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Running higher levels of dissolved solids with the High Matrix Kit on Attom ES

- **Run 5-10 times higher dissolved solids**
- **Simple setup and operation**
- **Low levels of signal drift**
- **Excellent long-term stability**

Introduction

When using ICP-MS for liquid samples, the sample is introduced as a fine aerosol through a pneumatic nebuliser. Typically, the liquid uptake flow is between 0.1 and 0.3mL/min with only a small proportion of that flow passing through a spray chamber and into the ICP torch. The plasma generated in the ICP torch, has a central channel with a temperature of 5000-6000K which is sufficient to desolvate the droplets, volatilise the solid compound, dissociate the molecules and then ionise the atomic species. The output from the ICP torch is positioned in close contact with the cooled cones of the mass spectrometer interface and this interface has a limit to the amount of condensing material that can be present in the output of the plasma before cone blockage occurs. The deposition of material on the cones leads to signal drift which can be gradual or less controlled as deposits build up and break off the skimmer cone particularly.

Sampler and skimmer cone designs have been refined over many years to provide a good compromise of sensitivity and stability with recent changes focussing on the temperatures at the tip of the cone so they operate well in the temperature of the plasma and maintain good performance over long periods. The generally accepted dissolved solids level before cones start to block is found to be about 0.2% by mass. The classic approach to running any higher matrix sample has been “dilute and shoot” which can be done in 3 different ways:

- Off-line: The sample is diluted manually or automatically off-line prior to loading the autosampler. Typical dilutions from 1:2 to 1:10,000 via serial dilution.

- On-line: The sample is diluted by the autosampler immediately before or even during the introduction of the sample to the nebuliser using systems like the ESI PrepFAST or Cetac SDX. Typical dilutions from 1:2 to 1:200 in one step.

- In-line: The sample is mixed with a diluent as it is introduced to the nebuliser, the diluent typically containing the internal standard elements removing a step in the sample preparation process. Typically 1:1.25 to 1:10 with the instrument’s peristaltic pump.

Liquid dilution techniques have the advantages of flexibility and high or low dilution ratios, they can often be combined as well but they all have the disadvantage of increasing the volume of liquid which subsequently has to be disposed of after the analysis is complete. Liquid dilution also carries the risk of contamination with the use of additional solvents and equipment.

Alternative dilution method

All of the sample processing steps in the plasma have to take place during the short time that the aerosol particle will have to pass through the torch to the cones. Some ICP-MS systems have changed to using torches with wider bore injectors so passing the same volume of gas leads to slower linear velocities and therefore longer residence times in the plasma. This has been reported to lead to better matrix handling but also the necessity of having an extra argon mass flow controller to provide additional gas independently of the nebuliser. The nebuliser optimises the formation of droplets at a particular flow and so relying on one gas flow to generate the droplets and optimise the volume of gas flowing through the torch is too compromising. Separating the processes allows the wider bore injectors to work effectively.

With the aerosol generation and gas flow through the torch now semi-independent, it is possible to vary the amount of the aerosol generated by the nebuliser that reaches the plasma. When delivering the sample to the nebuliser with the peristaltic pump, it is also possible to reduce the gas flow through the nebuliser below the optimum required for uptake through the Venturi effect of a glass concentric nebuliser. This effectively “starves” the aerosol and a dilution in the sample introduced to the plasma is seen which can be varied by the balance of flows between the nebuliser gas and the additional argon gas added after the spraychamber.

The Attom ES High Matrix Kit uses a 2.5 mm ID injector torch, a modified spray chamber elbow and the standard additional argon mass flow controller to provide sample dilutions of 10 times or greater.

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Analysis of 1% NaCl solution

The Attom was setup with a 10 ppb solution of tune elements in 1% nitric acid, sample uptake was pumped at 0.2 mL/min and the nebuliser and additional argon gas flows optimised to provide a sample dilution of ~15x (relative to the signal seen with the standard 1.5 mm ID torch injector) and a reduction of ~5x on the CeO/Ce ratio (which is an indicator of how well the sample matrix is broken down in the plasma). As the objective was to improve matrix handling, the RF power for the ICP was also increased to 1500 watts instead of the normal default of 1300 watts. The only difference in ion optics tuning compared to default was a reduced extraction voltage required due to the lower gas flow in the torch central channel. The typical conditions are shown in Table 1.

Table 1: Optimised conditions for sample matrix handling

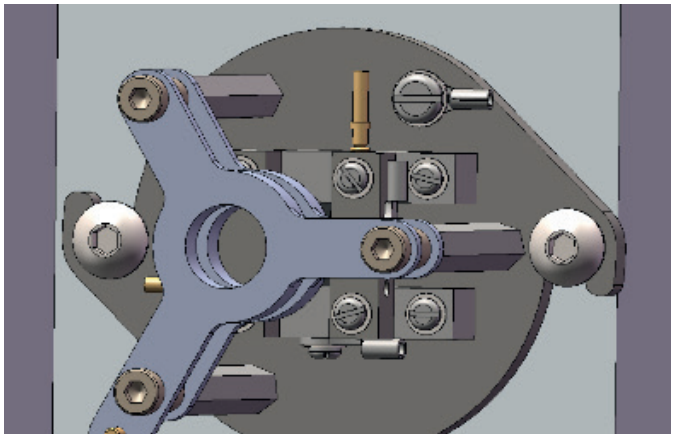
Parameter	High Matrix Kit	Standard Attom ES
Torch injector	2.5 mm ID	1.5 mm ID
Nebuliser uptake rate	0.2 mL/min	0.2 mL/min
Sample uptake method	Pumped	Free uptake aspiration
Nebuliser gas pressure	9-11 psi	28-35 psi
Additional argon gas flow	1.1-1.3 lpm	None
RF power	1500 watts	1300 watts
Extraction voltage	2200-2500 V	3000-3500 V
Typical 115In sensitivity	60k to 100k cps/ppb	1200K to 1800K cps/ppb
Typical CeO/Ce	0.2-0.3%	1.5-2%
Short term stability (10 minutes)	<1%	<1%
Long term stability (60 minutes)	<2%	<2%

A solution of 10 g/L of sodium chloride was prepared in 1% nitric acid which was then spiked with a multi-element stock to 10 µg/L of elements across the mass range from lithium to uranium. This solution was analysed without any further dilution in an automated sequence using an autosampler. With uptake, acquisition (ten cycles of 14 masses from Li to U) and washout for each sample took 9 minutes and 20 seconds and a check solution of 10 µg/L of tune elements in 1% nitric acid was measured after every 12 samples of high matrix. The complete analysis was repeated multiple times over 3 days without any maintenance of the interface, torch or sample introduction system. The data below is shown for a 14 hour run where the sequence of 13 samples was analysed 7 times.

For faster analyses, the use of a flow injection system such as ESI FAST or Cetac $ASX_{express}$ would dramatically reduce the sample uptake and wash times and reduce the overall sample timing to <5minutes using the acquisition parameters described above. Changing the sample analysis to a more common 3 cycle replicate would reduce the timing further such that each sample would be analysed in <3minutes.

Results

The CeO/Ce ratio was monitored throughout the run of samples and is reported below for the check solution run after every 12 high matrix samples. The error bars show the internal reproducibility for the 10 measurement cycles and the consistent measurement of the oxide level through the 14 hours shows how the plasma conditions and therefore gas flows remained constant



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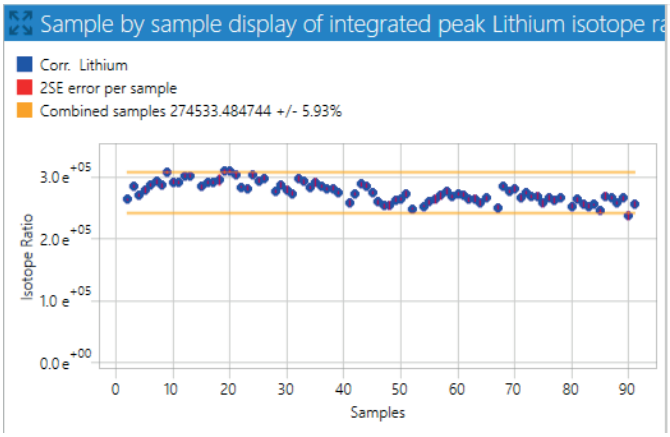
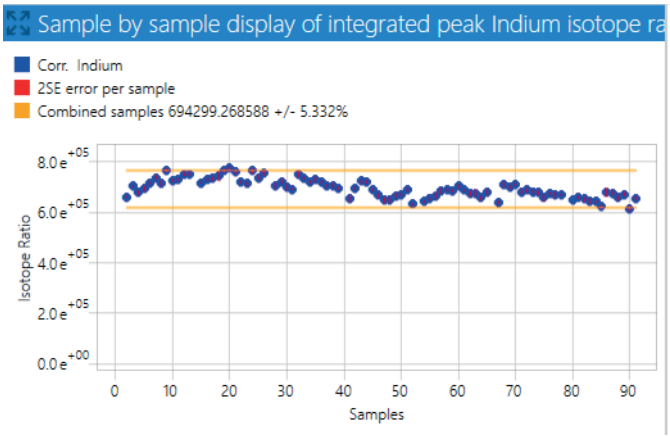
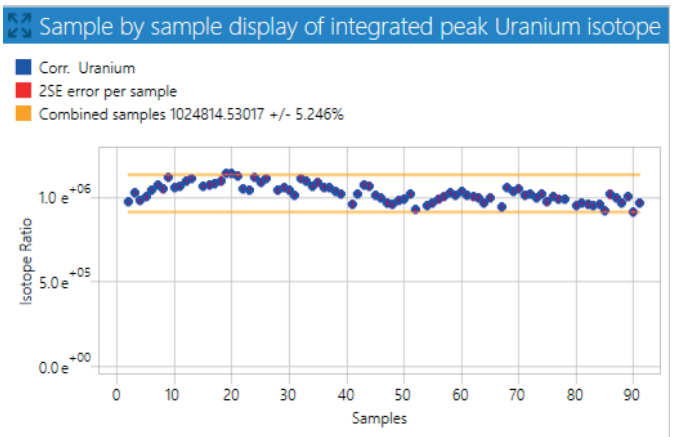
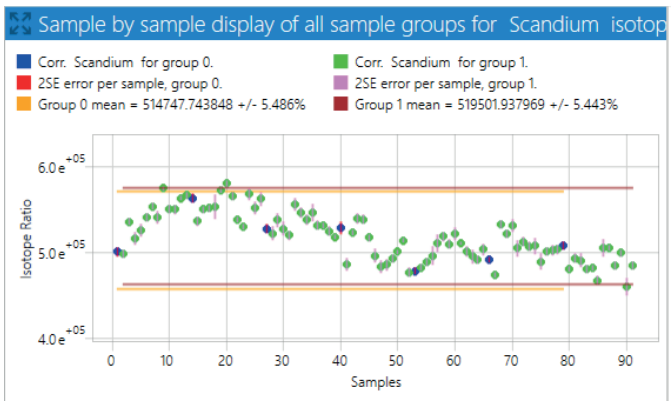
The signal measured for Li, In and U over 14 hours for the 10 ppb spike in undiluted 1% NaCl is shown with calculated RSDs of 5-6% over the whole batch. No systematic drift is seen indicating that the cones were not becoming blocked and the tuning was not affected by deposition of material on lenses.



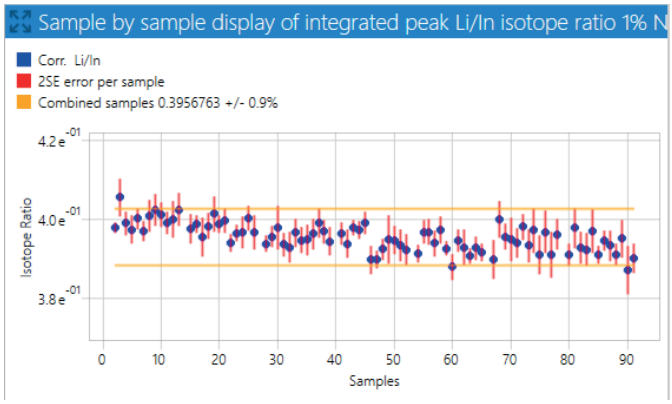


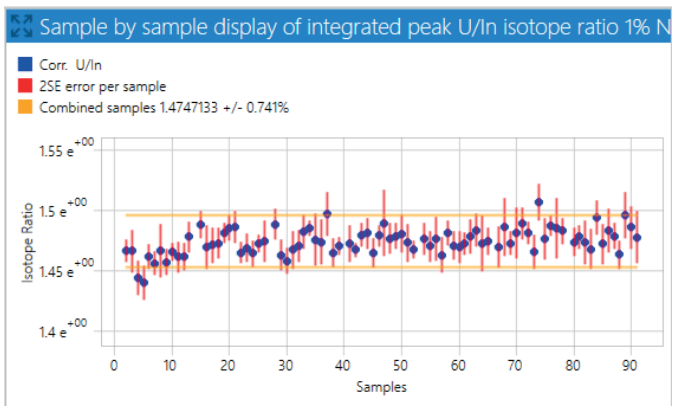


The variation seen was not due to ionisation changes in the plasma caused by the matrix as indicated by a 10 ppb standard in 1% HNO_3 run every 12 samples showing no difference relative to the 1% NaCl samples. In the chart below for scandium in the samples across the batch, the 1% HNO_3 standards are plotted as Group 0 and the 1% NaCl samples as Group 1. No difference in overall signal or variability was seen over the 14 hours.



The pattern of variation in signal across the batch was matched for all isotopes making it feasible to correct the data very easily with a single internal standard. The ratios of Li/In and U/In were plotted for the 14 hours and showed very little drift over the batch and RSDs of <1%.





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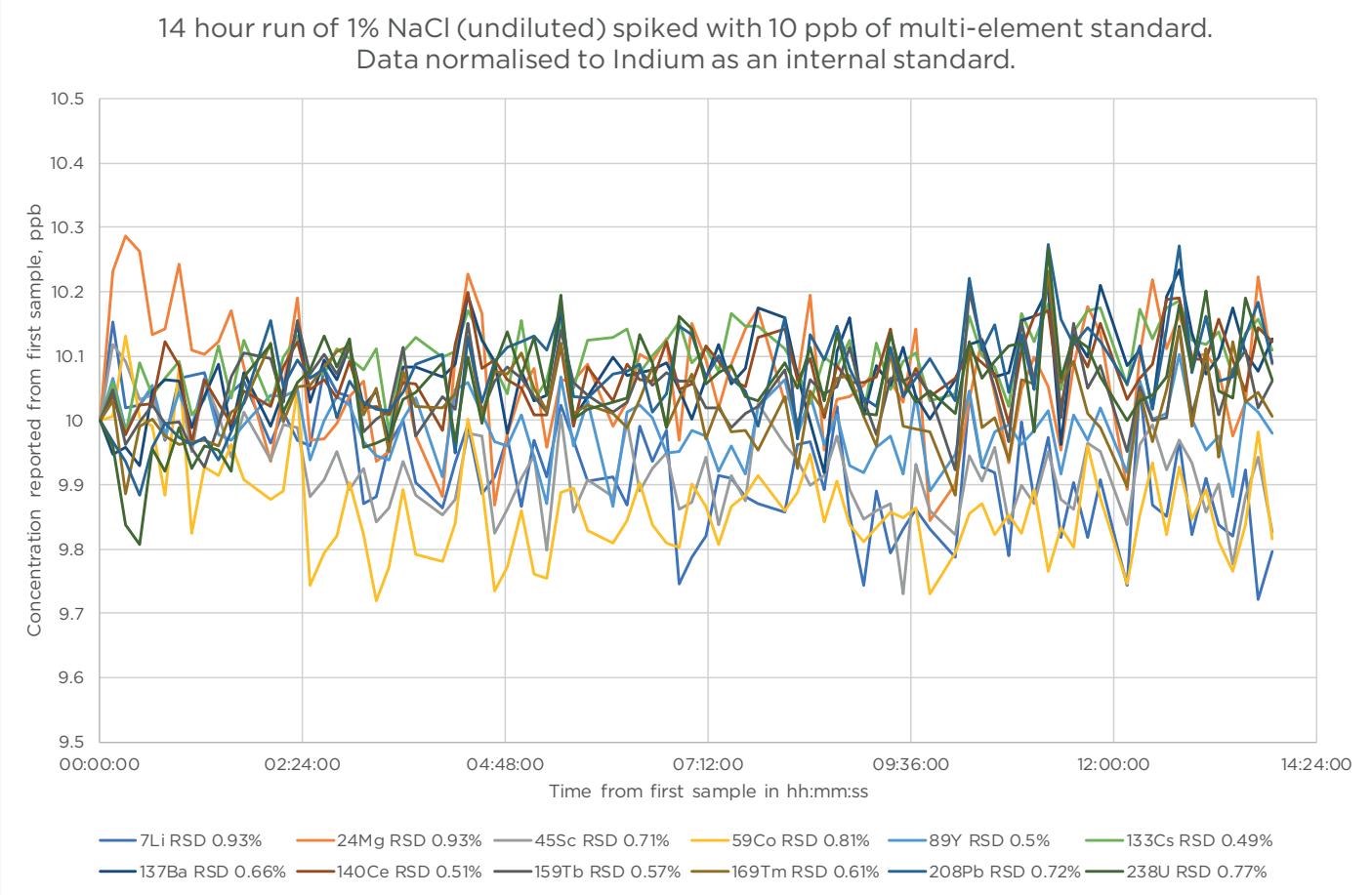
When the calibrated concentrations were reported for the 14 hours using indium as the internal standard, all the measured isotopes showed no significant drift and RSDs were 0.49-0.93%.



Discussion

The High Matrix Kit extends the level of dissolved salts that can be analysed with Nu Attom before the quality of the data is impaired. In this work the solutions measured were 5 times more concentrated than would normally be recommended for traditional ICP-MS. This could be extended further by adding the internal standard in-line using the peristaltic pump and thus effecting a further sample dilution as described in the introduction. The combination of in-line dilution and a flow injection sample introduction system would allow the analysis of samples with 5-10% dissolved solids taking only a few minutes per sample depending on the number of analytes to be measured.