DILUTE OR DIE – HOW TO HANDLE HIGH MATRIX SAMPLES BY ICP-MS

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Overview

Purpose: To illustrate the advantages and disadvantages of different dilution techniques, and to demonstrate robust, high-throughput analysis of high matrix environmental samples with ICP-Q-MS in He-KED mode using different dilution techniques.

Introduction

Dealing with high matrix samples in analytical measurements often means employing complicated analyte enrichment or matrix removal techniques. Disadvantages of those 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.

Automated dilution approaches were evaluated for their ability to dilute high matrix samples while overcoming some of the challenges and potential pitfalls with manual sample preparation.

Experimental

A Thermo Scientific™ iCAP Qc™ ICP-MS was coupled to an ESI prep*FAST*™ auto-dilution system. Argon Gas Dilution (AGD) combined with direct online dilution was also utilized on the iCAP Qc.

AGD Method: Solutions containing 25% NaCl were spiked with 23 analytes at 25 ppb. Samples were analyzed continuously over 4 hours, using He-KED mode. Sample accuracy and internal standard recovery was determined and the overall stability (RSD) of the system was calculated.

prep*FAST* Method: Semi saline waste water (up to 8% NaCl) was analyzed directly with the prep*FAST* system. The internal standard (IS) recovery limits (85 -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.

Methods

The following 2 dilution techniques were used for all sample analyses:

Argon Gas Dilution (Fixed Dilution Approach)

Samples are diluted through a combination of a reduced nebulizer flow and an additional argon flow added to the spray chamber (Fig. 1). To set up the AGD mode, a dedicated tuning procedure was used to tune the system with the additional Ar gas flow to achieve optimal sensitivity for all analytes.

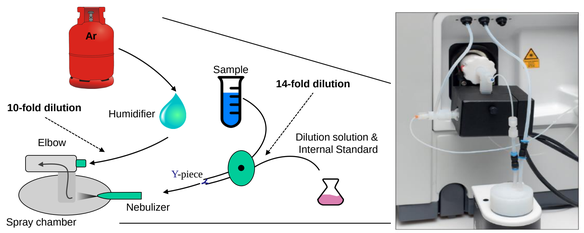

FIGURE 1 . Concept of an argon gas dilution approach coupled to online dilution.

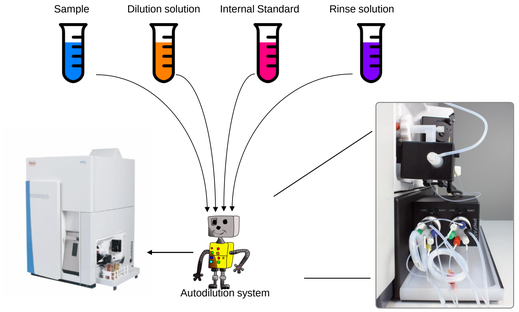

FIGURE 2. Concept of a fully automated dilution system.

prep*FAST* Dilution
(Automatic, Flexible Dilution Approach)

Samples are automatically diluted using a software-controlled valve system which provides flexible and prescriptive dilution for each sample. An internal standard solution can be added on-line as well.

Results

Argon Gas Dilution

A fixed 10-fold dilution (AGD) was used in combination with a 14-fold dilution (online liquid dilution). Results are displayed in Figure 3.

Recovery over the whole 4-hour sample run was between 80 and 120% for all analytes.

After a short stabilization time, the recovery of the internal standard was 80-120 % for all sample analyses.

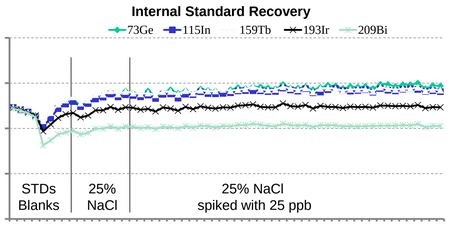

FIGURE 3. Internal std recovery during analysis of 25% NaCl samples (t=4 hrs)

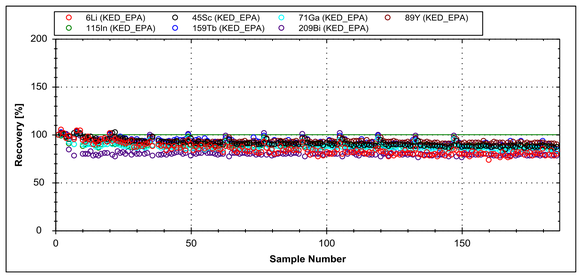

FIGURE 4. Internal standard recovery during analysis of tap water and QC samples. All recovery results are within the 60 – 125% range specified in EPA Method 200.8.

prep*FAST* and Routine Performance

Over 100 samples were analyzed according to EPA Method 200.8 requirements (see Figure 4).

Samples were analyzed continuously for 3 hours with a sample throughput of 68 s per sample.

All analytes were recovered within 90-110%, well within the EPA-mandated required range.

prep*FAST* Auto-dilution for Varying Matrix Samples

Semi-saline samples were initially measured with a prescriptive dilution factor of 40. Internal standard recovery results were below the defined threshold (85-120%) during the analysis of Sample 24, which triggered the auto-dilution process. The sample was iteratively diluted and analyzed until the internal standard recovery was within acceptable limits. Results are illustrated in Figure 5 below. All dilutions were calculated and executed through the ICP-MS software.

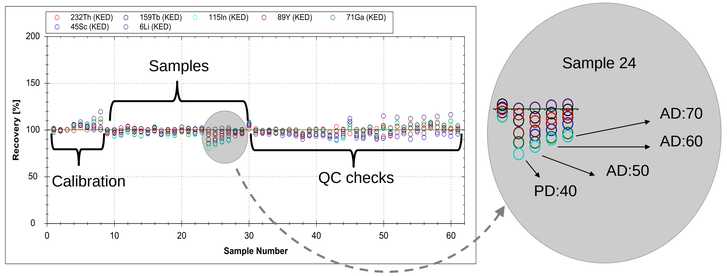

FIGURE 5. Internal standard response during semi-saline water analysis. Expanded software screenshot (right) illustrates automatic auto-dilution, triggered after analysis of Sample 24.

Conclusion

The iCAP Q, equipped with either a fixed or flexible dilution system, delivered reproducible data and good overall performance during the analysis of high matrix environmental samples. Results indicate that intelligent auto-dilution is the ideal solution for handling samples with varying levels of dissolved solids for routine, high-throughput analyses.

Attribute	AGD (fixed) dilution	prepFAST (flexible) dilution
Throughput	Significantly increases throughput	Significantly increases throughput
Ease of Use	Simple to set up and operate. Default tuning mode guarantees reliable optimization	Auto-dilution settings easily programmed into any sample analysis workflow
Flexibility	Inflexible. All samples are diluted with a pre-determined, fixed dilution factor	Automatic, intelligent prescriptive dilution provides complete flexibility

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