An Executive Summary

Trace Element Analysis Using ICP-MS for Environmental Samples, Part Two

Meeting Routine Monitoring and Research Challenges



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How ICP-MS addresses routine monitoring and research challenges.

Introduction

Inductively coupled plasma-mass spectrometry (ICP-MS) is one of the most powerful elemental analysis techniques used for environmental applications. It provides low detection limits, easy quantification, and high throughput. However, experience and best practices are necessary to take full advantage of all the technique can offer. Part 1 of this series covered routine regulatory monitoring; this manuscript summarizes Part 2 and is focused on solutions to improve productivity and overcome the challenges of high-matrix samples. Starting with a brief overview of ICP-MS, this summary discusses environmental sample analysis workflows and typical standard operating procedures, such as how software features can help standardize protocols and reduce operator workload. In addition, the use of triple-quadrupole ICP-MS to meet the needs of environmental researchers with specialty environmental applications is presented, including how to address environmental regulations in both the United States and Europe, tips and tricks for U.S. Environmental Protection Agency (EPA) Methods 200.8 and 6020, and the use of auto-dilution for productivity improvement for high-matrix samples.

Overview of ICP-MS

ICP-MS is a highly sensitive, multi-elemental, accurate, and rapid technique that efficiently meets the high demands of environmental analysis. With appropriate sample preparation, the method can measure nearly every chemical element in one sample run, and in practically any sample matrix. ICP-MS offers precise isotope ratio determinations, and when coupled with certain devices and used appropriately, species information, particle size, and composition information can be obtained.

ICP-MS can perform these applications because of the method's high-matrix tolerance, high sensitivity with a wide linear dynamic range, and the ability to remove elemental interferences that cause uncertainties in trace element quantification. The technique is based on producing, sampling, mass filtering, and detecting positive ions. The sample introduction system is typically a nebulizer and spray chamber system used to introduce acidified aqueous samples into the mass spectrometer as an aerosol.

After the sample has been turned into an aerosol, it is transported to the ICP itself where it is desolvated, atomized, and ionized to form positively charged ions. The ions then enter a high-vacuum region through an interface at low pressure.

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Once inside the high-vacuum region, any interferences present can be removed using collision reaction cell technology. Once interferences are removed, the ion beam is focused into the analyzing quadrupole to filter the analyte of interest into the detection system.

For most routine environmental analysis labs, a quadrupole mass analyzer is preferred because it is fast, easy to use, and relatively inexpensive to maintain.

After mass separation, the ion beam is converted to an electrical signal by the detector and reported as counts per second, which is essentially the rate at which ions of an element travel through the mass spectrometer.

Environmental Analysis Workflows and SOPs

A typical environmental analysis workflow involves sample preparation, sample analysis, and data analysis, and each step has challenges that affect the final data quality, as illustrated in **Figure 1**. For instance, challenges during sample preparation may include those associated with sample digestion, loss of volatile elements, or insufficient dilution for some samples within a batch. During sample analysis, potential problem areas include matrix suppression, matrix deposition on interface cones, or possible interferences from other analytes. Data analysis challenges can include preserving data quality and identifying inaccurate data that should be corrected by rerunning samples.

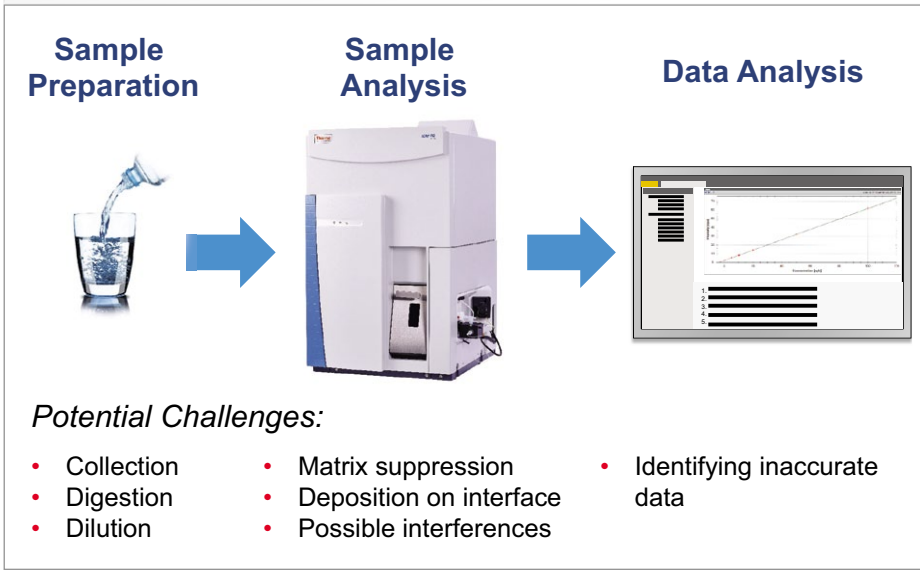
Environmental analysis standard operating procedures (SOPs) generally include instructions for instrument checks, preparing the system to operate properly, and the actual sample analysis. Determining that a system is set up correctly normally entails a visual check of the cones and the sample introduction system to ensure correct installation and cleanliness. It also involves checking the wear on the peristaltic pump tubing, cleaning or exchanging it as appropriate. Next, the plasma is turned on and, once the performance is verified, information can be entered into the software to conduct the analysis and direct the system to report or export the resulting data.

Instrument checks are greatly simplified by access to the two cones that transfer sample ions into the high-vacuum region of the mass spectrometer. Deposition from the high-matrix sample analyses can cause the orifices to reduce sensitivity over time. When a buildup of matrix on the cone tip affects the system's sensitivity, cleaning is recommended. Cleaning is facilitated on the Thermo Scientific™ iCAP™ RQ ICP-MS and Thermo Scientific™ iCAP™ TQ ICP-MS systems with a hinged drop-down door, which provides quick and easy access to the cones without visual obstructions.

The next instrument check is the sample introduction system, including the peristaltic pump tubing, which should be regularly inspected and replaced as necessary. Because samples are in contact with all parts of the sample introduction system, inert materials are favorable. Glassware cleaning is only needed when memory effects (e.g., an analyte gradually building up over time) cause detection limits or background equivalent concentrations to rise above acceptable limits. A second set of glassware is often recommended for laboratories with high sample turnover or highly varied sample types so that the sample introduction system can be quickly exchanged if necessary with minimal impact on downtime. Checking and exchanging the glassware is simplified with a simple torch assembly. The quick-connect assembly is self-aligning to ensure it is centralized within the torch; gas connections are necessary, thus reducing the potential for gas leaks.

Once the instrument checks are successfully completed, the plasma can be turned on and a performance check can be performed. Reliable and consistent ICP-MS data can only be produced by executing regular performance checks, preferably daily. Software procedures simplify the startup process; the "Get Ready" feature in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) platform software for the Thermo Scientific™ iCAP™ Qnova™ Series ICP-MS system is an automated procedure that starts the instrument, applies a predefined warm-up period, and then performs checks using the standardized tune solution. If the system does not meet the performance criteria, corrective action is triggered and automated tuning is run to ensure the system is brought within the specified criteria saving operator time and increasing reproducibility.

Figure 1: Typical workflow for environmental analysis.



Software workflows can also help to simplify the sample analysis procedure. Data are collected in an electronic lab book, which can easily be created from scratch or from a template. A template should include a collection of all the measurement parameters needed for analysis such as analytes, analysis times, sample list, structure, and quality control (QC) settings, and can be based on predefined protocols, such as EPA or US Pharmacopeia (USP) methods. The measurement parameters from the template are combined with sample details from several sources such as manual entry, a bar or QR code reader, or direct import from the laboratory information management system (LIMS) into the lab book. The lab book is then processed by a scheduler to deliver data that can be used to generate reports or be exported into a LIMS.

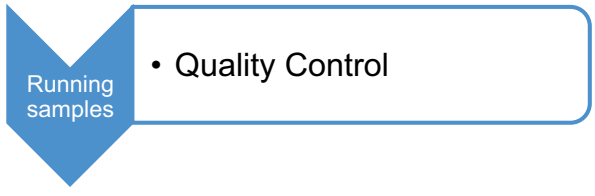
The performance and accuracy of the instrument and method are typically monitored using QC samples, as summarized in **Figure 2**. The blue table on the left of Figure 2 shows a shortened list of QC sample types, the type of quality assessment they are used for, and the limits for two environmental protocols (EPA 200.8 and EPA 6020). The Qtegra ISDS software includes the full set of QC sample types divided into six categories (i.e., blank tests, calibration tests, bad sample tests, spiked sample tests, continuous tests, and tests based on internal standard edition) that cover all EPA method requirements. Each QC test can have its own independent set of criteria such as user-defined limits for analytes and the actions that would be triggered upon failure.

The reporting editor in the Qtegra ISDS software can be tailored to list the data itself as well as information about the instrument and the operator's specific information. Data tables can be customized to report intensities and concentration ratios, or they can be customized per analyte or per sample. It is also possible to compare results from different lab books and operators, which is helpful when pooling data from two different sets for method validation. Reports can also be password protected, which benefits validated labs that must have controls on data security. Qtegra ISDS software is also equipped with useful visual aids to aid in reviewing data for quality and inaccuracies.

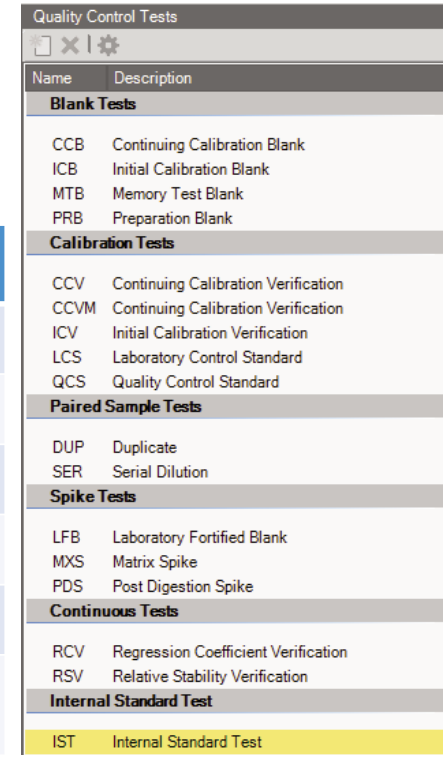
Overcoming Environmental Analysis Challenges

In general, environmental laboratories analyze three different kinds of samples: solids, gases, and liquids. When analyzing solid samples such as rocks or specific metal alloys directly, the homogeneity of the sample might be an issue so solid samples are often digested for analysis. Although analysts can directly analyze a gas sample with an ICP-MS instrument or an optical emission spectrometer system, gas samples are not very common for ICP optical or MS systems; they are more commonly analyzed with gas chromatography instruments. Liquid samples, however, are very common and digestion is often used as well. Successful, efficient digestions are characterized by obtaining clear liquids and

Figure 2: Setting up quality control – Typical examples from EPA methods.



QC Check	QC Assessment	200.8 limit	6020 limit
Sample RSDs	Instrument Performance	< 5% on 5 measurements	< 5% on 4 measurements
Lab Control Standard	Method Accuracy	+/- 10% certified value	+/- 20% certified value
Laboratory Reagent Blank	Laboratory Contamination	< 2.2 * MDL	< 3 * IDL
Calibration Verification	Calibration Accuracy	+/- 10% or within acceptance limits	+/- 10%
Lab. Fortified Matrix	Method Recovery	+/- 30%	+/- 25%
Internal Standardization	Analyte Recovery/Data Quality	60 - 125	70 - 130



good RSDs and spike-recoveries during sample analysis. Poor digestions can result in precipitates (e.g., silver, iron, and silicon), particles from undigested material, and the loss of volatile elements (e.g., mercury, arsenic, and selenium), which cause poor recoveries.

Therefore, it is often very useful to conduct spike recovery tests to determine the efficiency of the digestion procedure. The EPA has many guidance documents available to help choose appropriate digestion methods by sample type. For analyzing sediments, large soils, or oils, it is very useful to consult EPA Guidance 3051. For silica-based materials, lubricating oils, or botanical samples, methods are described in EPA Guidance 3052.

It is very important for almost all analytical approaches to pay attention to specific analytes that might be more difficult to determine than others. Arsenic and selenium, for example, can show increased ionization because of the carbon-enhancement effect, which can lead to overestimation. To overcome this issue, either a matrix-matched calibration or a microwave digestion can be performed to completely oxidize the carbon from the sample to carbon dioxide. Osmium and mercury are highly volatile elements, so it is very important to avoid long digested sample storage times or the use of closed-vessel microwave digestion.

Another difficult analyte is aluminum. At a high pH, aluminum can form aggregates leading to poor reproducibility and quantitation errors. Therefore, the pH should be kept low by adding hydrochloric acid, for example, to prevent colloid formation. A similar behavior is often observed for silica and boron when they have not been digested completely. For those elements, the addition of hydrofluoric acid can help to prevent poor reproducibility and quantitative errors.

For high-matrix samples, it is often useful to use an internal standard, and it is important to select the right one for the analysis of low levels of a certified 3 ppb uranium sample in seawater (see **Figure 3**). Using an external standard, a result of 2 ppb was obtained. By using iridium as an internal standard, all calibration and sample solutions recovery averaged 70%. By applying the internal standard correction, a uranium concentration of 3 ppb was obtained, matching the certified value.

The matrix is always one of the biggest challenges for chemical analysis and dilution solves many of the issues encountered. Dilutions can be performed manually or can be automated, for example using an argon gas or other auto dilution techniques as shown in **Figure 4**. A fully automated dilution system reduces the risk of sample contamination and lowers the error rate; however, several criteria should be considered, including bringing the analyte concentration in range with calibration standards, reduction of the matrix, addition of the internal standard, and flexibility for different sample types.

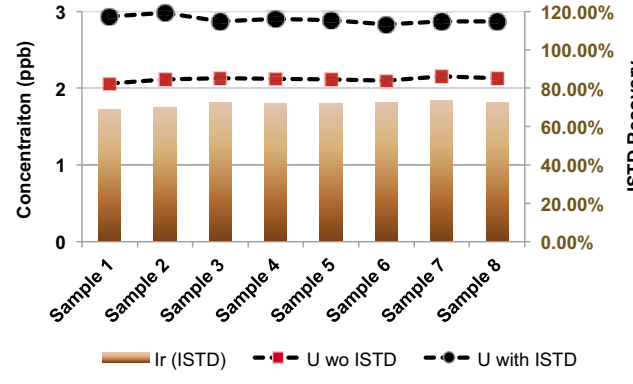
Two different kinds of autodilutions are available: prescriptive dilution, which is used for the dilution of samples before analysis or the creation of a calibration curve, and intelligent autodilution, which determines, based on set criteria, if a sample was measured accurately or if it should be remeasured.

Prescriptive dilution can be applied to the automated preparation of both samples and standards.

In prescriptive sample dilution, the sample is taken from the autosampler vial and diluted by a user-definable dilution factor before analysis. This feature is a clear advantage over

Figure 3: Why add an internal standard?

- Analysis details
  - Seawater sample
  - Salinity 33.5 (3.35%)
  - Samples were 5 fold diluted
  - Certified U conc. 3ppb
- Result
  - Measured concentrations of U too low without internal standard correction
- Internal standard is necessary when dealing with high matrix samples!



continuous dilution techniques that are limited to a single dilution factor for all analyses. In prescriptive standard dilution, a single standard stock solution can be used to generate multiple calibration standards—all without requiring additional positions in the autosampler rack. Atmospheric contamination of the standard is minimized by performing dilutions inside the valve head and errors in dilution are eliminated. Qtegra ISDS intelligent autodilution controls define the rules for over-calibration range analyses. The analyst defines the maximum calibration limit and the desired target concentration, both expressed as relative percentages of the top calibration point. An over-range analysis is automatically added to the analysis queue with a new automatically calculated dilution factor. The user also defines the acceptable internal standard recovery range, the autodilution factor, and the maximum number of dilutions; the software does the rest. When a high-matrix sample has initial internal standard recoveries outside the defined limits, the Qtegra ISDS software platform automatically and repeatedly dilutes the sample until the internal standard recoveries are within the defined range. Automation helps to ensure data quality, accelerate sample turnaround times, minimize maintenance, and save time and labor by performing on-line sample preparation, data reviews, and reruns.

Handling Matrix: Customized Interfaces for Maximum Flexibility

Different options are available to maximize performance based on the application. By using different sized skimmer inserts, the system can be optimized for a high- or a low-matrix load. A 4.5 mm insert is recommended for a very high matrix content in the sample and a linear calibration up to 2,000 ppm. This type of insert is mainly used for environmental and routine industrial applications. A 3.5 mm insert is the best compromise between sensitivity and matrix tolerance and is used for most applications for drinking water analysis or food safety. With the 2.8 mm insert, the system is optimized for the best sensitivity and signal-to-noise ratio. It allows measurements in the sub-ppt range and is recommended for customers who want to achieve very low detection limits in the geoscience or advanced materials research areas.

For environmental samples, high-calibration ranges can be required, and many protocols require that quantified levels in samples fall within the calibration range performed. Therefore, it is sometimes necessary to increase or decrease the internal standard within a given range. To calibrate to higher levels the signal can be attenuated by choosing a lower abundant isotope, by applying kinetic energy discrimination (KED) mode, or using higher instrument resolution settings. **Figure 5** shows the comparison of a 4.5 and a 3.5 mm insert. With the 4.5-mm

Figure 4: Dilution techniques.

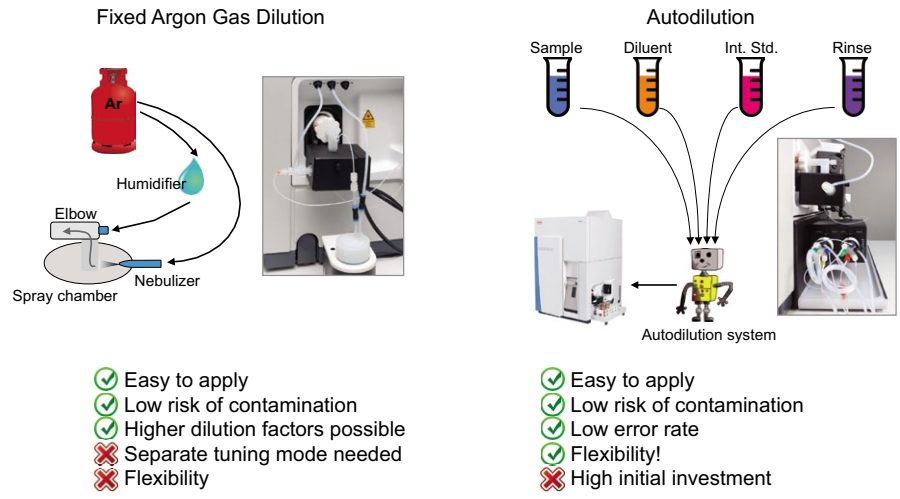
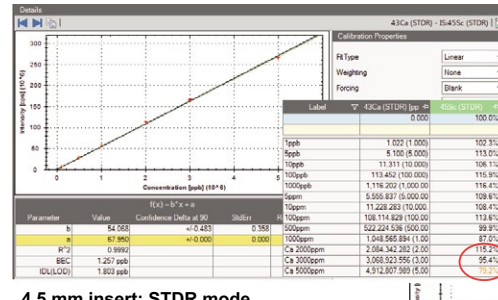
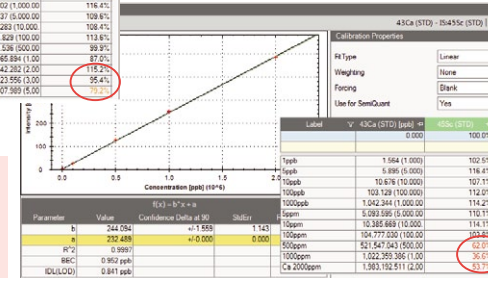


Figure 5: iCAP RQ vs iCAP Q – ^{43}Ca Calibration - STD.

- iCAP RQ: Maximum calibration **5000 ppm Ca**, ^{45}Sc (IS) > 70%
- iCAP Q: Maximum calibration 2000 ppm Ca, ^{45}Sc (IS) < 70%



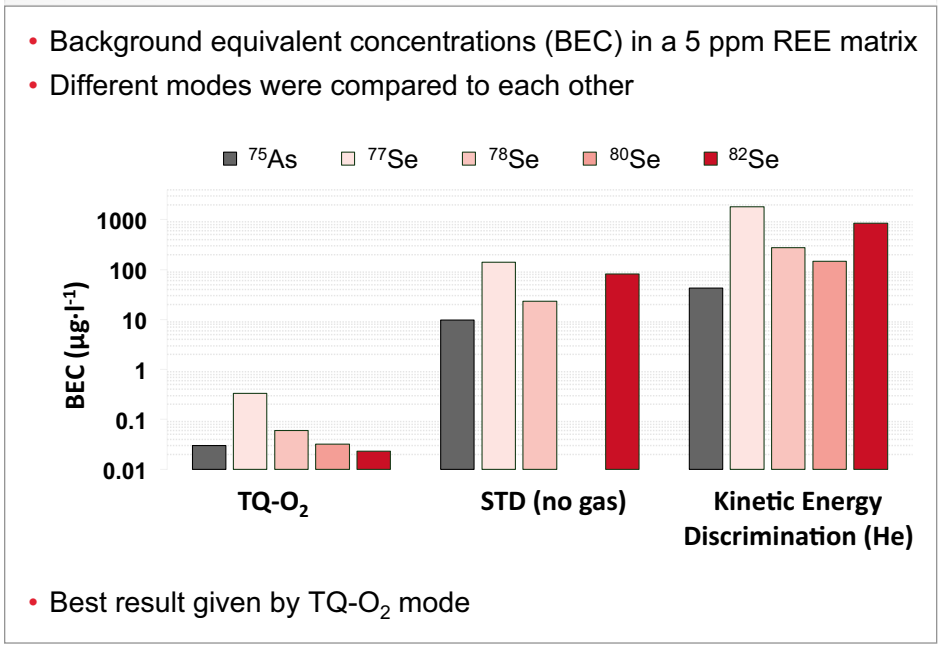
4.5 mm insert; STDR mode



3.5 mm insert; STD mode

- Reduced in sample suppression
- Linear calibration possible up to 5000 ppm within typical environmental method protocols

Figure 6: Arsenic and selenium in presence of high REE.



insert shown in the left of Figure 5, the internal standard decreased for a five-solvent ppm sample, falling to a value of 79%. When using a 3.5 mm insert, shown in the right of Figure 5, the two-solvent ppm calcium sample already causes an internal standard decrease of more than 40% down to a value of slightly above 60%. Due to the reduced sample suppression of the 4.5 mm insert, it is a useful tool for measuring a high-matrix content without the need for any further sample dilution.

For some applications, a single-quadrupole instrument is not sufficient. Analytes with isobaric interferences need reaction chemistry to mass shift them to a clean region of the mass spectrum, requiring a reaction cell. By using a triple-quadrupole instrument, potential interferences can be eliminated for the analysis of arsenic and selenium in the presence of high amounts of rare earth elements and zirconium/molybdenum. As shown in **Figure 6**, the best results are obtained in TQ-O_2 mode measured with the iCAP TQ ICP-MS instrument.

Conclusion

Routine maintenance and software solutions can help to reduce operator time, thus improving data quality and integrity. Such tools also provide clear and easy feedback, which helps to make quick decisions based on the data. A fully integrated, autodilution system can be valuable to many laboratories to extend run times and reduces reruns; other solutions such as customized interfaces and triple-quadrupole instruments can also offer solutions to answer the challenge of running heavy-matrix samples.