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Novel developments in ICP-MS: How can the analysis of complex samples be made simple?

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ABSTRACT

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is one of the key technologies used for the determination of trace element concentrations in almost any sample type. Following its initial development in 1980, it has seen an unparalleled ramp up, and grew from a high-end tool used in cutting edge research laboratories to a widely-used technique used in many thousands of laboratories across all regions.

In 40 years of being available, there have been developments to drive detection limits lower, hyphenation of separation techniques and accessories to allow for direct sampling of solids, increases in productivity and sample throughput, and, most of all, better removal of interferences. This presentation will provide an overview on novel developments in ICP-MS, providing an unmatched ability to tackle samples with outstanding complexity, both in terms of matrix load and interferences.

INTRODUCTION

Alongside the technological development, the complexity of samples to be analyzed using ICP-MS increased at the same level, and typical samples run by analytical testing laboratories today require the analysis of matrix levels previously analyzed using ICP-OES. This is particularly true for environmental monitoring, with region-specific standards and guidelines put in place to ensure that soil 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), which governs the analysis of soils, solid waste, and wastewaters.

MATERIALS AND METHODS

The Thermo Scientific™ 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. For the analysis of brine solutions, a PFA microflow nebulizer (Elemental Scientific (ESI), Omaha, USA) in conjunction with humidifier (Pergo, Elemental Scientific (ESI), Omaha, USA) was used. The sample introduction system components and instrument parameters used for this study are summarized in Table 1.

Table 1. Instrument configuration and operating parameters

Parameter	Value [EPA Method 6020 B]	Value [Analysis of brine]
Nebulizer	Micromist nebulizer (400 µl·min^{-1})	PFA MicroFlow ST, orange cap, 400 µL·min-1
Interface	Ni – tipped sample and skimmer	
Spray chamber & Injector	Cyclonic quartz, 2.5 mm ID	
Torch	Quartz torch	
Nebulizer flow (L·min^{-1})	0.26	0.22
AGD setting	Mid	High
Additional gas, argon (% of range)	65	70
Sampling depth (mm)	10	10
KED settings (gas flow rate in mL·min^{-1})	4.8 (with a 3V kinetic energy barrier)	
Number of sweeps	5	

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 elsewhere[2]. 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.

A brine solution containing 25% w/w of NaCl was prepared by dissolving 25 g of pure NaCl (Sigma-Aldrich, 99.0%) in 100 g 2% v/v HNO_3 (Optima™ grade, Fisher Scientific™). To demonstrate the capability of the instrument for accurate and precise analysis despite the challenging sample matrix, spike recovery tests were performed with brine solutions ranging from 0.5% w/w to 4% w/w, prepared from the original 25% w/w brine solution described earlier.

To test the performance of the method for the analysis of such sample types over longer periods and demonstrate analytical robustness for a high throughput orientated laboratory, a brine solution with a concentration of 2.5% w/w was analyzed over a period of 9 hours.

RESULTS

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).

Three default dilution levels (AGD-low, AGD-mid and AGD-high) are provided as an integral part of the Qtegra ISDS software and are readily available to use upon the instrument installation. Table 2 provides an overview on a wide range of typical samples containing high matrix loads together with the recommended dilution setting that will provide the most suitable solution for analysis. This table can be used as a first reference point when a method needs to be developed for a new sample type.

Table 2. Typical sample matrices, expected TDS level, recommended dilution modes for their analysis

Sample matrices	% TDS content	Recommended Dilution mode
Drinking water, surface water,	< 0.5%	AGD Low
Food Digests	0.5-1.0%	
Wastewaters	< 1.0%	AGD Mid
Soil Digests, Geological & Mining Samples	< 1.0%	
Brackish Waters, Fracking Flowback Solutions	< 1.5%	
Brackish Waters, Sea Water, Brine Solutions	< 3.0%	AGD High
Highly concentrated brine solutions	>3.0%	

EPA Method 6020 B (SW-846)

EPA Method 6020B is a performance-based method that includes analysis of a series of QC samples as part of the quality control protocol to ensure accuracy, precision, robustness, and reliability of the analytical data acquired during the run sequence.
Method accuracy was 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.

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

Analytes	NIST SRM 2709a Joaquin soil		NIST SRM 2711a Montana Soil II	
	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

A CCV standard was also analyzed every 10 samples to verify validity of the ongoing calibration. Concentrations of all the analytes in the CCV solution are presented in Table 2. The concentrations obtained for all the analytes in the CCV solution were found to meet the acceptance criteria of 90–110% of the true value of each analyte. Figure 1 presents the accuracy obtained for the analytes in the CCV solution for three consecutive days of measurements of unknown samples.

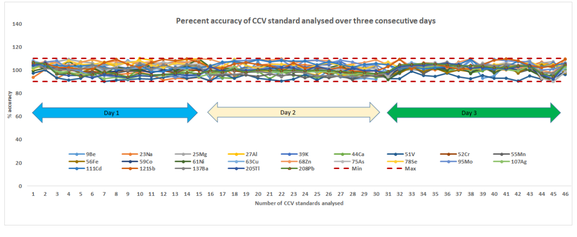

Figure 1. Percent accuracy of CCV standard analyzed on three consecutive days

Analysis of brine solutions

The analysis of samples containing higher levels of dissolved solids (typically above 0.5% w/v) is a known challenge in ICP-MS. The complexity of the sample matrix can significantly affect the sensitivity of the instrument, cause intensity fluctuation of the internal standard (suppression and drift), and lead to increased system maintenance with unwanted downtime due to clogging of the interface cone orifices, torch injector, or nebulizer tip.

It is important to validate the performance of any method to reliably allow the analysis of brine solutions over a wide concentration range. In this study, solutions containing between 0.5% and 25% w/w NaCl were analyzed and evaluated for the recovery of the internal standards and spike recovery at a level of 25 µg·L^{-1} for the common impurities. For all internal standards, a stable response with almost no suppression was observed against the initial readback in nitric acid. The only exception was tellurium, showing signal suppression in the range of 40% when analyzing solutions containing more than 3.0% of NaCl. This observation can be explained by the high ionization potential of tellurium (1st IP of 9.00 eV and degree of ionization of 66.74%).

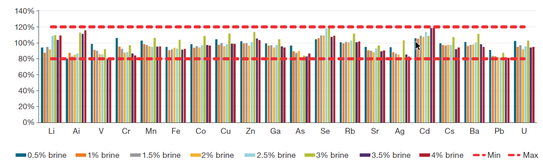

Figure 1. 25 µg·L^{-1} spike recovery performance with simulated brine water samples containing 0.5% to 4.0% w/w NaCl (N=3) for each concentration)

CONCLUSIONS

- All the requirements of EPA Method 6020B were met during the test period of three days, enabling the analysis of a total of 600 samples.
- 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.
- The highest dilution setting available for AGD allowed the aspiration of up to 25% w/w brine samples and allowed excellent MDLs to be obtained, while eliminating the need for labor-intensive manual sample dilution and accelerating sample throughput.
- Excellent CCV recovery and spike recovery results, as well as stable and consistent internal standards response, were obtained across a batch containing 120 samples of a 2.5% w/w brine solution, demonstrating the reliability of the method.

REFERENCES

1. Application Note 1592: Robust analysis of a variety of water and wastewater samples according to U.S. EPA Method 6020B (SW-846), Thermo Fisher Scientific
2. Application Note 1835: Accurate and robust analysis of challenging environmental samples for regulatory compliance, Thermo Fisher Scientific
3. Application note 1503: Managing the challenges of analyzing brine solutions of variable concentration using inductively coupled plasma mass spectrometry (ICP-MS) equipped with argon gas dilution, Thermo Fisher Scientific

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