GLASS EXPANSION NEWSLETTER

Quality By Design

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CONTENTS

NEW PRODUCTS

IsoMist Programmable Temperature Spray Chamber

ENHANCED PERFORMANCE FOR ICP-MS AND ICP-OES

Glass Expansion is pleased to announce the release of the new IsoMist Programmable Temperature Spray Chamber, providing the benefits of a temperature-controlled ICP sample introduction system in a compact, convenient package.

Figure 1. IsoMist

Peltier Effect Termperature Control

The temperature is electronically controlled using a powerful inbuilt Peltier device. You can select any temperature between –10°C and +60°C in 1°C increments to provide the optimum conditions for any application. The rapid response of the Peltier device allows a spray chamber temperature of –5°C to be reached within 15 minutes.

Bluetooth® Wireless Communication

For maximum convenience, the IsoMist can be controlled from your PC via a Bluetooth® wireless interface, although a standard USB network connection can also be used.

Reduced Oxide Interferences in ICP-MS

By introducing the sample at low temperature, the IsoMist reduces oxides as shown in Figure 2, resulting in fewer interferences and improved detection limits.

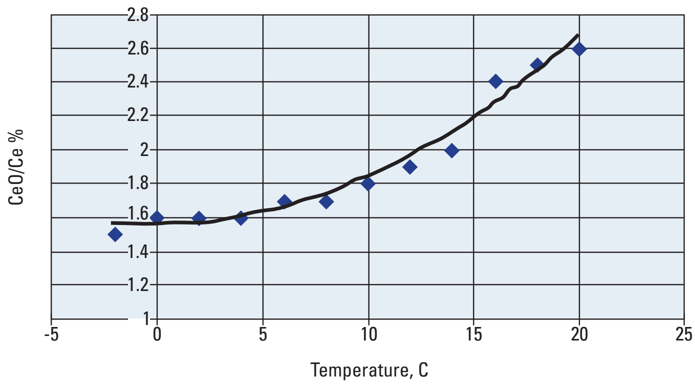

Figure 2. Effect of IsoMist Temperature on ICP-MS Oxide Ratio; Data Courtesy of David Jones, ALS Chemex.

Perfect for Volatile Organics

The temperature can be set as low as –10°C to reduce the solvent load on the plasma and allow the straightforward ICP-MS or ICP-OES analysis of even the most volatile organic solvents. The following table shows results for naphtha with a 10ppb spike obtained at –10°C. The two measurements were made 90 minutes apart using the same calibration data and demonstrate excellent stability for this very volatile sample.

	Conc, ug/L	Conc, ug/L
Cd	57	55
Cr	31	32
Cu	35	33
Fe	24	23
Mn	11	12
Ni	589	517
Pb	451	424
Sn	216	213
Ti	22	22
V	107	104

Figure 3. Reproducibility of naphtha results at –10°C (measurements at 90 minute interval)

Stable Temperature Improves Precision
By holding the spray chamber at a stable temperature, the IsoMist significantly improves long-term signal stability, increasing the likelihood of calibration checks passing.

Heating Mode Enhances Sensitivity
For samples with limited volume, the sensitivity can be enhanced by using a low-uptake nebulizer and running the spray chamber at an elevated temperature. The following table shows that the detection limit with a sample uptake of 20uL/min is better at 60°C than 21°C and is almost as good as that obtained with a standard system running at 21°C with a sample uptake of 2mL/min.

Temperature	60°C	21°C	21°C
Sample uptake	20uL/min	20uL/min	2mL/min
	DL, ug/L	DL, ug/L	DL, ug/L
Al	2.3	5.1	0.9
Cr	0.5	1.1	0.2
Cu	0.3	0.5	0.2
Ni	0.5	1.7	0.2
Zn	0.3	0.7	0.08

Figure 4. Detection limits at 21°C and 60°C

Proven Cyclonic Spray Chamber
The IsoMist incorporates the proven Twister cyclonic spray chamber, combining excellent sensitivity and precision with exceptionally fast washout. This spray chamber now incorporates Glass Expansion's proprietary Helix nebulizer interface which has a zero dead volume seal and provides for convenient nebulizer insertion and removal. For use with the IsoMist, the spray chamber is encapsulated with special thermally conducting material. This spray chamber is compatible with the full range of Glass Expansion nebulizers.

Figure 5. Encapsulated Twister Spray Chamber

Completely Self-Contained Ergonomic Package
The compact design includes a rugged, low maintenance, chemically-resistant polypropylene housing. It provides a much more convenient alternative to a jacketed spray chamber with an external chiller because it does not require an external source of coolant. It is compatible with almost all ICP-MS and ICP-OES models.

Contact enquiries@geicp.com for details on connecting the IsoMist to your specific model of ICP-MS or ICP-OES.

Figure 6. IsoMist on Perkin Elmer Optima

Figure 7. IsoMist on Varian Vista

Products to suit the Thermo Fisher iCAP 6000 and Varian 700-ES models

Glass Expansion offers a wide range of sample introduction components for the Thermo Fisher iCAP 6000 Series and the Varian 700-ES Series. You can see the full range through the following links to our website:

For the iCAP 6000 Duo: Click here
For the iCAP 6000 Radial: Click here
For the 700-ES Axial: Click here
For the 700-ES Radial: Click here

APPLICATION SPOTLIGHT

Determination of Impurities in Photoresists

INTRODUCTION

Photoresists are used during the manufacture of integrated circuits (IC) to protect a deposited layer on the surface of the silicon wafer that will ultimately become the chip. The photoresist is deposited on the wafer, covered with a mask, and then exposed to UV light. Those areas of wafer not protected by the mask are then etched away to create the chip. Impurities within the photoresist can result in electrical inconsistencies resulting in poor performance. A number of alkali and transition metals are the usual suspects.

Until recently, graphite furnace atomic absorption (GFAAS) was the most common means of reaching low detection limits for this application. However, because of the poor productivity, stemming partially from the inability to measure more than one element at a time, more productive techniques have grown in favor. Chi, et al,[1] described a laser ablation ICP-MS technique that yielded quantitative information on contaminants on the surface of the wafer. The advantages of this approach were the elimination of the need to either digest or dissolve the photoresist or to deal with liquids which may be difficult to deal with. However, since the technique is normally applied to solid samples, it is not easily adapted to measure contaminants in the solvents and liquid photoresist. Accessibility to accurate standards is another concern. A novel direct dilution approach was successfully used to measure sub ppb levels of sodium and potassium using flame atomic emission spectrometry (FAES) with a multichannel detector[2]. One channel was used on the analyte peak while another channel was positioned off-peak to simultaneously correct the rapidly changing background. The relatively low temperature flame yielded excellent detection limits for these easily ionizable alkali metals.

Both ICP-OES and ICP-MS have been employed in the direct dilution approach for this application. Takahashi and Yono describe a direct dilution ICP-MS method incorporating "cool plasma" conditions to minimize interferences[3]. The advantages of the direct dilution method are high precision and readily available standards. This paper will discuss the optimum conditions and sample introduction components of the direct dilution approach.

Sample Preparation

The solvent selected to dissolve the photoresist and keep it in solution will depend upon the chemical composition of the photoresist. Common solvents used are as follows:

- Ethyl lactate
- N-methyl-2-pyrrolidone (NMP)
- Propylene glycol monomethyl ether (PGME)
- 2-Ethoxy ethanol

Typically, a 1:10 dilution of the photoresist will ensure stability. Internal standards should be added to the sample during the dilution step. It is convenient to add the internal standard to the diluent prior to preparation of all samples and standards. It is not advisable to use in-line internal standard addition for this application since the sample is normally free aspirated rather than pumped and pumping provides the best accuracy for in-line addition. The solvents used are so powerful that it is difficult to find pump tubing materials that will hold up to them. For example, it was found that NMP strips polyimide (also known as Ultem®) of its bonding agents causing it to completely disintegrate after a brief exposure[4].

INSTRUMENT CONFIGURATION

For both ICP-MS and ICP-OES, the challenges are the same, as follows:

- Dealing with high and dynamic background signals
- Finding components that will stand up to the solvents
- Dealing with the high matrix associated with samples that can reach as high as 30% resin
- Preventing clogging within the sample introduction system
- Dealing with high carbon samples that can create deposits and result in both spectral and isobaric interferences

Optimizing the sample introduction system is key to overcoming these challenges. From the sample to the plasma, the proper components are critical.

Sample Line

The sample line must be made of an inert material. Because of its inertness, purity, and rigidity, PFA or PTFE (Teflon®) is a good choice. Many other materials, including those used to manufacture peristaltic pump tubing, may be subject to degradation by the solvent used. For this reason, it is preferable to self-aspirate sample with a pneumatic nebulizer rather than pump with a peristaltic pump.

Nebulizer

A self-aspirating micro-flow nebulizer made of glass or PFA is recommended. For example, Glass Expansion manufactures the MicroMist line of concentric glass nebulizers designed to achieve natural uptake rates of 50 to 600 ul/min (depending upon the specific model) and the OpalMist PFA nebulizer line with models that covers the same uptake rate range in addition to models with higher uptakes. All of these nebulizers are designed to achieve these nominal uptakes for aqueous solution and may yield substantially higher uptakes when used with solvents of lower viscosity.

Figure 1. MicroMist Nebulizer designed to achieve a natural uptake of 0.2ml/min

Figure 2. OpalMist PFA Nebulizer designed to achieve a natural uptake of 0.2ml/min

Spray Chamber

The spray chamber features that should be considered for this application include the following:

- All glass or quartz construction
- Minimal surface area for faster rinse out time
- Low internal volume to reduce equilibration time
- Cyclonic design to improve precision
- Small internal diameter (ID) central baffle designed to reduce the solvent load to the plasma
- Gravity drain in conjunction with an inert trap
- Auxiliary port for the addition of oxygen
- O'ring-free nebulizer fitting to eliminate the potential for aggressive solvents to degrade the o'rings
- Jacketed chamber for cooling

Figure 3. Jacketed Twinnabar Cyclonic Spray Chamber with Helix O'ring-Free Fitting and Auxiliary Port

Glass Expansion manufactures a low volume jacketed Twinnabar cyclonic spray chamber (20ml internal volume instead of the more standard 50ml) with a central baffle to reduce solvent transport. Although not shown in Figure 3, this spray chamber can be configured with a gravity drain to eliminate the need for pump tubing in the system. The auxiliary port can be connected to a source of oxygen such as a 20% oxygen/argon mixture. The function of the oxygen is to combust the high organic content to avoid carbon buildup and clogging within the injector and torch (and the cone orifice for ICP-MS). The Helix o'ring-free nebulizer fitting is very important for this application. Even ketone resistant o'rings are unlikely to hold up to these solvents for very long. They will either swell, making it very difficult to remove the nebulizer or shrink, resulting in air leaks. The jacket feature allows the spray chamber to be cooled to a temperature that further reduces sample transport and therefore plasma loading. The need for cooling and the degree of cooling must be empirically determined. Takahashi and Yono[3] used a Peltier cooled spray chamber integrated with the Agilent 7500 ICP-MS and cooled it to 2^{o}C when running PGME as the solvent. Glass Expansion has recently released a line of programmable Peltier spray chambers. Unlike many Peltier spray chamber accessories which require an external recirculator, the IsoMist line is self-contained. Please see the "New Products" section in this issue for more information.

Torch

This application produces a high degree of stress on the torch and its components for a number of reasons:

- The high organic content creates a greater load on the plasma, requiring higher forward power to sustain the plasma and efficiently excite the analytes. Higher energy places greater stress on the outer tube of the torch usually resulting in a shorter lifetime.
- Even with oxygen addition, carbonaceous deposits are likely to form eventually at the tip of the injector and the top of the outer and intermediate tubes.
- The viscous photoresist, even diluted 10X with solvent, has a tendency to deposit on the walls of the injector if precautions are not taken.

A single piece or demountable quartz torch provides the opportunity to clean the outer, intermediate, and injection tubes by placing them in a muffle furnace for 30 minutes at 500^{o}C. This process effectively removes all carbon deposits. A fully demountable torch (one that allows replacement of the outer and inner tubes separately) offers a cost benefit as well.

The injector tube may be the most critical component of the torch for this application. A narrow bore is recommended to reduce the sample load on the plasma. However, it is good practice to avoid a sharp taper of the internal injector diameter. The pressure change created by a sharp taper fosters deposition on the injector walls. For this reason, a capillary injector (uniform internal diameter) may be beneficial.

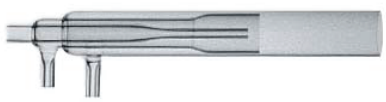

Figure 4. Single Piece Quartz Torch

Figure 5. Fully Demountable Torch

Sampling and Skimmer Cones
Whether adding oxygen or not, if ICP-MS is used, platinum tipped sampler and skimmer cones are preferable for this application. If not adding oxygen, the platinum cones will run hotter and keep the orifice clean longer. If adding oxygen, noble platinum cones will stand up better to the reactive environment.

Figure 6. Platinum tipped Sampler and Skimmer Cones for the Agilent 7500

CONCLUSION
The accurate quantification of impurities requires meticulous attention to detail. Solvents required can be both corrosive and toxic. Contamination must be controlled during all aspects of the analysis. Optimization of the sample introduction system is critical. We would like to acknowledge the help of Bob Almeida of Tyco Healthcare in Mansfield, MA, for his experience-based suggestions.

REFERENCES
1. Po-Hsiang Chi, Fu-Hsiang Ko, Chien-Teng Hsu, Hsuen-Li Chen, Chau-Kai Yang, Yuh-Chang Sun and Mo-Hsiung Yang, **Direct impurity analysis of semiconductor photoresist samples with laser ablation ICP-MS**, *J. Anal. At. Spectrom.*, 2002, **17**, 358-365.
2. Robert Almeida, **Trace analysis of sodium and potassium in photoresist by flame emission spectroscopy**, Pittcon Paper, March, 1999.
3. Junichi Takahashi and Koichi Yono, **Direct Analysis of Photoresist Using ICP-MS**, Application Note, Agilent Technologies.
4. Private communications with Dave Pfeil, Teledyne Leeman Labs, Hudson, NH; and Jerry Dulude, Glass Expansion, Pocasset, MA.

INSTRUMENT NEWS

From Spectro:

SPECTRO DELIVERS 25,000TH ANALYTICAL INSTRUMENT
SPECTRO has produced and delivered its 25,000th analytical instrument. The instrument, a SPECTRO CIROS VISION ICP-OES spectrometer, was purchased by Acme Analytical Laboratories Ltd. in Vancouver, British Columbia, to examine environmental and geological samples.

"Acme Analytical Laboratories, a laboratory service supplier, is one of our most important Canadian customers," notes Doug Keene, Sales Manager for SPECTRO Analytical Instruments in Kingwood, Texas. "Acme is active around the world, supporting its customers in all areas of geological analysis. The laboratory has ordered eight SPECTRO CIROS Vision ICP spectrometers since beginning ICP-OES analysis several years ago."

The SPECTRO CIROS VISION, with the special serial number marking its status as SPECTRO's 25,000th instrument, will be used by Acme in Vancouver for a wide range of applications. Acme employs ICP-OES technology to examine soil, sludge, water and waste water as well as rocks. Another important application for the CIROS VISION is measurement of the precious metal content in rock and ore samples.

ICP-OES analysis allows Acme to offer its customers a combination of analytical procedures. Rock samples, for example, are first analyzed with the CIROS VISION and then with an ICP mass spectrometer to achieve the lowest possible detection limits and to cover the entire spectrum of elements.

From Teledyne Leeman Labs:

NEW APPLICATION NOTE ON THE ANALYSIS OF SOIL USING EPA SW-846 METHOD 6010C
Technical note 1035, *"The Analysis of Soil using EPA SW-846 Method 6010c with the Prodigy ICP"* describes the analytical performance of the Prodigy High Dispersion ICP in analysis according to EPA SW-846 Method 6010c. In addition to soils, this method is applicable to ground waters, TCLP and Extraction Procedure (EP) toxicity extracts, industrial organic wastes, sludges and sediments.

As with other U.S. EPA mandated methods, 6010c requires adherence to specific procedures to ensure data quality. Some of these procedures are designed to demonstrate the initial performance of the instrument, while others assess the on-going performance of the laboratory.

To receive a copy of this technical note, contact Teledyne Leeman Labs by email at LeemanLabsinfo@Teledyne.com or visit their website at www.LeemanLabs.com

HINTS FOR THE OPERATOR

Running Organic Samples

Organic samples introduce several difficulties not encountered with aqueous samples. These include an unstable plasma due to vapourisation of the solvent, changes in sample uptake due to changes in viscosity, carbon deposits in the torch, and chemical incompatibility with sample tubing. These problems can be alleviated as follows:

Reduce plasma solvent load
A significant issue is the high amount of solvent delivered to the plasma. This makes the signal unstable and, in some cases, can even extinguish the plasma. There are several different methods that can be used to reduce the solvent load:

Low uptake nebulizer: A low uptake nebulizer is recommended. The MicroMist nebulizer is available with sample uptake rates of 50 to 600 uL/min. For most organic samples, an uptake of 200 to 600 uL/min is suitable.

Reduced sample pump rate: If a peristaltic pump is used to deliver the sample, then the sample uptake can be reduced by reducing the pump speed or using smaller diameter pump tubing. It is best to also use a nebulizer, such as the MicroMist, that is optimized for the lower sample uptake.

Narrow bore injector: We recommend an injector with a smaller internal diameter than that used for aqueous samples. Best performance with organic samples is also usually achieved with a capillary (uniform bore) injector. If different injectors are required for different samples, then a semi-demountable or fully-demountable torch is recommended.

Twister spray chamber: The Twister cyclonic spray chamber is recommended for organics because it filters out the larger sample droplets.

Helix Nebulizer Fitting: A spray chamber with the Helix nebulizer interface is also beneficial, since it is totally inert and does not contain any o-rings which could be attacked by the organic solvent.

Cooled spray chamber: With volatile solvents, reducing the temperature of the spray chamber is an effective method of reducing the solvent load on the plasma. A common practice is to pump a cooling solution from a chiller through a jacket surrounding the spray chamber. While this method is effective, it is rather cumbersome since it requires a bulky chiller and tubing to deliver the cooling solution to and from the spray chamber. A much more elegant solution is an electrically cooled spray chamber such as the IsoMist Programmable Temperature Spray Chamber. The IsoMist can be configured to operate with almost any ICP-OES or ICP-MS model and the temperature is programmable down to –10^{o}C.

Use higher RF power
Increasing the RF power applied to the torch can sometimes counter the increase in solvent load and improve the stability of the signal.

Increase argon coolant flow
A higher argon coolant flow to the torch, together with the higher RF power can also help overcome the effect of the higher solvent load and improve stability.

Select appropriate sample introduction materials
The glass and quartz materials generally used for nebulizers, spray chambers and torches are perfectly suited for use with organic solvents. However some types of o-ring and plastic tubing are not suitable. In order to avoid o-ring problems, a spray chamber with Helix is recommended. The standard PVC peristaltic pump tubing is not compatible with many organic solvents and Solva or Tygon MH tubing may be required. Alternatively, it may be preferable to dispense with the pump tubing altogether and use the natural aspiration of the nebulizer. In this situation, it is important that the viscosities of the samples and standards are well-matched. The MicroMist nebulizers provide reliable and consistent self-aspiration and can be supplied with the optimum sample uptake for each application.

Matrix match standards and samples
Different organic solvents can have quite different physical (eg. viscosity) and chemical properties, so it is very important that the standards and samples are closely matched.

Reduce carbon deposits
With organic solutions, it is very common to get carbon deposits in the torch, either at the tip of the injector or near the end of the outer tube. These can be removed by introducing a small amount of oxygen with the sample aerosol to burn off any carbon deposits. This may be bled in continuously or at periodic intervals. A torch with a slotted outer tube can also retard carbon build-up.

Glass Expansion can supply a sample introduction system optimized for organic samples to suit most ICP-OES and

ICP-MS models. Please email enquiries@geicp.com to find out what is available for your model.

GLASS EXPANSION NEWS

Pittcon

VISIT GLASS EXPANSION AT BOOTH 940

A wide selection of Glass Expansion products will be on display at Pittcon 2007, Chicago, Illinois, USA, February 26 to March 1, 2007. 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 940.

TECHNICAL PAPER TO BE PRESENTED

Glass Expansion technical personnel have submitted a paper entitled, "A Programmable Universal Peltier Cooled Spray Chamber for ICP-OES and ICP-MS", Jerry Dulude, Ron Stux, and Vesna Dolic. Mr. Dulude will be presenting on Tuesday, Feb. 27, at 1:50 PM in Room 502B (Session 1370 - New Tools and Techniques in Atomic Spectroscopy Analyses).

New Website Features

PUMP SPEED AND SAMPLE UPTAKE CALCULATOR

If you ever need to select the right peristaltic pump tubing or pump speed to give you the required sample uptake, or to find out what the sample uptake is with the pump tubing and pump speed that you are currently using, then try the convenient new Pump Speed and Sample Uptake Calculator on our website.

TRIDENT DILUTION FACTOR CALCULATOR

If you are using the Trident internal standard kit and you want to know how much dilution a particular pair of pump windings will apply, check the new online Trident Dilution Factor Calculator