

Environmental

Accurate and robust analysis of challenging environmental samples for regulatory compliance

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Goal

To highlight how most complex environmental samples, including soil digests and different water samples, can be analyzed with increased robustness and reduced downtime using the Thermo Scientific™ iCAP™ RQplus ICP-MS

Introduction

Environmental monitoring characterizes and assesses the safety and quality of the environment with the overarching objective of avoiding exposure to harmful substances, such as persistent organic pollutants (POPs) or heavy metals. Sample types frequently monitored include air, water, and soil; the latter two can be analyzed for elemental composition using atomic spectroscopy. Analysis of the elemental composition of soils for heavy metals, such as arsenic, lead, cadmium, and mercury, or nutritional factors, like phosphorous, is often carried out by analytical testing laboratories. To maximize the productivity of an analytical instrument, like an inductively coupled plasma mass spectrometer (ICP-MS), different sample types (for example, soil extracts and water samples) are ideally analyzed using a single method. There are region-specific standards and guidelines in place to ensure that the soil in the field, gardens, and other land areas is safe before any use of the land and to assure that toxic metals are not introduced after anthropogenic activities, such as the release of industrial waste, use of fertilizers, and mining. One key analytical method is U.S. EPA Method 6020B (SW-846),¹ which governs the analysis of soils, solid waste, and wastewaters.

However, the analysis of high matrix samples, such as soil digests and wastewater, present a unique challenge to ICP-MS analysis. Contract testing laboratories analyze hundreds of samples every day, leading to increased demand for cleaning and maintenance and thus causing downtime. In addition, the analysis of samples containing high dissolved solids may lead to enhancement or suppression of the analytical signal due to matrix effects and signal drift over time in a long analytical run, leading to failed samples and re-runs.

This application note discusses how the adverse effects of the sample matrix can be circumvented with an analytical workflow using the iCAP RQplus ICP-MS. The iCAP RQplus ICP-MS offers a comprehensive solution for effective and trouble-free analysis of high dissolved solids containing samples such as soil digests, wastewaters, and solid wastes. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to control the ICP-MS instrument and to generate, process, and report analytical data. The data presented in this application note was generated during an analysis of over 12 hours with more than 160 unknown samples, covering both soil extracts as well as typical water samples analyzed for environmental monitoring purposes.

Experimental

Instrument parameters and experimental conditions

The iCAP RQplus ICP-MS was used in this study, in conjunction with a Thermo Scientific™ iSC-65 autosampler. The instrument includes a full toolset to allow direct analysis of samples with increased levels of dissolved solids without prior dilution. Automated dilution of all blanks, standards, and samples in a batch can be accomplished using argon as a diluent added through the instrument. The addition of argon gas for dilution, together with a reduced nebulizer gas flow, not only improves the robustness of the plasma against elevated matrix loads, but also reduces the oxide formation rate significantly (generally below 0.5% using the conditions described here).

Another crucial challenge in ICP-MS analysis is interferences. The use of hydrochloric acid, a key reagent to assure effective digestions and improve the chemical stability of samples, leads to the formation of polyatomic interferences, affecting key contaminants under surveillance (i.e., monoisotopic $^{75}\text{As}^+$ can be positively biased through $^{40}\text{Ar}^{35}\text{Cl}^+$). The iCAP RQplus ICP-MS was operated using Kinetic Energy Discrimination (KED) mode, with pure helium as the only collision cell gas to remove potential polyatomic interferences on various analytes, even though oxide-based polyatomics are already reduced using argon gas dilution. The sample introduction system components and instrument parameters used for this study are summarized in Table 1.

Table 1. Instrument configuration and typical operating parameters

Parameter	Value
Nebulizer	MicroMist™ nebulizer (400 $\mu\text{L}\cdot\text{min}^{-1}$)
Interface cones	Ni – tipped sample and skimmer
Skimmer cone insert	High matrix
Spray chamber	Cyclonic quartz
Injector	Quartz, 2.5 mm i.d.
Torch	Quartz torch
Auxiliary flow ($\text{L}\cdot\text{min}^{-1}$)	0.8
Cool gas flow ($\text{L}\cdot\text{min}^{-1}$)	14
Nebulizer flow ($\text{L}\cdot\text{min}^{-1}$)	0.26
AGD setting	Mid
Additional gas, argon (% of range)	65
RF power (W)	1,550
Sampling depth (mm)	10
Number of replicates	3
Spray chamber temp ($^{\circ}\text{C}$)	2.7
KED settings (gas flow rate in $\text{mL}\cdot\text{min}^{-1}$)	4.8 (with a 3 V kinetic energy barrier)
Number of sweeps	5

Sample preparation

A total of ten different soil and five different water samples, including two standard reference materials (SRMs), were prepared for analysis. Soils were digested using microwave assisted acid digestion utilizing aqua regia as a digestion medium, as is described elsewhere². The SRMs were prepared according to the methodology described in EPA Method 6020B (SW 846).

The water samples comprised two wastewater samples, two brackish water samples, and one groundwater sample with approximate TDS ranging from 0.25 to 1.6% (w/w). These samples were then analyzed as technical replicates during a long-term measurement of more than 12 hours. The sample preparation accomplished with microwave digestion using aqua regia is suitable for analysis of extractable analytes but would not provide information regarding total content of the soil matrix. For determination of total content, samples need to be digested using hydrofluoric acid (HF) to ensure complete digestion of all components, especially silicates.

Calibration and quality control standards

Calibration curves were generated for 24 analytes using seven calibration standards and a calibration blank. The calibration standards were prepared by gravimetric dilution of intermediate stock solutions using a solution of 2% nitric acid and 0.5% HCl as the diluent. An internal standard solution containing 1,000 µg·L⁻¹ of ⁶Li, 200 µg·L⁻¹ of Sc, and 20 µg·L⁻¹ of Y, Rh, In, Tb, Ho, and Bi was added online continuously during the entire duration of the analysis. All regulated methods used for environmental monitoring require stringent quality control (QC) protocols to ensure data quality.

Typical QC checks include blanks tests (ICB and CCB to check for carryover of analytes and to verify that contract required detection limits can be met), calibration tests (ICV and CCV to monitor ongoing validity of the calibration curve), as well as spike tests (to check the digestion procedure and recovery of analytes), and the analyses of SRMs (to ensure accuracy). The Qtegra ISDS Software contains a full feature set to automatically perform the required QC checks and display results directly in the main results section. Automated actions upon QC warning or failures can be set up, starting from a simple rinse and repeat test up to aborting the entire sequence.

Results and discussion

Linearity and instrument detection limits

Instrumental detection limits (IDLs) for all analytes were calculated based on three times the standard deviation of the ten replicate measurements of the calibration blank. Excellent detection limits were achieved for all analytes with the correlation coefficients (R²) greater than 0.9995, which suggests excellent linear response for the established concentration range for each analyte.

System suitability checks – ensuring interference free analysis

A typical digested solution of soil contains naturally abundant elements such as Na, K, Ca, Mg, Fe, Al, P, and S at relatively high concentrations, which may vary significantly depending upon the soil sample and its collection point. These major constituents can also cause polyatomic or isobaric interferences on the masses of other trace level analytes, leading to the inaccurate determination of those critical toxic elements. EPA Method 6020B describes a dedicated test to ensure that the analytical system and the employed method are fit for purpose and that measurements are not biased due to the presence of potential interferents.

Two separate solutions were prepared to perform this study, often referred to as Interference Check Solution (ICS) A and AB, containing common interfering elements (ICSA) as well as

interferents and typical analytes at stated concentrations (ICSAB). The composition of both solutions is described in Table 2. Both solutions need to be analyzed at the beginning of the analytical batch of unknown samples and must return concentrations below a threshold value for common analytes in ICSA, as well as recovery within acceptable range in ICSAB. The results obtained indicate full compliance with the acceptance criteria mapped out in EPA Method 6020B.

Table 2. Analytes and interferents with their respective concentrations in solution A and solution B (all results expressed as µg·L⁻¹)

Analytes/ interferents	ICSA		ICSAB	
	Concentration and acceptance criteria [µg·L ⁻¹]		Concentration [µg·L ⁻¹] and acceptance criteria [%]	
Ag, As, Be, Cd, Co, Mn, Ni, Pb, Ti	0	<2	20 for all analytes except for Cu, Ni, Pb (25), Mn, Zn (30) and Cr (40)	80–120
Cr, Cu, Sb, Zn	0	<4		
ISe, V	0	<10		
Ba	0	<20		
Al, Ca, Fe, Mg, K, Na, P, S	100,000	80–120	100,000	80–120
C	200,000	N/A	200,000	N/A
Cl	1,000,000	N/A	1,000,000	N/A
Mo, Ti	2,000	80–120	2,000	80–120

Quality control results

The results obtained during the analysis of ICB and analysis of CCB solutions in the required intervals were found to be less than the IDL achieved for each analyte. The results demonstrated that no considerable carry-over was present from sample to sample, and analysis of unknown samples could be continued without the need of any corrective action. The concentrations for each analyte in the ICV solution were found to be within 90–110% of the true value, confirming that the initial calibration standards are at the correct concentrations.

Continuing calibration verification (CCV) – ensuring accurate quantification of every sample

To verify the ongoing validity of the calibration curve throughout the analytical run and to confirm that the analytical data acquired for unknown samples is consistently accurate, a CCV check solution containing all analytes at a concentration level located in the middle of the calibrated range was analyzed periodically. The percent accuracy for each analyte was calculated directly within Qtegra LabBook and was within 90–110% of the true value in all CCV samples analyzed throughout the analytical sequence.

Method accuracy – analysis of standard reference materials

Method accuracy was further assessed by analyzing two different SRMs, which were prepared in the same way as all unknown samples. The National Institute of Standards and Technology (NIST) SRM 2709a Joaquin Soil (Baseline Trace Element Concentrations) and NIST SRM 2711a Montana Soil II were the two SRMs analyzed in this study. Table 3 summarizes the analytes and their concentration ranges based on results obtained by several Contract Laboratory Program (CLP) laboratories and the measured concentrations. As shown, the recoveries achieved for most analytes were within the generally accepted concentration ranges, demonstrating the accuracy of the results from the method developed.

Method robustness – enabling long-term analysis of challenging matrices

Continuous and long-term analysis of high and varying matrix containing samples may lead to the deposition of solids on the

interface cones, mass specific signal drift over time, QC failures, and suppression or enhancement in the response of internal standards. These challenges lead to more frequent maintenance of the system and/or dilution of samples to reduce matrix content, followed by reanalysis of the samples, consuming more time and resources.

An indication of instrument robustness is the ability to analyze samples of varying matrices over an extended period with minimum suppression and drift in the internal standard response. Figure 1 shows the response of all internal standards monitored during an analytical run sequence containing both soil digests and wastewater samples analyzed continuously for 12 hours. Within the run sequence, soil samples and water samples were analyzed alternately resulting to the analyses of at least 80 of each sample type.

Table 3. Analyte concentration ranges and measured concentrations from SRM analyses

Analytes	NIST SRM 2709a		NIST SRM 2711a	
	Concentration range (mg·kg ⁻¹)	Measured concentration (mg·kg ⁻¹)	Concentration range (mg·kg ⁻¹)	Measured concentration (mg·kg ⁻¹)
Be	0.5–0.72	0.7	0.73–1.1	1.00
Na	460–610	565	140–210	210.76
Mg	9,700–11,000	11,342	5,000–6,000	7,019
Al	13,000–17,000	23,797	9,800–15,000	19,444
K	2,600–4,000	3464	3,300–4,600	4,562
Ca	12,000– 14,000	13,276	14,000–17,000	16,313
V	43–71	66.5	24–34	33.98
Cr	46–67	65.2	12–18	18.6
Mn	380–450	447	450–580	511.8
Fe	22,000–26,000	27,415	14,000–18,000	19,817
Co	8.2–13	11.6	5.5–9	7.9
Ni	59–71	67.5	13–18	17.1
Cu	24–28	27.2	120–160	123.3
Zn	69–87	82.5	310–380	343.4
As	6.4–10	9.3	81–110	93.3
Se	0.69–1.9	2.2	1.4–1.9	2.8
Ag	0.14–4.1	0.3	4–6.1	7.00
Cd	0.33–0.66	0.3	43–56	49.6
Sb	1.2–1.5	0.2	2.8–7.2	4.43
Ba	350–400	384.2	170–200	177.5
Hg	0.79–0.92	1.0	6.3–8.3	7.6
Tl	0.74–1.6	0.2	0.71–3.1	1.97
Pb	8.1–11	10.9	1,100–1,400	1,361

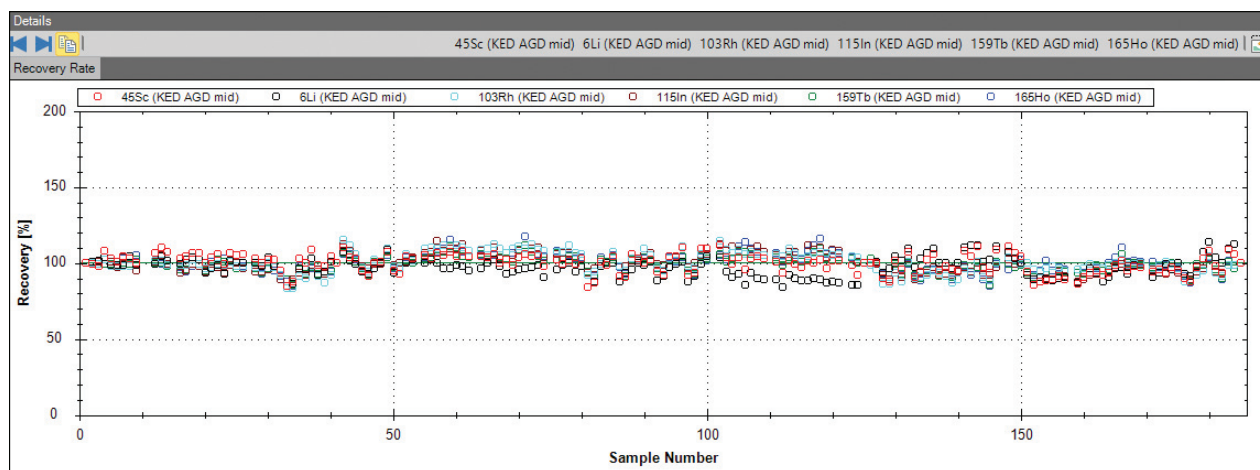


Figure 1. Internal standards response obtained over a period of 12 hours of continuous measurements

As shown, the response for all internal standards was between 80 to 120% of the initial response in the calibration blank, well within the acceptable range of $\pm 30\%$ described in EPA Method 6020B. There is no systematic pattern recognizable, which would indicate that one of the matrix types under investigation here would create a more severe impact on the overall stability of the system. Internal standards Y and Bi were found to be present in some of the soil samples, causing erroneously high responses, hence they are excluded from the plot and were not used in any of the calculations.

Conclusion

The quality of analytical data obtained during this study indicates that the iCAP RQplus ICP-MS equipped with argon gas dilution for controlled and automatic dilution of the sample aerosol offers the desired robustness and matrix tolerance, enabling contract testing laboratories to perform the analysis of challenging environmental samples with improved productivity. Some of the key highlights and findings of this study are summarized below:

- The instrument detection limits and correlation coefficients achieved for each analyte suggest that the proposed method can be used for sensitive determination of target analytes with wider linear range, enabling reliable analysis of samples with varying elemental composition.

- The accuracy of all analytes obtained from the analyses of the ICS solutions indicates that KED mode using helium as the cell gas offers effective interference removal, enabling the use of a single mode method for accurate and rapid determination of target analytes.
- The accuracy of analytes obtained during measurement of the CCV standards suggests that the method developed for this study was optimized for the sample types and that the initial calibration was verified consistently throughout the run sequence.
- The accuracy determined by the analyses of two NIST SRMs further highlights the capability of the iCAP RQplus ICP-MS in delivering reliable data.
- The consistent internal standards recovery of 80–120% observed during the analysis of a mixed batch of typical samples, analyzed in a period of 12 hours, demonstrates the robustness of the system and the absence of physical interferences causing signal drift and suppression or enhancement.
- Qtegra ISDS Software provides comprehensive QC functionalities that enable the automatic calculation of recoveries and precision.

References

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