Improving data quality for ICP-MS in high throughput environmental laboratories

Wei Liu[1] , Marcus Manecki[2],Daniel Kutscher[2] , Maura Rury[1], and Shona McSheehy Ducos[2]
[1]Thermo Fisher Scientific, Sunnyvale, United States, [2]Thermo Fisher Scientific, Bremen, Germany

OVERVIEW

Purpose: To demonstrate robust high throughput analysis of high matrix environmental samples using ICP-MS in He-KED mode with different dilution techniques. To demonstrate the accurate determination of arsenic and selenium in sediments and rocks that contain elevated levels of rare earth elements (REE) using triple quadrupole ICP-MS

Methods: Thermo Scientific™ iCAP™ RQ ICP-MS coupled to the ESI prep*FAST*™ auto-dilution system was used for the analysis and the Thermo Scientific™ iCAP™ TQ ICP-MS was used for As and Se measurements.

Results: Internal Standard and analyte recoveries of 80-120% were achieved for different high matrix sample sets with automated online auto-dilution for long term measurements. Ultra low background data was achieved by using triple quadrupole technology for As and Se determination

INTRODUCTION

Dealing with high matrix samples in analytical measurements often means complicated analyte enrichment or matrix removal (e.g. reverse osmosis) techniques have to be used. Disadvantages of these methods are that they are expensive, time consuming and increase the risk of sample contamination. Dilution of the samples often leads to much better results as long as the analytes of interest are not diluted below the limit of detection of the analyzing instrument. Therefore, intelligent auto-dilution was evaluated handling higher matrix and overcoming issues of manual sample preparation in high throughput labs.

In addition, automation is also one of solutions for high throughput lab. But when analyzing unknown environmental samples some analytes might be very challenging. Arsenic and selenium, for example, are difficult to analyze in the presence of REE due to multiple spectral interferences. These doubly charged REEs lead to false positive results and as such lead to incorrect conclusions and actions based on that data. Therefore, we compared different techniques, including triple quadrupole technology, to overcome these problems.

METHODS

Automated dilution system

A fully automated system (prep*FAST* system, Elemental Scientific Inc.) was prepped with the necessary solutions (diluent, internal standard, rinse solution). The whole dilution process for all sample types is controlled by the Thermo Scientific Qtegra™ Intelligent Scientific Data Solution™ Software (ISDS).

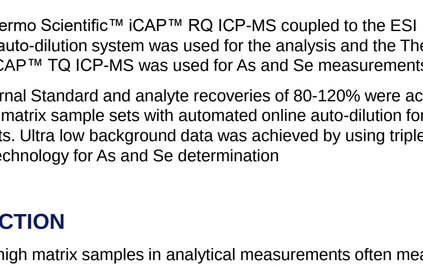

FIGURE 1. Concept of a fully automated dilution system with an ICP-MS

For the first data set a long term measurement of >500 analyses against the EPA Method 200.8 (Rev. 5.5) method for drinking water was performed. The data set contains standards, samples and quality controls required by EPA Method 200.8.

In the second experiment semi saline waste water (up to 8% NaCl) was analyzed directly with the fully automated dilution system. The Internal Standard (IS) recovery limits of between 85 to 120 % were defined by the method. All samples were run with a 40-fold prescriptive dilution (PD) and if a sample was not in the defined range, an automated 10-fold auto-dilution (AD) of the sample was triggered

Advanced interference removal technique for As and Se in presence of REE

Calibration standards of arsenic and selenium were prepared in a mixture of 2% (v/v) HNO_3 and 2% (v/v) methanol (MeOH). Mixtures of REE for interference evaluation were prepared by diluting appropriate volumes of the single element standards dysprosium, gadolinium, neodymium, samarium and terbium in 2% (v/v) HNO_3/2% (v/v) MeOH. The final solution contained 1 mg·L^{-1} of each REE. The Background equivalent concentrations (BEC) for As and Se were determined by using different measurement modes:

- **SQ-STD** – single quadrupole mode with no collision/reaction cell (CRC) gas.
- **SQ-H_2** – single quadrupole mode with CRC pressurized with pure hydrogen as a reaction gas.
- **SQ-KED** – single quadrupole mode with CRC pressurized with helium as a collision gas and Kinetic Energy Discrimination (KED) applied.
- **TQ-O_2** – triple quadrupole mode with CRC pressurized with oxygen as a reaction gas, Q1 set to analyte mass (M^+) and Q3 set to product ion mass (MO^+).

To test the robustness and the accuracy of the approach, two samples, a deep sea sediment and a geochemical reference standard, were analyzed under optimal conditions.

RESULTS

prep*FAST* and routine performance

Over 500 analyses were run against EPA Method 200.8. The throughput in single measurement mode was 66s per sample. Concentrations of all analytes and internal standard recovery were measured over a period of 3 h (Fig. 2). All analytes remained within the recovery range of 90 to 110% which is required by EPA Method 200.8.

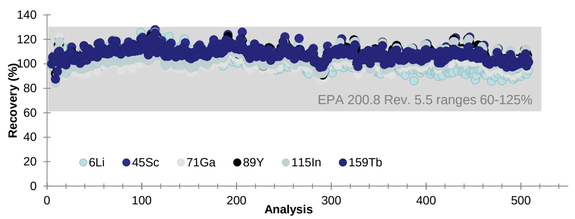

FIGURE 2. Internal standard response of running tap water and QC samples. The recoveries are well within the 60 – 125% range specified in EPA Method 200.8.

prep*FAST* auto-dilution for varying matrix samples

Different semi saline samples were measured directly with a PD of 40 (Fig. 3). Sample 24 triggered the auto-dilution process in the Qtegra software because the internal standard recovery was lower than the limits (85-120%) set in the method. The first auto-dilution step increased the original PD factor by 10 and the sample was reanalyzed after a (40+10) 50-fold dilution. The internal standard recovery was still not in range and another two measurements were triggered. After the 3rd automated dilution the internal standard recovery was within the range of 80 to 120 percent and the system continued on to the next sample analysis without any manual intervention. Qtegra ISDS software provided all required features needed for this high throughput analysis of environmental samples.

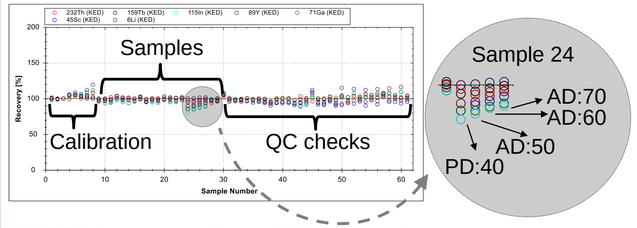

FIGURE 3. Screenshot of Qtegra (ISDS) software. Internal standard response of running semi saline water and QC samples (left). Automatically triggered auto dilution of sample 24 is shown in the right circle.

Advanced interference removal technique for As and Se in the presence of REE

External calibrations for arsenic and selenium in the range 0.2 to 5 µg·L^{-1} show excellent linearity and LODs of 0.17 ng·L^{-1} and 2.02 ng·L^{-1} for ^{75}As and ^{78}Se respectively, when using TQ-O_2 mode. The corresponding BEC for every measurement mode and isotope is shown in Fig. 4.

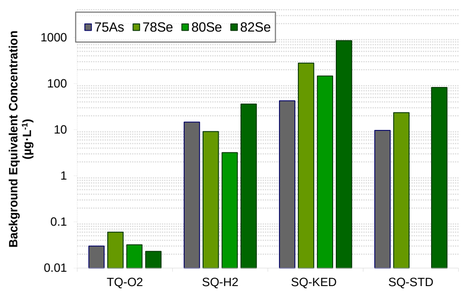

FIGURE 4. BECs of arsenic and selenium isotopes in a 5 mg·L-1 REE solution using four different measurement modes

The quantitative data for arsenic and selenium measured in the AGV-1 CRM and the deep seas sediment are shown in Table 1. The measured concentration of 0.446 µg·L^{-1} As in the diluted AGV-1 sample corresponds to a recovery of around 100% of the certified value. Both samples were also spiked with 1 µg·L^{-1} of arsenic and selenium (Table 1).

Table 1. Quantitative data for arsenic and selenium in AGV-1 and a deep sea sediment using TQ-O_2 mode (calculated back to the solid and reported in µg·g-1).

AGV-1	Content in original sample (µg·g^{-1})	Content in original sample (µg·g^{-1})	Recovery (spike recovery)
75As	0.892	0.88	101% (95%)
78Se	< LOQ		(94%)
Deep Sea Sediment			
75As	1.303		(98%)
78Se	0.109		(98%)

CONCLUSIONS

The iCAP RQ ICP-MS equipped with an ESI autosampler and prep*FAST* auto-dilution system was tested for the analysis of different high matrix samples and showed very reproducible data and a good overall performance. It is ideal for measuring environmental samples in a high throughput laboratory. All settings are easily programmed into the workflow and provide the basis for prescriptive and intelligent dilution. Manual sample preparation and data post processing is significantly reduced when using auto-dilution, saving valuable time for skilled technicians to work on other lab tasks.

When analyzing for challenging samples like soils, sediments or in general matrices containing a high amount of REEs the future proof technology of iCAP TQ ICP-MS is the best method to achieve the highest data quality for As and Se in the presence of REEs. Using TQ-O_2 mode gives the lowest LODs and BECs compared to single quadrupole techniques.

REFERENCES

1. Application Note 43323 - Fully Automated, Intelligent, High-Throughput Elemental Analysis of Drinking Waters Using SQ-ICP-MS
2. Application Note 43285 - Accurate determination of arsenic and selenium in environmental samples using the Thermo Scientific iCAP TQ ICP-MS

TRADEMARKS/LICENSING