GLASS EXPANSION
Quality By Design

APPLICATION SPOTLIGHT

Applications of a Temperature Controlled Spray Chamber

Jerry Dulude, Vesna Dolic & Ron Stux, Glass Expansion.

Article 010407

INTRODUCTION

We have known for many years that the temperature of a sample introduction system has a profound effect on the performance of an inductively coupled optical emission spectrometer (ICP-OES) and an inductively coupled plasma mass spectrometer (ICP-MS). We use cooled spray chambers to reduce the volatility of certain solvents so that the plasma is sustained. We know that heating a spray chamber results in higher sample transport. We know that controlling the temperature of a laboratory can be critical to long-term stability. Yet only a small percentage of the instruments in the field either monitor or control the temperature of the sample introduction system.

The IsoMist™ Programmable Temperature Spray Chamber (see Figure 1) is a convenient and universal device for both controlling and monitoring spray chamber temperature. Its characteristics are listed below:

- It uses a solid-state Peltier device to control temperature in the range of -10 to +60C in 1 degree increments.
- It incorporates a baffled Twister cyclonic spray chamber which is encapsulated in a conductive resin for intimate contact with the Peltier heat transfer block (see Figure 2). This enables it to go from room temperature to -5C in less than 15 minutes.
- Configurations are customized for each make and model of ICP-OES or ICP-MS system.
- The IsoMist is controlled through a standalone software application with a single interface screen through which spray chamber temperature can be set and monitored for up to 24 hours in a down-loadable file.
- Communication to the IsoMist is performed either by a standard USB cable or through wireless BlueTooth® technology. Once programmed, a PC connection is not required.

Figure 1. IsoMist Programmable Temperature Spray Chamber with Perkin Elmer adaptor.

Figure 2. Twister Spray Chamber encapsulated with conductive resin.

Because of its unique features, the IsoMist can be used to facilitate a number of applications as described below.

DIRECT ANALYSIS OF VOLATILE SOLVENTS

Volatile organic solvents can be troublesome due to the high transport efficiency to the plasma which creates excessive load and typically results in plasma instability and, in the worse case, cessation. One of the most difficult commonly analyzed solvents is naphtha. The petrochemical industry is interested in the metal content of naphtha for many reasons. These metals can interfere with the "cracking" process during the refining of oils. They can also cause serious degradation of the expensive catalysts used in the process. Furthermore, there are environmental concerns related to the release of metals during combustion. And lastly, the specific metal or metals found and their relative concentrations are informative markers in the determination of both the origin and migration of oil reserves.

Because of the high volatility of naphtha, it is usually diluted a factor of 10 with a more "friendly" solvent such as kerosene or Xylene. However, analysts would like to reach lower detection limits than this dilution will allow. The IsoMist run at -10C allows the direct analysis of naphtha without dilution.

Instrument Conditions

This work was performed on a Perkin-Elmer Optima 2100DV using the axial mode and the conditions listed in Table I (page 2). The IsoMist mounts inside the sample compartment of the ICP as shown in Figure 3 (page 2).

Several of the instrument parameters require some explanation. The nebulizer gas flow was significantly lower

than that commonly used for this nebulizer in order to decrease sample transport. The injector used had a small 1mm bore for similar reasons. The IsoMist temperature of -10C was required to achieve stability. A temperature of -5C was insufficient. The sample uptake rate was critical and higher rates resulted in instability.

Forward Power	1500Watts
Coolant Flow	20L/min
Auxiliary Flow	1.8L/min
Nebulizer Gas Flow	0.35L/min
Injector	1mm capillary bore
IsoMist Temperature	-10C
Nebulizer	SeaSpray glass concentric
Sample Uptake Rate	0.3mL/min

Table I. ICP-OES parameters for the analysis of naphtha.

Figure 3. IsoMist mounted on the Optima 2100DV.

Sample Preparation

Blanks and standards were made from 100% kerosene and S-21 Conostan organometallic standards. Samples were 100% naphtha. All blanks, standards, and samples were spiked with 0.5ppm cobalt as an internal standard in the form of an organometallic (also Conostan).

Results

To measure the reproducibility of the technique, a naphtha sample was twice analyzed for 11 elements 90 minutes apart. The results are shown in Figure 4. With the exception of phosphorus, reproducibility was quite acceptable. Phosphorus demonstrated severe instability in naphtha.

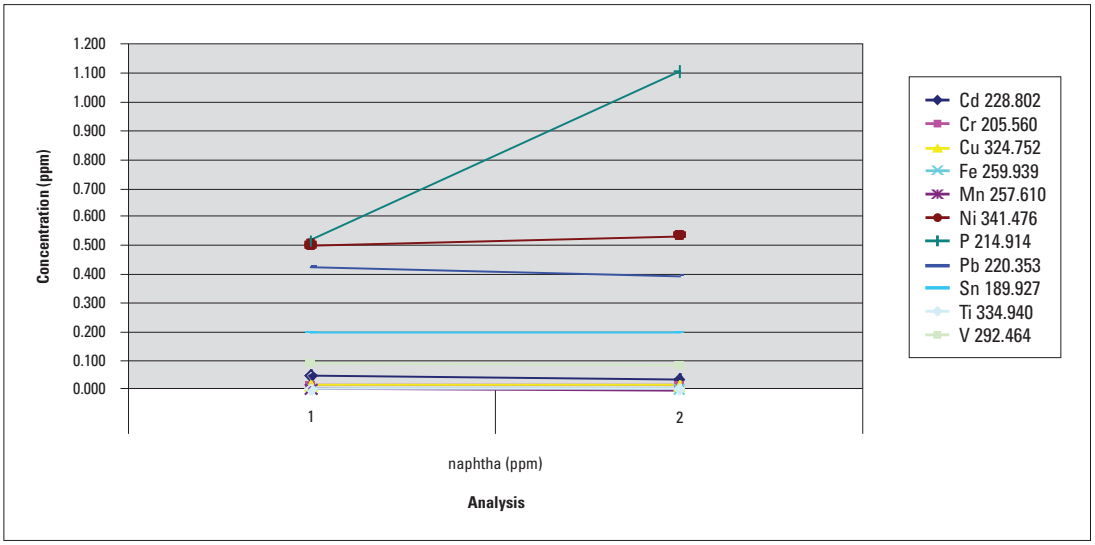
The sample was spiked at a level of 0.1ppm for all metals monitored and the results are shown in Figure 5 (page 3).

Figure 5 shows good recoveries for all elements except P, Ni, and Pb. Phosphorus was discussed above. Nickel and lead show poor recoveries indicating that the response in naphtha is very different from the response in kerosene, so much so that internal standardization is inadequate. Although further investigation is under way, it may be that the forms of nickel and lead used are rendered more volatile by the naphtha matrix resulting in premature losses of the metals.

ANALYSIS OF LIMITED SAMPLE VOLUMES

Sample size can be quite small for many ICP applications. Clinical and pharmaceutical laboratories are often faced with the daunting task of achieving trace measurements of metals in small samples such as neonatal blood samples. Forensic labs must sometimes deal with micro samples which can be traced through their metal content. Another application where micro sampling is desirable is in the

Figure 4. Reproducibility of naphtha results taken 90 minutes apart.



analysis of radioactive samples. Here the goal is to minimize or eliminate waste due to the expense of disposal. Typical ICP methods use sample uptake rates of 0.5 to 2ml/min., which is unsatisfactory for micro samples. Therefore, micronebulization is recommended. However, sensitivity and hence limit of detection is often unavoidably sacrificed with this technique. Techniques which have been used to regain sensitivity are high efficiency nebulizers (HEN) and direct injection nebulizers (DIN) or a combination of the two, direct injection high efficiency nebulizers (DIHEN). Drawbacks of these approaches are the requirement of high gas pressure, increased likelihood of clogging, and excessive micro droplet velocity all of which limit the utility of the approach.

We used a MicroMist nebulizer configured to run at an uptake rate of 20ul/min. and compared the results taken at different temperatures using the IsoMist. All instrument conditions and gas flows and pressures were standard. Figure 6 compares the relative sensitivity at 3 different temperatures for 17 different analytical wavelengths. On average, sensitivity is enhanced to a factor of 2 to 2.5 by going from 21C to 40C and a factor of 3 to 3.5 at 60C.

We also evaluated the effect of temperature on detection limit using the same conditions as above and the results are shown in Figure 7 (page 4). In this case the normalized value is the detection limit obtained at 2 ml/min uptake at 21C. Plotted against this are the results obtained at 20ul/min uptake at both 21C and 60C. The results at 21C represent the type of degradation in detection limit expected using micronebulization and are a factor of 5 to 10 poorer. The results at 60C demonstrate a degradation of on average only a factor of 2. To put this in perspective, we used an uptake rate of 1% of the normal uptake rate yet only sacrificed a factor of two in performance.

Figure 5. Recovery of spiked metals in naphtha.

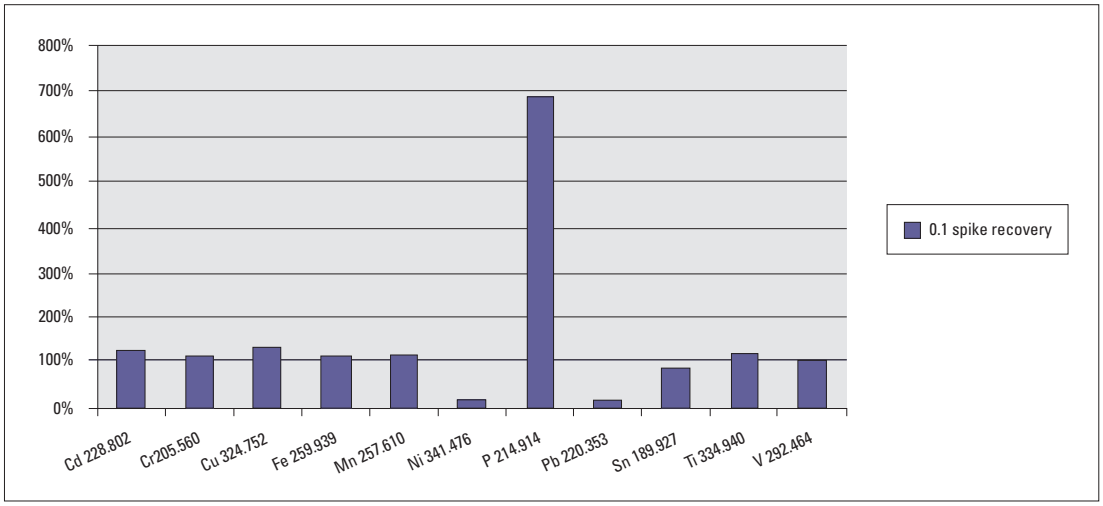
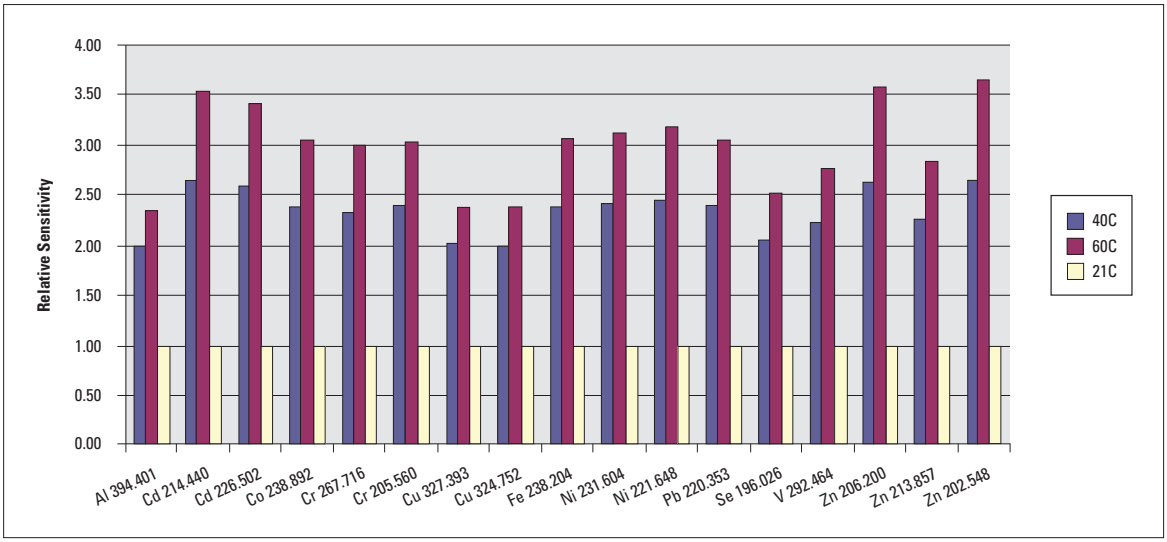


Figure 6. Sensitivity comparison of 20ul uptake rate at different temperatures.



OXIDE REDUCTION IN ICP-MS

The formation of metal oxides in the plasma can result in isobaric interferences on a number of analyte ions in ICP-MS (see Table II).

Element / Isotope	Interference
$^{56}Fe^{+}$	$^{40}Ar^{16}O^{+}$
$^{51}V^{+}$	$^{35}Cl^{16}O^{+}$
$^{44}Ca^{+}$	$^{14}N^{14}N^{16}O^{+}$
$^{48}Ti^{+}$	$^{32}S^{16}O^{+}$
$^{52}Cr^{+}$	$^{34}S^{18}O^{+}$
$^{64}Zn^{+}$	$^{32}S^{16}O^{16}O^{+}$
$^{64}Zn^{+}$	$^{48}Ca^{16}O^{+}$

Table II. Isobaric oxide interferences in ICP-MS[1].

The CeO/Ce pair was selected to study the effect of temperature on oxide formation. A Perkin Elmer Sciex Elan 6000 ICP-MS was used with a Glass Expansion Conikal nebulizer run at 1.1L/min of argon flow and an uptake rate of 0.5ml/min. Power was set at 1400Watts. The spray chamber was a baffled cyclonic style. A 10ppb Cerium standard was used for testing. Results are shown in Figure 8.

As shown, the ratio of cerium oxide to cerium is decreased by a factor of two at 0C, enough to significantly reduce the interferences for many analytes.

STABILITY ENHANCEMENT

The long-term stability of an ICP spectrometer is paramount in achieving financial success within a service laboratory. Regulatory agencies require laboratories to run frequent calibration verifications in order to report payable sample results. The temperature of the sample

Figure 7. Detection limit comparison at different temperatures.

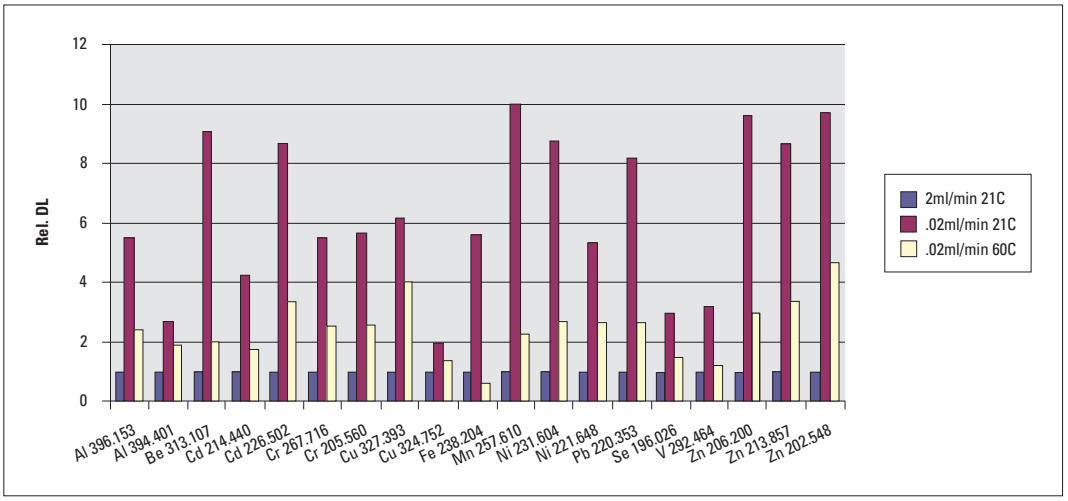
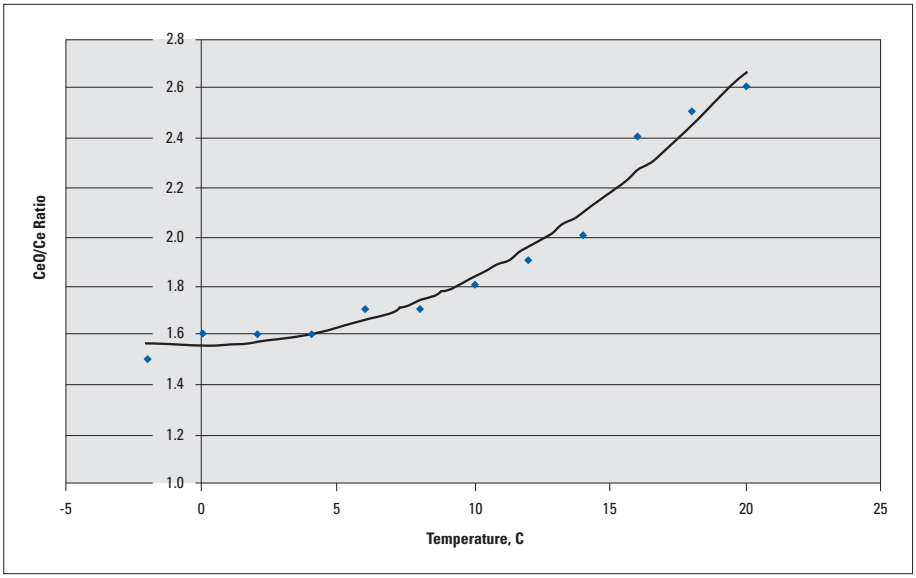


Figure 8. Effect of spray chamber temperature on oxide ratio[2].



introduction system is only one factor resulting in sensitivity drift. Others include detector contortions and changes in the nebulizer, spray chamber, torch, and RF coil. However, temperature is probably the main contributor to drift especially with the solid state detectors used by most manufacturers today. Many ICP-MS instruments and the vast majority of ICP-OES instruments rely soley on stable room environment to control the temperature of the sample introduction system. Analysts have learned through experience not to install an ICP near a heating or cooling vent. The IsoMist can be operated at any temperature from -10 to 60C and therefore can be used to simply maintain a stable temperature within the sample introduction system. Figure 9 shows the drift in sensitivity for a range of analytes over a 4 and a half hour period without the IsoMist, while Figure 10 shows the stability over a 6 hour period using the IsoMist to control temperature at 25C. Without the IsoMist, results drift over a range of 8% while a drift of only 3% results over a 6 hour period when the IsoMist is incorporated.

SUMMARY

In application after application, the IsoMist Programmable Temperature Spray Chamber facilitates successful analysis. Applications utilize the full range of temperature to achieve stable, sensitive results with fewer interferences.

REFERENCES

1. Robert Thomas, **Practical Guide to ICP-MS**, Marcel-Dekker, NY, 2004.
2. Data courtesy of David Jones, ALS Chemex, Brisbane, Australia, 2006.

INTERNATIONAL
Glass Expansion
15 Batman Street
West Melbourne VIC 3003
Australia
Telephone: +61 3 9320 1111
Facsimile: +61 3 9320 1112
Email: enquiries@geicp.com
Web: www.geicp.com

AMERICAS
Glass Expansion
4 Barlows Landing Road
Unit #2
Pocasset, MA 02559
USA
Telephone: 508 563 1800
Facsimile: 508 563 1802
Email: geusa@geicp.com

Figure 9. Long-term stability of 16 analytes by ICP-OES without the IsoMist.

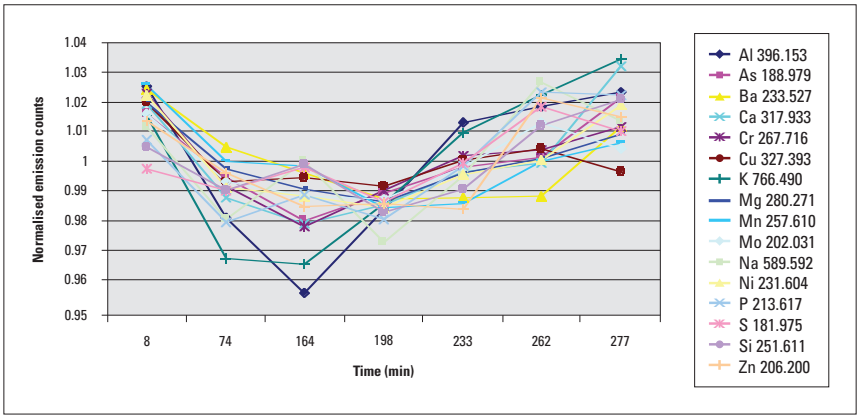


Figure 10. Long-term stability of 20 analyte wavelengths with the IsoMist at 25C.