On-line isotope dilution analysis with the 7700 Series ICP-MS: Analysis of trace elements in high matrix samples

Application note

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Abstract

This work describes a simple, accurate and precise ICP-MS method for the direct determination of trace elements in high matrix samples by on-line isotope dilution analysis (OIDA). The use of isotope dilution eliminates the need for time-consuming external calibrations and corrects for matrix suppression as well as signal drift, eliminating the need for periodic recalibration or drift correction. The effective dynamic range for the method is more than 4 orders of magnitude (0.1 to 1000 µg/L). The capability of an Octopole Reaction System ICP-MS (ORS-ICP-MS) operated in helium collision mode to remove all matrix-based polyatomic interferences in complex matrices is important, since OIDA requires two interference-free isotopes of each analyte (or an interference-free tracer isotope in the case of monoisotopic elements). High Matrix Introduction (HMI) with aerosol dilution was also used to allow the routine analysis of high matrix samples. The combination of OIDA and ORS-ICP-MS with HMI proved to be an ideal solution for routine high matrix sample analysis, increasing sample throughput and improving the quality and reliability of the analytical results.

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Introduction

The analysis of trace metals in high matrix samples such as seawater, sludge or urine often generates data with large uncertainty values and poor repeatability. Such high matrix samples are difficult to analyze by ICP-MS due to their complex and often variable composition and the fact that high levels of matrix elements give rise to unpredictable matrix-based polyatomic interferences that affect many commonly required analytes. The very high total dissolved solids (TDS) levels in these types of samples (up to 3% w/v for seawater) can also cause matrix deposition on the interface, which gradually clogs the cone orifices and leads to a reduction in signal intensity and poor long-term stability.

Isotope dilution analysis (IDA) or isotope dilution mass spectrometry (ID-MS) is a well-known analytical technique based on the measurement of isotope ratios in samples where the isotopic composition has been altered by the addition of a known amount of an isotopically enriched element [1]. It is an absolute quantitative method (traceable to the primary isotopic standard) and is commonly used for applications where high accuracy and certainty is required, for example in National Metrology Institutes. Also, since the quantification solely depends on the measurement of the isotope ratio in the sample itself and does not involve the use of external calibration, IDA is significantly less prone to matrix effects. IDA offers the possibility to determine major to ultra-trace concentrations of elements in virtually any matrix, with superior accuracy and precision compared to external calibration and is often used as a reference method for certified reference material characterization [2].

However, in routine testing laboratories, IDA is often perceived to be a 'complicated' analytical method with limited applicability for routine multielement measurements. IDA calculations are not trivial if errors that affect the isotope ratio determination have to be corrected, the technique cannot be applied to monoisotopic elements, and its application range is limited compared to external calibration. Furthermore, sample preparation for conventional IDA is time-consuming, since a determined amount of the isotopic spike solution has to be added to each sample individually. The development of on-line IDA (OIDA), where a mixture of enriched isotopes is added to the samples on-line using a T-connector prior to the ICP-MS nebulizer, eliminates many of these issues and simplifies both the sample preparation and the quantitative calculations [3].

Conventional IDA requires at least two isotopes free from spectral interferences, but all the isotopes of almost all the elements below m/z 80 can be affected by polyatomic interferences in common sample matrices. The Agilent 7700x ICP-MS system with 3rd generation Octopole Reaction System (ORS^3) operates in helium collision mode (He mode) with KED, which has proven to be effective in removing a wide range of plasma and matrix-based polyatomic species. The key benefit of He mode is that it filters out polyatomic interferences without generating any of the new and unpredictable interferences that are characteristic of cell systems that operate with reactive gases — even hydrogen. The use of helium mode allows the accurate determination of both primary (preferred) and, where available, secondary (confirmatory) isotopes for all elements in a single run. The effective removal of interferences on multiple isotopes of every analyte is critical for accurate IDA with quadrupole ICP-MS. Helium mode conditions are independent of the sample matrix, so a single set of conditions can be used, which simplifies method development and reduces the total acquisition time. Finally, Agilent's High Matrix Introduction (HMI) technology enables the direct analysis of samples with high (up to several %) TDS levels [4], so the need for sample dilution with high matrix sample types is largely eliminated.

IDA can easily be adapted to routine analysis by combining OIDA with the unique performance of the Agilent 7700x ICP-MS ORS^3 system and HMI. This combination has the potential to be an ideal solution for high matrix sample analysis, providing increased sample throughput and improved productivity, as well as better accuracy, absolute quantification, and reduced uncertainty. Furthermore, monoisotopic elements can be determined in the same run, without the need for external instrument calibration, using a 'pseudo isotope dilution' approach.

Experimental

Instrumentation

An Agilent 7700x ICP-MS, which includes the High Matrix Introduction (HMI) kit and Octopole Reaction System (ORS^3), was used throughout. The ORS^3 was operated in helium collision mode only; all elements were measured using a single set of operating conditions without switching cell gas modes. The sample introduction system consisted of a MicroMist glass concentric nebulizer and a quartz double-pass Scott-type spray chamber maintained at a temperature of 2 °C. A standard quartz torch with 2.5 mm internal diameter (ID) injector was used. HMI conditions were ultra robust plasma with medium level aerosol dilution, auto-tuned using the 7700 MassHunter software. The instrument was equipped with an Agilent I-AS integrated autosampler, and the standard on-line internal standard addition kit was used for the on-line addition of the multielement isotopic spike solution. Instrumental conditions including HMI settings are summarized in Table 1. Total analysis time per sample, including wash-in and wash-out, was 2.5 minutes.

Table 1. Agilent 7700x ICP-MS operating conditions

Instrument parameter	Value
Forward power	1550 W
Plasma gas	15 L/min
Plasma conditions	Ultra robust
Aerosol dilution level	Medium
Kinetic energy discrimination (KED)	3 V
Helium collision gas	4.5 mL/min
Acquisition parameter	**Value**
Acquisition mode	Spectrum
Points/mass	1
Integration time/point	0.2 s
Replicates	3

Standards

The seawater Reference Material NASS-5 was obtained from the National Research Council of Canada (Ottawa, Canada). The wastewater SPS-WW1, the urine NIST-2670a and the sewage sludge BCR-146R were obtained from LGC Standards (Barcelona, Spain). A multielement isotopically-enriched standard IES-WAK, employed for the multielement trace metal determination, was obtained from ISC-Science (www.isc-science.com, Oviedo, Spain). A synthetic high matrix solution was prepared by dissolving the following matrix components in 1 liter of deionized water:

- 24 g $NaCl$
- 11 g $MgCl_2.6H_2O$
- 4 g Na_2SO_4
- 2 g $CaCl_2.6H_2O$
- 0.7 g KCl
- 0.1 g KBr
- 0.03 g H_3BO_3
- 0.005 g $NaSiO_3.9H_2O$
- 0.04 g $SrCl_2.6H_2O$
- 0.003 g NaF
- 0.002 g NH_4NO_3
- 0.001 g $Fe_3PO_4.4H_2O$

On-line isotope dilution

Sample spiking consisted simply of an automated on-line addition using the autosampler and standard peristaltic pump of the 7700x ICP-MS, with no further modification to instrument setup. The only change to the conventional setup was that the normal internal standard solution was replaced by the multielemental isotopically-enriched spike solution. The sample or natural standard (reference standard) and spike solutions were pumped to the nebulizer and the two solution streams were combined before the nebulizer, using the online ISTD addition kit. The multielement isotopic spike solution was delivered continuously using one channel of the peristaltic pump, with the samples and natural standards delivered from the autosampler vials by a second channel of the pump.

Analyte concentrations in the samples were calculated using the simplified OIDA equation [3]:

$$C_s = C_{st} \times \frac{R_{st}R_n - 1}{R_m R_n - 1} \frac{R_{sp} - R_m}{R_{sp} - R_{st}}$$

Where,

- C_s concentration of the analyte in the sample (the result to be calculated)
- C_{st} concentration of the analyte in the natural reference standard (st) (certified value)
- R_{sp} isotope ratio of spike (sp) (certified value)
- R_n natural isotope ratio of analyte (IUPAC value)
- R_m measured isotope ratio of the mixed sample and spike solution (s + sp)
- R_{st} measured isotope ratio of the mixed reference standard and spike solution (st + sp)

From the above, it is apparent that the isotope ratios R_{st} and R_m are the only unknown parameters that have to be determined in order for the sample concentration (C_s) to be calculated. The raw data (CPS) of each isotope was easily exported from the MassHunter data analysis table directly into a custom-designed Microsoft® Excel spreadsheet (included on CD-ROM with the IES-WAK standard), where the isotope ratios were calculated and then incorporated into the equation for the calculation of the concentration (C_s) of each analyte. The natural (IUPAC) isotope ratio values for (R_n) and the certified ratios in the multielement isotopically-enriched standard IES-WAK (R_{sp}) are summarized in Table 2. The ratios are all shown as Isotope 2 abundance/Isotope 1 abundance, where Isotope 1 is the normally preferred isotope for each element.

The concentrations of the monoisotopic elements were obtained using a 'pseudo isotope dilution' approach [4] in which the internal standard (Sc or Th) was used as a 'tracer isotope' and the analyte concentrations calculated using the above equation.

Table 2. Certified/reference R_n and R_{sp} values for the natural elements and the isotopic standard IES-WAK.
* Denotes monoisotopic analyte: tracer isotope used.

	Isotope 1	Isotope 2	R_n	R_{sp}
B	11	10	0.248	302.0
Cr	52	53	0.113	14.38
Mn*	55	45 (Sc)		
Fe	56	57	0.023	31.64
Co*	59	45(Sc)		
Ni	60	61	0.044	8.721
Cu	63	65	0.446	63.85
Zn	66	67	0.147	22.64
As*	75	45(Sc)		
Se	78	77	0.321	1,120
Sr	88	86	0.119	33.38
Mo	95	98	1.516	0.009
Ag	107	109	0.929	151.0
Cd	111	114	2.245	0.009
Sn	120	119	0.268	11.83
Sb	121	123	0.748	73.46
Ba	137	138	6.385	0.073
Hg	202	199	0.565	116.3
Tl	205	203	0.419	36.31
Pb	208	207	0.422	32.65
U*	238	232(Th)		

In Isotope Dilution Analysis, the amount of spike added to the sample is usually optimized by calculating the ideal ratio using the 'error magnification factor' [5]. This factor depends on the isotopic abundances of the enriched element spike, as well as of the natural isotopic abundances of that element in the samples. For OIDA, the spike amount is constant, but it is preferable to 'over-spike' the samples to yield better counting statistics and therefore less uncertainty in the isotope ratio measurements. The effective quantitative range of OIDA depends on the concentration of the reference standard for each analyte. The concentration of each element in the reference standard should ideally be midway between the lower and upper quantification limit: this gives a quantification range of at least 4 orders of magnitude. Therefore the concentration levels of analytes in the multielement isotopic standard are matched to the reference standards used. Because all

analytes are present in the multielement standard at the appropriate level, the spike standard can be added on-line, automating the spike addition. Table 3 shows the working quantification range of the multielement standard IES-WAK. Note that the lower limit can vary depending on the instrument and working conditions. For example reagent quality and blank levels can affect the lower limit of the analytical range.

Table 3. Working quantification range of the multielement isotopic standard IES-WAK. All concentrations are in µg/L except Ca, Mg, K and Na (mg/L).

Analyte	Units	Lower limit	Upper limit
Aluminum (Al)	µg/L	0.1	10,000
Antimony (Sb)	µg/L	0.1	1000
Arsenic (As)	µg/L	0.1	1000
Barium (Ba)	µg/L	0.1	10,000
Boron (B)	µg/L	0.1	5000
Cadmium (Cd)	µg/L	0.1	1000
Calcium (Ca)	mg/L	0.05	500
Chromium (Cr)	µg/L	0.1	1000
Cobalt (Co)	µg/L	0.1	1000
Copper (Cu)	µg/L	0.1	2000
Iron (Fe)	µg/L	0.1	5000
Lead (Pb)	µg/L	0.1	2000
Lithium (Li)	µg/L	0.1	1000
Magnesium (Mg)	mg/L	0.05	500
Manganese (Mn)	µg/L	0.1	1000
Mercury (Hg)	µg/L	0.1	100
Molybdenum (Mo)	µg/L	0.1	5000
Nickel (Ni)	µg/L	0.1	2000
Potassium (K)	mg/L	0.05	500
Selenium (Se)	µg/L	0.1	1000
Sodium (Na)	mg/L	0.05	500
Strontium (Sr)	µg/L	0.1	1000
Thallium (Tl)	µg/L	0.1	1000
Tin (Sn)	µg/L	0.1	1000
Uranium (U)	µg/L	0.1	1000
Zinc (Zn)	µg/L	0.1	5000

Sample analysis

Figure 1 shows the sequence for the analysis of the high matrix samples. The first step was the measurement of the reference standard, which serves as an online calibration for mass bias correction, and simplifies the IDA calculation. An initial quality control (QC) standard was measured to calculate the lower limit of quantification (LOQ) of the method, and then the unknown samples were analyzed. Further QC samples were measured periodically every 10 samples to confirm that the test runs were valid and results were reliable. Three different QCs were used, prepared in a synthetic high matrix solution and covering the working quantification range (lower, midpoint and upper limit of quantification).

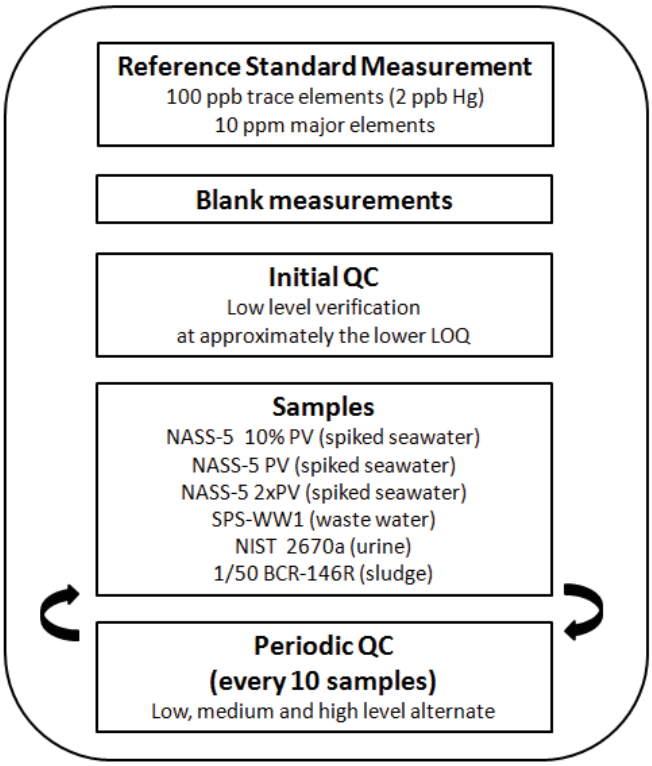

Figure 1. Measurement sequence — high matrix samples

Analysis of certified reference materials

In all, four different certified reference materials were analyzed. These included seawater (NASS- 5), wastewater (SPS-WW1), urine (NIST 2670a low level) and sewage sludge (BCR-146R). The seawater, wastewater and urine were analyzed undiluted, without any sample preparation. The sewage sludge was diluted

50-fold after microwave digestion and then analyzed. The microwave digestion method was 0.5 g sample + 7 mL HNO_3 + 1 mL $HClO_4$, 10 minutes to 220 °C and hold for 20 minutes, dilute to 15 mL final volume. The seawater was spiked at three different concentration levels: at the parametric value (PV), which is the maximum allowable concentration according to Spanish regulations [6], at 0.1x (10%) the PV, and at 2x the PV. Each reference material was measured 10 times over the course of the sequence and the average concentration and standard deviation of the mean recoveries were calculated for each element.

Results and discussion

The results obtained are given in Table 4. The concentrations found in the wastewater, urine and sewage sludge certified reference materials were in good agreement with the certified values for all analytes. The recoveries for the spiked seawater fell within 10% for all elements in all three spike levels, demonstrating accurate measurement at a level 10% of the parametric value. The use of IDA corrected for any possible matrix effects and signal drift. The multielement isotopic standard acts as both a calibration standard and an internal standard. Because the enriched isotope has the same chemical and physical properties as the analyte element, it is the ideal internal standard for elements where ionization is affected by the matrix components of the sample.

OIDA completely eliminates the drift, recalibration and re-analysis of samples that often has to be carried out when running long sequences of high matrix samples using conventional external calibration. As a result, high productivity is achieved through the combination of high sample throughput and the elimination of periodic recalibration and reanalysis. On-line addition of the mixed multielement IDA spike completely eliminates the increased sample handling required for individual sample spiking in conventional IDA.

Table 4. Mean measured values and recoveries for all elements in four certified reference materials analyzed.
* Parametric Value. Regulated elements and maximum allowable limits for seawater in Spain.

Analyte	Wastewater SPS-WW1 (µg/L)		Sewage Sludge BCR-146R (mg/L)		Urine NIST 2670a (µg/L)		Seawater recoveries (%) at			
	Found	Certified	Found	Certified	Found	Certified	PV (µg/L)*	10% PV	PV	2x PV
Aluminum	1965 ± 37	2000 ± 10	-	-	-	-	209	93.8	94.5	97.2
Antimony	-	-	-	-	1.02 ± 0.07	0.971 ± 0.033	5	103.5	107.3	96.7
Arsenic	96 ± 5	100.0 ± 0.5	-	-	-	-	25	94.6	95.2	96.6
Cadmium	19 ± 1	20.0 ± 0.1	19.2 ± 0.2	18.4 ± 0.4	0.051 ± 0.005	0.0591 ± 0.0034	5	93.4	94.4	98.2
Chromium	195 ± 5	200 ± 1	173 ± 8	174 ± 7	-	-	5	94.8	98.6	97.9
Cobalt	61.6 ± 0.9	60.0 ± 0.3	6.8 ± 0.2	6.5 ± 0.4	0.122 ± 0.004	0.166 ± 0.040	-	-	-	-
Copper	395 ± 15	400 ± 2	872 ± 20	838 ± 16	-	-	25	95.0	96.3	98.4
Iron	1055 ± 17	1000 ± 5	-	-	-	-	200	96.5	98.8	98.1
Lead	98 ± 2	100.0 ± 0.5	555 ± 17	583 ± 17	0.40 ± 0.05	0.49 ± 0.16	10	95.7	96.2	96.9
Manganese	405 ± 6	400 ± 2	288 ± 2	298 ± 9	2.65 ± 0.04	2.6 ± 0.7	50	95.8	96.3	96.7
Mercury	-	-	8.2 ± 0.2	8.4 ± 0.3	0.069 ± 0.003	0.0663 ± 0.0058	1	92.1	92.9	103.6
Nickel	1042 ± 38	1000 ± 5	69 ± 2	65 ± 3	-	-	25	95.1	99.6	98.7
Selenium	-	-	-	-	7.32 ± 0.56	8 ± 3	10	90.2	93.8	96.9
Zinc	605 ± 35	600 ± 6	2959 ± 75	3040 ± 60	108 ± 2	130 ± 30	60	94.1	95.6	97.4

Conclusions

The combination of OIDA, helium collision mode, and the enhanced matrix tolerance provided by HMI has proven to be an excellent solution for accurate multielement determinations in high matrix samples, providing the following advantages:

- In combination with helium mode for interference removal on both primary and secondary (qualifier) isotopes, IDA has been simplified and adapted for routine analysis, allowing the simultaneous determination of all analytes including monoisotopic elements.
- The multielement isotopic standard acts both as a calibration standard and as an ideal internal standard, providing complete correction of matrix effects such as ionization suppression and signal drift.
- Sample throughput is increased and productivity is improved, since sample preparation is eliminated in most cases, no external calibration of the instrument is required, and time-consuming reruns are avoided.
- Accuracy and precision of the method was excellent; good agreement with certified values and good spike recoveries were obtained — even in challenging samples such as undiluted seawater and urine.

Note: The method has been implemented in a large number of testing laboratories in Spain and is used successfully for the analysis of several different high matrix samples (wastewater, seawater, soils, and so forth) on a routine basis. Custom multielement isotopic standards, prepared specifically to individual requirements (isotopes, concentrations) are available from www.isc-science.com

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