# GLASS EXPANSION NEWSLETTER

Quality By Design

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# APPLICATION SPOTLIGHT

## Determination of Impurities in Metal Alloys

### INTRODUCTION

The determination of trace impurities in metals and metal alloys presents unique challenges to the ICP analyst. A host of interferences must be properly dealt with to achieve the desirable accuracy and precision, both of which may be crucial. Examples of this application include the following:

- Precious metal assays – Currency mints all over the world are understandably concerned with the purity of the gold and silver used to mint coin. For years, mint analysts relied upon the fire assay method to quantitate precious metals. This is in essence a gravimetric method which follows the separation and conglomeration of impurities. Today, both ICP-OES and ICP-MS have been successfully employed to facilitate the production of higher purity precious metals.
- Stainless steel analyses – There are numerous types and grades of stainless steel, each of which has its own unique set of properties that make it the preferred material for certain applications. The properties are determined by the precise concentrations of alloying metals that are mixed with iron during the smelting process. In addition, the alloying metals are expensive, so manufacturers need to meet their specifications while minimizing the use of these components. In this case, the analyst must precisely measure the added elements as well as quantitate the total impurities present.

Solid sample analyses are viable alternatives to ICP analyses and indeed can be combined with this technique in the form of laser ablation and spark ablation sampling. A major challenge of these approaches is to locate solid standards that closely match the sample and are accurately certified. This paper focuses on solution analyses.

### CHALLENGES

Starting with the solid sample and working toward the final result, there are a number of potential stumbling blocks.

*Sample Preparation*

A large enough sample must be used to be representative of the sample as a whole. On the other hand, the larger samples are more difficult to dissolve. Contamination of the metal sample by the tool used to cut or grind is also a concern. Although reference materials produced by organizations such as the US National Institute of Standards and Technology (NIST) are prepared in filings that are designed for easy sampling, real world samples may not be so accommodating. Typical sample weights range from 0.1 to 1.0gram and require an analytical balance capable of weighing to 4 decimal places. Static electricity can cause errors (as well as present a nuisance factor) and should be minimized if necessary with anti-static devices which are readily available.

Volumes have been written on the dissolution of various metal alloys and a rigorous discussion is not practical here. Both hot plate and microwave methods are commonly used. Some concerns during the dissolution process are as follows:

- Choosing the proper acids and proportions to achieve total dissolution.
  - A common solvent for precious metals is *aqua regia*, a solution of nitric and hydrochloric acids (typically 1:3 or 1:4).
  - Many alloys require the addition of hydrofluoric acid to achieve complete dissolution.
  - In some cases, the addition of strong oxidizers such as perchloric acid and hydrogen peroxide are necessary particularly if significant carbon is present.
- Microwave digestions can usually speed the dissolution and, due to the combination of high temperature and pressure, facilitate the dissolution of very refractory metals. Due to size and pressure limitations, sample size is usually limited to 0.3 to 0.5grams.

• In the end, the sample typically exists as a 0.5 to 2.0% solution of the metal. This solution should be clear with no precipitates. A cloudy solution indicates incomplete dissolution.

*Standard Preparation*

Matrix matching techniques are commonly employed for the determination of impurities in metals and metal alloys. The major constituent or constituents are well characterized. Preparing calibration standards with the same concentrations of the major elements as in the sample is an excellent way to eliminate many spectral and matrix interferences. However, it may also be a good idea to use an internal standard to compensate for variations in the resultant acid concentrations from the sample preparation process. This can easily be achieved in ICP-OES without the addition of a separate element by using a very weak line of a major constituent. For ICP-MS, in-line addition of the internal standard is the recommended method for matrix variation compensation. Careful selection of appropriate analyte lines or masses is quite challenging due to the complexity of the matrix. For ICP-OES, an iron matrix which is present at 1% (10,000ppm) results in spectral lines that cover the entire analytical region. A spectrometer that has full wavelength coverage and allows the selection of a wide range of lines for each analyte will be advantageous. Background correction points must also be carefully chosen to accurately subtract even sloping baselines. For ICP-MS, the high matrix creates a multitude of isobaric interferences which must be considered in the selection of the proper analyte isotope to monitor. The use of a reaction cell and isobaric correction factors may still be required when only very low abundance isotopes of the analyte are interference free.

*Sample Introduction*

The presence of high concentrations of total dissolved salts (TDS) and corrosive acids such as hydrofluoric (HF) require that the proper sample introduction components be employed.

• **Torch:** The presence of metal salts will hasten the devitrification of the quartz outer tube in particular. To lessen the financial impact of deteriorating outer tubes, a fully demountable torch is recommended, in which case the outer tube can be easily replaced without disposing of the whole torch. An example of such a torch is shown below.

*Figure 1. Varian ABC Fully Demountable Torch*

• **Argon Humidifier:** Although sample solutions generally do not exceed 2% dissolved solids, many of the metal salts may have a relatively low dissociation constant, and therefore may be prone to salting out at the tip of the nebulizer or injector tube. The Capricorn argon humidifier shown below has a bypass switch which allows you to turn off argon humidification as needed by flipping a switch; there is no need to disconnect lines when humidification is not required.


*Figure 2. Capricorn Argon Humidifier with Bypass*

• **Injector:** An injector tube is needed which will stand up to both the high dissolved solids and the presence of hydrofluoric acid. For this, a wide bore alumina injector is recommended.

• **Nebulizer:** An OpalMist nebulizer shown below is made of inert PFA and is designed to tolerate up to 20% TDS. Since it is also a self-aspirating nebulizer, the pulsations from the peristaltic pump are damped, resulting in tight precision.

*Figure 3. OpalMist Nebulizer*

• **Spray Chamber:** An inert Tracey cyclonic spray chamber (shown below) will provide excellent precision and sample transport and yet is unaffected by metal salts and HF. We recommend a PTFE inert chamber for OES applications and a high purity PFA chamber for MS applications.

*Figure 4. Inert Tracey PFA44 Cyclonic Spray Chamber*

• **In-Line Internal Standard:** For ICP-MS, the in-line addition of the internal standard solution is an excellent means of compensating for variations in acid composition which can result in physical interferences. The Trident™ in-line addition kit shown below combines a rugged tee with an efficient mixing chamber and a totally modular design.

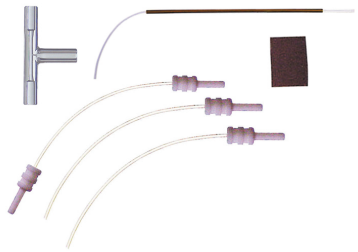

*Figure 5. Glass Expansion In-Line Internal Standard Kit*

• **Pump Tubing:** Inexpensive PVC tubing will stand up to the corrosive metal solutions and is therefore recommended for this application. If using in-line addition of an internal standard, flared-end tubing will facilitate the insertion of the internal standard capillary tubing into the small ID internal standard pump tubing.

**CONCLUSIONS**

The determination of impurities in metals requires a host of considerations not normally applied to other applications. The successful analysis is one where the complete process has been considered, from sample selection to standardization to sample introduction. Although these samples in solution present challenges to the analyst, proper selection of wavelengths or masses coupled with an appropriate combination of sample introduction components will dramatically improve the analysis.

# NEW PRODUCTS

**NEW RF COILS FOR AGILENT, HORIBA JOBIN YVON AND THERMO MODELS**

Glass Expansion has expanded its range of RF coils to include coils for the Agilent 7500, Horiba Jobin Yvon models, Thermo iCAP 6000 series and Thermo Iris Radial. These coils are available with silver or gold plating, with silver giving the most efficient energy transfer but gold being more resistant to corrosion. The coils for the Thermo models also have a Teflon coating to help protect against corrosion. Each coil is supplied on a plastic former, ensuring correct dimensions are maintained during transport and simplifying installation. A re-usable installation kit, which includes instructions on CD-ROM, is also available.

Glass Expansion RF coils are also available for Varian, Perkin Elmer and other Thermo models. For details on our full range of RF coils, check our website at: www.geicp.com/cgi-bin/site/wrapper.pl?c1=Products_coils

*Figure 6. RF Coil for Agilent 7500*

*Figure 7. RF Coil for Horiba Jobin Yvon*

*Figure 8. RF Coil for Thermo iCAP 6000*

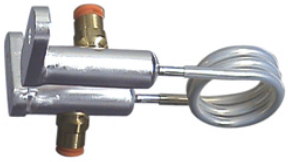

*Figure 9. RF Coil for Thermo Iris Radial*

# INSTRUMENT NEWS

**FROM HORIBA JOBIN YVON:**

**OPTIMIZING MULTI-LINE ANALYSIS IN ICP-AES FOR ENHANCED RELIABILITY OF QUANTITATIVE RESULTS USING INTERACTIVE ASSISTANCE TOOLS**

The aim of any analytical system is to provide highly accurate results in quantitative analysis. HORIBA Jobin Yvon has developed tools, associated with the CCD-based ACTIVA ICP-AES, to emphasize the use of multi-line analysis. Besides an efficient use of the information emitted by the ICP, i.e. 165-800nm spectra, the use of several lines per element allows the analyst to verify possible outliers due to unexpected interferences, provided that dedicated tools are present to facilitate the task of the analyst. Multi-line selection is facilitated by the MASTER (Multi-line Analysis, Selection Tool for Enhanced Reliability), based on a proprietary ICP-based spectra database. The database is used through a filtering procedure to select lines with appropriate sensitivity and no spectral interferences. An interactive display procedure combines single-element spectra as a function of the expected composition of the sample, allowing for a final validation of both lines and positions of background

correction. Once concentration measurements for each line have been obtained, the SOS (Statistics for Outliers Survey) tool verifies possible outliers from an ANOVA-based statistical test. A reliable, single concentration per element is given.

**FROM SPECTRO:**
**NEW SMART ANALYZER VISION ICP-OES SOFTWARE OFFERS IMPROVED AUTOMATION AND EASIER OPERATION**
Newly ordered SPECTRO CIROS VISION and SPECTRO GENESIS ICP-OES spectrometers now include the latest version of Smart Analyzer Vision analytical software. The current release of the Smart Analyzer Vision software, first introduced in 2003, now has added functions for unattended laboratory operation. The latest version of the software also is equipped with a proprietary spectra-based background correction for extremely high measurement accuracy.

1,000 Samples per Day without Supervision: SPECTRO's software development team added two important capabilities to the Smart Analyzer Vision software that comprehensively automates sample processing. It is now possible to assign any number of methods to an automated test series, and the software is now equipped with event-controlled control logic.

New Correction Extension for Improved Results: Other highlights of the new Smart Analyzer Vision software include a proprietary "Smart Background Correction," a spectra-based background correction that easily corrects elemental and molecular interferences and structured backgrounds, and "Intelligent Rinse/Move" functions for control of the autosampler. "Intelligent Rinse" monitors and controls the rinsing procedure between every measurement based on the concentrations. "Intelligent Move" optimizes the movements of the autosampler. This prevents carry-over effects and dramatically reduces sample throughput times.

**FROM TELEDYNE LEEMAN:**
**NEW TECHNICAL NOTE ON TIME RESOLVED ANALYSIS**
The ability to acquire elemental data on an intensity versus time basis, sometimes called Time Resolved Analysis, is important to many applications. Two of the more prominent applications include element specific chromatographic separations and spatially resolved laser ablation experiments (e.g., depth profiling and/or linear traverses across a sample). Teledyne Leeman Labs' technical note T1006, *"Time Resolved Analysis with the Prodigy ICP Spectrometer"* provides an overview of the time resolved data acquisition capabilities of the Prodigy High Dispersion ICP.

To receive a copy of this technical note, email: LeemanLabsinfo@Teledyne.com or visit our website at www.LeemanLabs.com

**FROM THERMO:**
**THERMO'S iCAP 6000 SERIES ICP EMISSION SPECTROMETER WINS GOLD INSTRUMENT BUSINESS OUTLOOK INDUSTRIAL DESIGN AWARD**
Thermo Electron Corporation, world leader in analytical instrumentation, announces that its iCAP 6000 Series of ICP emission spectrometers has won the Gold Award at the Instrument Business Outlook (IBO) Design Awards 2006. The IBO award is for excellence in industrial design of analytical and life science instruments, portable analytical instruments and laboratory equipment. Each year, IBO honors those instruments that demonstrate the most original, functional and user-friendly industrial design, thus being aesthetically appealing while enhancing the end-user's experience. Specifically suited to the needs of general and elemental analysis laboratories in the environmental, petrochemical, metal, food and beverage, geo chemical and cement industries, Thermo's iCAP 6000 Series features the most compact ICP emission spectrometers available on the market.

With bench space being at a premium in today's modern laboratories, a small instrument footprint is of utmost importance, making transportation and installation far simpler and easier. Thermo's iCAP 6000 Series features an advanced, high efficiency, close coupled optical design with orthogonal fore optics, which increases the amount of light reaching the detector. Additionally, the ergonomic design of a large 270° door allows unrestricted access to a large sample compartment and peristaltic pump, while the inner enclosure has a large viewing window for convenient observation of the plasma. For more information on Thermo's new iCAP 6000 Series of ICP emission spectrometers, please e-mail analyze@thermo.com or visit www.thermo.com/elemental

# HINTS FOR THE OPERATOR

## Running Samples Containing High Levels of Dissolved Solids

Samples containing high concentrations of dissolved salts require thoughtful optimisation of the sample introduction system. Salts can cause interferences and can also be deposited in the sample flow path, causing blockages in the narrow channels of the nebulizer or injector and accelerating devitrification of the torch. Some of the issues that need to be considered are as follows:

**Dilution:** Minimise the salt concentration by diluting the samples as much as possible while maintaining the analytes at sufficiently high concentration for accurate analysis. If analyte concentrations are low, the scope for dilution may be severely limited.

**Rinse:** Always rinse between samples and aspirate the rinse solution for several minutes at the end of a run. Always have a rinse solution aspirating whenever the plasma is on and samples are not being analysed. Keep the time when there is no solution aspirating to an absolute minimum. This is when the sample can dry out and leave salt deposits. Once salt deposits start to form, they act as a seed for further deposits. The Niagara Rapid Rinse Accessory helps in this regard, since it switches immediately to rinse as soon as the sample measurement is completed.

**Nebulizer:** Concentric nebulizers have traditionally been associated with blockage problems when running high salt solutions. However, the Glass Expansion SeaSpray concentric glass nebulizer and OpalMist PFA concentric nebulizer have both been designed to accommodate high levels of dissolved solids without clogging. For example, both of these nebulizers can routinely handle up to 20% NaCl solutions. However, they are still susceptible to blockage by particulates. If the samples contain particulates as well as dissolved solids, the Quartz VeeSpray or Ceramic VeeSpray nebulizers are recommended.

Regular nebulizer maintenance is important to prevent salt build-up. If the nebulizer's sample capillary becomes blocked, use the Eluo nebulizer cleaning tool to clean it. If there are salt deposits that cannot be removed with the Eluo, we recommend soaking the tip of the nebulizer in a 25% solution of Fluka RBS-25 or similar surfactant. It should be soaked for 24 hours and then flushed with warm water using the Eluo. After a few flushes with warm water it can then be flushed with methanol so that it will dry faster.

**Spray Chamber:** The Tracey cyclonic spray chamber is recommended. The excellent sensitivity obtained with this spray chamber means that the highest possible dilution can be used. This spray chamber also has a very efficient rinse mechanism so that there is no carry-over between samples. The Helix nebulizer interface virtually eliminates all dead volume to further enhance the rinse process.

**Torch:** The two potential problem areas are the injector and the outer tube. Salts can be deposited in a narrow-bore injector, impeding sample flow and eventually blocking it.

This problem can be minimized by choosing wide-bore and/or capillary injectors. The salts are normally deposited at the point where the bore of a tapered injector narrows. Capillary injectors have parallel sides and no taper, so this problem is significantly reduced.

With high TDS samples, it is common to get salt deposits near the end of the outer tube. Salt deposits accelerate devitrification of the quartz, leading to a significant reduction in torch life. This problem can be tackled as follows:

- The length of the outer tube can be reduced. Although this leads to some signal loss, the torch lifetime is improved.
- The quartz outer tube can be replaced with a ceramic tube that does not suffer from devitrification.

The fully demountable torch offers significant benefits for high TDS applications. It allows different injectors and outer tubes to be used. And, if the lifetime of the components cannot be improved, it provides a significant reduction in replacement cost.

**Argon Humidifier:** An argon humidifier helps prevent salt deposits in the sample introduction system. When the argon supply to the nebulizer is saturated with water, it is much less likely to cause droplets to dry out and leave salt deposits. The Capricorn argon humidifier is suitable for use with all ICP models.

**Internal Standard:** High TDS levels can cause interferences and an internal standard is often used to correct for them. The Trident internal standard kit is available with either glass or HF-resistant mixing t-piece.

**Advice:** If you need any advice about running samples with high levels of dissolved solids please send an email to enquiries@geicp.com. Our ICP experts will be happy to assist you.