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Trace elemental analysis

Robust and reliable analysis of soil samples using single quadrupole ICP-MS

Authors

Sukanya Sengupta, Tomoko Vincent, Daniel Kutscher

Thermo Fisher Scientific, Bremen, Germany

Keywords

ICP-MS, iCAP MSX, robustness, matrix tolerance, Argon Gas Dilution, quality control, soil analysis, accuracy

Goal

To highlight the use of the Thermo Scientific™ iCAP™ MSX ICP-MS for robust and accurate analysis of soil samples

Introduction

Soil is an essential part of our ecosystem and plays an important role in the development and sustainability of the biosphere. Maintaining fertility and quality of soil is an ultimate prerequisite for ensuring human and animal health. Environmental pollution is an important cause for concern in modern society, and applicable regulations and standards focus on regularly testing soils and sediments from different areas. For similar reasons, sludges, which are often used as fertilizers, are also regularly tested to detect harmful elements and compounds that may degrade soil quality and eventually pose a threat to human health and safety. Researchers and applied testing laboratories work to fully understand the root cause and potential impact of soil pollution, as well as its distribution through mobilization or diffusion. Accurate and rapid analysis of the content of metal substances in soil is a key step in accomplishing this important task.

Inductively coupled plasma mass spectrometry (ICP-MS) is a technique that is widely used for the elemental analysis of complex samples such as soil and sludge digests. In this application note the new Thermo Scientific™ iCAP™ MSX ICP-MS was used for the analysis of soils, sludges, and sediments. Argon Gas Dilution (AGD) reduced the manual work involved in sample dilution, and at the same time, enhanced the overall matrix tolerance of the system to different environmental samples. This study demonstrates how AGD can be used to readily deliver repeatable and reliable results with high accuracy and sensitivity in laboratories tasked to analyze high sample loads.

Experimental

Instrument parameters

An iCAP MSX ICP-MS instrument was used for the analysis of major and trace elements, including heavy metals, in different soil samples and reference materials. Digested and filtered soil samples were directly introduced into the ICP-MS and diluted online using argon gas, supplied from directly within the instrument (AGD). This minimized matrix effects that would affect data quality within a sequence (i.e., matrix effects or drift/suppression of the internal standard) but also reduced the impact of the matrix on the instrument, leading to an extension of maintenance intervals. Intelligent Matrix Handling, a unique feature of the Thermo Scientific™ iCAP™ MX Series, additionally reduces the impact of the matrix on the sample introduction system. The analysis was carried out in the kinetic energy discrimination (KED) mode using helium as a collision cell gas to eliminate typical polyatomic interferences caused by the matrix and the acids used in the digestion procedure. All instrument parameters are listed in Table 1.

Table 1. Instrument parameters

Parameter	Value
Nebulizer	iCAP MX Series Nebulizer
Interface cones	Ni – tipped sample and skimmer
Spray chamber	Cyclonic quartz
Spray chamber temp. (°C)	2.7
Injector	Quartz, 2.5 mm ID
Torch	Quartz torch
Auxiliary flow (L·min^{-1})	0.8
Cool gas flow (L·min^{-1})	14
Nebulizer flow (L·min^{-1})	0.348
CRC gas	Pure helium, 4.4 mL·min^{-1}
KED	3 V
AGD setting	AGD Level 10
RF power (W)	1,550
Sampling depth (mm)	8
Number of repeats	3

Samples and reference materials

Two soil samples and three soil, sediment, and sludge standard reference materials (SRM)—namely, SRM 2702 -Inorganics in Marine Sediment, SRM 2709a Joaquin Soil, and SRM 2781 Domestic Sludge—were analyzed in this study.

Sample preparation

The dry samples and reference materials were prepared using closed vessel microwave digestion (ETHOS™ EZ SK10, Milestone SRL). Homogenized aliquots of 0.25 ± 0.05 g of each sample were accurately weighed in and mixed with 5 mL of freshly prepared aqua regia (35–37% HCl: 67% HNO_3 = 3:1, TraceMetal™ Grade, Fisher Scientific™). The samples were digested and allowed to cool, and the solutions were quantitatively recovered to a final volume of 50 mL with ultrapure water. The digests were filtered before introduction into the ICP-MS, but no further manual dilution was performed prior to analysis.

Standards

The calibration ranges for the studied elements were chosen according to their expected concentrations in the SRMs that were selected for this study (Table 2). The standards were prepared using single element standards (SPEX CertiPrep™, Metuchen, NJ, USA).

An independently prepared solution containing 10 µg·L^{-1} of the elements in Groups 1–3 and 50 mg·L^{-1} of the Group 4 elements in Table 2 was used as a quality control (QC) standard for regularly checking the data quality during uninterrupted analysis of a large number of samples. An internal standard (IS) solution containing 40 µg·L^{-1} of In, Rh, Re, and Ir each was added online via a Y-connector to all solutions continuously during the analytical runs. The calibration blank, calibration standards, as well as both the QC and the IS solutions were prepared in an acid matrix of 2% HNO_3 and 0.5% HCl (v/v).

Table 2. List of calibration standards and their concentrations (in µg·L^{-1} for Groups 1-3, and in mg·L^{-1} for Group 4). The calibration block also included a calibration blank at zero concentration level for all analytes.

Group	Elements	Calibration range
1	Ag, As, Ba, Be, Cd, Co, Cr, Mo, Ni, Pb, Sb, Se, Tl	1–500 µg·L^{-1}
2	Al, Cr, Cu, V	0.005–5 mg·L^{-1}
3	Mn, Zn	0.005–10 mg·L^{-1}
4	Ca, Fe, K, Mg, Na	10–200 mg·L^{-1}

Software

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software was used for the analysis. It allows effortless instrument tuning with readily available AGD tune sets, setting up measurement sequences and data acquisition, as well as straightforward data evaluation.

Results and discussion

Linearity and sensitivity

A wide analytical range was covered for the different analytes, as listed in Table 2, and excellent linearity was obtained for all analytes (correlation coefficients >0.9995) in the selected concentration ranges. Excellent sensitivity was obtained for all analytes in the AGD Level 10 KED mode, indicated by the instrument detection limits (IDL) which are automatically calculated within the Qtegra ISDS Software, based on repeated analysis of the calibration blank (Table 3).

Table 3. List of target analytes and sensitivity expressed as instrument detection limits (IDL) in AGD Level 10 KED mode. The values in blue are in mg·L^{-1} and other values are in µg·L^{-1}.

Analyte	LOD	Analyte	LOD
^{9}Be	0.072	^{63}Cu	0.011
^{23}Na	0.016	^{66}Zn	0.026
^{24}Mg	0.010	^{75}As	0.051
^{27}Al	0.004	^{78}Se	0.079
^{39}K	0.007	^{95}Mo	0.014
^{44}Ca	0.006	^{107}Ag	0.017
^{51}V	0.007	^{111}Cd	0.031
^{52}Cr	0.067	^{121}Sb	0.025
^{55}Mn	0.003	^{138}Ba	0.002
^{57}Fe	0.012	^{205}Tl	0.005
^{59}Co	0.013	^{208}Pb	0.003
^{60}Ni	0.013		

Accuracy

The method accuracy was assessed by analyzing three different soil/sediment SRMs, prepared in the same way as the unknown soil samples. The certified, reference, and information values for the concentrations of the different elements in the SRMs, as well as the recoveries obtained during the analysis in this study compared to those certificate values are listed in Table 4. Very good recoveries were obtained within 80–120% for the different elements. The chosen digestion method does not

Table 4. List of standard reference materials (SRMs) analyzed in the current study, the expected concentrations of the different elements in the SRMs (certified values, *reference values, **information values), and the concentration recoveries obtained, expressed as a percentage compared to the certified values. All reported concentrations were derived from the 200-fold diluted digested measurement solutions. The expected concentrations are expressed in mg·kg^{-1} unless otherwise specified in the table.

Element	SRM 2781 Domestic Sludge		SRM 2709a Joaquin Soil		SRM 2702 -Inorganics in Marine Sediment	
	Certificate concentrations	Recovery%	Certificate concentrations	Recovery%	Certificate concentrations	Recovery%
Be	613.3 µg·kg^{-1} ± 24.7*	86.9 ± 3	-	-	-	-
Na	0.21% ± 0.01%*	93.3 ± 11	-	-	-	-
Mg	0.59% ± 0.02%*	109.6 ± 2	1.46% ± 0.02 %	86.4 ± 4	0.990% ± 0.074 %*	86.8 ± 4
K	0.49% ± 0.03%*	82.0 ± 8	-	-	2.054% ± 0.072 %	
Ca	3.9% ± 0.1%*	99.4 ± 3	3.36% ± 0.07%	82.6 ± 3	0.343% ± 0.024 %*	83.2 ± 4
V	-	-	110 ± 11	89.3 ± 3	357.6 ± 9.2	83.7 ± 5
Cr	202 ± 14	94.8 ± 5	130 ± 9	98.9 ± 7	352 ± 22	
Mn			529 ± 18	98.9 ± 5	1757 ± 58	97.8 ± 2
Fe	2.8% ± 0.1%*	98.2 ± 2	3.36% ± 0.07 %	90.0 ± 5	7.4 %**	97.7 ± 7
Co			12.8 ± 0.2	94.8 ± 4	27.76 ± 0.58*	90.7 ± 4
Ni	80.2 ± 1.8	87.1 ± 3	-	-	-	-
Cu	627.8 ± 18.4	97.1 ± 6	33.9 ± 0.5 *		117.7 ± 5.6	90.8 ± 4
Zn	1273 ± 68	103.4 ± 10	-	-	485.3± 4.2	85.3 ± 4
As	7.81 ± 0.67	102.3 ± 5	10.5 ± 0.3*	96.2 ± 2	45.3 ± 1.8	86.3 ± 1
Se	16.0 ± 1.5	99.9 ± 8			-	-
Ag	-	-	-	-	0.622 ± 0.078*	119.9 ± 2
Cd	12.78 ± 0.63	97.2 ± 3	0.371 ± 0.002	96.0 ± 7	0.817 ± 0.011	95.8 ± 3
Pb	200.8 ± 4.2	94.0 ± 6	-	-	132.8 ± 1.1	88.5 ± 3

involve a complete digestion of soil samples, as the use of HF had to be avoided. Thus, a complete extraction of elements bound within the silicate fraction of the samples could not be expected. Therefore, the recoveries for some elements have not been reported for soil and sediment SRMs. For the extractable elements in the respective SRMs, the recoveries were very good, thus verifying the accuracy of the method.

The method accuracy was additionally monitored by measuring a QC standard with elements at concentration levels of 10 μg·L^{-1} (Groups 1–3 elements, Table 2) and 50 mg·L^{-1} (Group 4 elements, Table 2). Very good recoveries were obtained for all elements, ranging on average between 83–105% for eight replicate measurements of the QC during a long analytical sequence (Figure 1).

Robustness

To test the suitability of the method and the iCAP MSX ICP-MS for running a high number of samples in an uninterrupted long analytical sequence of several hours, as is a typical requirement in environmental testing laboratories, a robustness test was carried out as a part of the present study. The sequence included an initial single calibration block, followed by regular QC checks, run first as initial calibration verification (ICV) and then as continued calibration verification (CCV), in between blocks of unknown samples and SRMs throughout the sequence of 8 hours. All QC checks passed successfully as described in the section on accuracy above and illustrated in Figure 1. The IS recovery was free of matrix suppression and drift, as evident from stable response within 80–120% over 8 hours of analysis (Figure 2). The acceptable ranges of IS recoveries in laboratories analyzing samples like soils, sediments, etc. is often much larger (e.g., 70–130%); thus, the performance of the iCAP MSX ICP-MS exceeds the analytical requirements with respect to soil analysis.

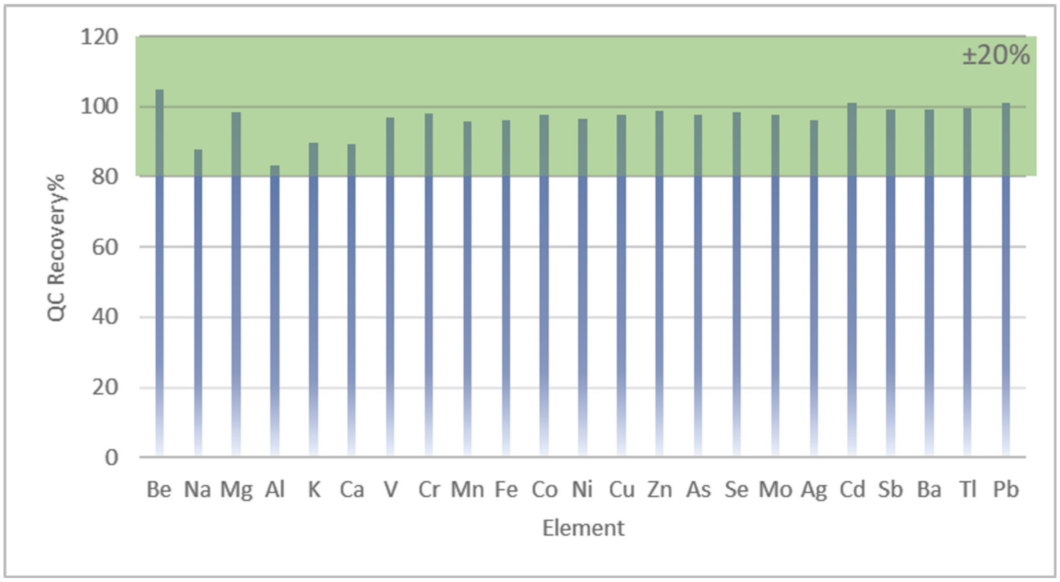

Figure 1. Quality control sample analytes recoveries for eight replicate runs during a long analytical sequence. The elements Ca, Fe, K, Mg, and Na were present at 50 mg·L^{-1} concentration level in the QC sample; all other elements were present at 10 μg·L^{-1} concentration level.

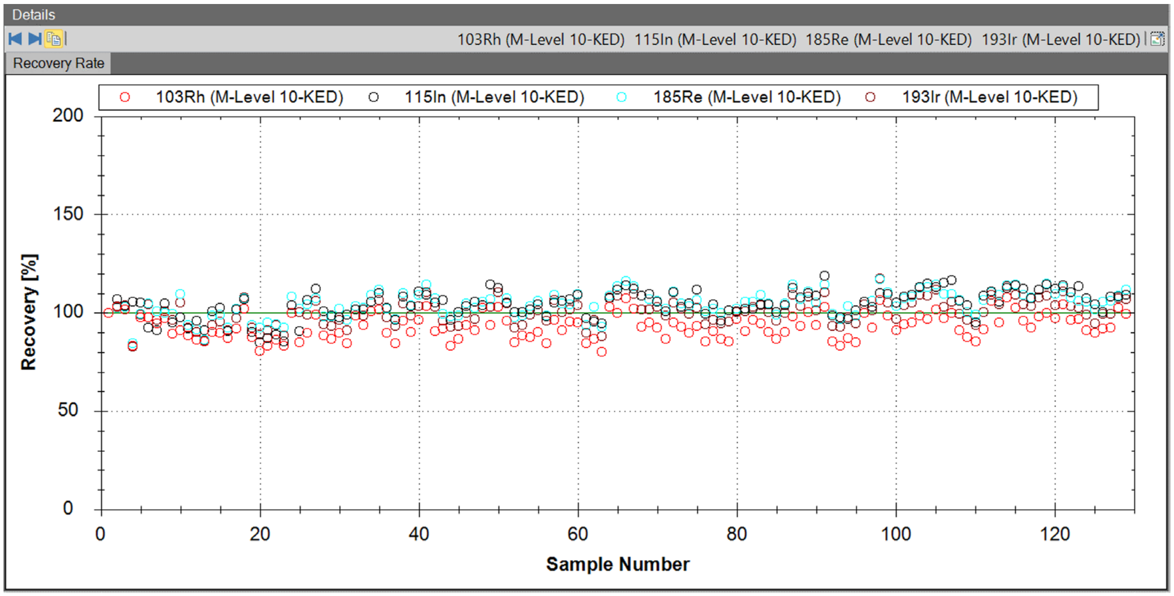

Figure 2. Stable response within 80–120% of the internal standards over 8 hours of robustness test including calibration blank and standards, and different soil and sediment samples and reference materials

Conclusions

The iCAP MSX ICP-MS is an excellent choice for laboratories performing soil and sediment digests with varying compositions. It provides the robustness and matrix tolerance needed to analyze the often challenging samples, yet at the same time provides the sensitivity required to detect important contaminants at relevant levels. The integrated argon gas dilution for controlled and automatic dilution of the sample aerosol effectively minimizes matrix effects without the need for laborious additional sample preparation. Robustness combined with accuracy and high sensitivity, enabling the analysis of several major as well as trace elements in soil samples with high reliability, makes this method an ideal option for seamless analysis of hundreds of soil samples daily. The most important results of this study are summarized below:

- The use of AGD Level 10 combined with KED mode measurements yielded excellent linearity, wide linear dynamic range, high sensitivity, and interference free data for a range of different elements in soil samples.
- Online sample dilution using integrated AGD offers an automatic solution for diluting soil sample digests to the desired extent and results in accurate and reliable analysis with minimal to no matrix induced signal variation.
- The accuracy of the method is confirmed by the SRM recoveries as well as the stable QC analyte response which were both found to be within 80–120% for the different analytes on repeated analysis over several hours.
- The internal standard recoveries remained stable and extremely consistent within 80–120% throughout the 8-hour robustness test, proving that a reliable uninterrupted and robust high-quality analysis of different types of soil samples can be easily carried out using the iCAP MSX ICP-MS.

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