

# Analysis of high matrix samples using argon gas dilution with the Thermo Scientific iCAP RQ ICP-MS

## Keywords

Argon gas dilution, AGD, High matrix samples, Seawater

## Goal

To critically assess the use of Argon Gas Dilution (AGD) on the Thermo Scientific iCAP RQ ICP-MS for the direct analysis of high matrix samples such as seawater.

## Introduction

High matrix samples remain a challenge in ICP based applications. For example, high levels of dissolved solids can cause ionization suppression that reduces sensitivities during the analysis of real samples by both ICP-OES and ICP-MS. For ICP-MS the situation is further complicated as high matrix levels may lead to blockage of the narrow aperture cones used in the interface between the ICP ion source and the mass spectrometer. While continual advances in interface design have improved ruggedness, manual or automated sample dilution using a suitable solvent (usually dilute acid) is still commonly used to reduce sample matrix levels to ~0.2% total dissolved solids (TDS) before ICP-MS analysis. Depending on both the application and required sample throughput level, however, this may not be ideal as it increases both the risk of contamination and the cost per analysis (due to the additional time and consumables).

Argon Gas Dilution (AGD) is a useful technique to address these fundamental limitations. In AGD-ICP-MS analyses, the argon (Ar) gas flow through the nebulizer is reduced while the total Ar gas flow to the plasma is maintained by the addition of a make-up Ar gas flow to the aerosol leaving the spray chamber. The sample aerosol is therefore diluted with Ar gas inside the ICP-MS sample introduction system. Since the absolute amount of sample entering the plasma is limited, the dissociation of heavy matrix samples in the ICP is improved, reducing matrix deposition on the ICP-MS interface. Overall plasma robustness improves in AGD mode as demonstrated by a reduction in metal oxide formation.

Additionally, dilution with clean Ar gas minimizes contamination by reducing sample handling without increasing analysis times or requiring extra (potentially costly) consumables.

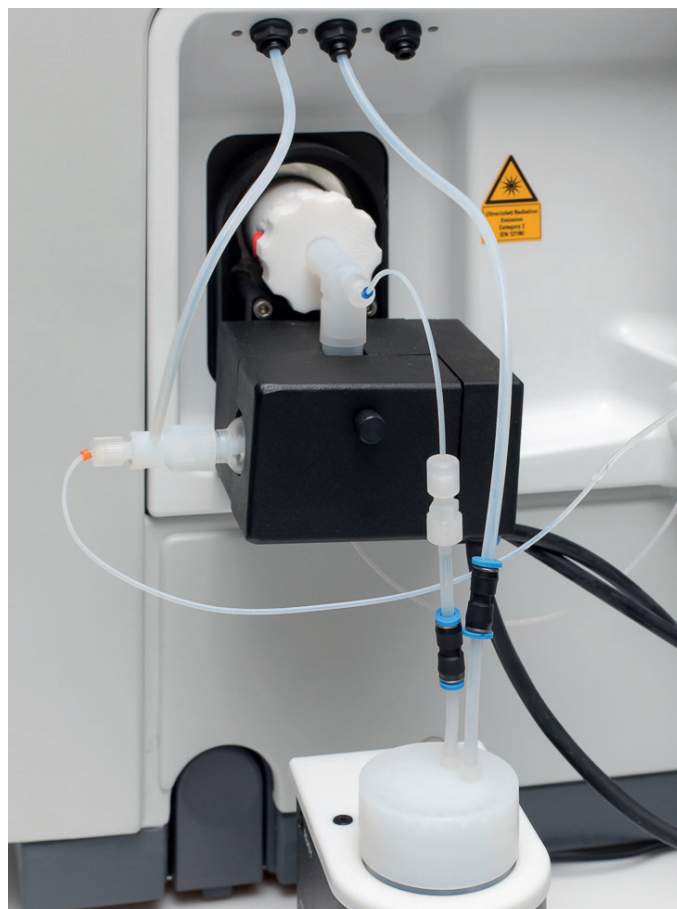
The use of AGD is not, however, without disadvantages. In contrast to automated, sample specific dilution, all samples are diluted in AGD mode, reducing absolute instrumental sensitivity. Furthermore, since the proportion of sample to Ar delivered to the ICP is reduced, the plasma runs slightly “drier” lowering the ionization efficiency for elements with higher 1<sup>st</sup> ionization potentials (Zn, Cd for example) leading to reduced recoveries. Approaches to overcome this inherent characteristic of Ar gas based sample dilution, including re-humidifying the plasma and the addition of excess carbon, are investigated in this note.

### Instrument configuration

A Thermo Scientific™ iCAP™ RQ ICP-MS fitted with the Argon Gas Dilution Kit was used for all analyses (see Figure 1). As part of this kit, a *pergo* Argon Nebulizer Gas Humidifier (Elemental Scientific, Omaha, US) is used to humidify an additional argon gas supply added to the sample aerosol. Instrument parameters are shown in Table 1.

**Table 1. Instrument parameters.**

Parameter	Value
Forward Power	1550 W
Nebulizer	Glass, concentric (pumped, 400 $\mu\text{L}\cdot\text{min}^{-1}$ )
Nebulizer Gas Flow	0.25 $\text{L}\cdot\text{min}^{-1}$
Add. Gas Flow (Ar)	0.95 $\text{L}\cdot\text{min}^{-1}$
Interface	Ni sampler and skimmer cones High matrix insert
Sample Introduction	Orange/Yellow tubing, 20 rpm
QCell Conditions	5 $\text{mL}\cdot\text{min}^{-1}$ He, 3V KED



**Figure 1. Argon Gas Dilution, AGD (PN: 1371830) on the iCAP RQ ICP-MS.**

### Method development

In order to assess the AGD technique, the iCAP RQ ICP-MS was used to determine trace elements in undiluted seawater (NRCC CASS-5 and NASS-6 reference materials) using a series of different AGD conditions. Seawater, with approximately 3.5% (35,000  $\mu\text{g}\cdot\text{mL}^{-1}$ ) total dissolved solids (TDS), over a factor of 10 higher than the normal TDS limit for ICP-MS analysis, was chosen for these tests as it is one of the most challenging sample matrices analyzed by ICP-MS.

The two seawater samples were spiked with a multielement standard solution at concentration levels between 20 and 200  $\mu\text{g}\cdot\text{L}^{-1}$ . A sample of 2%  $\text{HNO}_3$  spiked at the same level was also prepared.

An internal standard solution, containing Sc, Ge, Rh and Ir in 2% HNO<sub>3</sub> (and 10% isopropanol, where appropriate), was added to all samples via a T-piece (a 1:1 online dilution) before entering the spray chamber. Higher dilution factors (of up to 1:9) can be achieved by combining peristaltic pump tubing with different internal diameters so that samples with higher amounts of total dissolved solids can be analyzed using the same configuration.

The following AGD configurations were tested:

- Argon gas dilution using dry Ar.
- Argon gas dilution using humidified Ar.
- Argon gas dilution using humidified Ar + 1% CH<sub>4</sub> (in Ar) added after the humidifier at a flow rate of 100 mL·min<sup>-1</sup>.
- Argon gas dilution using humidified Ar + 10% (v/v) isopropanol in the internal standard solution.

The spiked seawater and 2% HNO<sub>3</sub> samples were then analyzed using the four AGD settings on the iCAP RQ ICP-MS.

## Results

Relative recovery values, calculated from blank subtracted intensities in the seawater and 2% HNO<sub>3</sub> matrices, were used to assess the extent of signal suppression for each AGD setting tested. No internal standard correction was made. As an acceptance criteria, signal recovery in the seawater matrix should be between 80–120% for all elements, as commonly accepted for environmental analysis.

Relative recovery values for each AGD configuration tested are shown in Figure 2.

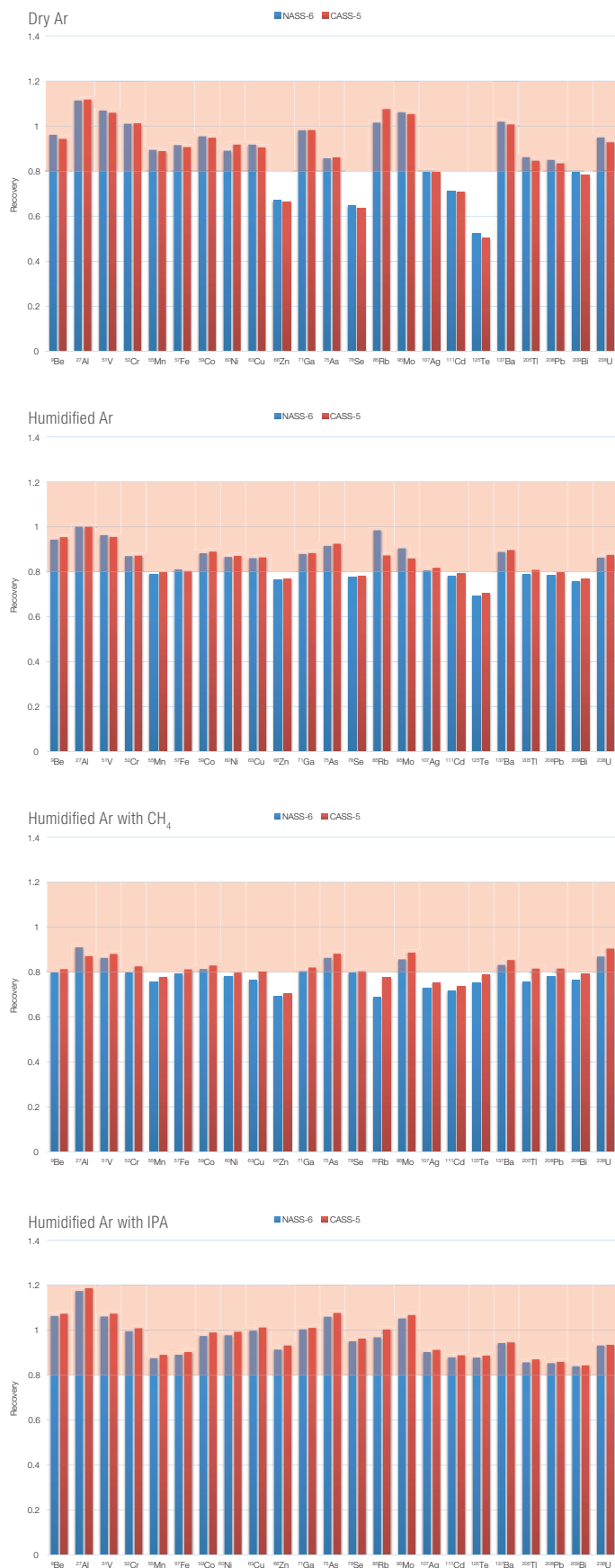


Figure 2. Trace metal recoveries for each AGD configuration in undiluted seawater relative to 2% HNO<sub>3</sub>. Red-shaded areas indicate recoveries of between 80–120%.

Results for the four AGD settings tested are summarized below:

- **Dry Ar:** Dilution with dry Ar shows acceptable (80–120%) recoveries for most trace metals in the ICP-MS analysis of the two seawater samples analyzed. Significant signal suppression is observed, however, for several critical analytes with relatively high 1<sup>st</sup> ionization potentials (Zn, Se, Cd and Te), where recoveries as low as 50% (Te in CASS-5) are observed. These low recoveries demonstrate the unsuitability of dry Ar for multielemental AGD-ICP-MS analysis of high matrix samples such as seawater.
- **Humidified Ar:** With an argon humidifier to “re-wet” the plasma for AGD-ICP-MS analysis, signal recoveries for the higher ionization potential (IP) elements are improved, but still do not meet the 80% lower recovery limit commonly used in environmental analyses.
- **Humidified Ar with CH<sub>4</sub>:** The introduction of carbon to the plasma in the form of methane addition (1% CH<sub>4</sub> in Ar) does not significantly improve recoveries for the higher IP elements and a slight reduction in recovery is observed for others.
- **Humidified Ar with IPA:** When carbon is introduced to the plasma via the addition of isopropanol (10% v/v) to the internal standard solution, AGD-ICP-MS recoveries for all trace elements, including those with higher 1<sup>st</sup> ionization potentials, are between 80–120%.

To verify the robustness of the humidified Ar with IPA approach for AGD-ICP-MS analysis, the two spiked seawater reference materials (CASS-5 and NASS-6) were quantified against an external calibration curve (prepared in dilute HNO<sub>3</sub>) and analyzed over a 7.5-hour period regularly interspersed with quality control samples.

The AGD-ICP-MS method developed minimizes signal suppression so that undiluted seawater can be quantified against simple HNO<sub>3</sub> calibration standards. During the entire analysis, minimal signal drift was observed, as shown in Figure 3.

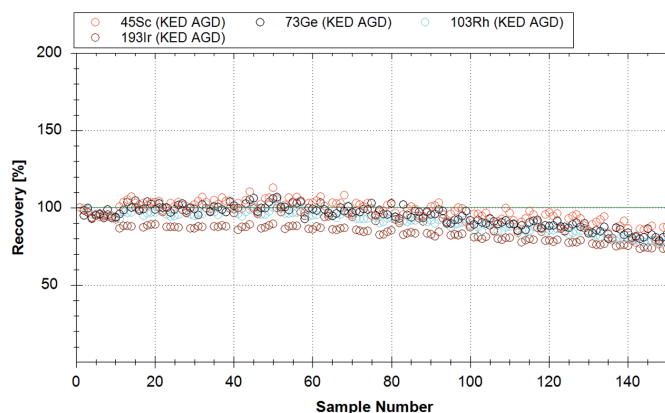


Figure 3. Internal standard recoveries during a 7.5-hour analysis of undiluted seawater.

Average recoveries and precisions over the 7.5-hour analysis sequence for the spiked CASS-5 and NASS-6 seawaters are shown in Table 2.

Table 2. Accuracy and precision data from a 7.5-hour AGD-ICP-MS analysis of the spiked seawater reference materials CASS-5 and NASS-6 using the iCAP RQ ICP-MS. Average trace metal accuracies are expressed as the relative percentage of the spiked concentrations.

Isotope	CASS-5		NASS-6	
	Recovery (%)	Precision (%RSD)	Recovery (%)	Precision (%RSD)
<sup>51</sup> V	95	2.2	96	2.2
<sup>52</sup> Cr	95	3.5	97	2.9
<sup>55</sup> Mn	86	4.2	89	4.7
<sup>56</sup> Fe	85	2.9	85	4.2
<sup>59</sup> Co	91	2.8	91	2.5
<sup>60</sup> Ni	91	3.4	91	3.1
<sup>63</sup> Cu	94	2.7	97	2.3
<sup>68</sup> Zn	85	2.7	86	1.9
<sup>71</sup> Ga	95	3.1	96	2.7
<sup>75</sup> As	101	2.3	103	2.2
<sup>78</sup> Se	90	2.5	90	2.4
<sup>85</sup> Rb	99	2.7	99	2.9
<sup>95</sup> Mo	100	1.5	101	1.6
<sup>107</sup> Ag	89	1.2	80	1.3
<sup>111</sup> Cd	87	2.2	88	1.7
<sup>137</sup> Ba	99	3.1	99	3.2
<sup>205</sup> Tl	94	1.6	93	3.5
<sup>208</sup> Pb	93	1.9	93	2.0
<sup>209</sup> Bi	85	2.0	86	2.0
<sup>238</sup> U	95	2.0	96	1.9

As can be seen from the percentage recovery data in Table 2, the AGD-ICP-MS method developed for the iCAP RQ ICP-MS provides accurate data for all trace metals determined in the spiked seawater reference materials. Concentration precisions of below 5% RSD demonstrate the robustness of the AGD-ICP-MS technique for the long term direct analysis of undiluted seawater.

### Software implementation

AGD based analysis on the iCAP RQ ICP-MS is fully supported by the Thermo Scientific Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Both nebulizer and additional gas supplies are controlled by Qtegra ISDS Software and an AGD specific autotune is provided, making method development straightforward. Instrument performance under AGD conditions can be assessed using a Qtegra ISDS Software supplied Performance Report.

AGD can be integrated with any Thermo Scientific QCell™ based solution for interference removal, i.e. collision based He KED or reaction based CCT. Multi-mode AGD analysis methods can be easily defined to provide accurate, interference-free analyses in even the most challenging sample matrices.

### Performance

Lowering the nebulizer gas flow in AGD based analyses reduces sample transfer to the plasma decreasing absolute instrumental sensitivity when compared to non-AGD based conditions. At the same time however, metal oxide formation is reduced. Typical performance in STD, STD-AGD and KED-AGD analysis modes is shown in Table 3. While oxide and doubly charged formation are shown as percentages.

**Table 3. Typical performance of an iCAP RQ ICP-MS in STD, STD-AGD and KED-AGD analysis modes. Sensitivities are expressed as cps/ppb<sup>-1</sup>.**

	STD	STD-AGD	KED-AGD
<sup>7</sup> Li	78081	4134	23
<sup>59</sup> Co	113645	7627	3350
<sup>115</sup> In	279640	21739	8953
<sup>238</sup> U	383232	35082	42380
CeO/Ce	1.8%	0.9%	0.5%
Ba <sup>++</sup> /Ba <sup>+</sup>	1.8%	1.0%	1.8%

### Conclusion

Argon gas dilution significantly improves plasma robustness allowing the direct analysis of high matrix samples such as undiluted seawater using the iCAP RQ ICP-MS. Optimum performance for high IP analytes in such samples is only possible, however, after online addition of water vapor and carbon.

Find out more at [thermofisher.com/SQ-ICP-MS](http://thermofisher.com/SQ-ICP-MS)