GLASS EXPANSION NEWSLETTER

Quality By Design

October 2004

CONTENTS

APPLICATION SPOTLIGHT

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

INTRODUCTION

In the previous issue, we discussed the analysis of non-volatile organic samples such as wear metals in kerosene-diluted engine oils. This issue will focus on the following non-routine applications involving the analysis of organic solvents:

1. Volatile organic solvents such as gasoline, methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), acetone, toluene, methanol, and ethanol.
2. Volatile organic matrices with volatile analytes such as tetraethyl lead in gasoline.
3. Analysis of active pharmaceutical ingredients (API) after dissolution in dimethyl formamide (DMF).

INSTRUMENTATION

All commercially available ICP-AES and ICP-MS systems can be configured to handle organic solvents. For the analysis of volatile organic solvents, special consideration should be given to the sample introduction system. On the other hand, DMF can be analyzed with the standard aqueous configuration.

For volatile organic solvents, the procedures previously considered for kerosene analysis are even more important:

• Even higher forward RF power may be required to maintain the plasma since close to 100% of the solvent reaches the plasma. In addition, it may be necessary to reduce the sample uptake rate to limit the mass of solvent reaching the plasma.

• Higher auxiliary gas flows and the addition of oxygen to the plasma gas are both recommended in order to reduce carbon buildup on the torch.

ANALYSIS OF VOLATILE ORGANIC SAMPLES

The prudent selection of sample introduction components can facilitate the analysis of volatile organic solvents by preventing system failures, reducing maintenance, and maximizing analytical performance.

Nebulizer

A concentric glass nebulizer is recommended for this type of sample. However, because of the high volatility of the sample, a much higher portion of the nebulized sample will reach the plasma (in some cases, 100%) in comparison to aqueous samples which have a transport efficiency of 2 to 5%. This produces a dramatically higher load on the plasma, which in the worst case will extinguish it and in the best case degrade analytical performance. For pumped nebulization, selecting a small ID pump tubing and lowering the pump rate is sufficient to reduce the uptake. However, to achieve the optimum droplet size distribution, it is recommended to operate a nebulizer close to its natural (free-aspiration) uptake rate. A low uptake MicroMist nebulizer will provide the optimum performance in this situation. The operator can choose from 50 uL/min to 600 uL/min, depending upon the sample volatility.

In some cases, it may be desirable to free-aspirate the sample and eliminate the pump tubing. Reasons for doing this could include:

• Interaction of the sample with the tubing material.
• A risk of contamination for ultra-trace determinations.
• A need to reduce carryover and washout times.
• Difficulty of working with small ID pump tubing (See the internal standard kit in the New Product section).

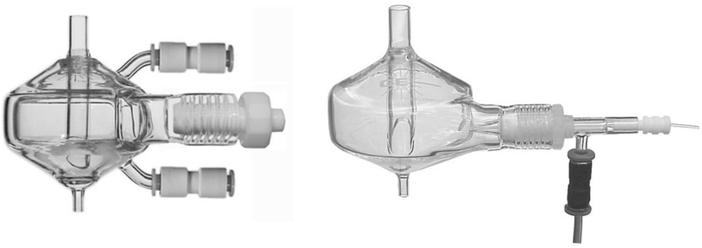
When free-aspiration is chosen, note that the nominal uptake rates of the MicroMist nebulizers are specified for aqueous samples and may differ for non-aqueous samples. In the case of volatile solvents which are also low in density and viscosity, the uptake rates achieved will be significantly higher than those specified. The uptake rate for each nebulizer model is determined by a combination of nebulizer design and the sample uptake capillary ID and length. The smallest ID capillary normally utilized is 0.25mm (P/N EZT-025) for the 50 and 100 uL/min configurations. For volatile samples, smaller ID EzyFit connectors are available with 0.18 (P/N EZT-16-18), 0.13 (P/N EZT-16-13), or 0.07 (P/N EZT-16-07) mm ID.

MicroMist Concentric Glass Nebulizer with EzyFit sample connector and EzyLok argon connector.

Spray Chamber

The preferred spray chamber for this application is either the Twister or Twinnabar cyclonic spray chamber. These spray chambers each have a central baffle that prevents large solvent droplets from reaching the torch. The major difference between the Twister and the Twinnabar is in internal volume; the Twister has 50mL while the Twinnabar has 20mL. The Twinnabar is preferred for use with the MicroMist nebulizers to minimize washout times. Both spray chambers feature the Helix o-ring-free nebulizer fitting. The absence of o-rings is particularly beneficial for organic solvents, many of which affect the o-ring material, causing it to either swell or become dried.

Even when using low-flow nebulizers, the solvent load on the plasma may be too great and cause the torch to extinguish. In this case, a jacketed spray chamber (as shown below) and an external chiller are recommended. The purpose of the chiller is to reduce the volatility of the solvent to an acceptable level.



Jacketed Twister and Twister Cyclonic Spray Chambers with Helix Fitting.

Torch & Injector

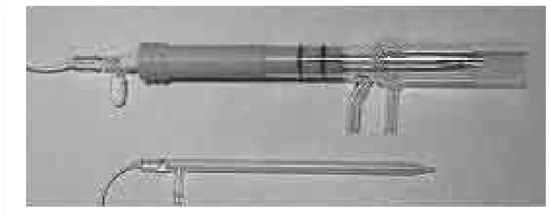
As with other organic solvent applications, a smaller bore injector is recommended - typically 1.0 to 1.2mm. This will decrease the loading of the plasma by the energy-absorbing organic solvent. In addition, it has been found that a capillary bore injector takes longer to show signs of carbon build-up than a tapered bore injector.

Pump Tubing

The pump tubing that accommodates the widest variety of organic solvents is made from Tygon MH. This tubing material has been specially designed to stand up to solvents that have traditionally been difficult to deal with, including MEK, MIBK and acetone. This tubing is available in a number of ID sizes with either 2 tabs (P/N's ending with "MH") or 3 tabs (P/N's ending with "MH3").

DETERMINATION OF VOLATILE ANALYTES IN A VOLATILE MATRIX

In order to direct volatile analytes into the plasma rather than down the drain, it is sometimes advisable to use a direct injection nebulizer such as the Glass Expansion Vulkan system. The Vulkan combines the nebulizer and the torch injector and eliminates the spray chamber. The nebulizer/injector is designed to provide an uptake rate of 50uL/min. In most cases, a specially modified torch is required. These systems are available for most ICP and ICP-MS models and an example is shown below.



The Vulkan In-Torch Nebulizer System

SWITCHING TO AQUEOUS

Because the solvents to which the sample introduction system has been exposed are volatile, switching to aqueous solvents should not require any significant cleaning. However, to switch back to the organic solvent, the sample introduction system should be rinsed with acetone and allowed to dry.

ANALYSIS OF ACTIVE PHARMACEUTICAL INGREDIENTS (API)

The information in this section was contributed by one of our readers, Jeffrey Weber, of Pfizer Global Manufacturing in Kalamazoo, Michigan. Although many of these compounds require an acid digestion prior to presentation to the ICP-AES, Jeffrey has found a way to avoid this time consuming step for ~30% of the samples analyzed. For this application, the sample introduction system is fairly straight forward, because the sample matrix is treated like an aqueous sample analysis. Dissolution of the API is accomplished with dimethyl formamide (DMF). It is necessary to mix the DMF with a dilute acid in the proper proportion - too dilute will result in incomplete dissolution and too concentrated will degrade pump tubing and o-rings. Experimentally, the proper ratio was found to be 80% DMF to 20% dilute acid (1 - 2% hydrochloric or nitric).
A typical sample preparation is as follows:
1. Add 25 mL of the 80% DMF solution to 0.5g of sample and mix well.
2. Allow 5 minutes at room temperature for complete dissolution.

3. Standards and blanks are prepared from the same 80/20 DMF/0.1M acid solution.

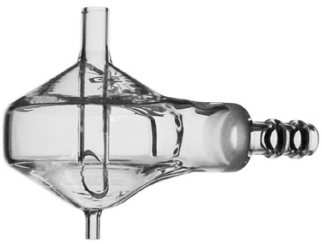
Although this matrix runs like an aqueous sample, its transport efficiency is much greater than water. The nebulization appears to be more of a fog than a mist. For this reason, it is necessary to reduce the volume of sample reaching the plasma so that excessive plasma loading does not occur. Jeffrey uses a Scott style spray chamber in combination with a SeaSpray nebulizer. An uptake rate of 0.5mL/min is used along with a standard torch with a 2.5mm injector. To achieve faster washout and high precision, a cyclonic spray chamber and a MicroMist nebulizer (0.2mL/min) would be a viable alternative. All other conditions are the same as for standard aqueous samples.

PRODUCT DESIGN FOCUS

The Helix

The interface between the nebulizer and the spray chamber in an ICP spectrometer needs to fulfill several criteria:
1. Seal the spray chamber from the external environment
2. Ensure that the nebulizer is always in the same position
3. Allow the nebulizer to be easily removed to be cleaned or replaced
4. Not contaminate the sample
5. Minimise carryover from one sample to the next

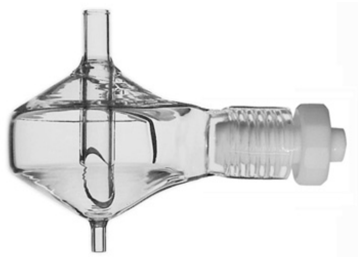
With early spray chambers, an attempt was made to satisfy these criteria by constructing the spray chamber with a glass arm containing grooves for o-rings as shown below:



While this design was generally satisfactory, there was a tendency for the o-rings to bond to the glass nebulizer. If this happened, the nebulizer could be difficult to remove, and it was not uncommon for operators to break either the spray chamber arm or the nebulizer.

The introduction of the plastic nebulizer adaptor, as shown below, made the spray chamber much more robust and alleviated the problem of the spray chamber arm being broken. However, this design still used o-rings, and the problem of the o-rings bonding to the nebulizer remained. Also, there is no o-ring material that is impervious to all of the solvents used with an ICP. In particular, some organic solvents cause the o-rings to degrade rapidly, leading to potential contamination and necessitating frequent o-ring replacement.

The new Helix, shown below, eliminates all of the problems with the older designs. A smooth lock and release mechanism enables the nebulizer to be simply and easily inserted or removed. The Helix is made from Teflon, which is totally inert to all of the organic solvents and strong acids normally used in ICP analyses. This minimizes any possibility of contamination and the Helix is expected to last indefinitely. It also eliminates dead volume around the nebulizer seal, leading to faster washout times and higher sample throughput.



Contact enquiries@geicp.com for information about a spray chamber with Helix for your ICP.

NEW PRODUCTS

INTERNAL STANDARD KITS
Internal standards are often used to improve stability. The internal standardization process involves the addition of a known concentration of a particular element to every sample. This can be a very time-consuming procedure. The new Glass Expansion Internal Standard Kit allows the internal standard to be automatically mixed with each sample during sample introduction, thus saving considerable sample preparation time. We can also supply packs of special peristaltic pump tubing with flared ends to facilitate easy connection to the sample tubing.

SAPPHIRE AND PLATINUM INJECTORS
Glass Expansion offers a wide range of injectors for both

Semi Demountable and Fully Demountable Torches. Quartz is usually used for normal aqueous or organic samples and, for routine analysis of samples in HF, an alumina ceramic injector is the lowest cost option. However, for the most demanding ultra-trace analyses where highest purity components and lowest background are required, sapphire and platinum injectors are recommended. Sapphire or platinum injectors are also necessary for low level Si or Al determinations. Glass Expansion sapphire and platinum injectors are available in a range of bore sizes to suit specific applications.

HINTS FOR THE OPERATOR

Care and maintenance of RF Coils

The RF coil is a key link in the delivery of power from the RF generator to the plasma and it is important that it is well maintained. Any degradation of the coil will reduce the efficiency of power transfer, causing stress to the RF generator components and/or reduced analytical signal. Copper, silver and gold are used as coil materials because they have high conductivity. Most coils are constructed from copper tubing which is often plated with gold or silver. Because of their high conductivity, these materials enable power to be delivered efficiently to the plasma. However, their oxides do not have the same high conductivity. So if the coil is oxidized or corroded, then the conductivity is reduced and the efficiency of power transfer is also reduced.

It is therefore essential that the coil be kept clean. Gold is the most corrosion-resistant material, followed by silver and then copper. In some situations, copper may be oxidized quite quickly, leading to possible arcing between turns of the coil and reduced energy transfer to the plasma. For this reason, gold-plated or silver-plated coils are usually preferred. However, due to the harsh environment in an ICP torch box, even gold will be corroded in time. Any coil should be inspected regularly and cleaned whenever it shows discoloration. A metal polish should be used for gold-plated coils and a tarnish remover for silver-plated coils. It is important not to over-polish a gold-plated or silver-plated coil since the plating will wear off in time and the coil will then need to be replaced.

Regular cleaning will extend the life of the coil, ensure that the RF power system is always operating at optimum efficiency, and produce a more consistent plasma. This in turn will lead to better analytical results. When the coil becomes so worn that it cannot be effectively cleaned, it is important that it is replaced so that the RF generator is not placed under stress and is able to maintain optimum power in the plasma.

INSTRUMENT NEWS

FROM AGILENT

Agilent Technologies has introduced a new version (rev. B.03) of the 7500 ICP-MS ChemStation software with enhanced user interface and additional functions. The new version enables up to 15 user-defined tuning masses and mass ratios on the tuning screen. It allows the user to monitor sensitivity, oxides, doubly-charged ions, background and interferences, all at the same time. The new intelligent rinse function improves throughput and minimizes the possibility of carry-over from an unusually high sample. The calibration user interface has been significantly simplified and improved. Enhanced semiquant includes isotopes previously unavailable to semiquant analysis due to interferences. This new feature is beneficial and very powerful when using the He mode with the ORS system. The data archival functions and new diagnostic and support tools have also been added to this version. More information about the Agilent 7500 Series ICP-MS can be found at www.agilent.com/chem/icpms.

FROM THERMO

New ICP-MS Instrument Coupling Packages for Elemental Speciation Analysis.

Metal speciation is increasingly important in a wide range of analytical areas. It is recognized that the determination of the chemical form of metals within bio-medical, environmental, nutritional, industrial, and geochemical samples is essential for the correct evaluation of their beneficial or toxic affects and hence their potential impact on the environment and mankind. To advance this vital discipline, Thermo Electron Corporation has developed Speciation Coupling Packs for the X Series ICP-MS which provide integration of ICP-MS with HPLC (Finnigan™ Surveyor™ or Finnigan SpectraSYSTEM™) and GC (Finnigan FOCUS™ or Finnigan TRACE™) instrumentation. The simple instrument coupling and intelligent software facilitate high sample throughput and the automation of quantitative element speciation analysis. Furthermore, rapid and simple interchangeability between ICP-MS, GC-ICP-MS and HPLC-ICP-MS configurations is achievable with the open sample introduction architecture of the X Series ICP-MS. For more information on the X Series ICP-MS coupling packages, visit www.thermo.com/elemental.

Iris Intrepid II - Setting new standards for ICP performance.

Thermo Electron Corporation now offers improved performance with its next generation XDL and XSP ICP spectrometer – the Iris Intrepid II. The instrument increases sensitivity and extends detection limits beyond those previously achievable with much shorter integration times, resulting in reduced analysis times, less gas consumption and lower cost of ownership. The Iris Intrepid II benefits from three major enhancements which make the instrument unique on the market:

- Based on the rugged and well proven optical design of the Iris family of instruments, the Iris Intrepid II features an ultra temperature stabilized optical tank with new high efficiency components to improve energy throughput.
- The patented Charge Injection Device (CID) detector has been updated to use the enhanced 38API chip, which is chemically etched to improve sensitivity and has optimized pixel structure with lower read noise. The result is a detector with unparalleled sensitivity and signal to noise ratio.
- The plasma source has a dual compensation RF and plate current control with directly coupled autotune impedance control. Together with mass flow gas control this ensures that a robust and stable plasma is achieved even with the most difficult of sample matrices.

For more information about the Iris Intrepid II, please email analyze@thermo.com

GLASS EXPANSION NEWS

ONLINE PRICE LIST AND SHOP

We have recently upgraded our website (www.geicp.com) to make it even easier for you to get prices or place orders. The product range available online includes nebulizers, spray chambers, torches, RF coils, ICP-MS cones, accessories and consumables. Products are listed by instrument model, and over 70 current and past models from all of the major manufacturers are covered. Even if you do not wish to order online, you may still get access to the current Glass Expansion prices through the website.

NEW 2004 CATALOGUE

If you do not yet have your own copy of the new 2004 Glass Expansion catalogue, please send your mailing address to enquiries@geicp.com and we will rush a copy to you.