GLASS EXPANSION NEWSLETTER
Quality By Design
June 2006

CONTENTS

APPLICATION SPOTLIGHT

Internal Standardization for ICP-OES and ICP-MS

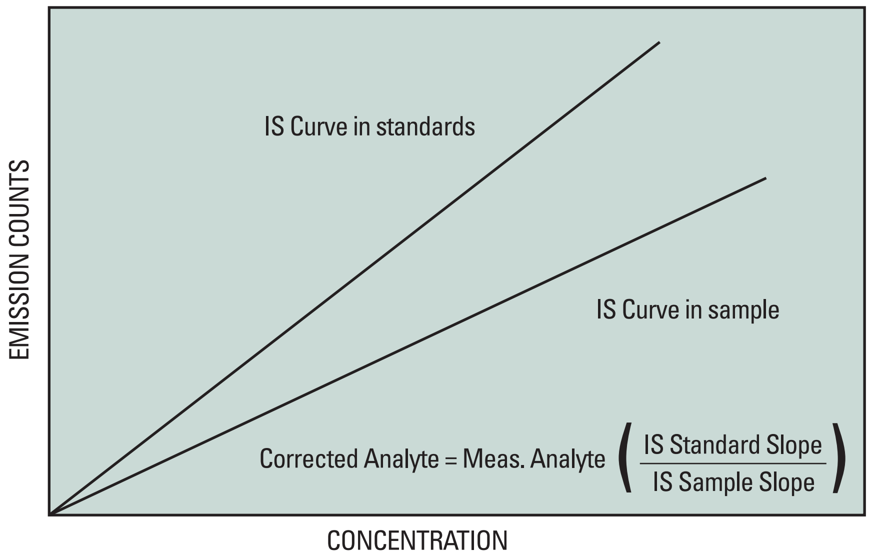
INTRODUCTION

Internal standardization has long been used to effectively compensate for matrix based interferences. It is similar to the method of standard additions (MSA) in that the response of an element in a sample as opposed to the standard is used to calculate concentration. In MSA, one or more additions of the analyte are added to the sample and the in-sample calibration curve is used to calculate concentration. MSA is typically used with atomic absorption spectrometry (AAS) determinations (particularly with a graphite furnace) since the matrix effects differ in severity between elements. For ICP-OES, it is generally assumed that matrix effects are similar for all elements (an assumption that is not rigorously valid, as will be discussed below). For ICP-MS, matrix effects can be reasonably accurately predicted based on the mass/charge of the analyte. Therefore, concentration is corrected based upon the response of an added element (or elements) not otherwise present in the sample (see Figure 1 below). All commercially available ICP spectrometers have the capability of performing this correction automatically.

It should be recognized that internal standardization does not correct for all interferences. For example, it does not correct for background or spectral/mass overlap interferences.

In ICP-OES, matrix interferences stem from several mechanisms as follows:
1. Differences between the viscosity or surface tension of the sample and standards can alter the transport efficiency of the sample introduction system.

Figure 1. Internal Standard Calculation



2. The presence of high concentrations of dissolved solids is quite common and may result in “plasma loading” such that the amount of energy available is decreased. The effects of this tend to be more severe on those “hard” lines that require more energy for efficient excitation. It should also be noted that this type of interference predominantly affects ion lines. Atom lines are more robust (except in the case of the easily ionizable elements discussed below), while the ion lines tend to be suppressed. It is therefore important to link analyte ion lines with internal standard ion lines and similarly for atom lines. Commonly employed internal standard lines for Yttrium and Scandium are ion lines. Experience has shown that atom lines often do not require an internal standard to compensate for plasma loading effects. Indeed, linking an analyte atom line to an internal standard ion line may result in an erroneously high concentration.

3. Easily ionizable element (EIE) effects are more pronounced for axially viewed plasmas where a small slice of the plasma is not easily isolated. Elements such as sodium, potassium, lithium, and cesium exist predominantly as ions in an ICP. However, the only intense emission lines are for atomic species, the population of which is fragile and can be altered by the presence of other easily ionizable elements. Rather than an internal standard, an ionization suppressant consisting of a high concentration of an easily ionizable element that is not of analytical interest can be added to all solutions to serve as a buffering agent. Often, the ionization suppressant is mixed with the internal standard(s) and added simultaneously.

In ICP-MS, interferences are similar with some distinctions. EIE effects are dramatically reduced in comparison to axial ICP-OES since for ICP-MS, the ion populations are of analytical interest and these are not significantly affected by the presence of other easily ionizable elements. However, ICP-MS does suffer from mass related interferences which occur at the sampling interface and thus are not seen in ICP-OES. In essence, the presence of high concentrations of high mass ions has a suppressive effect on elements of lower mass. To compensate for this type of interference, a multiple element internal standard solution is used to cover the mass range of interest.

CHOOSING INTERNAL STANDARDS

The rules for choosing internal standards are as follows:
• Choose an element that is not of analytical concern.
• Choose an element which is extremely unlikely to be present in the samples. Precious metals or rare earths are often selected as internal standards for this reason.
• Choose an element that behaves similarly to the elements to which it will be linked.
• Choose an analytical wavelength or mass for the internal standard that behaves similarly to that to which it will be linked and one that has a clean background in the sample type of interest.
• Choose an internal standard element concentration that gives a signal that is within a high precision range.

MANUAL VS. IN-LINE ADDITION

Manual Addition

Certain types of samples incorporate a significant and consistent dilution as part of the workup, for example metals and oils. In these cases, it is easy and accurate to add the internal standard(s) to the diluent. When sample dilution is undesirable, individual small volume additions to each solution must be performed. For multiple internal standard additions, a “soup” may first be prepared of all elements and then an aliquot of this added to each analytical solution. Some concerns are as follows:
• If sample volumes are small, the degree of dilution will be greater.
• As internal standard aliquots become smaller, the accuracy of addition suffers.
• Each addition carries a finite error which is the propagation of the errors of sample and internal standard volume and concentration measurements.
• Use of micropipettes to add internal standard may result in the uptake of an air bubble which will adversely affect accuracy.

Furthermore, manual addition can be quite time consuming and labor intensive. For these reasons, many analysts elect to add internal standard automatically via an in-line system.

In-Line Addition

Automatic addition of internal standard is usually accomplished by teeing the internal standard solution into the sample line using an available position on the existing peristaltic pump (see figure 2 below).

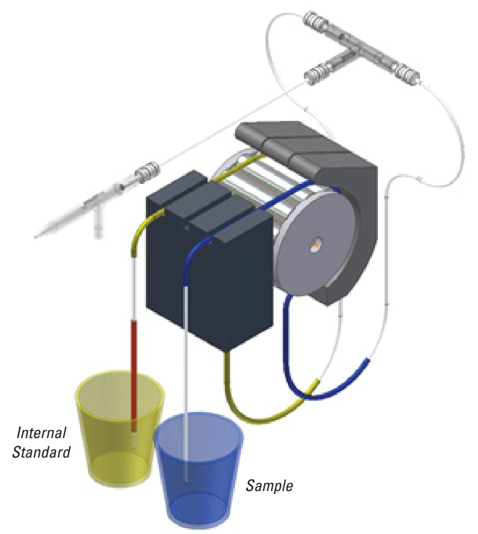


Figure 2. Schematic of In-line Internal Standard Addition

Concerns regarding the in-line addition approach are as follows:

• The ID of the pump tubing used for the two solutions (sample and internal standard) will determine the degree of dilution of both the solutions.

• The combined solution flow of sample and internal standard should not exceed the uptake rate for which the nebulizer is designed.

• Accurate matrix compensation often requires intimate mixing of the internal standard with the sample.

• The addition of the mixing tee increases the washout time of the sample.

In order to provide a general recommendation, two examples will be given, one for ICP-OES and the other for ICP-MS.

ICP-OES

First, standard conditions without using in-line addition will be described. Typically, uptake rates of between 1 and 3 ml/min are employed and therefore 2ml/min will be used in this example. To accomplish this, 0.76mm ID pump tubing is used at the appropriate pump speed. A commonly used internal standard element is either Scandium or Yttrium at a concentration of 1ppm in the analytical sample.

For in-line addition, to minimize dilution of the sample, a pump tube of 0.19mm ID is recommended for the internal standard (see the System-Set-up section on how to connect small ID pump tubing). Since volume (and hence flow rate) vary as the square of the radius, this would result in 6% dilution of the sample and 94% dilution of the internal standard. The sample dilution is negligible with respect to the effect on detection limits and on appropriate nebulizer consumption and therefore the pump speed can remain unchanged. The internal standard reservoir should be prepared at 15ppm to deliver approximately 1ppm in the sample.

ICP-MS

Conditions without in-line addition are as follows. Lower uptake rates are commonly employed in ICP-MS to both reduce oxides and enhance ionization. For this example, an uptake rate of 0.4ml/min will be used. For this uptake rate, a low-flow nebulizer is recommended such as the Glass Expansion MicroMist or PFA OpalMist models. To achieve the desired uptake rate in a pumped mode, the 0.38mm ID pump tubing can be used at the appropriate pump speed for the sample.

For in-line addition, and again to minimize sample dilution, a pump tube of 0.13mm ID is recommended for the internal standard (see the System-Set-up section on how to connect small ID pump tubing). In this case the sample will be diluted by 10% and the internal standard by 90%. To maintain optimum nebulizer performance, it is recommended to decrease the pump speed by 10%. The internal standard reservoir should be prepared with each element at a concentration that is a factor of 10 times greater than that desired in the sample.

System Set-up

Standard supplies are available from most lab supply houses to allow the assembly of a “home made” internal standard in-line addition kit. The following components are recommended:

• A merging tee. Inexpensive plastic tees are available. Exercise care in the handling of these as they can be somewhat fragile and susceptible to leaks if handled harshly.

• Appropriate pump tubing, either 2 tab or 3 tab as your pump dictates. For the small ID pump tubing recommended above, some type of stretching tool is recommended to enable the connection of the pump tubing to the capillary tubing (for example, a 1.3mm OD capillary needs to be inserted into a 0.13mm ID pump tube). Care must be exercised to avoid contamination of the tubing. Alternatively, flared-end pump tubing is available which obviates the need for tube stretching (see below).

• A mixing chamber; often a small length of larger bore tubing that allows the merged solutions to intimately mix.

• Air-tight connections for the four junctions as follows:
    ◦ Sample to tee
    ◦ Internal standard to tee
    ◦ Tee to mixing chamber
    ◦ Mixing chamber to nebulizer

• Capillary tubing to connect all components.

To facilitate the creation of this kit, Glass Expansion offers a ready-to-use modular in-line addition kit (see Figure 3) that has the following attributes:

• Combination merging tee and mixing chamber. Made from borosilicate glass, this component combines zero dead volume ports for the sample and internal standard with a measured mixing chamber on the outlet side of the tee. This guarantees minimal washout times along with intimate mixing of the solutions. This mixing tee is also available in HF resistant plastic.

• All capillary tubing is included and equipped with EzyFit connectors for air-tight seals to the mixing tee and nebulizer.

• A sipper probe with integrated capillary is included to facilitate uptake of internal standard solution.

• Squares of sandpaper are included to facilitate the connection of the pump tubing to the capillary tubing.

• The kit is compatible with Glass Expansion’s line of trace metal free flared-end pump tubing so that even very small ID tubing can easily be mated to the capillary tubing.

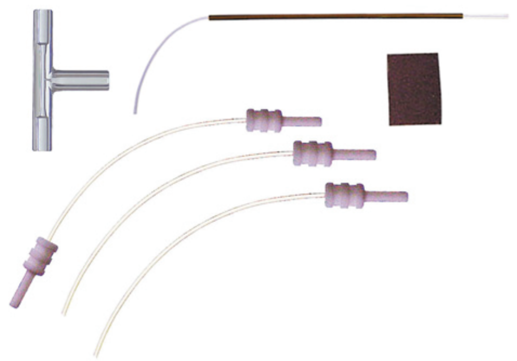


Figure 3: Glass Expansion In-line Internal Standard Kit

CONCLUSION

For both ICP-OES and ICP-MS internal standardization is a useful and often necessary tool to help achieve a high level of accuracy. The automatic in-line addition of internal standards to every sample, standard, blank and control is an effective method to achieve high accuracy of addition and minimize sample dilution while reducing labor and saving time.

NEW PRODUCTS

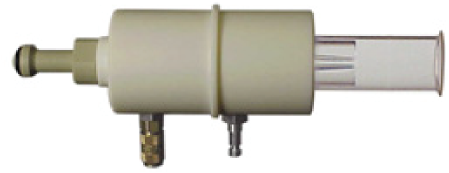
TORCH FOR OILS ANALYSIS WITH PERKIN ELMER OPTIMA 4300V/5300V

The analysis of oils is a common ICP application but organic solutions can significantly degrade the life of quartz torches. To overcome this problem, we have developed a fully demountable torch for oils analysis on the PerkinElmer 4300V and 5300V. Optional ceramic inner and outer tubes are available for this torch. The ceramic tubes are not susceptible to the same failure as quartz torches and the torch life is greatly extended.

Fully Demountable Torch with Ceramic Tubes for Perkin Elmer Optima 4300V/5300V

FULLY DEMOUNTABLE TORCH FOR SPECTRO EOP

We have extended our range of fully demountable torches to include a version for the Spectro Genesis and CIROS EOP models. This torch allows the quartz inner tube, outer tube and injector to be independently replaced. Ceramic injectors, inner tubes and outer tubes are also available to extend the torch life or for use with samples containing HF.



Fully Demountable Torch for Spectro EOP

INSTRUMENT NEWS

FROM AGILENT TECHNOLOGIES - NEW ICP-MS CHEMSTATION SOFTWARE

Agilent has introduced a new revision of ICP-MS ChemStation software (rev. B.03.03). There are several new functions and user interfaces to enhance ICP-MS capability and ease of use. The “Pre-Run Monitor” function is a screen to display the current signal before starting data acquisition. It is useful to shorten the stabilization time with limited volume samples. Also it visually determines appropriate stabilization time for method setup. The “Offline Acquisition Editor” enables you to edit an acquisition method while a separate sequence is running. It enhances productivity and multi-tasking. The Tuning window is also renewed to enhance productivity. There are more than 30 improvements for enhanced ease of use on this new revision. More information about the Agilent 7500 Series ICP-MS can be found at:
www.agilent.com/chem/icpms

FROM SPECTRO - AMETEK FORMS NEW MATERIALS ANALYSIS DIVISION

AMETEK Inc. has announced the formation of its new Materials Analysis Division. The new division brings together the recently acquired SPECTRO Analytical Instruments Division and EDAX, formerly a business unit of AMETEK’s Process & Analytical Instruments Division.

Both SPECTRO, based in Germany, and EDAX, based in the United States have strong organizations. AMETEK will leverage the manufacturing operations, technological capabilities and distribution competencies of these two businesses to further improve the support and services of its customers around the world. It also will continue to invest in new product development to ensure that its customers have the most advanced products available on the market today.

AMETEK’s Materials Analysis Division is a global leader in applying analytical instrumentation to satisfy the materials analysis needs of its customers. The products and technologies available include arc/spark and ICP optical emission spectrometers, energy dispersive and EBSD microanalysis systems, and X-ray fluorescence spectrometers for the fast accurate analysis of solids, liquids, and powders. AMETEK's Materials Analysis Division, built upon the SPECTRO and EDAX business units, provides analytical instrumentation for applications in the metals, environmental, R&D, petrochemical, pharmaceutical, electronics, and forensic science markets.

Please contact Tom Milner for additional information. E-Mail: info@spectro.com

FROM TELEDYNE LEEMAN - NEW HF RESISTANT SPRAY CHAMBER IMPROVES PERFORMANCE

Analysts often must add surfactants to samples containing hydrofluoric acid (HF) to overcome memory effects seen with polypropylene spray chambers. This added step is not only cumbersome but may introduce unwanted contamination. A new PTFE cyclonic spray chamber designed by Glass Expansion provides faster washout than an analogous polypropylene chamber.

At Teledyne Leeman Labs, we ran a 10ppm multi-element standard followed by 30 blank replicates for the polypropylene (PP) chamber with and without Triton X-100 added and for the PTFE (TFE) spray chamber without Triton X-100. In the absence of Triton X-100, the polypropylene chamber required 10 replicate blanks before baseline was reached (Figure 1). In addition, it showed occasional signal spikes (most significantly for iron). Both phenomena were eliminated by the addition of Triton X-100. The PTFE spray

Figure 1. Polypropylene Spray Chamber without 0.01% TX-100

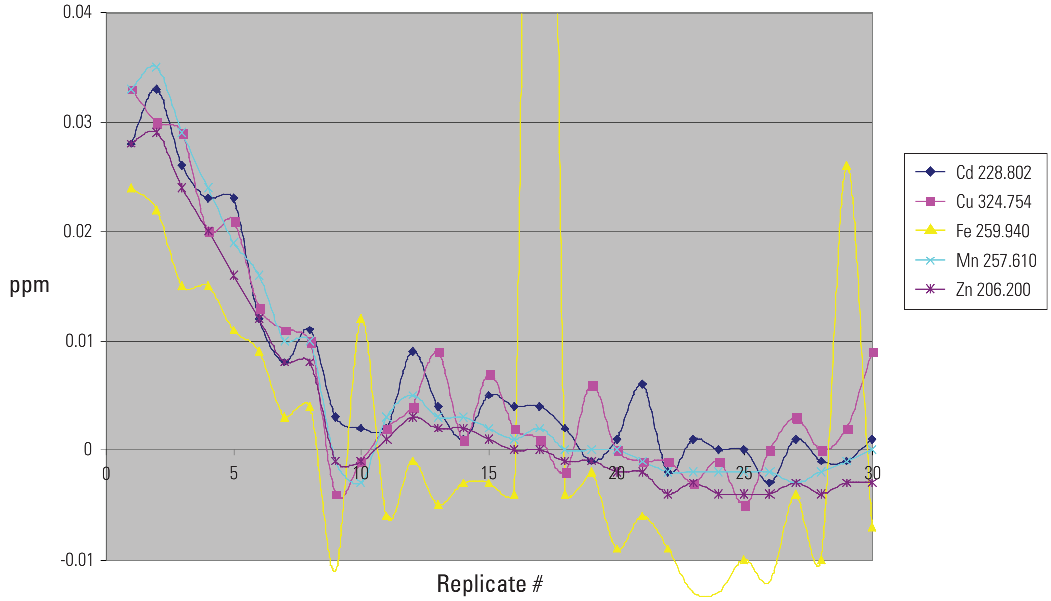
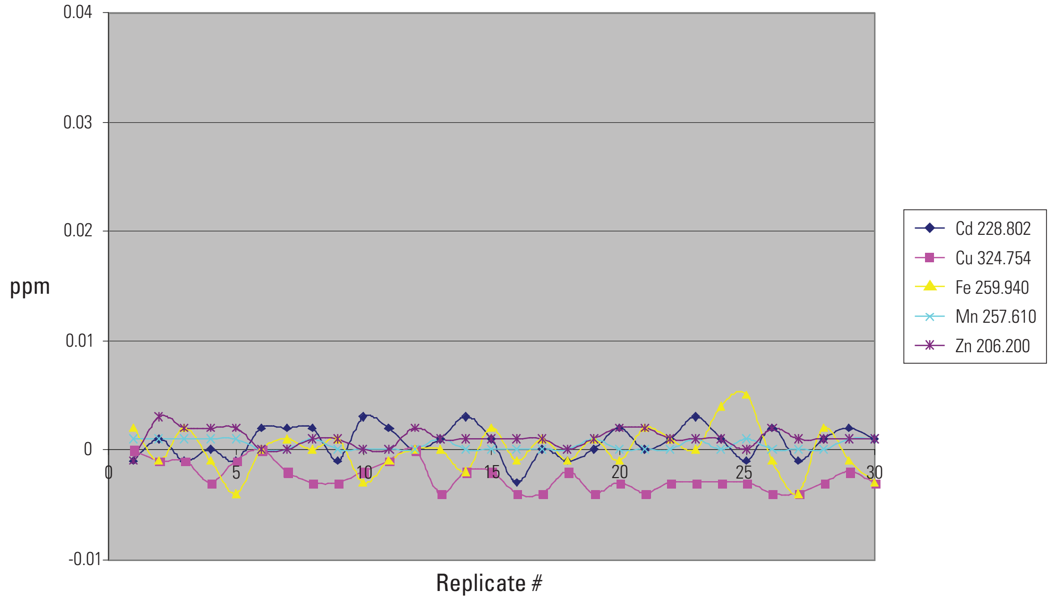


Figure 2. PTFE Spray Chamber without 0.01% TX-100



chamber showed no significant memory effects or signal spikes even when Triton X-100 was absent (Figure 2).

The new PTFE spray chambers are now available as part of an HF resistant sample introduction kit for all configurations of our Prodigy and Profile ICP spectrometers.

To receive additional information, please contact Leeman Labs. E-Mail: LeemanLabsinfo@teledyne.com

FROM THERMO - THERMO OFFERS TWO COMPREHENSIVE TRAINING COURSES ON THE USE OF ITS INNOVATIVE iCAP 6000 SERIES

Thermo Electron Corporation has designed two new training courses in support of its recently launched innovative iCAP 6000 Series, the fastest and most sensitive ICP emission spectrometers available on the market. The new courses have been specifically developed to provide iCAP users with the necessary skills to operate these instruments efficiently in a variety of different application areas and allow plenty of hands-on experience. The course manual, which is given to all attendees includes application notes, hints and tips, data, experiments, detection limits and much more and has proved to be a comprehensive reference source. The innovative iCAP 6000 Series, which was recently given an "honorable mention" in the Editor Awards at PITTCON® 2006, improves performance up to five times and dramatically cuts purge gas consumption, significantly decreasing annual operating costs.

The comprehensive four-day course has been exclusively developed for scientists who are unfamiliar with the operating technology of ICP emission spectrometers. The course aims to provide participants with a complete understanding of ICP theory and demonstrate the vast range of applications of the technique. Thermo has also designed a two-day course for more experienced users who already have a basic understanding of the ICP theory. This course is also ideal for those migrating from Thermo's IRIS Intrepid II to the iCAP 6000 series.

For more information about Thermo's new iCAP 6000 Series training courses, please email analyze@thermo.com or visit: www.thermo.com/elemental

FROM VARIAN - THE WORLD'S BEST IN ICP-OES

Varian, Inc. introduces its new range of ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometer) instruments, the 700-ES series, to meet the needs of scientists working in a variety of application areas ranging from environmental to pharmaceutical. This new range of ICP-OES instruments complements Varian's broad range of AA (Atomic Absorption) and ICP-MS (Inductively Coupled Plasma - Mass Spectrometer) instruments and strengthens the company's global position in elemental analysis.

The 710-ES series is an entry-level instrument designed for budget-conscious laboratories performing routine ICP-OES analyses. These instruments are ideal for educational institutes and for industries that need to comply with environmental protection laws and regulations such as the European Union's directives on the Restriction of the use of Hazardous Substances (RoHS) and on Waste Electrical and Electronic Equipment (WEEE).

The 720-ES and 730-ES series set a new benchmark in speed and performance. Core to both the 720-ES and 730-ES series is a patented CCD detector that delivers the world's best performing and fastest ICP-OES platform, ideal for high-throughput contract laboratories in environmental, petrochemical and geological applications.

With Varian's new range of ICP-OES instrumentation, laboratories can obtain capabilities that match both their demanding analytical needs and budget. The Varian 700-ES Series of ICP-OES delivers more value to customers, strengthening its position as a leading global supplier of elemental analysis instruments.

For more technical information about Varian's ICP-OES instrumentation, please visit:
http://www.varianinc.com/products/spectr/icpoes/

HINTS FOR THE OPERATOR

Running samples containing HF

Glass and quartz are excellent materials to use in ICP sample introduction systems for most solvents. They provide excellent precision and sensitivity, low background, and are not affected by most acids and organic solvents. However, they are not suitable for use with samples containing hydrofluoric acid (HF). Even low concentrations of HF will attack glass and quartz, degrading both sensitivity and reproducibility. Therefore, glass and quartz should be avoided. Many polymer and ceramic materials are impervious to HF and are to be preferred.

Nebulizer - Glass Expansion manufactures nebulizers from PFA, polyimide and ceramic, all of which are suitable for use with HF. The PolyCon nebulizer has a rugged polyimide construction which provides the best durability and stability for ICP-OES systems. The OpalMist PFA nebulizer is even more inert, and the exceptional purity of the PFA material makes the OpalMist ideal for ultra-trace ICP-MS analyses. The Ceramic VeeSpray nebulizer is made from alumina ceramic and it provide the highest tolerance to samples containing particulates and high total dissolved solids.

Spray Chamber - There are many plastics that are not affected by HF but the main challenge in manufacturing an HF-resistant spray chamber is to match the performance obtained with glass spray chambers. Many plastic spray chambers do not drain evenly and suffer from poor precision and sensitivity. Glass Expansion has conducted extensive experiments with different materials and surface treatments and has released a new range of PFA and PTFE (Teflon) cyclonic spray chambers that provide near equivalent performance to the glass cyclonic spray chambers. The PTFE spray chambers are recommended for ICP-OES systems and the PFA spray chambers are preferred for ICP-MS analyses due to their exceptional purity.

Torch - The most vulnerable part of the torch is the injector. The injector is in intimate contact with the sample and any HF in the sample will rapidly degrade a quartz injector. The solution is to replace the quartz injector with one made from HF-resistant material. If the injector is to be replaced, a semi-demountable or fully-demountable torch must be used. With a semi-demountable torch, the inner and outer tubes are constructed as one-piece quartz but the injector is a separate piece. With a fully-demountable torch, the injector, inner and outer tubes can all be separately replaced. Both the semi-demountable and fully-demountable torches enable the quartz injector to be replaced with one made from an HF-resistant material such as alumina ceramic, sapphire or platinum.

HF Resistant Sample Introduction System

Glass Expansion can supply HF-resistant nebulizers, spray chambers and torches for most ICP-OES and ICP-MS models. Please email enquiries@geicp.com to find out what is available for your model.

GLASS EXPANSION NEWS

NEW ICP SPECIALIST

We are pleased to announce the addition of Ron Stux to our staff in the US. Ron has over 30 years of experience in atomic spectroscopy. He started his career in the analytical instrument business with Varian in Australia. He then moved to the US, where he became international marketing manager, and later product manager, for the Thermo line of ICP instruments. Ron has always been particularly interested in the effects of sample introduction on instrument performance, and in determining the best sample introduction system components for different sample matrices. Ron is available for consultation any day of the working week between the hours of noon and 4pm at his Florida office, tel. 954-571-2222 or email rstux@geicp.com. Please feel free to take advantage of Ron's depth of experience in the field of ICP spectrometry.

2006 EXHIBITION DATES

Goldschmidt Geochemistry Conference

A wide selection of Glass Expansion products will be on display at the 16th Annual V.M. Goldschmidt Conference, Melbourne, Australia, August 27 to September 1, 2006. The display will include nebulizers, spray chambers, torches, RF coils and accessories. Glass Expansion specialists will be on hand to answer your questions and assist you to choose the optimum components for your ICP.

JAIMA Show 2006

A full range of Glass Expansion products will also be on display at the JAIMA Show, Tokyo, Japan, August 30 to September 1, 2006 and Glass Expansion specialists will be on hand to assist you.

FACSS 2006

Ron Stux will be presenting a paper entitled, "Approaching a Universal Pneumatic Nebulizer - The Next Step" at the 33rd Annual FACSS Meeting, Lake Buena Vista, Florida, September 24-28, 2006.

NEW 2006 CATALOGUE

If you do not yet have your personal copy of the new 2006 Glass Expansion catalogue (Issue 5), please send your mailing address to enquiries@geicp.com and we will rush a copy to you.