L}\cdot\text{min}^{-1}$
Injector	2.0 mm i.d., sapphire
Plasma Power	1550 W
Cooling Gas	14 $\text{L}\cdot\text{min}^{-1}$
Auxiliary Gas	0.80 $\text{L}\cdot\text{min}^{-1}$
Nebulizer Gas Flow	1.1 $\text{L}\cdot\text{min}^{-1}$
Measure mode	STD and KED
Scanning mode	Peak jumping
Number of scans	40
Dwell time	0.02s
Cell gas flow	He 4.8 $\text{mL}\cdot\text{min}^{-1}$
KED Voltage	3V
Interface	Robust skimmer cone insert, 4.5 mm
Time per sample	2 min

Each day of analysis, the instrument was started, and, after ignition of the plasma, left to warm up for approximately 10 minutes. A daily performance check was executed in order to verify that the instrument's performance was according to the manufacturer's specifications. This includes sensitivity across the mass range, but also key plasma parameters such as oxide ratio ( $^{140}\text{Ce}^{16}\text{O}^{+}/^{140}\text{Ce}^{+}$ ) and doubly charged ion formation ( $^{137}\text{Ba}^{++}/^{137}\text{Ba}^{+}$ ). If necessary, an automated tuning procedure was executed to optimize the system and re-gain performance.

The composition of typical geological and mineral samples is complex, containing for example high amounts of silicates, but also oxides from various elements, such as aluminum, potassium or iron. Moreover, argon and nitrogen from the plasma gas and ambient air,

hydrogen and oxygen derived from the aqueous matrix of the samples, chlorine from the acids used during sample preparation, are easily forming a variety of polyatomic species, which cause interference on the elements of interest. For the analysis of soil samples, two different measurement modes were applied, standard mode (STD, with the collision/reaction cell acting as an ion guide) and kinetic energy discrimination mode (the collision/reaction cell flushed with helium for removal of polyatomic interferences). Whereas STD mode offers higher sensitivity for especially low mass analytes, only KED can eliminate polyatomic interferences leading to significant false results for elements especially in the mass range between 40-150 u. Although the sensitivity is reduced compared to standard mode, the signal to noise ratio for critical, but strongly interfered analytes such as vanadium, chromium or arsenic are greatly improved.

In order to address this and considering the advantages of the STD and KED modes, the STD mode was used to detect Li, Be and Ga, while all other elements were detected using the KED mode.

To calibrate the system for analysis of soil samples, a two-point calibration curve was generated using mixed standard solutions (Spex Certiprep, Metuchen, NJ) with concentrations of  $20 \mu\text{g}\cdot\text{L}^{-1}$  and  $50 \mu\text{g}\cdot\text{L}^{-1}$ , each prepared through serial dilution from a  $2 \text{ mg}\cdot\text{L}^{-1}$  stock solution. To compensate for matrix effects caused by the sample matrix and instrument drift during the analysis of a large number of samples, an internal standard solution (containing rhodium and rhenium at a concentration of  $10 \mu\text{g}\cdot\text{L}^{-1}$ ) was added online using a T-piece.

### Sample Preparation

(The described sample preparation protocol requires the use of hazardous chemicals. Appropriate personal protective gear such as lab coat, safety glass and gloves are required)

Soil and sediment samples (0.1 g aliquots per incoming soil sample) were homogenized and accurately weighed, placed into a polytetrafluoroethylene (PTFE) crucible and moistened with 3 mL of water. Next, 4 mL of an acid mixture ( $\text{HF}:\text{HClO}_4=5:1$ , Fisher Scientific™ Tra-

ce Metal™ grade) was added to the crucible, and the sample was and heated up to  $260^\circ\text{C}$  on an electric hot plate digestion system (APL Instruments Co, Ltd.). This was followed by a second addition of 4 mL of the acid mixture ( $\text{HF}:\text{HClO}_4=5:1$ ) which was then heated until the emission of white smoke had ended. In a second step, 2 mL of aqua regia ( $\text{HCl}:\text{HNO}_3=3:1$ ) were added to re-dissolve the mixture. After that, 10 mL 10% aqua regia was added to extract the sample until the solution became clear and transparent. A volume of 2 mL  $\text{HNO}_3$  was added to the cooled solution and the sample extract was then transferred to a PTFE volumetric flask and made up to a final volume of 100 mL using ultra pure water (18.2 MΩm, Thermo Scientific™ Barnstead™ Water Purification System). The sample was vortexed, and an aliquot was transferred to a 10 mL PTFE test tube for ICP-MS analysis. To keep background contamination at a minimum, as it can significantly affect the measurement of trace elements at low levels, it is important to strictly control the cleanliness of all materials that get in contact with the sample, such as crucibles, reagents, acids and ultra-pure water, volumetric flasks and test tubes. For the same reason, it is required to carefully follow the protocol for sample preparation as incorrect amounts of acids added can lead to incomplete digestion (leading to reduced accuracy and precision) or increased blank values.

### Results and Discussion

In order to demonstrate the potential of the proposed method to accurately determine the concentration of different trace elements in soil samples, four national primary standard substances were selected for the test, including GBW07304a, GBW07308a, GBW07402 and GBW07408. For each standard, 12 individual measurements were carried out in order to assess the accuracy of the results. The experimental results are summarized in table 2 and indicate that the measured values were consistent with the standard values, with high accuracy, whereas relative standard deviation between individual repeats were less than 5%, indicating a good reproducibility.

Table 2. Accuracy and Precision of the Method

GBW07304a					GBW07308a			
Element	Measured value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	RSD (%)	Standard value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Recovery (%)	Measured value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	RSD (%)	Standard value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Recovery (%)
7Li	38.1	1.1	39	97.7	22.5	1.4	22	102.3
9Be	1.9	1.5	2.0	95.0	3.3	1.2	3.5	94.3
45Sc	10.6	0.47	11.0	96.4	9.2	0.42	9.0	102.2
51V	98.7	1.9	99	99.7	32.3	0.13	31	104.2
52Cr	67.3	0.98	70	96.1	12.3	1.4	11.6	106.0
55Mn	983	1.3	1010	97.3	630	0.31	645	97.7
59Co	15.5	1.0	16.0	96.9	6.0	0.88	6.8	88.2
60Ni	27.7	0.35	28	98.9	2.6	1.5	3.0	86.7
63Cu	31.5	0.68	33	95.5	5.1	2.3	5.8	87.9
66Zn	136	1.0	139	97.8	78.7	0.60	80	98.4
71Ga	17.1	0.69	15.2	112.5	19.7	0.51	18.5	106.5
85Rb	86.7	1.4	89	97.4	229	1.3	232	98.7
88Sr	141	0.80	143	98.6	51.1	0.25	52	98.3
93Nb	17.5	1.1	20	87.5	26.5	0.30	27	98.1
95Mo	1.6	1.2	1.6	100	1.4	0.58	1.3	107.7
114Cd	0.91	1.7	0.90	101.1	0.15	3.2	0.16	93.8
133Cs	7.1	0.68	7.3	97.3	9.3	2.1	9.7	95.9
137Ba	360	0.43	369	97.6	625	0.47	620	100.8
181Ta	1.20	1.3	1.38	87.0	1.69	1.6	1.88	89.9
182W	2.5	1.3	2.6	96.2	3.5	0.62	3.3	106.1
205Tl	1.12	1.7	1.28	87.5	1.48	1.4	1.60	92.5
208Pb	67.4	0.31	68	99.1	35.7	0.35	37	96.5
209Bi	0.69	0.33	0.70	98.6	0.19	0.42	0.18	105.6
232Th	13.1	0.17	13.6	96.3	20.3	0.47	20.5	99.0
238U	2.8	1.0	3.2	87.5	4.4	0.22	4.7	93.6

GBW07402					GBW07408			
Element	Measured value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	RSD (%)	Standard value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Recovery (%)	Measured value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	RSD (%)	Standard value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Recovery (%)
7Li	21.3	1.9	22	96.8	33.8	2.7	35	96.6
9Be	1.8	0.56	1.8	100	1.8	2.8	1.9	94.7
45Sc	10.3	2.2	10.7	96.3	11.1	2.3	11.7	94.9
51V	63.1	0.82	62	101.8	80.7	1.1	81	99.6
52Cr	44.5	0.55	47	94.7	66.7	1.0	68	98.1
55Mn	498	0.26	510	97.6	627	1.2	650	96.5
59Co	8.1	0.42	8.7	93.1	12.3	0.68	12.7	96.9
60Ni	18.7	1.3	19.4	96.4	32.0	0.55	31.5	101.6
63Cu	15.4	0.49	16.3	94.5	23.0	1.3	24.3	94.7
66Zn	41.1	0.50	42	97.9	66.7	0.82	68	98.1
71Ga	13.5	0.25	12	112.5	16.1	1.8	14.8	108.8
85Rb	88.7	0.81	88	110.8	94.2	1.4	96	98.1
88Sr	183	0.78	187	97.9	238	0.75	236	100.8
93Nb	25.1	0.31	27	93.0	12.7	0.63	15	84.7
95Mo	1.12	2.0	0.98	114.3	1.26	1.8	1.16	108.6
114Cd	0.067	4.0	0.071	94.4	0.13	3.5	0.13	100
133Cs	4.5	1.2	4.9	91.8	7.1	1.5	7.5	94.7
137Ba	926	0.33	930	99.6	470	0.49	480	98.0
181Ta	0.63	0.49	0.78	80.8	1.00	0.48	1.05	95.2
182W	1.16	1.5	1.08	107.4	1.8	1.3	1.7	105.9
205Tl	0.55	1.8	0.62	88.7	0.54	1.1	0.58	93.1
208Pb	19.1	0.65	20	95.5	20.4	0.12	21	97.1
209Bi	0.37	1.1	0.38	97.4	0.31	0.83	0.30	103.3
232Th	16.1	1.2	16.6	97.0	11.2	0.43	11.8	94.9
238U	1.2	1.2	1.4	85.7	2.4	0.44	2.7	88.9



Please note that due to the complexity of the sample matrix with high concentrations of elements such as zirconium and molybdenum, some adjustments to the standard isotopes selected for key elements were required in order to avoid interferences. For example, although for the analysis of Cd, the preferred isotope is often  $^{111}\text{Cd}$  due to the absence of isobaric overlaps from other elements and reasonable abundance, the experimental results of  $^{111}\text{Cd}$  were not as good as those of  $^{114}\text{Cd}$ . The reason was that  $^{111}\text{Cd}$  was significantly biased from polyatomic interferences such as  $^{94}\text{Zr}^{16}\text{O}^{1}\text{H}^{+}$  and  $^{95}\text{Mo}^{16}\text{O}^{+}$ , despite the use of kinetic energy discrimination for removal of such interferences. Although  $^{114}\text{Cd}$  is susceptible to isobaric overlaps from  $^{114}\text{Sn}$ , as the content of Sn in soil samples and water sediments is generally low, mathematical correction of the contribution can be applied with good accuracy. The required correction equations are readily available in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ Software. For all other elements, the default isotopes for analysis could be used without any further correction.

The instrumental detection limits achieved for this analysis are summarized in table 3. These limits were calculated based on the standard deviation observed for 12 subsequent measurements of a blank solution using the  $3\sigma$  criterion. Please note that achievable instrument's detection limits significantly depend on the overall laboratory conditions, i.e. cleanliness of acids, vessels, standards.

Table 3. Detection Limits of the Elements

Element	Detection limit (ng·g <sup>-1</sup> )	Element	Detection limit (ng·g <sup>-1</sup> )	Element	Detection limit (ng·g <sup>-1</sup> )	Element	Detection limit (ng·g <sup>-1</sup> )	Element	Detection limit (ng·g <sup>-1</sup> )
7Li	0.14	9Be	0.0012	45Sc	0.028	51V	0.014	52Cr	0.085
55Mn	0.18	59Co	0.0042	60Ni	0.040	63Cu	0.020	66Zn	0.24
71Ga	0.016	85Rb	0.19	88Sr	0.072	93Nb	0.017	95Mo	0.022
$^{114}\text{Cd}$	0.0018	$^{133}\text{Cs}$	0.0012	$^{137}\text{Ba}$	0.087	$^{181}\text{Ta}$	0.0027	$^{182}\text{W}$	0.12
$^{205}\text{Tl}$	0.0024	$^{208}\text{Pb}$	0.054	$^{209}\text{Bi}$	0.0084	$^{232}\text{Th}$	0.0036	$^{238}\text{U}$	0.0015

## Conclusion

This application note demonstrates the comprehensive analysis of a large number of soil samples using a simplified sample preparation procedure using cost effective acid digestion in combination with the robust and sensitive iCAP-RQ ICP-MS. The iCAP RQ ICP-MS is perfectly suited for this type of application because of its user-friendly design combined with outstanding analytical performance. The unique design of the QCell CRC combining kinetic energy discrimination with an automatically adjusted low mass cut off allows to significantly reduce the impact of false positive signals caused by polyatomic interferences. A preliminary validation showed that excellent accuracy and precision was obtained for different relevant standard materials. The Qtegra ISDS Software allows analysts to leverage a full suite of embedded quality control tests and tools for data visualization for rapid screening of the data after analysis. Using the proposed method, laboratories can perform a full multi-element analysis of soil samples in a timely and cost-effective manner. The combination of KED mode with the high sensitivity of STD mode of the iCAP RQ ICP-MS enables the full analysis of all elements in one run in the shortest possible time, but with optimal detection limits.

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