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GLASS EXPANSION NEWSLETTER

Quality By Design

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CONTENTS

APPLICATION SPOTLIGHT

Spray Chamber Temperature: A Critical Parameter in ICP Experiments

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The following is based on paper TH13 presented at the 2008 Winter Conference on Plasma Spectrochemistry, in Temecula, CA, January 6-12, 2008. The original PowerPoint presentation is accessible at our web site.

INTRODUCTION

If you examine the literature on ICP-OES over the past 20 years, you will find that the temperature of the spray chamber is rarely included as a documented parameter. In this paper, we will show that spray chamber temperature is as critical a parameter as nebulizer gas flow or plasma power. We will characterize its effects on intensity, detection limits, plasma robustness, and matrix suppression.

EXPERIMENTAL

We performed all experiments on a PerkinElmer 2100DV ICP-OES. Parameters are listed below.

- Power: 1450 watts
- Coolant gas: 15LPM
- Aux. gas: 0.2LPM
- Neb. gas: 0.7LPM
- SeaSpray concentric glass nebulizer
- IsoMist Programmable Temperature Spray Chamber with Twister Baffled Cyclonic

Figure 1. IsoMist and PE Optima 2100DV

The IsoMist is a compact self-contained accessory which possesses the following characteristics:

- Covers the range of -10 to +60ºC
- Maintains temperature to within 0.1ºC
- No external plumbing
- Customized to fit each model of ICP-OES and ICP-MS

RESULTS AND DISCUSSION

Low Uptake Rate

This paper begins where a previous paper ended. At the 2007 Pittcon Conference in Chicago (1) we presented data demonstrating the benefits of heating the spray chamber to 60ºC when a small (20ul/min) uptake was employed. Compared to a standard 2ml/min uptake, detection limits were improved from a factor of 8 degradation to a factor of only 2 degradation when heated at 60ºC. The improvement in detection limit was commensurate with the increase in intensity with increasing temperature (Figure 2).

Initially, we attributed the increase in intensity to the greater transport efficiency realized at elevated temperatures. However, after examining the data, we realized that there must be another mechanism at work as well. Figure 3 shows the transport efficiency with respect to uptake rate at room temperature.

It is clear from this data that the 20ul/min uptake rate is already at 60% transport efficiency at room temperature;

the highest theoretical increase is therefore 66% (40/60). In Figure 2 we can see that a 200% increase in intensity is realized at 60ºC. Therefore the majority of the intensity increase cannot be attributed to transport efficiency.

A search of the literature yielded two theories to explain the discrepancy. Mermet and Todoli (2) stated that, for a robust plasma, the addition of water to the plasma will create an increase in hydrogen ions which would increase the thermal conductivity of the plasma locally. This would be expected to result in a higher energy plasma which would explain the enhanced emission intensity found here. To test this theory we conducted an experiment using our Capricorn argon humidifier. The Capricorn has a bypass valve which allows the analyst to shut off or activate humidification by flipping a switch; no need to shut down the plasma or change any parameters (Figure 4).

Figure 4. Capricorn argon humidifier with bypass

We analyzed a standard at 100ul/min without humidification and then flipped the switch and reran the standard with

Figure 2. Effect of spray chamber temperature on intensity for 20ul/min uptake

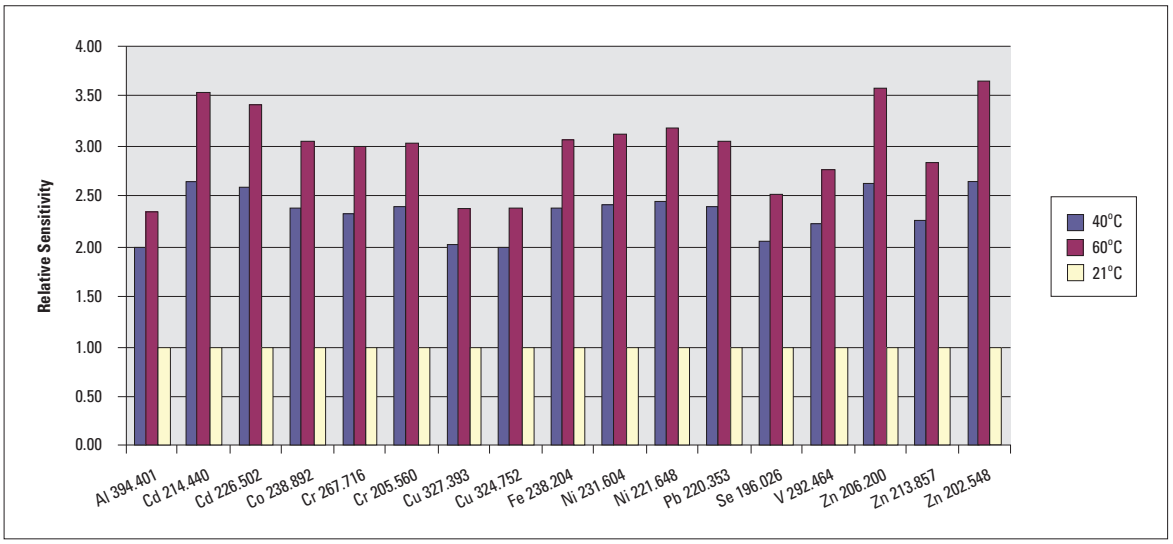
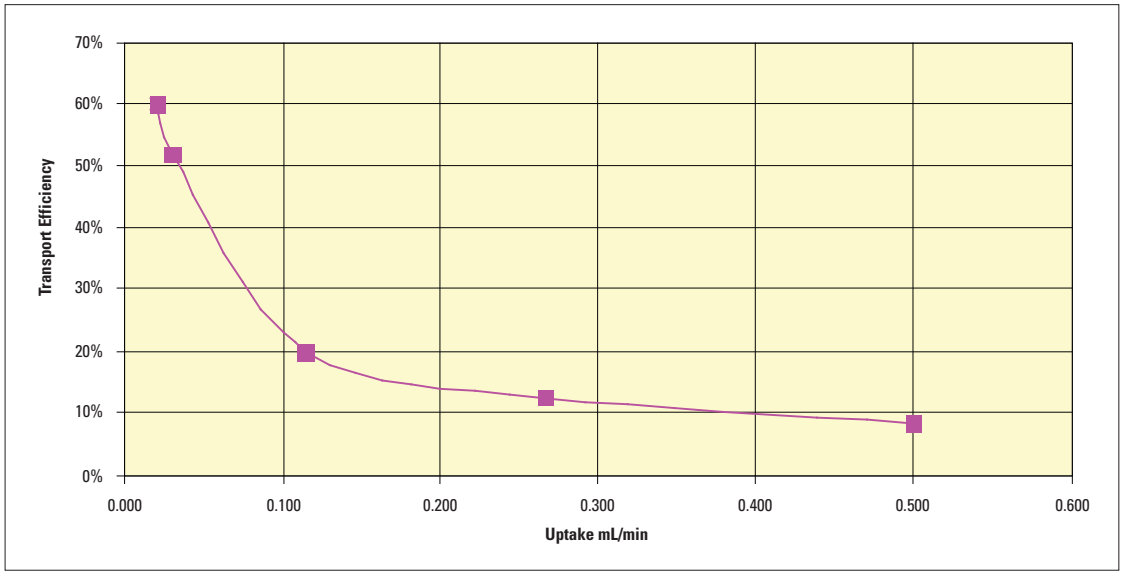


Figure 3. Effect of sample uptake rate on transport efficiency at room temperature



humidification. An elevated intensity when humidification was employed would support the theory. The results are shown in Figure 5.

Clearly, humidification did not increase intensity. On the contrary, humidification caused a decrease in intensity of about 10%. Therefore, under the conditions used here, the added ion density theory does not appear to explain the increased intensity found.

A second theory espoused by Longerich and Diegor (3) and Browner and Zhu (4) suggests that the size of the droplets entering the torch is inversely proportional to spray chamber temperature. It is reasonable to expect that a smaller droplet would lead to faster desolvation, atomization, and excitation (as well as ionization). Although not yet proven experimentally, this is the theory we believe to be responsible in large part for the intensity enhancement observed here.

Standard Uptake Rate

Although analysis with micro flow nebulizers has its place, particularly in clinical and forensic laboratories, the majority of applications employ uptake rates in the 1 to 2 ml/min range. How does spray chamber temperature affect performance under these conditions? A major difference between the two cases is that, for low uptakes, the vapor created is not saturated while a vapor created from larger uptake rates would be. Figure 6 shows the effect of spray chamber temperature on average intensity for a 1ml/min uptake rate. A few points are observed; first a steady increase in intensity is found with increasing temperature; second, a change in slope is noticed at 25°C such that intensity increases faster above this inflection point. It should be noted that the maximum temperature employed (35°C) was determined by the point at which the plasma became unstable due to excessive sample loading.

In the low uptake rate experiment, we found the increase

Figure 5. Effect of argon humidification on signal intensity

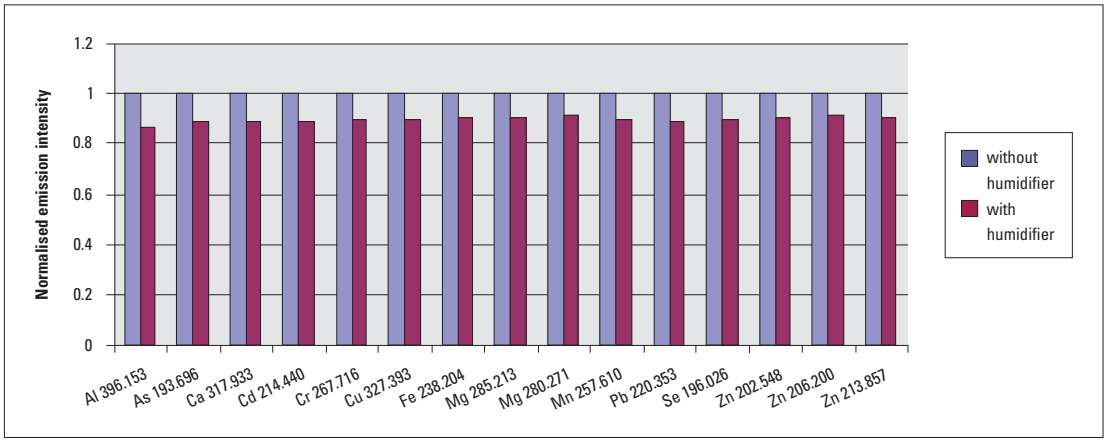
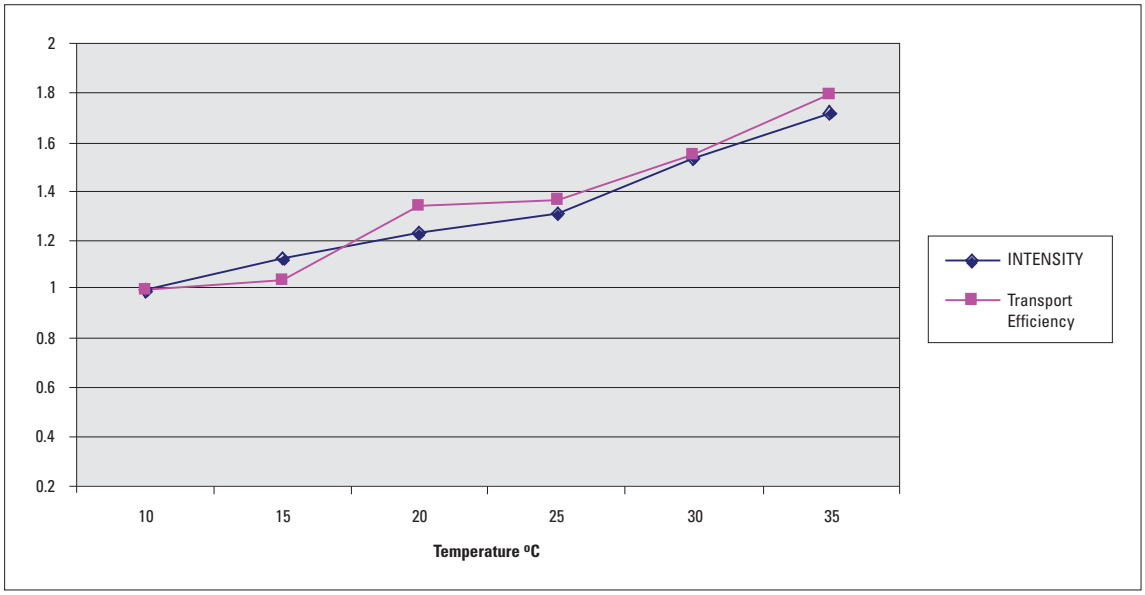


Figure 6. Normalised graph of intensity and transport efficency vs. spray chamber temperature



in intensity to far outpace the increase in sample transport. We examined that relationship for the 1ml/min data as well. A plot of transport efficiency vs. temperature is superimposed on the intensity graph in Figure 6. Both plots are normalized to unity. The graphs track each other within experimental error. Therefore, in the case of the larger uptake rate, the increase in transport efficiency with temperature adequately explains the increase in intensity. It is likely that the difference in behavior between the low and high uptake rates is due to the degree of saturation of the vapor.

Since more solution is reaching the plasma at higher temperatures, it would be interesting to investigate how this affects plasma robustness and analyte suppression. Intuitively, we might reason that the greater sample load would result in a less robust and less stable plasma. We might also expect that the presence of dissolved salts would create greater analyte suppression at the higher sample loads, i.e. temperature. We therefore investigated both of these phenomena. Plasma robustness was measured as the ratio of intensity of a Mg ion line to a Mg atom line. This experiment was conducted both in a clean standard and in an interference sample consisting of added sodium (1000ppm), potassium (1000ppm) and calcium (500ppm). Figure 7 shows the results.

Interestingly, for both solutions the plasma robustness increases with increasing temperature. A negative offset is seen for the salt solution but this, we believe, is due more to the easily ionizable element (EIE) effects of the added salts (commonly reported for axially viewed plasmas) rather than a degradation of robustness. We believe that the presence of smaller droplets created by the warmer spray chamber outweighs the added sample loading and results in a more robust plasma.

Figure 7. Effect of spray chamber temperature on plasma robustness for a standard and a salt solution

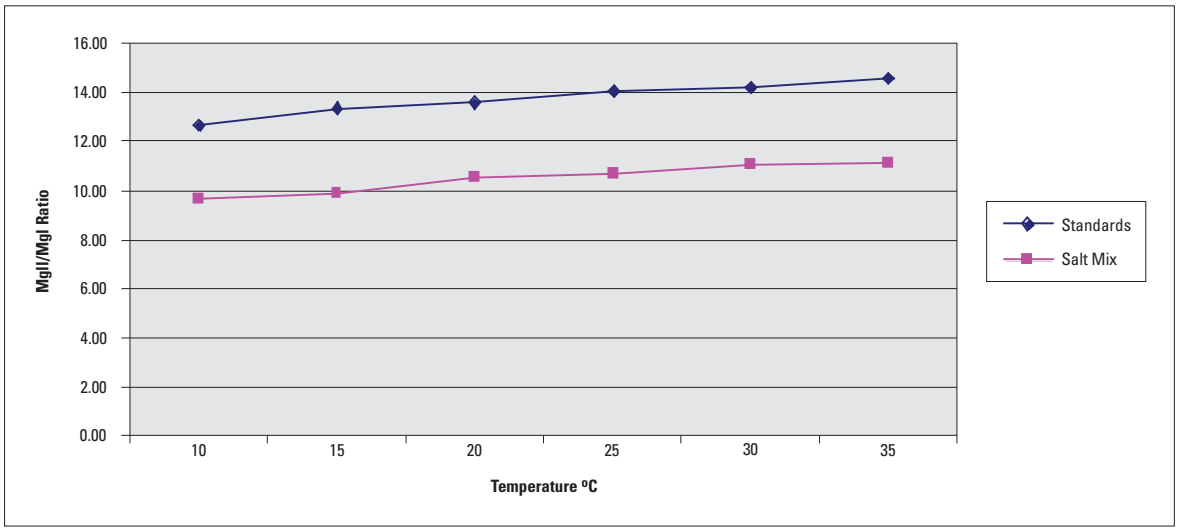
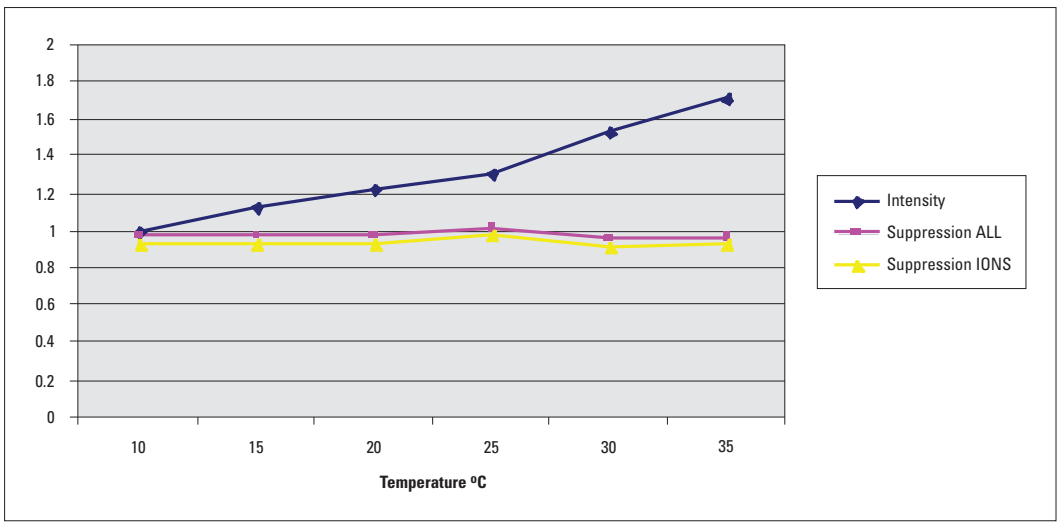


Figure 8. Average suppression of a salt solution vs. temperature (all lines and ion lines only) overlaid on normalised plot of intensity vs. temperature



It is reasonable to assume, therefore, that the degree of suppression caused by added salt may indeed be no greater at the elevated temperatures. Figure 8 overlays the intensity vs. temperature graph on a plot of analyte suppression (due to the interference sample described above) vs. spray chamber temperature using the average of the 18 lines selected. Indeed, we can see that the degree of suppression is both small and constant across the temperature range while the intensity increases by 70%. Also shown in this graph is the average suppression of only the ion lines which are typically more sensitive to matrix effects. The greater suppression of the ion lines is supported by this data but they are equally as insensitive to spray chamber temperature as is the average suppression of all lines.

The data in Figure 8 is significant in that, under the conditions employed, intensity can be increased without any negative effects from the sample matrix simply by increasing the temperature of the spray chamber.

CONCLUSIONS

Experimental data has shown that spray chamber temperature has a profound effect on the performance of an ICP spectrometer. At low uptake rates, elevated temperature increases line intensities via two mechanisms; increased sample transport and, more significantly, increased excitations due to a smaller mean droplet size. At larger standard uptake rates, only the first mechanism appears significant. Plasma robustness also increases with increasing temperature under the conditions employed here, although the reason for this is not yet clear. Suppression effects, however, are relatively insensitive to spray chamber temperature. It must be noted that the specific parameters and conditions under which the instrument is operated may play an important role on these results.

(1) Jerry Dulude, Ron Stux, and Vesna Dolic, Pittcon 2007 in Chicago, #1370, "A Programmable Universal Temperature Controlled Spray Chamber for ICP-OES and ICP-MS"
(2) Todoli and Mermet, JAAS, 1998, 13, p.730
(3) Longerich and Diegor, JAAS, 2001, 16, p.1196-1201.
(4) Browner and Zhu, JAAS, 1988, 3, p.781-789.

NEW PRODUCTS

D-Torch for PerkinElmer Optima 4300V/5300V

The D-Torch is a new demountable torch design that provides the benefits of a fully demountable torch at a significantly lower cost. Interchangeable outer tubes made of quartz or ceramic are available. The ceramic outer tube is of particular benefit with oils analysis, where quartz outer tubes often suffer from short lifetime. The ceramic outer tube has a much longer lifetime, greatly reducing interruptions and downtime due to torch failure.

The D-Torch is now available for the PerkinElmer Optima 4300V/5300V. We will soon be releasing the D-Torch for other ICP models. Please contact enquiries@geicp.com for information on the availability of the D-Torch for your ICP.

Ceramic D-Torch for PerkinElmer Optima 4300V/5300V

Fluka RBS-25 Cleaning Solution

Tests over many years have shown that Fluka RBS-25 is the most effective cleaning agent for nebulizers and spray chambers. It is more effective than other detergents and is even more effective than acids. It is manufactured by Sigma-Aldrich and is available through Sigma-Aldrich sales offices or agents. However, some of our customers have reported difficulty in obtaining it. We have therefore decided to offer it for sale in 1L bottles. Please contact enquiries@geicp.com or your local Glass Expansion distributor for details.

INSTRUMENT NEWS

From PerkinElmer:

LOCALIZED LANGUAGE ICP WINLAB32™ SOFTWARE

PerkinElmer has announced the availability of its WinLab32™ software with a complete Japanese and Simplified Chinese user interface to offer convenience and support for PerkinElmer's user base in China and Japan. The software is compatible with the Optima™ line of Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) systems.

WinLab32 requires the Windows XP® Service Pack 2 to give customers all the tools needed to analyze samples, report and archive data, and ensure regulatory compliance.

The new releases of WinLab32 provide support for:

• Ethernet connectivity on the Optima™ 5x00 series ICP
• Integration of the new PerkinElmer S10 Autosampler
• The latest generation of computer hardware
• Improved software usability

For more information, please visit:
http://las.perkinelmer.com/Catalog/default.htm?CategoryID=ICP+Optical+Emission+%5bICP-OES%5d

From SPECTRO:

NEW APPLICATION REPORTS ON RELIABLE BIOFUELS TESTING

Biofuels are quickly becoming an important ecological alternative to gasoline and diesel. Elemental analysis with XRF and ICP-OES is well suited to the monitoring of bio-fuel components and biofuel blend quality and contents. Drawing on years of practical experience analyzing conventional fuels, SPECTRO offers a comprehensive information package for analyzing bio-fuels available on the internet at www.spectro.com. New application reports document continuous monitoring of the quality of bio-fuels with four SPECTRO instruments, while remaining in compliance with the relevant fuel regulations and specifications. Visitors to the site also will find a new online brochure with information dealing with current fuel legislation.

"Within the framework of climate protection, biofuels are receiving a great deal of attention as well as political backing. In many industrial nations, laws facilitating the use of alternatives to gasoline and diesel are under consideration or already in place," explains Dirk Wissmann, Product Manager for X-ray fluorescence analysis at SPECTRO. "The European Union is leading the way: Their 2003/30/CE directive compels fuel manufacturers to increase the share of bio-fuels on the fuel market from today's 2 percent to 5.75 percent by 2010."

The SPECTRO iQ II and SPECTRO PHOENIX II XRF instruments are well suited to measurement of sulfur content. The SPECTRO iQ II also can be used to screen for phosphorous, potassium, calcium, copper and lead. The SPECTRO ARCOS and SPECTRO GENESIS ICP-OES instruments are capable of monitoring relevant limiting values for all of the above.

From Thermo Fisher:

SPECIATION ANALYSIS CAPABILITIES FOR HIGH RESOLUTION ICP-MS

Thermo Fisher Scientific Inc. announces the addition of a new kit for coupling Gas Chromatography (GC) to the Thermo Scientific high resolution ICP-MS Element 2 and Element XR. Designed to enable scientists to use a high resolution magnetic sector field ICP-MS as a detector for GC, the kit extends traditional ICP-MS capabilities for elemental speciation analysis of volatile compounds. This novel system is the latest offering, further expanding the unique and comprehensive capabilities of the Thermo Scientific Element 2 and Element XR which are manufactured at the company's Mass Spectrometry Center of Excellence, based in Bremen.

Thermo Fisher already offers a GC coupling kit for the Thermo Scientific X Series 2 quadrupole-based ICP-MS and has used the same dual sample introduction for the high resolution ICP-MS. This offers simple instrument set up and internal standardization using simultaneously nebulized solutions in parallel to the GC sample gas stream. This new GC-ICP-MS interface for high-resolution ICP-MS is unique in the market.

The new Thermo Scientific coupling kit enables high resolution ICP-MS to work alongside any GC system, giving customers the ability to detect species using high resolution with their existing GC system. For more information on the Thermo Scientific GC coupling kit for high resolution ICP-MS analysis, please email analyze@thermofisher.com or alternatively visit www.thermo.com/elemental.

From Varian:

A wide selection of Varian, Inc. products will be on display at Pittcon, New Orleans, Louisiana, USA March 1-7, 2008. On display at the Varian, Inc. booth (# 4621), you will find Varian ICP-OES and ICP-MS instrumentation plus consumable items such as nebulizers, spray chambers, torches and accessories. Varian specialists will be on hand to answer your questions and assist you to choose the optimum instrumentation for your ICP needs.

There will also be several different in-booth talks being presented, including one to be presented by Dr. Doug Shrader, Atomic Spectroscopy Market Development Manager for Varian, Inc. titled **"Innovative Atomic Spectroscopy Solutions for your Laboratory"**. This presentation describes a new GF-AAS tube design which improves sensitivities, detection limits and tube lifetime; a new ICP axial sheath gas torch for improved high dissolved solids performance; and Varian's unique Collision Reaction Interface (CRI) ICP-MS for simple, fast, interference-free analysis. Presentation times are 10 am Monday, 12 pm Tuesday and 2 pm Wednesday.

Varian specialists will also be actively involved in the Technical program with the following oral presentations and posters planned for presentation:

Tuesday, March 4 – 9:00 am to 4:30 pm at Exposition Floor – Hall C, Aisles 3000-3400
Poster Title: Analysis of Nutraceutical Supplements and Raw Materials Using Collision Reaction Interface ICP-MS (Abstract # 1210-12P)

Thursday, March 6 – 9:00 am to 2:00 pm at Exposition Floor – Hall C, Aisles 3000-3400
Poster Title: Analysis of Complex Geological Samples: Rapid, Accurate and Precise by Axial ICP-OES (Abstract # 2740-3P)

Thursday, March 6 – 3:25 pm Room 241
Title: Advancing Performance in the Analysis of High-Dissolved-Solids Solutions by ICP-OES through Innovative Design

HINTS FOR THE OPERATOR

Care and Maintenance of ICP-MS Cones

WHEN TO CLEAN

The frequency at which the cones are cleaned depends very much on the application and the workload of the instrument. If the samples are clean and the usage is low, the cones may only need cleaning monthly. But if the instrument is in continuous use and/or the samples contain high levels of dissolved solids or are highly corrosive, the cones may need cleaning daily.

The cones should be cleaned if there are visible deposits near the orifice or if the orifice is blocked or distorted. Deterioration in the performance of the ICP-MS can also indicate that the cones may need cleaning. In particular, watch for increased background signal, memory effects, loss of sensitivity or distorted peak shapes. A change in the instrument vacuum reading can also be an indication of cone problems. If the orifice gets blocked, the vacuum will increase (pressure decrease), although there will usually be a deterioration in performance before this point. If the vacuum decreases (pressure increases), this could indicate that the orifice is worn and has increased in size. If this happens the cone needs to be replaced.

The sampler cone, being exposed to the plasma, will usually need cleaning more often than the skimmer cone. If the performance of the instrument does not recover when the cones are cleaned, then you may need to replace them.

WHAT TO USE

The method of cleaning will also depend on the application. If the samples are relatively clean, a gentle cleaning process will be sufficient. But, if the samples contain high levels of dissolved solids or are highly corrosive, a more aggressive cleaning procedure will be required. A Citranox solution is a gentle and effective cleaning agent and we recommend that it be tried first. If Citranox is not effective, it may be necessary to use a more aggressive cleaning agent such as nitric acid. However, we recommend that nitric acid not be used unless it is necessary. Nitric acid is more corrosive than Citranox and prolonged use will reduce the lifetime of the cones. Note that even Citranox will attack copper cones so the cones should not be exposed to high concentrations of Citranox or exposed for long periods. When cleaning cones which have a screw thread, be particularly careful that the thread is not contacted by nitric acid. Pre-soaking the cones in a detergent such as Fluka RBS-25 prior to cleaning with Citranox or nitric acid will help the cleaning process. Citranox is manufactured by Alcanox Inc. (www.alcanox.com) and Fluka RBS-25 by Sigma-Aldrich. Both are available from most suppliers of laboratory chemicals.

HOW TO CLEAN

WARNING: Always use safety glasses and protective gloves. Be careful when handling the cone – the tip is very easily damaged. Hold the cone by its edge and only use light pressure with your hand when cleaning the tip. Never use tools for cleaning cones.

The cleaning process does not necessarily need to reproduce the original as-new polished appearance. Sample deposits need to be removed, but it is not usually a problem if the cone is discolored. This may actually result in a more stable signal.

There are three common methods of cleaning cones. From the simplest and gentlest to the most thorough and aggressive, these are:

A. Soak in Citranox -
Daily or weekly, depending on application:
1. Soak the cone overnight in a 25% solution of Fluka RBS-25.
2. Rinse with deionized water.
3. Place the cone in a 2% Citranox solution and soak for about 10 minutes.
4. Wipe with a soft cloth or Kimwipe dipped in the Citranox solution.
5. Wash thoroughly with deionized water.
6. Place the cones in deionized water and soak for 2 minutes to remove any residual Citranox.
7. Replace the deionized water and repeat Step 6 at least twice, ie. the cones should be washed at least 3 times, using fresh deionized water each time.
8. Rinse with deionized water and allow to dry or blow-dry with clean argon or nitrogen. Make sure the cones are

completely dry. It may help to heat them in a laboratory oven at about 60°C.

B. Sonicate in Citranox -
Daily or weekly, depending on application:
1. Soak the cone overnight in a 25% solution of Fluka RBS-25.
2. Rinse with deionized water.
3. Be very careful to avoid damaging the cone tip. The cone should not be placed in the ultrasonic bath without being supported or contained. One way to avoid damage is to place the cone in a ziplock plastic bag half filled with a 2% Citranox solution and float the bag in the ultrasonic bath. Ensure that the bag is floating so that the cone is not resting on the bottom or touching the walls of the bath. This also minimizes the volume of Citranox used since the bath can be filled with water.
4. Sonicate for 5 minutes.
5. Wipe with a soft cloth or Kimwipe dipped in the Citranox solution.
6. Wash thoroughly with deionized water.
7. Replace the Citranox with deionized water and sonicate for 2 minutes to remove any residual Citranox.
8. Replace the deionized water and repeat Step 7 at least twice, ie. the cones should be washed in the ultrasonic bath at least 3 times, using fresh deionized water each time.
9. Rinse with deionized water and allow to dry or blow-dry with clean argon or nitrogen. Make sure the cones are completely dry. It may help to heat them in a laboratory oven at about 60°C.

C. Sonicate in nitric acid -
Weekly or monthly, depending on application:
1. Soak the cone overnight in a 25% solution of Fluka RBS-25.
2. Rinse with deionized water.
3. Be very careful to avoid damaging the cone tip. The cone should not be placed in the ultrasonic bath without being supported or contained. One way to avoid damage is to place the cone in a ziplock plastic bag half filled with 5% nitric acid and float the bag in the ultrasonic bath. Ensure that the bag is floating so that the cone is not resting on the bottom or touching the walls of the bath. This also minimizes the volume of nitric acid used since the bath can be filled with water.
4. Sonicate for 5 minutes.
5. Wipe with a soft cloth.
6. Wash thoroughly with deionized water.
7. Replace the nitric acid with deionized water and sonicate for 2 minutes to remove any residual nitric acid.
8. Replace the deionized water and repeat Step 7 at least twice, ie. the cones should be washed in the ultrasonic bath at least 3 times, using fresh deionized water each time.
9. Rinse with deionized water and allow to dry or blow-dry with clean argon or nitrogen. Make sure the cones are completely dry. It may help to heat them in a laboratory oven at about 60°C.

The recommended concentrations of the Citranox and nitric acid, and the wash times, should be used as a guide only. Given the wide range of ICP-MS applications, you may need to experiment a little to find the best cleaning procedure for your application. We recommend that you do not use nitric acid any more than is necessary since it will attack the cone materials. If nitric acid is used excessively, the size of the cone orifice may be increased. If this happens, or if the tip is damaged or deformed, then the cone needs to be replaced.

PLATINUM CONES
The cleaning procedures outlined above can be used for platinum cones as well as nickel cones. Since platinum is more chemically resistant than nickel, platinum cones can usually be used for longer before they need cleaning. Platinum cones consist of a platinum insert in a nickel or copper base, so aggressive cleaning solutions still need to be avoided as they may attack the base. Platinum cones also run hotter, which helps slow deposition. The lifetime of a platinum cone is typically much longer than that of a nickel cone, and can be further extended by refurbishment.

We offer free refurbishment on the platinum cones that we sell for the life of the cone. Note that, if the orifice is worn to the extent that the diameter is outside specification, or if the tip is badly damaged, the cone may not be able to be refurbished. In this case, we will give a credit for the value of the platinum.

Please contact enquiries@geicp.com if you have any questions regarding the care of your ICP-MS cones.

Care of Other Products

For hints on the care and maintenance of other products, please refer to our website as follows:

For nebulizers:
http://www.geicp.com/cgi-bin/site/wrapper.pl?c1=Care_gencareneb

For glass spray chambers:
http://www.geicp.com/cgi-bin/site/wrapper.pl?c1=Care_gencaresprayglass

For PTFE and PFA spray chambers:
http://www.geicp.com/cgi-bin/site/wrapper.pl?c1=Care_gencaresprayptfe

For torches:
http://www.geicp.com/cgi-bin/site/wrapper.pl?c1=Care_gencaretorch

For RF coils:
http://www.geicp.com/cgi-bin/site/wrapper.pl?c1=Products_coils_general_benefits

GLASS EXPANSION NEWS

PITTCON 2008

A wide selection of Glass Expansion products will be on display at Pittcon 2008, New Orleans, USA, March 2 to 7, 2008. The display will include nebulizers, spray chambers, torches, RF coils, ICP-MS cones and accessories (including the new IsoMist Programmable Temperature Spray Chamber). Glass Expansion specialists will be on hand to answer your questions and assist you to choose the optimum components for your ICP. Please visit us at Booth 4913.