GLASS EXPANSION NEWSLETTER

Quality By Design

June 2004

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APPLICATION SPOTLIGHT

Analysis of Organic Solvents by ICP-AES (Part One)

INTRODUCTION

Although both ICP-AES and ICP-MS have been used to determine metal concentrations in organic solvents, ICP-AES has been the more widely used technique for these applications and will be the focus of this discussion. However, many of the recommendations are equally applicable to ICP-MS. For the purpose of this discussion, the topic will be divided into four categories as follows:

1. Non-volatile organic matrix; examples of this include the following:
   a. Analysis of kerosene-diluted fuel oil for metal contaminants
   b. Analysis of kerosene-diluted vegetable oils for alkali metal contaminants
2. Non-volatile organic matrix with particulates, the primary example of which is the determination of wear metal in used engine oils.
3. Volatile organic solvents such as gasoline, methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), acetone, toluene, methanol, and ethanol.
4. Volatile organic matrix with volatile analytes such as the determination of tetraethyl lead in gasoline.

The first two categories will be addressed in the current issue. The balance of the categories will be addressed in the next issue of this newsletter

INSTRUMENTATION

All commercially available ICP-AES systems can be configured to handle organic solvents. For the determination of metals in kerosene-diluted oils, radial viewed plasma is typically preferred due to its relative freedom from interferences, wide linear range, and the relatively undemanding levels of detection required.

Because organic solvents create a greater load on the plasma, a higher forward power should be applied, usually from 1.3 to 1.5kW. The high carbon content matrix has a tendency to form carbon deposits on the outer and intermediate tubes and the inside of the injector. Clogging of the injector with carbon has the more immediate ramifications. This can be lessened somewhat by employing a higher than normal auxiliary flow of argon, one to two liters per minute. The higher flow lifts the plasma off the injector, decreasing the extent of solvent breakdown within the injector. Some analysts have found that bleeding 0.1 to 0.2 L/min of air into the argon line prior to the nebulizer further reduces the carbon buildup by combusting the carbon, thereby converting it to carbon dioxide.

SAMPLES

Oils are typically diluted in a solvent such as kerosene prior to presentation to the instrument. Kerosene is a popular solvent choice for several reasons as listed below:

- It is relatively inexpensive and readily available.
- It is free of significant elemental contamination in reagent grade form.
- It is "plasma friendly" unlike other more volatile solvents.
- Although flammable, its vapors are not irritants at room temperature.

A 5X or 10X dilution is usually adequate to reduce the viscosity of the oil so that it travels well in the uptake tubing and nebulizer but not so excessive as to degrade

detection unacceptably. Because of varying viscosities (and hence, densities), dilutions are usually performed by weight rather than volumetrically. For the same reason, it is common to employ an internal standard to correct for inter-sample differences in nebulization efficiency. Since it is generally not found in these types of matrices, beryllium is often selected as the internal standard and added to the kerosene diluent. All standards are prepared by weight using organometallic standards. Automatic oil dilution accessories are available from some ICP manufacturers. These save time by eliminating the laborious dilution by weight.

SAMPLE INTRODUCTION SYSTEM

The sample introduction systems recommended for these two categories of application are similar; only the nebulizer is different.

NEBULIZERS

Oils without Particulates - Conikal or MictroMist

A standard Conikal concentric glass nebulizer is the preferred means of vaporizing kerosene-diluted oil samples. The nebulization efficiency of kerosene is much higher than that of water, thereby introducing more sample to the plasma. If the lowest detection limits are not required, it may be beneficial to use a MicroMist low uptake concentric glass nebulizer. The lower volume of sample and solvent reaching the torch will provide a more rugged system and more robust plasma.

Concentric Glass Nebulizer with EzyFit Connector and EzyLok Argon Connector

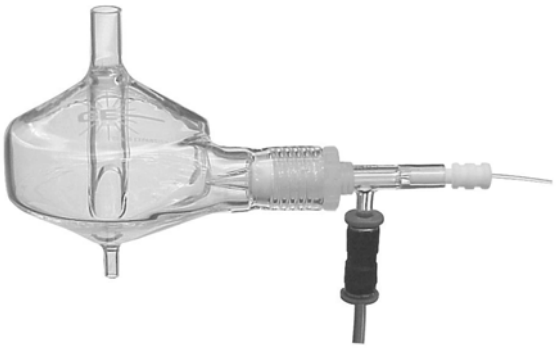
Oils with Particulates - Slurry or VeeSpray

The determination of wear metals in used engine oils is typically performed by technician-level analysts and for hundreds of samples per day. For these reasons, this assay must be rugged and simple. Although most particulates suspended in engine oil (from the wear of metal engine components) are less than 1 micron in diameter, it is possible for larger particles to be present. Where a Conikal nebulizer can handle particles up to 75 microns in size, the Slurry concentric glass nebulizer is designed to accommodate particles as large as 150 microns. The VeeSpray modified Babington style nebulizer can accommodate particles up to 300 microns without clogging. Unlike the VeeSpray nebulizer, the Slurry nebulizer is self aspirating and therefore exhibits less pulsing due to the revolutions of the peristaltic pump. For this reason and the unlikelihood of the presence of particles greater than 150 microns, the Slurry is the preferred nebulizer for this application.

VeeSpray™ Modified Babington Nebulizer

SPRAY CHAMBER

The Twister Cyclonic spray chamber (shown below) will provide optimum performance and prevent large solvent droplets and particulates from reaching the torch. This spray chamber also has the beneficial feature of the Helix o'ring-free nebulizer fitting. With this design, the knurled plastic knob of the Helix is loosened to allow installation of the nebulizer. When the knob is tightened, the nebulizer is locked into position. With the same motion, a PFA ferrule is sealed against the inside of the nebulizer port preventing any buildup of solvent around the nebulizer. For high throughput operations such as the determination of wear metals in used engine oils, the reduced dead volume of the system will result in faster washout times and thus higher productivity.



Twister Cyclonic Spray Chamber with Helix Fitting

TORCH AND INJECTOR

The torch assembly should be capable of withstanding a muffle furnace at 450ºC. This treatment will be necessary periodically to remove carbon buildup from the injector and the outer and intermediate tubes. Glass Expansion offers three types of torches for various ICP models as follows:

- Single piece quartz torch with integral injector

- Semi-demountable quartz torch with demountable injector

• Fully demountable quartz torch with demountable injector, outer tube, and intermediate tube

Each of the above can be cleaned in a muffle furnace. Where available, the fully demountable torch is the most cost effective and convenient design. The torch in this application is subjected to unusually high temperatures in comparison to aqueous analysis, primarily because of the higher plasma power employed. The higher temperature may cause the torch outer tube to deteriorate prematurely. Use of the fully demountable torch allows the operator to clean or replace only the components in need of attention.

In order to limit the mass of sample reaching the plasma per unit time, a smaller bore injector is recommended, typically 1.0 to 1.2mm. This will decrease the loading of the plasma by the energy-absorbing organic solvent. In addition, it has been found that a capillary bore injector takes longer to show signs of carbon build-up than a tapered bore injector.

PUMP TUBING

By many accounts, the longest lasting pump tubing for this application is that made of a solvent flex form of PVC. In our catalog, this tubing has the suffix "SF". Fluran (Viton®) tubing is also commonly used for kerosene ("VS" prefix in the GE catalog).

SWITCHING TO AQUEOUS

If the same spectrometer will also be employed to analyze aqueous matrices from time to time, it is necessary to carefully clean the entire sample introduction system prior to aspirating water. Failure to do so may result in the formation of emulsions which will degrade performance. Rinsing with acetone followed by a drying step is an effective method to do this. The same procedure should be applied when switching from aqueous to organic solvents. In order to avoid this laborious cleaning process, many analysts elect to use a separate dedicated sample introduction system for organic and aqueous solvents.

PRODUCT DESIGN FOCUS

The RF Coil

The RF Coil is a critical component of the electical system which delivers energy to the plasma. The major issues to be considered when purchasing a replacement RF coil are:

1. Concentricity. The turns of the coil must all be concentric in order to generate a correctly shaped plasma.
2. Alignment. Each coil must be able to be positioned correctly in relation to the torch.
3. Dimensions. Any changes in the dimensions of the coil (diameter of the tubing, diameter of the coil, space between turns) will affect the tuning of the RF generator.
4. Material. The material must be highly conductive in order to efficiently transfer energy to the plasma and it must also be able to withstand the harsh environment inside the torch compartment.

CONDUCTIVITY

The higher the conductivity of the coil, the lower will be the energy loss in the coil and the higher will be the efficiency of the energy transfer to the plasma. Of the readily available materials, silver has the highest conductivity with an IACS (International Annealed Copper Standard) of 105. Copper is close behind at IACS 100 and gold is IACS 74. So, from the conductivity point of view, pure silver would be the best material from which to make the coil. Copper is only a little below silver in conductivity and significantly below in price. This has led to the use of copper coils by many manufacturers. Since the RF current travels in the surface layer of the coil, the best efficiency at reasonable cost can be obtained with silver plating over a copper base.

CORROSION RESISTANCE

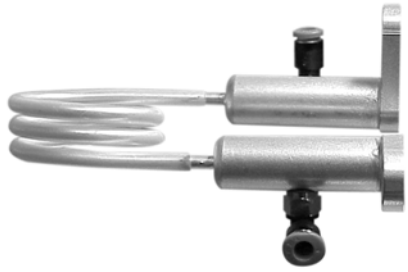
In the selection of coil material, the environment in which it operates must be considered. The environment inside the torch compartment of an ICP spectrometer is very harsh, with high temperatures and corrosive gases. In this environment, the surface of a pure copper coil may soon become corroded. This will reduce the conductivity, reduce the efficiency of energy delivery to the plasma, and place additional stress on the components of the RF generator. Silver is more resistant to corrosion than copper, so a silver-plated coil will provide better efficiency over a longer period than a pure copper coil.

Oxides will form on the surface of both silver and copper coils. Copper oxides have much lower conductivity than silver oxides so the efficiency of a copper coil will degrade much more than the efficiency of a silver coil as the surface oxidizes.

Although the conductivity of gold is lower than that of silver, gold is more resistant to corrosion. This has led to the increasing popularity of gold-plated coils. The plating process is critical for gold-plated coils. Gold plating can

produce a porous coating which will allow chemical attack of the underlying copper and copper migration through the gold plating to the surface of the coil. The plating process used in the production of Glass Expansion gold-plated coils is designed to minimize the porosity of the plating and maximize the life of the coil.

All Glass Expansion coils are available with your choice of silver or gold plating. Some models are available with Teflon coating for added corrosion protection. Some models are also available in unplated copper but these are not generally recommended.



PACKING AND INSTALLATION

The majority of commercial RF coils have a base of copper tubing and are therefore quite pliable. It is critical that there is no distortion of the coil shape during transport or installation. Every Glass Expansion coil is supplied on a rigid plastic former, ensuring that correct dimensions are maintained during transport and installation. Each coil is shipped in a special container for added protection. Glass Expansion's reusable installation kits provide the tools and instructions for straightforward do-it-yourself installation. Contact enquiries@geicp.com for more information on Glass Expansion RF coils.

NEW PRODUCTS

NEW LOWER-COST CAPRICORN ARGON HUMIDIFIER

Glass Expansion has released a new, lower-cost version of the popular Capricorn Argon Humidifier. An argon humidifier is commonly used in ICP analyses involving samples with high dissolved solids concentration. Prior to being introduced to the nebulizer, the argon is bubbled through a water vessel so that it becomes saturated with moisture. This helps to prevent salt buildup inside the sample introduction system, allowing uninterrupted and maintenance-free operation. The new version of the Capricorn is for users who need to use a humidifier for most of their analyses, since it does not have an online bypass. The original version of the Capricorn with the online bypass is still available. This version has a toggle valve which allows the user to bypass the humidifier without extinguishing the plasma. This version is for users who only need to use a humidifier with some samples. Contact enquiries@geicp.com for details.

OPALMIST NEBULIZER WITH 10uL/MIN UPTAKE

Glass Expansion has released a new version of its OpalMist nebulizer with an ultra-low sample uptake of 10uL/min. This is designed for ICP-MS applications where the sample volume is very limited. (Other versions of the OpalMist are available with natural uptake rates of 50uL/min to 2mL/min.) The high purity of the PFA material eliminates potential contamination, making the OpalMist ideal for ultra-trace analyses such as those in the semi-conductor industry. Also, PFA is one of the most chemically inert materials known and can be used with reagents such as HF, sulfuric acid and hydrogen peroxide. The OpalMist provides strong and consistent self-aspiration and so can be used without a peristaltic pump. The elimination of the peristaltic pump removes the pump tubing as a potential source of contamination, eliminates potential instability due to pump pulsations, and speeds sample throughput by reducing the overall length of sample tubing. The OpalMist is also able to aspirate high salt concentrations without clogging and is available with a range of argon pressures and flows to match all current ICP-MS and ICP-AES models.

EL-1 EZYLOK KIT

All Glass Expansion glass concentric nebulizers with the "E" suffix are now supplied with the EL-1 EzyLok kit at no extra charge. The EzyLok connectors facilitate quick connection between the argon gas tubing and the nebulizer. You no longer need to purchase the fittings separately. This means that nebulizers with the "EL" suffix are now obsolete and have been replaced by nebulizers with the "E" suffix.

HINTS FOR THE OPERATOR

Analysing Low Volume Samples

There are many applications where the volume of sample available is limited. In these cases, the sample introduction components must be carefully chosen to enable reliable measurements to be made using only a small volume of sample. The best results with low volume samples are obtained when a low-volume spray chamber is combined with a low-uptake nebulizer. This combination is much more efficient than standard components, so the loss of signal is not as great as might be expected. For example, a MicroMist nebulizer with 50uL/min sample uptake combined with a Cinnabar 20mL spray chamber is 50% efficient. This compares with 2% efficiency for a standard system operating at 2mL/min. So, even though the amount of sample used has dropped by a factor of 40, the sensitivity drops by less than a factor of 2. This enables reliable measurements to be made with very small volumes of sample.

Glass Expansion manufactures MicroMist glass concentric nebulizers with a range of natural uptakes down to 50uL/min to suit all models of ICP-MS and ICP-AES. Cinnabar spray chambers are also available for all instrument models. For samples containing HF, the OpalMist PFA and PolyCon polyimide nebulizers are available with uptakes down to 50uL/min as are polymer versions of the Cinnabar spray chamber. An OpalMist nebulizer with a natural sample uptake of 10uL/min has also been recently released (see New Products section for details).

DISTRIBUTOR PROFILE

S.T. JAPAN

S.T. Japan has been selling a wide range of analytical instrument accessories and FTIR Raman database software for more than 20 years. Their main products can be seen at their demonstration facilities in Tokyo and Osaka. They have sales offices in the USA, Europe and South Korea and sell their own products all over the world. Since 1993, they have been selling ICP/ICP-MS accessories, including Glass Expansion Products, to the Japanese market. Their range of products can be seen on their website at www.stjapan.co.jp.

INSTRUMENT NEWS

FROM AGILENT

Agilent Technologies has introduced the new Agilent 7500ce ICP-MS for trace-metals analysis in environmental applications. The 7500ce meets the demands of the routine trace metal analytical lab that requires high performance from reliable, robust and simple to use instrumentation. It is equally suited to the toughest analytical challenges found in the clinical, foods, petrochemical, metals, pharmaceutical, forensic and geological industries. The 7500ce's Octopole Reaction System features redesigned ion optics and a new, high-transmission reaction cell, which allow the 7500ce to detect analytes at ppt levels even in samples with high amounts of dissolved solids. The sample introduction system comprises a quartz torch and a double-pass spray chamber fitted with a highly efficient and precise MicroMist nebulizer, made by Glass Expansion, for excellent sensitivity and stability. The New brochure (5989-0774EN), Agilent ICP-MS Journal Issue 19 (5989-1147EN) and several application notes are also available now. More information about the Agilent 7500 Series ICP-MS can be found at www.agilent.com/chem/icpms.

GLASS EXPANSION NEWS

THE NEW 2004 CATALOG NOW AVAILABLE

The new Glass Expansion catalog is now available. This 124-page full colour catalog lists nebulizers, spray chambers, torches, RF coils, ICP-MS cones and other parts for over 70 ICP-AES and ICP-MS models. If you would like your personal copy, please send your mailing address to enquiries@geicp.com and we will rush a copy to you.

JAIMA SHOW 2004

A wide selection of Glass Expansion products will be on display at the JAIMA Show, Tokyo, Japan, September 1-3, 2004. 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.