Technical note | 001705

Thermo Fisher SCIENTIFIC

Environmental

Achieving robustness and improving productivity every day using a simplified approach of argon gas dilution (AGD) with ICP-MS

Authors

Bhagyesh Surekar, Daniel Kutscher

Thermo Fisher Scientific
Bremen, Germany

Keywords

ICP-MS, iCAP RQplus ICP-MS, total dissolved solids (TDS), high matrix, robustness, productivity, aerosol dilution, AGD

Introduction

Inductively coupled plasma – mass spectroscopy (ICP-MS) is a popular technique for analysis of elemental impurities in a wide variety of sample matrices due to its excellent detection capability, wide linear dynamic range, and specificity. However, the quality of acquired analytical data can be impacted while analyzing samples that contain higher amounts of TDS, typically above 0.2% (m/v). The composition of samples under investigation plays a vital role as different matrices affect data differently. The typical indicator of sample matrix affecting the quality of analytical data is the suppression or enhancement of the internal standard response compared to the initial calibration blank. Various regulated methods specify the acceptance criteria for internal standard recovery, and any sample failing to meet those criteria need to be re-analyzed after appropriate dilution. Other typical challenges associated with analysis of these types of samples are signal drift, QC failures, and loss of sensitivity, which lead to repeated sample measurements, adversely impacting productivity of an analytical laboratory. In addition to the impact on data quality, continuous measurement of these types of challenging matrices contributes to other instrument health related problems, such as deposition of solids on interface cones and salt-up on the injector tip and torch. This leads to frequent cleaning of the respective instrument components being required in order to ensure that the required instrument performance is achieved.

The Thermo Scientific™ iCAP™ RQplus ICP-MS, which is specially designed for effective handling of varying sample matrices, offers a built-in solution for on-line sample dilution using an argon gas dilution (AGD) accessory. The readily available default measurement modes, which correspond to the different levels of sample dilution, provide the user with the flexibility to choose the appropriate dilution level. Depending on the matrix load and application requirement, one of the three variable and user-selectable dilution levels can be utilized for the intended application. This technical note will highlight how the use of AGD helps to achieve higher robustness and productivity.

ACT. The Environmental Impact Factor Label

thermo scientific

Choice of measurement mode and expected dilution level

Three default dilution levels (AGD-low, AGD-mid, and AGD-high) are provided as an integral part of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software and are readily available to use upon the instrument installation. These modes are optimized and designed to handle a variety of real-world samples, such as food and beverages, environmental waters and soils, or industrial samples, which all have completely different matrix compositions. Since robustness and detection sensitivity are the key requirements for many sample types across a range of industries, it is critical to maintain balance between the dilution factor applied and the subsequent reduction of the analytical signal. The typical dilution ranges achieved for each of the three default levels can be best assessed using the sensitivity (cps/µg·L^{-1}) of indium (^{115}In). The achieved dilution factor depends on the analyte mass, and indium was selected here as it represents an analyte in the middle of the assessable mass range.

Table 1 summarizes the different measurement modes, achievable dilution factors, and detection limits for key analytes.

Table 1. Available dilution modes, corresponding dilution factors, and achievable detection limits of key analytes. All measurements were accomplished using kinetic energy discrimination (KED) to remove common polyatomic interferences.

Measurement mode	Approximate dilution factor	Detection limit (µg·L^{-1}) in KED mode			
		As	Cd	Pb	Hg
No gas dilution	0	0.004	0.0002	0.0003	0.005
AGD-low	4–6	0.011	0.002	0.001	0.06
AGD-mid	20–25	0.031	0.004	0.002	0.051
AGD-high	75–80	0.077	0.019	0.008	0.106

Table 2 provides an overview of 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, and recommended dilution modes for their analysis

Sample matrices	Detail	% TDS content of samples	Recommended dilution mode
Drinking water, surface water	Predominantly alkaline and alkaline earth elements, dissolved organic matter	<0.5%	AGD-low
Food digests	Mixed matrix composition, highly variable	0.5–1.0%	AGD-low
Wastewaters	Alkaline and alkaline earth elements, potentially elevated levels of transition/heavy metals, such as Fe, Cu, Zn, etc.	<1.0%	AGD-mid
Soil digests, geological and mining samples		<1.0%	AGD-mid
Brackish waters, fracking flowback solutions	Predominantly alkaline and alkaline earth elements, transition, and heavy metals	<1.5%	AGD-mid
Brackish waters, diluted sea water and dilute brine solutions		<3.0%	AGD-high
Highly concentrated brine solutions and undiluted sea water		>3.0%	AGD-high

Standard sample introduction system for various sample matrices

While using argon gas dilution in the AGD-low and AGD-mid modes, the recommended components of the sample introduction system remain unchanged compared to the standard configuration. This includes the glass concentric nebulizer (400 µL·min^{-1}), baffled cyclonic spray chamber, 2.5 mm injector, and quartz torch. The same set-up can be used for analysis using AGD-high mode depending upon the TDS content (<3%) of the sample solution under investigation. For analysis of samples containing more than 3% TDS, such as undiluted seawater, the use of a PFA microflow nebulizer (Elemental Scientific (ESI), Omaha, USA) in conjunction with a humidifier (*pergo*™, Elemental Scientific (ESI), Omaha, USA) is the best option. This combination of nebulizer and humidifier is an effective solution that enables laboratories to run challenging samples containing high levels of TDS without the potential trouble of nebulizer blocking and salt deposition on the injector tip in the long run. The suggested sample introduction system for each mode is optimized to deliver robust, accurate, and consistent instrument performance day after day without the need of frequent system maintenance and instrument downtime. Table 3 summarizes the recommended components of the sample introduction system.

Table 3. Recommended sample introduction system components for different dilution modes. More details and corresponding part numbers can be found in the Consumables and Parts Catalog.

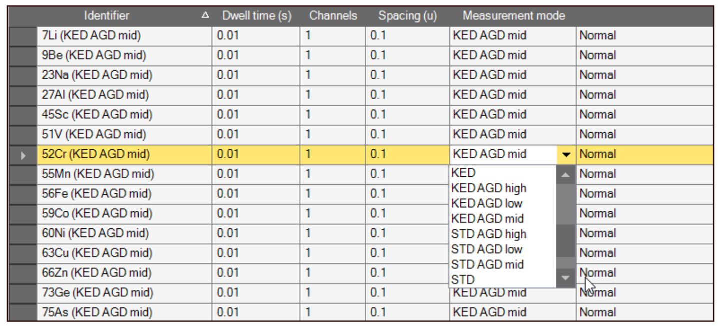
Sample introduction system component	Dilution level		
	Low	Mid	High
Glass concentric nebulizer	√	√	
Baffled cyclonic spray chamber	√	√	√
2.5 mm i.d. quartz injector	√	√	√
Torch (quartz/Thermo Scientific™ PLUS torch)	√	√	√
Skimmer cone/inset (high matrix)	√	√	√
Humidifier			√
PFA-ST micro-flow nebulizer			√

User-friendly hardware and intuitive method set-up

The integrated accessory for argon gas dilution in the iCAP RQplus ICP-MS allows the user to switch between no dilution to the different dilution levels very quickly and easily without the need for any manual intervention or modification in the sample introduction system. The additional stream of argon used for sample dilution is provided by an integrated and software-controlled mass flow controller before entering the plasma.

Tuning of the different dilution levels is fully integrated within the Qtegra ISDS Software to allow for easy and reliable operation by staff of all levels of experience.

Method creation is accomplished in an intuitive and guided workflow in Qtegra ISDS Software. The overall user-centric workflow for hardware set-up and method creation incorporating the various dilution levels offers unique user-friendliness and enables analysts to utilize their available time for other analysis-related important activities, improving the overall productivity of an analytical laboratory. Figure 1 is a screen capture taken from a Qtegra LabBook, which highlights the user-selectable choice of measurement mode from the available options.



Identifier	Dwell time (s)	Channels	Spacing (u)	Measurement mode	
7Li (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal
9Be (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal
23Na (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal
27Al (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal
45Sc (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal
51V (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal
52Cr (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal
55Mn (KED AGD mid)	0.01	1	0.1		Normal
56Fe (KED AGD mid)	0.01	1	0.1		Normal
59Co (KED AGD mid)	0.01	1	0.1		Normal
60Ni (KED AGD mid)	0.01	1	0.1		Normal
63Cu (KED AGD mid)	0.01	1	0.1		Normal
66Zn (KED AGD mid)	0.01	1	0.1		Normal
73Ge (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal
75As (KED AGD mid)	0.01	1	0.1	KED AGD mid	Normal

Figure 1. User-selectable choice of measurement modes during method set-up within the user-friendly interface of Qtegra ISDS.

Improved matrix robustness – analyze multiple samples with varying matrices in a single analytical batch

The approach of automatic sample dilution using AGD minimizes matrix effects to accommodate various sample matrices in a single run by eliminating the need for matrix-matching or standard addition calibration. The most common way of evaluating matrix effects on an analytical measurement is monitoring the internal standard response against the calibration blank during the measurement of each sample of the analytical batch.

To demonstrate the effectiveness of AGD and assess the robustness of the iCAP RQplus ICP-MS when analyzing various sample matrices in a single batch, a series of different sample types were run using the most appropriate dilution level (Table 2), and the average recovery of common internal standards was recorded. The results are summarized in Table 4.

Table 4. Typically observed internal standard recoveries for a variety of different sample types. Approximate TDS levels are indicated.

Sample matrices	Typcial TDS level	Internal standard recovery [%]							
		^{45}Sc	^{73}Ge	^{89}Y	^{103}Rh	^{115}In	^{175}Lu	^{193}Ir	^{205}Tl
Food digests[1]	0.5 to 1%	98 ± 6	N/A	99 ± 5	94 ± 4	N/A	100 ± 2	N/A	97 ± 6
Drinking water[2]	0.4 %	105 ± 5	102 ± 5	N/A	N/A	102 ± 4	N/A	101 ± 4	N/A
Surface water[3] **Wastewater**[3]	0.4 to 1%	101 ± 5	N/A	97 ± 3	103 ± 5	N/A	103 ± 5	N/A	103 ± 5
Brackish water[3]	0.75%	107 ± 7	N/A	105 ± 6	104 ± 7	N/A	97. ± 5	N/A	91 ± 5
Saline water[3]	1.6%	94 ± 7	N/A	89 ± 8	91 ± 7	N/A	92 ± 7	N/A	85 ± 4
Brine[4]	[2.5% m/m]	101 ± 6	N/A	105 ± 6	101 ± 4	N/A	98 ± 5	N/A	N/A

N/A – Not available

As can be seen from the data, the internal suppression observed across a variety of commonly used internal standards and a series of different sample types, all typically analyzed in analytical testing labs, indicates predictable responses and stable performance over time. In all cases, there was no requirement for maintenance if data collection took place over two or more consecutive days. This means that analytical testing laboratories with high demand on the number of samples run per day, or tight deadlines to deliver results back to clients, can rely on the iCAP RQplus ICP-MS to help them deliver on the expectation, even when different sample types are mixed in a single batch.

Consistency in day-to-day performance

The analysis of samples containing elevated matrix load will eventually and unavoidably lead to more frequent maintenance of the system, i.e., cleaning of the nebulizer, spray chamber, or cones. Dilution, either manual or automatic, using liquid or gas, will reduce the impact to the performance of the system, but not eliminate it. However, consistent performance with plannable downtime is a key requirement in analytical testing laboratories.

The Thermo Scientific™ Hawk™ Consumables and Maintenance Assistant available in the Qtegra ISDS Software allows monitoring of the instrument performance over time and therefore enables the user to track changes in the performance effectively and take corrective actions—such as maintenance—well in advance of an interruption in the laboratory workflow. In addition, the Hawk Consumables and Maintenance Assistant tracks the runtime of the key components of the sample introduction system and allows configuration of alerts to inspect, maintain, or replace the corresponding parts in a predictive manner. Once maintenance has been executed, the action is logged in the maintenance log to provide traceability for all operators of the system and to assist in effective troubleshooting, if needed.

Figure 2 highlights the consistency in the performance of the iCAP RQplus ICP-MS for the monitoring of contaminants in drinking and surface waters. The plot shows the sensitivity of the system in AGD mode, determined daily using the factory-provided performance report. During ten days of continuous operation, involving measurement of more than 2,800 drinking water samples, performance was consistent with no unplanned interruptions for maintenance.

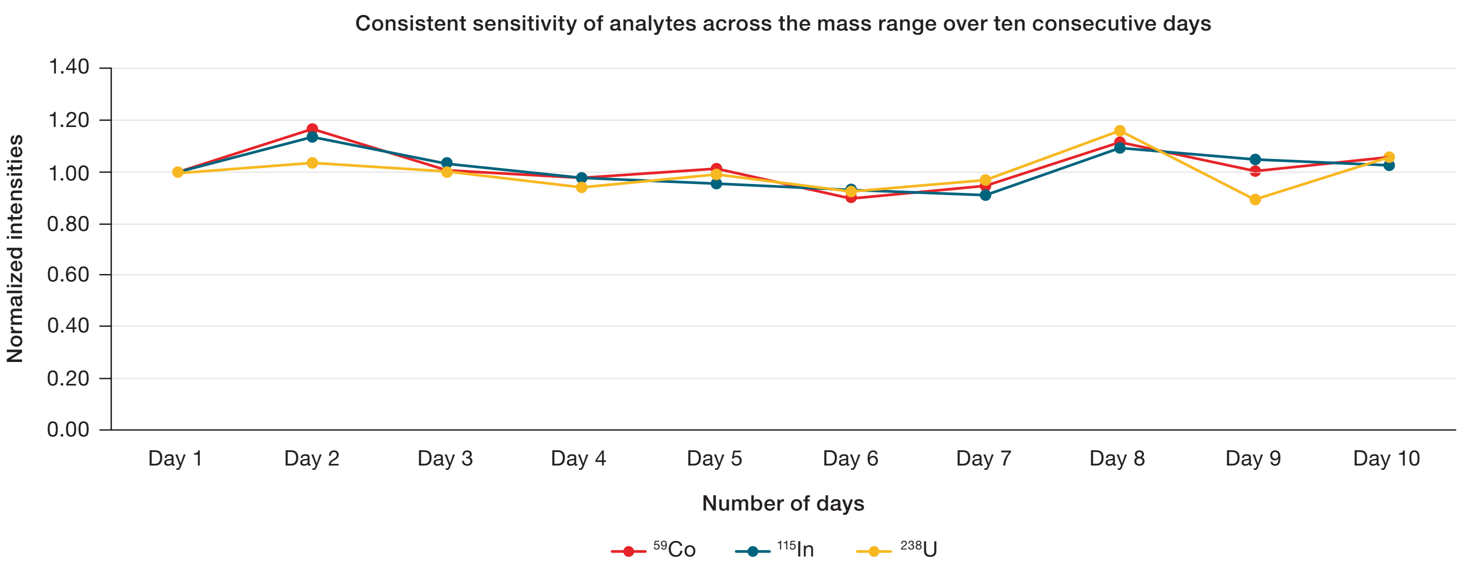


Figure 2. Consistency in the instrument performance observed over period of 10 days of continuous analysis of more than 2,800 water samples

Extended linear range with improved detector lifetime

One of the key features of ICP-MS is its wide linear dynamic range, especially when compared with other atomic spectroscopy techniques like atomic absorption (AA) and ICP – optical emission spectroscopy (ICP-OES). However, sensitive determination of typical contaminants occurs in the $\mu g{\cdot}L^{-1}$ and $ng{\cdot}L^{-1}$ concentration range, whereas major elements need to be determined at high $mg{\cdot}L^{-1}$ levels or above. Therefore, the concentration range that needs to be covered in a single analysis often exceeds the typical linear range of an electron multiplier used in ICP-MS (equivalent to 10 orders of magnitude). When analyzing solutions containing high $mg{\cdot}L^{-1}$ (or even %-levels), saturation of the detector and rapid aging when performing this analysis over extended periods is often a consequence. Detector signal saturation limits the analysis of higher concentrations that can be analyzed reliably with ICP-OES with good linearity. This limitation generally requires samples to be run in two dilution levels or re-analysis of samples after further dilution, in both cases ensuring that measured concentrations are within the calibrated range. For busy analytical laboratories, this presents a big obstacle in achieving productive operation.

The automatic dilution of typical high matrix samples helps to overcome these issues. As fewer ions reach the detector, a reduction in signal intensity is achieved that allows users to run even high concentrations of typical major elements, such as sodium, potassium, or calcium, with excellent linearity. Figure 3 shows a calibration curve for ^{39}K in the range of 0.025 to 1,000 $mg{\cdot}L^{-1}$ using AGD-mid. At the same time, analysis of trace and ultra-trace contaminants in the range of 0.01 to 25 $\mu g{\cdot}L^{-1}$ is demonstrated by the calibration curve for cadmium (^{111}Cd) in Figure 4. A correlation coefficient (R^2) value of greater than 0.9999 was observed during this experiment, which demonstrates the extension of the upper calibration limit, further helping analytical laboratories to significantly reduce sample analysis time and improve productivity. A further extension of the dynamic range for individual analytes can be achieved by adjusting the quadrupole resolution to a narrow peak width, again limiting the number of ions arriving at the detector during a measurement.[5]

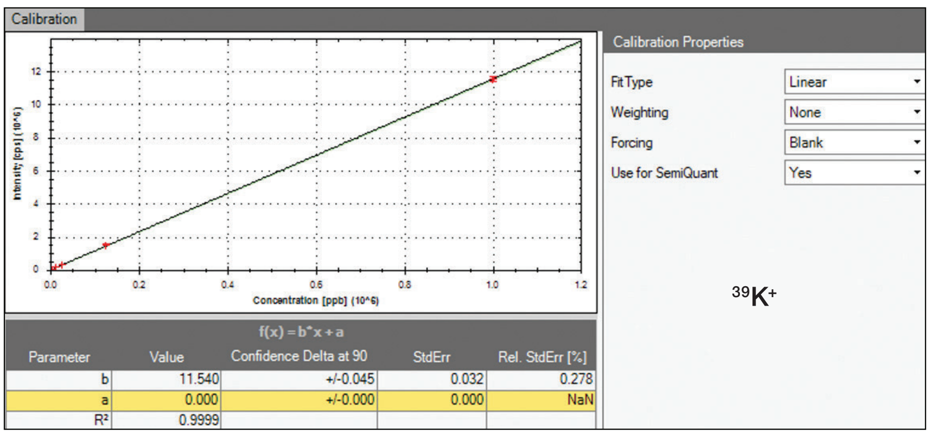


Figure 3. Linearity graph for ^{39}K plotted in the range of 0.025 to 1,000 $mg{\cdot}L^{-1}$ highlighting improvement in linear range using the dilution approach. The plot shows the uncorrected signal intensity recorded by the detection system.

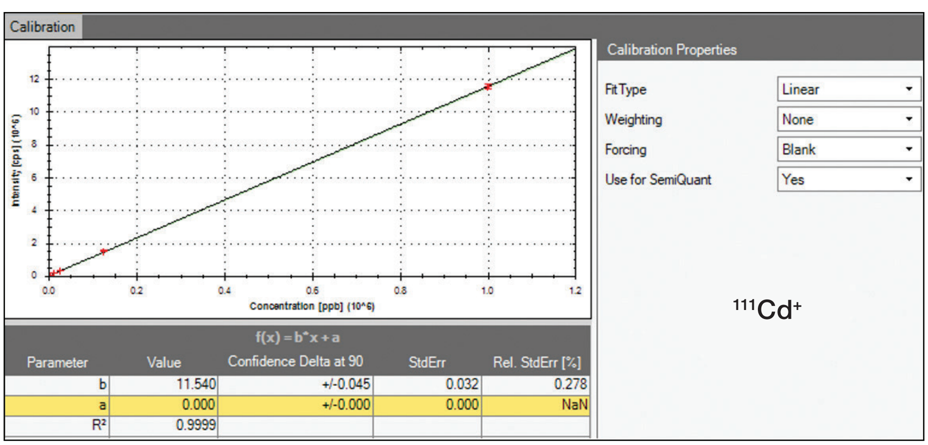


Figure 4. Linearity graph for ^{111}Cd plotted in the range of 0.01 to 25 $\mu g{\cdot}L^{-1}$ highlighting ability of detecting trace level analytes using the argon gas dilution approach. The plot shows the uncorrected signal intensity recorded by the detection system.

Conclusion

The approach of automatic sample dilution using argon gas provides a comprehensive solution for effective handling of heavy matrices with varying sample composition. It allows laboratories to run different sample matrices in a single analytical run without the need for any additional modification in the instrumental set-up and analytical method.

- The default measurement modes allow three different dilution levels to be achieved, enabling the robust analysis of different sample types with the required sensitivity.
- The sample introduction system is configured identically for analysis with and without dilution, offering the highest flexibility for switching between modes without any manual intervention.
- The setting of the right dilution level is embedded in the intuitive workflow of Qtegra ISDS Software to further simplify method development in the analytical workflow. Dedicated autotune routines for each mode enable reliable day-to-day operation with assured consistency in the instrument performance.
- The considerable decrease in the sample load that reaches the plasma due to aerosol dilution reduces solid deposition on the interface cones and lessens the frequency of system maintenance. This helps in lowering the instrument downtime and improves the overall productivity of the laboratory.

References:

1. Thermo Fisher Scientific Application Note 001533: Accurate and robust long-term analysis of food and beverage samples using single quadrupole ICP-MS.
2. Thermo Fisher Scientific Application Note 001529: Reliable analysis of surface and drinking waters following ISO method 17294 using single quadrupole ICP-MS.
3. Thermo Fisher Scientific Application Note 001592: Robust analysis of a variety of water and wastewater samples according to U.S. EPA Method 6020B (SW-846).
4. Thermo Fisher Scientific Application Note 001503: Managing the challenges of analyzing brine solutions of variable concentration using inductively coupled plasma mass spectrometry (ICP-MS) equipped with argon gas dilution.
5. Thermo Fisher Scientific Technical Note 43399: Linear Dynamic Range Performance of the Thermo Scientific iCAP Qnova Series ICP-MS.