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Resolving the challenges of analyzing samples with high and variable matrix content using Argon Gas Dilution (AGD) with ICP-MS

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Introduction

Among the key advantages of ICP-MS are its outstanding sensitivity and its ability to carry out analysis with relatively low matrix effects with many sample types. However, this statement is essentially only true for samples containing a maximum matrix load of less than 0.2% (m/v) total dissolved solids (TDS). For samples above this level, ICP-OES has been and still is the workhorse for analysis. In modern laboratories, increasing numbers of samples contain dissolved solids above the 0.2% (m/v) level but still need to be analyzed using ICP-MS to meet the required detection limits, or should be analyzed on an ICP-MS system to fully leverage the productive time and the fast throughput abilities of this instrument. It is easily possible to do so, but it normally requires some form of dilution to circumvent potential adverse effects, leading to potential drift, QC failures, or the need to perform maintenance more frequently.

When analyzing solutions with increased levels of TDS (beyond 0.5% and up to several %), there are two main challenges to be considered:
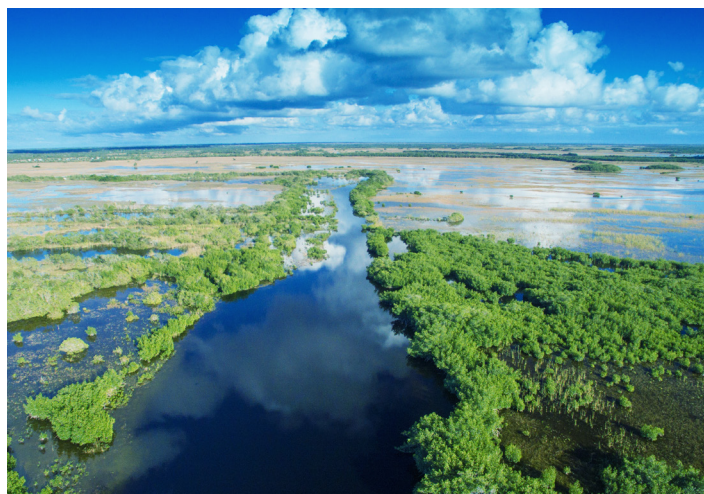
- The plasma needs to fully decompose the matrix and effectively ionize the analytes of interest to achieve the required detection sensitivity. Matrix effects can alter the observed signal intensity for a given concentration of an analyte versus the signal intensity obtained when calibrating in a clean acid matrix, and hence cause inconsistent results. Although internal standardization is a way to account for signal suppression, it must still fall in an acceptable range to assure reliable correction (typically 80–120%).

- The matrix can deposit on the interface region of the system, more specifically the sample and skimmer cones, and over time clog the narrow orifice connecting the plasma with the mass spectrometer, meaning a

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sudden drop of the signal to potentially no signal at all. The consequence is stopping the analysis and a delay in providing results back to clients.

The solution to both challenges is dilution of the sample to an appropriate level. Liquid dilution is a way to reduce the matrix load in a sample, but often it is not preferred in an applied testing laboratory, since it causes additional labor (which may be reduced when using an automated dilution system), cost (as clean diluent solutions need to be provided), and risk of contamination or errors during dilution.

The use of argon gas, provided directly from the instrument, is an attractive way to dilute the sample online at no additional cost. Samples can be placed as received onto the autosampler and analyzed directly, with the dilution carried out inside the instrument. This solution, known as Argon Gas Dilution (AGD), is available for the Thermo Scientific™ iCAP™ RQ ICP-MS, as well as the Thermo Scientific™ iCAP™ TQe ICP-MS and the Thermo Scientific™ iCAP TQ™ ICP-MS.

The Argon Gas Dilution interface uses an additional flow of argon gas, provided from a dedicated mass flow controller inside the instrument, to dilute the sample. With AGD, the quantity of sample delivered to the plasma is reduced by lowering the nebulizer gas flow, while at the same time adding argon via the additional mass flow controller such that the overall gas flow to the plasma remains constant. The dilution is accomplished by addition of the extra argon gas flow to the aerosol, leaving the spray chamber via a port located between the spray chamber and the torch (Figure 1). The sample is therefore diluted with argon gas inside the ICP-MS sample introduction system. Since the absolute amount of sample entering the plasma is lower than with the conventional setup, the dissociation of the matrix in the ICP is improved and deposition on the ICP-MS interface is reduced. AGD can be combined with all operation modes of the QCell collision/reaction cell for interference removal, using either helium cell gas with kinetic energy discrimination (KED) or reactive gases such as oxygen, hydrogen, or ammonia.

The AGD approach has two important consequences:

- The plasma conditions are changed towards a drier plasma, observed by a reduction of the cerium oxide to cerium ratio from less than 2% to typically less than 0.5%. This means that more robust plasma conditions are achieved, enabling more effective decomposition of the sample and provision of enough energy for complete ionization of the analytes.

- Clogging and obstruction of the cone orifices is avoided, and maintenance cycles can be reduced.

Different dilution factors can be realized by variation of the nebulizer gas and dilution gas ratio. However, within an analysis sequence, a fixed dilution factor must be applied for all samples, regardless of whether a lower or higher dilution factor would be beneficial for a particular sample in the sequence. Changing the argon flows for different samples in a run would require the calibration standards to also be run under the changed conditions, as well as requiring additional stabilization times to assure consistent performance, thus limiting the achievable sample throughput. The general settings tuned for by the autotune routine provided with the Thermo Scientific™ Qtegra™ ISDS Software optimize AGD at around 0.25–0.30 L·min⁻¹ nebulizer gas flow. Under these conditions, the amount of sample reaching the detector is decreased significantly. Note that this tuning reduces the typically achieved sensitivity of the system by a factor of 10; however, the sample load is reduced more significantly, such that resulting method detection limits (MDLs) are often at least comparable to liquid dilution by a similar factor.

Sample dilution occurs automatically inside the instrument

Dilution gas (humidified argon)

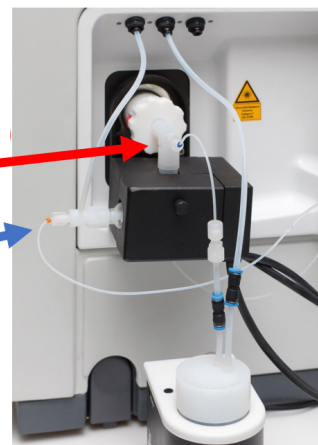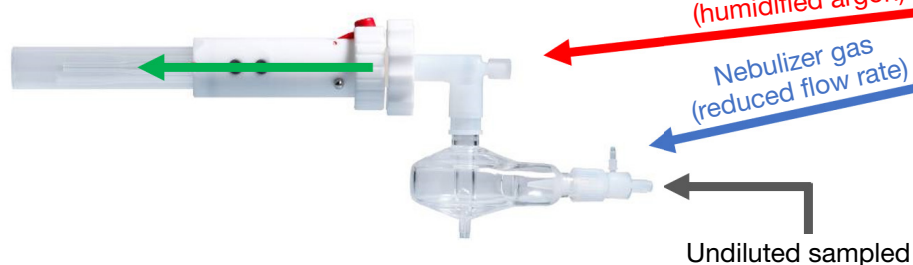Nebulizer gas (reduced flow rate)

Undiluted sampled

Figure 1. Principle of Argon Gas Dilution and setup on an iCAP RQ ICP-MS

In some cases, predominantly for samples with a TDS content of between 0.5% and 1%, the use of a different skimmer cone insert available for the Thermo Scientific™ iCAP™ Qnova Series ICP-MS instruments can be an alternative to avoid dilution of the sample. This assures the best possible sensitivity and optimized detection limits, while maintaining the intended robustness. For previously digested samples (either using a microwave system or a hot plate digestion) that cannot be diluted further due to the need to detect impurities at the lowest possible level, use of the robust skimmer cone insert can be particularly beneficial.

Application examples

Argon Gas Dilution allows direct analysis of a wide variety of sample types that would otherwise require dilution upfront (either accomplished manually or automatically). In the following, a series of examples are shown.

Direct analysis of water samples

The analysis of water samples is one of the key applications for ICP-MS. Between the different types of waters (i.e., drinking water, river or lake water, waste water, and sea water) there are significant differences in the total matrix content and composition, so that a robust approach is needed to analyze all types of waters in a single method. In environmental research applications, such as analysis

of the extent and potential origin of contamination,[2] it is key to not only reliably detect contaminants at low levels but also avoid any contamination in the process of sample collection and preparation. Being able to directly analyze the sample without any further handling in the laboratory is therefore beneficial. With the necessary measures of careful sample handling and clean workspaces, it is possible to analyze typical environmental contaminants, such as arsenic, mercury, cadmium, or lead at ultra-trace levels, even in sample types such as estuarine and sea water, as shown in Table 1.

One of the challenges many laboratories face is that a method needs to include a variety of sample types with variable matrix load and composition to make the most efficient use of the instrument. At the same time, all sample matrices need to pass applicable QC acceptance criteria, for example, recovery of the internal standard. In a subsequent study,[3] the analysis of different types of water samples has been studied. To simulate a high sample volume, a larger sample batch was scheduled for analysis, including drinking, surface, and sea water. The total number of solutions analyzed was 171 samples (including 120 unknown samples), requiring a total analysis time of approximately 9 hours. The recovery of the internal standards throughout the analysis is shown in Figure 2.

Table 1. Results obtained for the analysis of estuarine waters without prior dilution. Critical contaminants like cadmium and lead were accurately determined in a certified reference material at ultra-trace levels. Potential polyatomic interferences on arsenic ($^{40}Ar^{35}Cl^+$ on $^{75}As^+$) are fully removed using both single and triple quad ICP-MS. Data was acquired using standard addition, no internal standard was used.

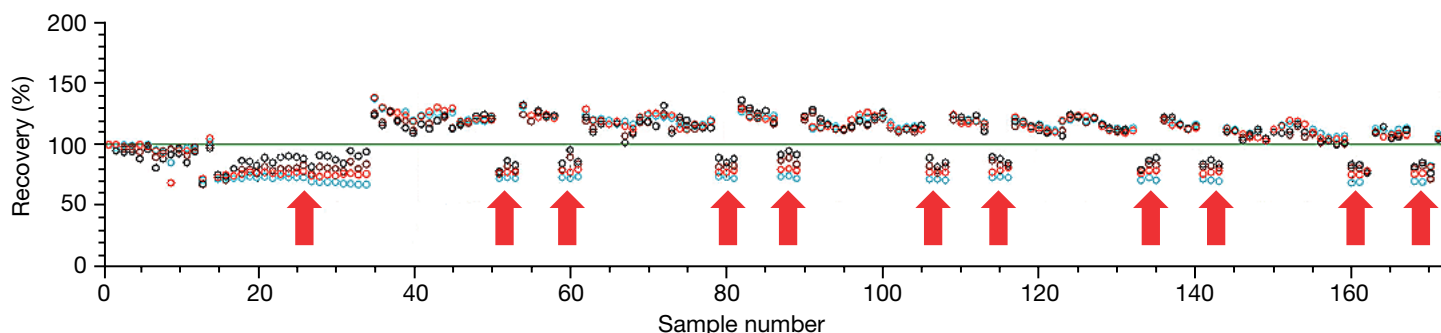| Element	Cu	Zn	As		Cd	Pb
Mode	SQ-KED	SQ-KED	SQ-KED	TQ-O$_2$	SQ-KED	SQ-KED
Result CASS & CRM [µg·kg^{-1}] (N=4)	0.57 ± 0.012	1.89 ± 0.23	1.04 ± 0.11	1.09 ± 0.08	0.027 ± 0.004	0.013 ± 0.002
Certified value [µg·kg^{-1}]	0.530 ± 0.032	1.27 ± 0.18	1.04 ± 0.10		0.0217 ± 0.0018	0.0106 ± 0.0040
Concentration range in samples [µg·kg^{-1}]	0.31–0.56	0.41–2.34	1.32–1.88		0.017–0.058	0.023–0.042

Figure 2. Response of the internal standards in a batch covering about 9 hours of uninterrupted analysis of 171 samples. Samples with lower recovery (approx. 70%) correspond to undiluted sea water.

All internal standards showed reliable and predictable recovery (within approximately 69% to 122%) over the entire runtime of the batch, demonstrating robust analytical performance. It is important to note that those samples causing a suppression of the internal standard were, in every case, undiluted sea water. Whereas an internal standard recovery of around 70% still allows for accurate correction of matrix effects and potential drift, it is far more important that the signal of the internal standard immediately and reliably returns to expected levels (approximately 110% in this example) when switching back to lower matrix samples (e.g., 2% HNO_3 for QC checks or less saline water types). This ultimately demonstrates the system´s ability to effectively analyze a variety of different sample types with vastly different TDS load in a single batch.

At the same time, the performance of a method for different sample types must also allow regulatory requirements to be met.[4] As mentioned previously, even if the sample is placed on the autosampler without any upfront dilution, with AGD a dilution step takes place during the analysis. This means that instrumental detection limits (IDLs) are slightly worse compared to the standard tuning of the instrument, but method detection limits (MDLs) are often at least equivalent or better. This is proven by the data shown in Table 2, summarizing the analytical figures of merit as well as the results of a preliminary validation of a method using argon gas dilution for the analysis of different types of water samples using single quadrupole ICP-MS.

Analysis of food samples

Food materials are typically digested using a microwave assisted digestion system, and ideally the digested sample is analyzed immediately to avoid time and labor-intensive dilutions. As food samples consist of a mostly organic matrix, which is converted into CO_2 and evaporated during the process of digestion, direct analysis of the sample after minimal dilution (to reduce the acid concentration in the sample digest) is feasible even though the calculated level of total dissolved solids is still higher than 0.5%. In such cases, the use of argon gas dilution may be suitable to assure robust long-term analysis, but direct analysis is also possible using a slightly different configuration of the interface, and operation using a standard tuning of the plasma. Using this approach, a total of 283 samples were successfully analyzed in approximately 14 hours,[5] with the internal standard response and QC checks falling well within regulatory limits.

Table 2. Results for the CASS-5 sea water and drinking water samples. Analyte concentrations are reported as µg·L⁻¹. The spiked concentration was varied between 0.5 and 20 µg·L⁻¹ for different analytes and sample types. Analysis was accomplished on an iCAP RQ ICP-MS.

	LOD [µg·L⁻¹]	BEC [µg·L⁻¹]	CASS-5 sea water CRM [µg·L⁻¹]		Spike recovery [%]	
			Measured (N=24)	Reported value	Sea water (N=24)	Drinking water (N=24)
Be	0.004	0.001	0.004 ± 0.003	–	98	102
Al	0.233	2.800	2.12 ± 0.42	–	115	97
V	0.034	0.044	1.50 ± 0.24	1.32 ± 0.14	–	–
Cr	0.055	0.211	0.145 ± 0.072	0.106 ± 0.013	106	96
Mn	0.022	0.011	2.72 ± 0.15	2.62 ± 0.20	102	94
Fe	0.072	0.240	1.67 ± 0.12	1.44 ± 0.11	107	98
Ni	0.054	0.112	0.315 ± 0.03	0.33 ± 0.023	102	94
Cu	0.061	0.163	0.381 ± 0.04	0.38 ± 0.028	100	97
Zn	0.023	0.033	0.624 ± 0.04	0.719 ± 0.068	105	97
As	0.025	0.032	1.62 ± 0.12	1.24 ± 0.09	106	94
Se	0.143	0.084	< LOD	–	103	91
Cd	0.006	0.002	0.020 ± 0.01	0.0215 ± 0.0018	93	99
Sb	0.009	0.008	0.46 ± 0.03	–	98	98
Pb	0.007	0.013	0.011 ± 0.002	0.011 ± 0.002	101	105

Determination of impurities in refined nickel

Nickel (Ni) is a widely used constituent of many alloys, as it confers chemical resistance and anti-corrosion properties. Nickel alloys are frequently used in the manufacturing of mechanical parts in various industries, batteries, and electronics.[6] Considering the importance of such Ni-alloys for some industries (for example, aircraft engine turbine blades), it is imperative to control potential impurities as they can cause weaknesses in the alloy that lead to fracturing and, ultimately, total material failure. A challenge related to this application is the requirement to analyze high concentrations of the sample matrix, typically resulting in a matrix concentration of nickel of between 1,000 and 8,000 mg·L^{-1}. Upfront dilution is often not feasible to ensure that impurities can still be detected at required levels.

However, when using Argon Gas Dilution such analysis is feasible with high accuracy. This is demonstrated by the data presented in Figure 3, showing the recovery of two QC checks containing a series of impurities subject to analysis and a QC check to verify the concentration of nickel in the sample.
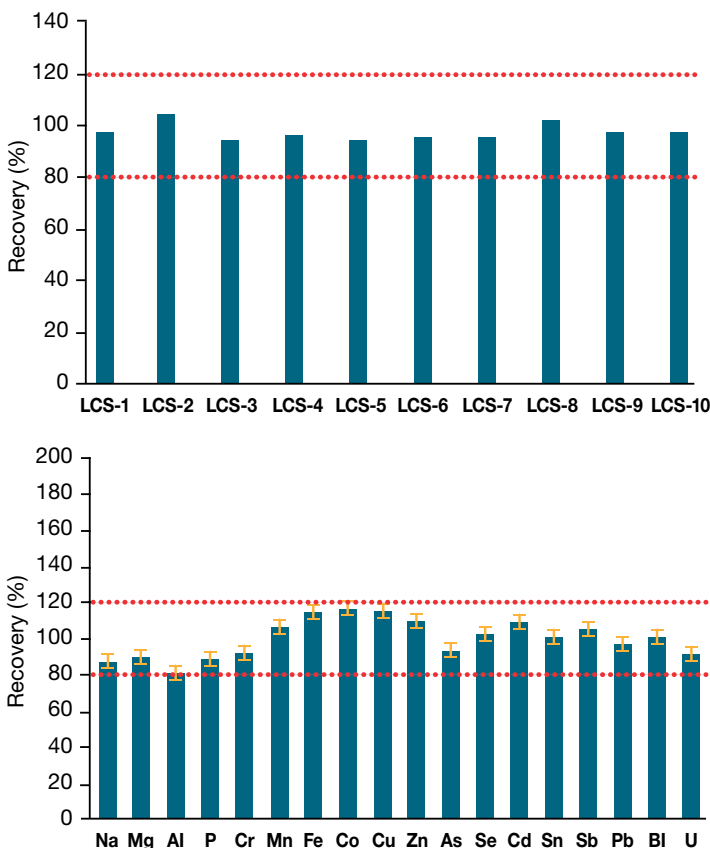

Figure 3. Recovery of applicable QC checks for the analysis of impurities in solutions containing up to 7,000 mg·L^{-1} nickel.
Upper: A solution containing 7,000 mg·L^{-1} nickel. Lower: QC standard (continuing calibration verification standards). All results fall well within the accepted range between 80–120% recovery.

Analysis of solutions containing up to 25% TDS

With minor modifications to the setup, the instrument´s capability to handle matrix load can be extended from 3–4% (as shown previously) up to 25%.[7] In most cases, an exchange of the standard nebulizer for a so-called V-groove nebulizer is sufficient. Especially in industrial applications, the need to analyze samples with such heavy matrices without upfront dilution is needed. In this example, good long-term stability (recovery between 70% and 120% over 4.5 hours) and spike recovery (85–116%) were observed.

Conclusion

Argon Gas Dilution is a way to overcome the challenges associated with the analysis of samples with matrix content outside the commonly defined limit of around 0.2% (m/v) TDS.

- Dilution with argon gas is accomplished automatically inside the instrument with no additional sample handling required.

- The optimized plasma conditions allow higher robustness, and lead to an improved decomposition of the sample matrix, meaning fewer matrix effects and reduced signal drift.

- Contamination and errors in sample preparation are effectively avoided.

- Samples with 3–4% TDS can be analyzed directly, but also samples with ultra-high matrix content (up to 25%) can be run with minor modifications.

- AGD is fully integrated and supported in the Qtegra ISDS Software, so that it is easy to set up and operate.

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