NEWS

Glass Expansion Newsletter | February 2014 | Issue 33

APPLICATION SPOTLIGHT

TROUBLESHOOTING GUIDE FOR ICP OPTICAL EMISSION SPECTROMETERS

Introduction

In this report, we will examine the causes and corrections for five common problems that can arise for ICP optical spectrometers as follows:

- Poor precision
- Carryover
- Drift
- Degraded detection limits
- Inaccuracy

The order of these is important in that each problem can only be addressed once all characteristics above it have been resolved. For example, inaccuracy issues can only be addressed when the instrument is demonstrating acceptable short-term precision and carryover, negligible drift and adequate limits of detection. Precision is the first peel of the onion and must always be optimized first.

To facilitate troubleshooting, you should have periodically generated data (control charts) that gauge an appropriate selection of criteria for each spectrometer. This will make it easier to find the cause when something goes wrong and these will be detailed below.

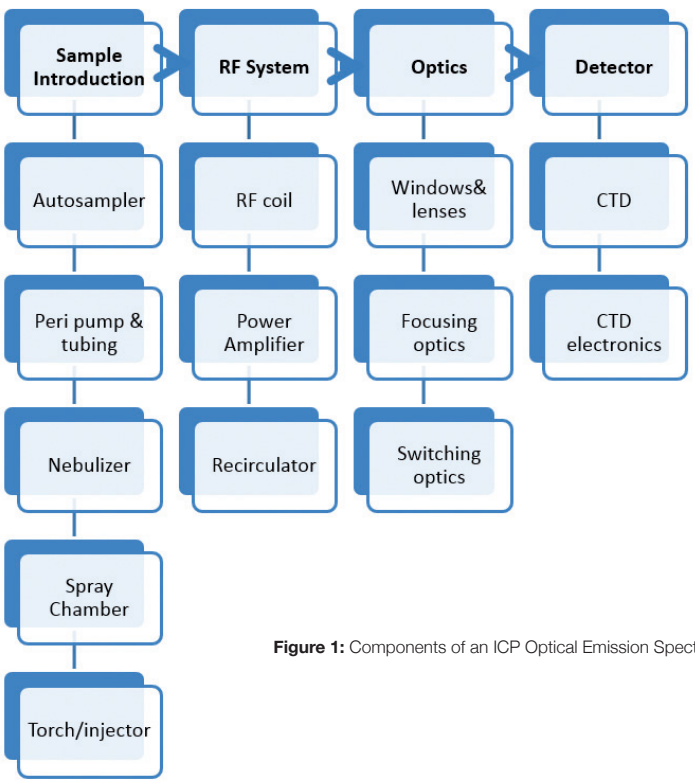

Figure 1: Components of an ICP Optical Emission Spectrometer

GE NEWS

Pittcon 2014

A wide selection of Glass Expansion products will be on display at Pittcon 2014, Chicago, Illinois, USA, March 2 - 6, 2014. The display will include nebulizers, spray chambers, torches, RF coils, ICP-MS cones and accessories. You will also be able to see a demonstration of the new Assist CM and Niagara Plus CM enhanced productivity systems. 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 2253.

PITTCON 2014 CONFERENCE & EXPO

Videos

We have compiled informative videos on:

Nebulizer cleaning

Assembly of nebulizer and spray chamber

D-Torch assembly

Niagara Plus CM

Assist CM

These can be viewed at:

www.youtube.com/user/RGBgeicp/videos

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GE GLASS EXPANSION
Quality By Design

The components of an ICP optical spectrometer are shown in Figure 1. Since the sample comes in contact only with the sample introduction system and only photons come into contact with the spectrometer and detector (unlike an ICP-MS), the majority of maintenance is required for the sample introduction system and that is the first place to look when troubleshooting. Poussel, Mermet, and Samuel developed a number of diagnostic tests to isolate the cause of a problem[1]. A combination of only three elements is needed to perform all tests and multi-element stock solutions with these elements are commercially available. Although these tests were designed to test sequential photomultiplier (PMT) based spectrometers, many are applicable to today's charge transfer device (CTD) based systems (see Table I). Due to differences in CTD's, these tests are useful to make intra-instrument, but not inter-instrument, comparisons. Therefore, these tests should be implemented regularly and the results stored and preferably graphed for each spectrometer.

Test	Measurement	PMT Component	CTD Component
Ba II 233nm line profile	UV resolution	Dispersive system	Camera
Ba II 455nm line profile	VIS resolution	Dispersive system	Camera
Mg II 280/Mg I 285	Atomization/ionization	Generator	Generator
Ar I 404nm intensity	Light Absorption	Collimation/detector	Camera
BKG 400nm/BKG200nm	Lens/Mirror degradation	Optics	Optics
SBR Mg I 285nm	Transport efficiency	Nebulizer/Spray Chamber	Nebulizer/Spray Chamber
RSD Mg I 285nm	Nebulizer precision	Nebulizer/Spray Chamber	Nebulizer/Spray Chamber
SD BKG at 190nm	Background noise	Detector	Camera
SD BKG Plasma off	Detector noise	Detector	Camera
RSD Ar I 404nm	Drift	Generator Stability	Generator Stability

Table 1: Diagnostic Tests for ICP Optical Spectrometers

The magnesium ion line to atom line ratio is a popular test to measure the robustness of the plasma. Low results can cause reduced intensities and greater interferences. Significant changes in the four tests listed directly underneath this test are significant only if the Mg II/Mg I test results have not changed materially.

Poor Precision

This is determined by first performing the Mg I 285 RSD test in Table I. If poor precision is indicated, you can glean more details by analyzing a high multi-element standard (containing the elements in your method) with at least 3 replicates. You should achieve less than 1% RSD for all lines measured, assuming that you have selected lines and concentrations that have sufficient intensities. As mentioned above, if you have a control chart for the performance of that standard and can determine that the precision is significantly poorer than the historical average, then even 1% RSD may be indicative of a precision problem. The first thing you should do is to look carefully at the data. The problem is most likely **not** in the sample introduction system if the answer to any of the questions below is affirmative.

- If the spectrometer is a dual view model, is there a difference between the axially and radially viewed lines in terms of precision? If yes, then before calling for service, make sure that all accessible optics used in the troubled view have been thoroughly cleaned.
- If the CTD uses a different exposure for high and low wavelengths, is there a difference in precision between the two regions? If yes, the problem points to the switching optics or dispersive system. Use the two barium tests in Table I to confirm.
- Is there a significant difference in performance between atom and ion lines? If yes, the problem points to the RF system. Ion lines are typically more sensitive to RF fluctuations. Use the Mg II/Mg I test to confirm. Examine the condition of the load coil and replace if necessary. Glass Expansion offers an **RF coil installation kit** to ensure proper installation and correct alignment each time you install a new RF coil. A full line of copper, gold, and Teflon coated silver **RF coils** are available from Glass Expansion.
- Is the first or last reading different from the others for all lines measured simultaneously (If it is a sequential system you need to look at the first and last line measured)? If yes, the problem is likely due to improperly set stabilization and/or rinse times (see **Carryover** below).
- Is there degradation in either of the two background measurement tests (SD BKG at 190nm and SD BKG Plasma off) listed on Table I? If yes, then the detector is suspect.

If the answer to all of the above questions is no, the problem most likely resides in the sample introduction system. Figure 2 is a decision tree to take you through the above troubleshooting procedures. The procedures below are based on the assumption that the sample introduction system is suspect.

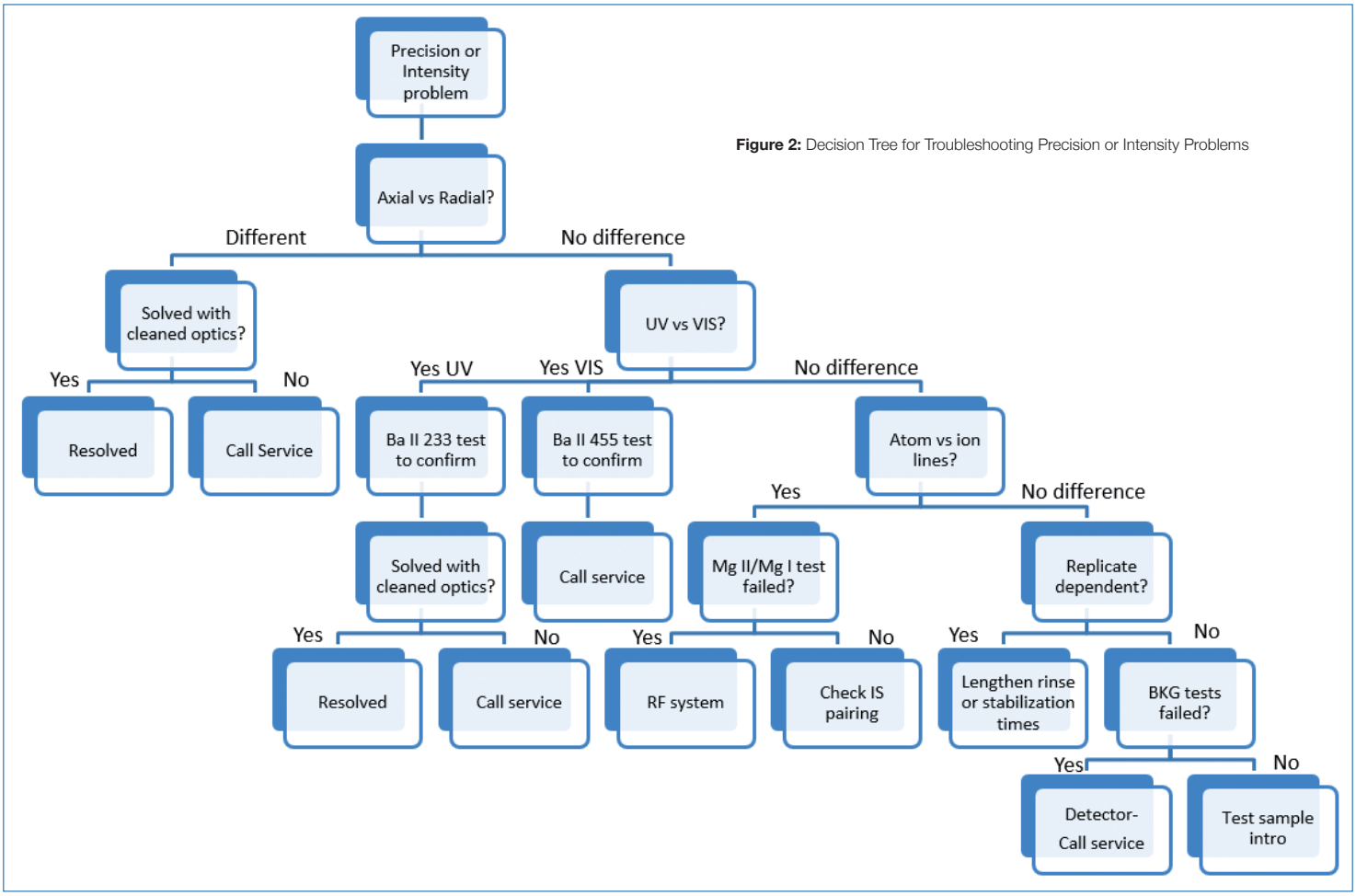


Figure 2: Decision Tree for Troubleshooting Precision or Intensity Problems

Peristaltic Pump: The first component to replace is the peristaltic pump tubing for both sample and internal standard (if applicable). Glass Expansion offers a full line of **peristaltic pump tubing**, with 2-tag, 3-tag and continuous tubing in a wide range of diameters and materials to suit most analyses. We also supply Contour™ flared-end peristaltic pump tubing to facilitate the connection between the pump tubing and the sample capillary tubing.

HINT: If using in-line addition of internal standard (IS), look at the uncorrected analyte results. If the precision looks much better without IS correction, something is wrong with the IS concentration, wavelength or pump tubing.

One visual test is to watch the flow of an air bubble in the capillary tubing to see if it is smooth. If not and you have already changed the pump tubing, optimize the tension on the pump tubing and visually inspect the pump rollers. Finally, observe the peristaltic pump for jerky movement. You can isolate the culprit faster if you have a device to accurately measure the uptake rate in real time (such as the **TruFlo Liquid Flow Monitor** from Glass Expansion). If fluctuations in uptake rate are observed, the problem is likely due to one of the following:

- Peristaltic pump
  - Worn pump tubing
  - Worn pump roller
  - Improper tension
  - Faulty pump
- Clogged nebulizer

Nebulizer: If no fluctuations in sample uptake are found, you can eliminate the peristaltic pump but not the nebulizer. Even though the nebulizer is not blocking liquid flow, it can still be the cause of imprecision. Use the Mg SBR and Mg RSD tests to determine if the problem is due to low transport efficiency or poor nebulizer precision, respectively. Sometimes you can identify a nebulizer problem visually by examining the aerosol spray; look for “spitting” or pulsations in the mist inside the spray chamber. The best way to test the nebulizer is to replace it with a new or proven nebulizer. For this reason, some labs keep a proven nebulizer handy for test purposes. If the new nebulizer solves the problem, then try to clean the questionable one. With regards to an efficient cleaning procedure, we have found that soaking the nebulizer tip (last 3-5mm) in a 25% solution of FlukaRBS25 (GE P/N FLUKA25) for 5 hours is sufficient to restore the nebulizer to its original operating condition. Thorough flushing would also be required to remove the Fluka; two flushes with warm water (60°C) and one flush with methanol using the **Glass Expansion Eluo Nebulizer Cleaning Tool** (GE P/N’s: 70-Eluo, 70-Eluo-OP, and 70-Eluo-OPD, depending on nebulizer model) was found to be sufficient. Please note you can only use the warm water with the glass nebulizers. The PFA capillary of the DuraMist, OpalMist, and PolyCon may be damaged when flushing with hot water.

For the plastic nebulizers use room temperature DI water in place of the warm water. If the nebulizer still performs poorly, it is probably damaged beyond repair. Glass Expansion also provides a service for evaluation and repair of its nebulizers, please contact us at **enquiries@geicp.com** for a return authorization form.

Spray Chamber: If replacing the nebulizer shows no improvement, look to the spray chamber. A dirty spray chamber is a common cause of degraded precision and is usually evidenced by droplet formation on the interior surface. If it is a glass or quartz chamber and you can see the droplets, proper cleaning is indicated (soak in 25% Fluka solution for 24 hours). If it is an inert PFA or PTFE chamber purchased from Glass Expansion, first soak it in the Fluka solution. If that does not improve the precision, the interior surface treatment may need refurbishing (a service provided by Glass Expansion). As described for the nebulizer, replacing with a new or proven spray chamber is a sure method to incriminate or eliminate the spray chamber. Other potential trouble spots for the spray chamber are as follows:

- Kinked or plugged drain tubing. Replace with new UniFit kit.
- Worn drain tube peristaltic pump tubing (if pumped drain). Replace pump tubing.
- Droplet buildup in the transfer tube to the torch. This is more common with axial or dual view systems where the transfer tube needs to turn 90 degrees. Clean the transfer tube with Fluka or refurbish the interior surface.

Torch: If the spray chamber is cleared, move on to the torch. The usual suspect is the torch injector, which takes the brunt of sample contact. Look for a deposit around the tip of the injector and clean if found. Other points to check are as follows:

- Injector misalignment- this is more likely with a demountable injector which may not have been re-installed concentrically.
- Torch misalignment- this possibility varies from instrument to instrument depending upon whether or not the torch is adjustable or the instrument performs an automatic alignment.
- Devitrification of the torch- exposure to salts at high temperature can cause severe devitrification of the quartz and even breakage. If observed, replace the torch (or just the outer tube if you have a demountable torch such as the **Glass Expansion D-Torch**).

Carryover

Acceptable carryover is typically considered to be 0.1%. For example, if you run a 100 ppm standard, the blank immediately following it should read less than 0.1ppm. If you need less carryover for your specific application, you will need to use a higher test standard. For example, to achieve 0.01% carryover, run a 1000ppm standard; you should read less than 0.1ppm on the subsequent blank. As mentioned above, a high first replicate can be indicative of excessive carryover. The degree of carryover is not the same for all elements. Some elements such as boron, mercury, arsenic, silver, molybdenum, and thallium are “stickier” than others. The easiest way to resolve carryover is to use a longer rinse time between samples but this adds time to the analysis, which may be undesirable. Other more productive approaches are listed below:

- Incorporate a fast flush between samples. This is programmable for most spectrometers and it allows a faster flush between samples to more efficiently and quickly flush the sample introduction system. You should note that this introduces more liquid per minute into the plasma and thus changes the load on the plasma. It therefore requires a 10 to 15 second equilibration time for the plasma to “settle” after returning to the measurement uptake rate. So you have to weigh the time saved against the equilibration time.
- Load the autosampler rinse station with a more vigorous rinse solution. Some autosamplers and software allow the use of multiple rinse solutions to more efficiently clean the system.
- Install a switching valve accessory such as the **Niagara-CM Rapid Rinse Accessory** or the **Niagara Plus-CM**. These provide a dual benefit for reducing carryover as follows:
  - Reduces the amount of time that the sample introduction system comes into contact with the sample.
  - Switches to rinse as soon as the analyte measurement is complete.
  - With the Niagara Plus, sample does not come into contact with the peristaltic pump tubing.

Drift

Most quality protocols such as the US EPA Contract Laboratory Program (CLP) have a drift specification. In that case, drift is not to exceed 10% and checks run every 10 samples must verify that. Other more demanding applications such as precious metals analysis require drift to be as small as possible. Causes of drift can include the following:

- ***Gradual deposit build-up on the nebulizer tip.*** Intuitively, one would expect this to always cause a downward drift, but there are exceptions. With spectrometers using a mass flow controller for the nebulizer gas, a decreasing nebulizer orifice will result in the same flow rate but at higher pressure, which could cause an upward drift. Also, if using an internal standard, drift may be random, depending upon the relationship of the analyte line to the internal standard line. Although you can sometimes observe the presence of a deposit with the naked eye, you may need a microscope in some cases. The solution is to clean the nebulizer in Fluka as described previously and to subsequently incorporate an argon humidifier such as the **Glass Expansion Capricorn™** to minimize future deposits. Also ensure that you have a nebulizer suited for your sample type, see the Glass Expansion June 2013 Newsletter for a helpful guide to nebulizer selection.[2]
- ***Gradual deposit build-up on the injector tip.*** With the exception of the internal standard effect, this always causes a negative drift for two reasons as follows:
  - The smaller orifice reduces the mass flow rate of sample to the plasma
  - The smaller orifice increases the pressure and hence the speed of analyte through the plasma reducing the analyte residence time.

  Similarly, the solution is to clean the injector in Fluka and incorporate an argon humidifier. Also if you are dealing with samples high in total dissolved solids (TDS), ensure that you are using a large bore injector, e.g. between 2.0 and 3.0 mm ID.

- ***Room temperature drift.*** As described in the February 2008 Glass Expansion newsletter article[3], the temperature of the room in which the spectrometer resides has a marked effect on the transport efficiency of the sample introduction system (tertiary transport). The measured effect was as much as 3% per °C change in temperature. So a temperature change of as little as 4°C can cause a failure of a CLP calibration check. If your lab suffers from temperature swings, this may be the cause of the drift. The solution is to stabilize the temperature of your spray chamber. Glass Expansion offers the **IsoMist Programmable Temperature Spray Chamber** for most ICP models to accomplish this.
- ***Faulty nebulizer gas pressure regulator or mass flow controller.*** This problem is best diagnosed by installing a digital flow meter in the nebulizer gas line. Alternatively, it is detected by the process of elimination. If suspected, call a service engineer.
- ***Power generation system.*** This includes the RF coil, the generator, and power amplifier tube (if applicable). Running the Ar I 404 tests for both RSD and intensity over 30 minutes is a good diagnostic. The most common culprit (and the least expensive to replace) is the RF coil. Visual signs of wear usually accompany a faulty coil and, as described above, replacing the coil yourself is not difficult with the Glass Expansion RF coil installation kit.
- ***Optics.*** The optical components are typically sealed, with the exception of the outer window to the spectrometer. If an optic is getting dirty gradually, you will see a downward trend in intensities which is much more severe for the UV lines. Clean all accessible optics with methanol or acetone (for magnesium fluoride windows).
- ***Detector.*** Use the SD BKG at 190nm and SD signal plasma off tests to diagnose detector issues. Call a service engineer if suspected.

Degraded Detection Limits

Since detection limits are determined by the ratio of signal to background noise, both parameters must be evaluated separately to isolate the cause of the problem. This can be done very simply with the following two tests:

- SBR Mg I 285nm for signal
- SD BKG at 190nm for noise

If it is determined to be a problem with low signal, use the decision tree in Figure 2 to isolate the cause. If it is determined to be a noise problem, check the RF system and the detector as described above.

Inaccuracy

Accuracy is probably the most important goal of an analysis but the most difficult to assess. One method is to analyze a known sample. This of course requires that you have a standard reference material (SRM) or certified reference material (CRM) that closely matches your unknown samples. The US National Institute for Science and Technology (NIST) has available a plethora of SRMs. In addition, certified reference materials (CRM) are available from other sources such as Inorganic Ventures and are traceable to NIST SRMs. Another approach is to use matrix matching for the standards but this too requires detailed knowledge of the sample. Two ways to circumvent this problem is to do recovery spikes in a representative sample or use the method of standard additions in all samples, both of which add time to the process. There are four general causes of inaccuracy as follows:

- ***Sample preparation*** – Depending upon the sample type, preparation can vary from the very simple acidification to complex acid digestion procedures or salt fusions. Potential problems include the following:
  - Contamination – This is easy to spot with the inclusion of procedure blanks; controls included in the sample preparation process in which all reagents added to the samples are added to the blank.
  - Inaccurate dilution – The inclusion of a pre-digestion sample spike is an easy way to determine dilution accuracy
  - Incomplete dissolution – Usually characterized by a cloudiness of the sample or the presence of visible particulates.
  - Loss of analyte – This is best identified by comparison of pre-digestion and post-digestion sample spikes.
- ***Physical interferences*** – These result when certain physical characteristics of the sample, such as density, viscosity, or surface tension, differ from that of the standards. Physical interferences can best be resolved by either matrix matching or internal standardization. Since accurate matrix matching is not always possible, the most common solution is internal standardization. Glass Expansion offers the **Trident In-line Reagent Addition kit** to automate the in-line addition of internal standard. For the most accurate on-line addition of internal standard, Glass Expansion's **Assist syringe-driven sample introduction system** is available. With the Assist, the internal standard is delivered by a precision syringe drive, ensuring that the ratio of internal standard to sample is accurately maintained. Any fluctuations in this ratio that may occur when the internal standard is delivered by peristaltic pump are eliminated, improving the analytical accuracy.
- ***Chemical interferences*** – Although rare in ICP optical spectrometry, chemical interferences are sometimes found when the plasma is viewed axially. One commonly recognized chemical interference is the effect of easily ionized elements (EIE) on one another. For example, varying concentrations of sodium can affect the signal for potassium. The best way to resolve this problem is a form of matrix matching called ionization suppression. By adding a high concentration of an EIE to all solutions, the interference is minimized. This can be done by adding the ionization suppressant to the internal standard solution described above.
- ***Inter-element interferences*** – Spectral overlap is the most common inter-element interference and is resolved primarily by selecting an interference-free wavelength. For most wavelengths (but not all) an inter-element interference is obvious from a scan of the suspect sample. For some metalloid elements such as As, Bi, and Se, where line selection is severely limited, inter-element correction factors can be used to compensate for the effects.

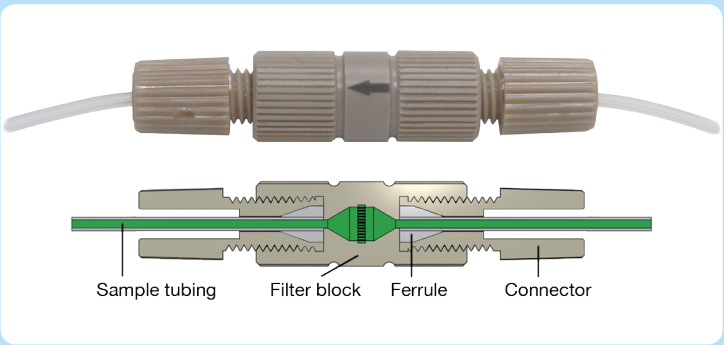
Summary

A careful methodical examination of data can greatly facilitate the isolation and resolution of a problem which has been identified on an ICP optical spectrometer. The periodic recording of specified performance data facilitates the troubleshooting process. In this report, we have identified the data which should be recorded and provided a step-by-step approach to the resolution of any of the five problems discussed.

References

1. E. Poussel, J.M. Mermet, and O. Samuel, Simple experiments for the control, evaluation, and diagnosis of Inductively Coupled Plasma Sequential Systems, Spectrochimica Acta Part B, **48**, 1993, 743-755.
2. Glass Expansion Newsletter, June, 2013, A Nebulizer Update.
3. Glass Expansion Newsletter, February, 2008, Spray Chamber Temperature: A Critical Parameter in ICP Experiments.

NEW PRODUCTS

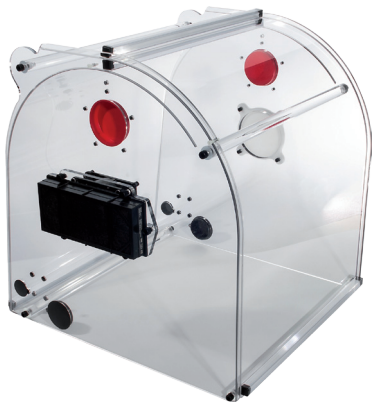


Inline Particle Filter

If there are particulates in your samples, there is a risk that they may get trapped in the fine channels of your sample line or within the nebulizer. The Inline Filter provides a simple and effective way to eliminate this risk. This filter is easily inserted in the sample tubing between the autosampler probe and the nebulizer. It incorporates a 120 micron filter and is suitable for use with 1/16 inch (1.6mm) OD sample tubing. If you require a filter for different tubing, please email Glass Expansion at **enquiries@geicp.com**.

The purpose-built clog-resistant design is ideal for ICP samples. Any particle build-up is easily removed by back-flushing and ultrasonic cleaning. And the PEEK material is suitable for use with all of the most common ICP solutions.

Part No.	Description
70-803-1108	Inline Filter for 1/16 inch Tubing



WindTunnel Autosampler Enclosure

The WindTunnel autosampler enclosure will protect your samples against airborne contaminants and also protect the operator against fumes and odours. And its versatile configuration makes it suitable for the most common laboratory situations:

Filtered positive pressure enclosure. When fitted with the optional fan and HEPA filter, the WindTunnel provides a positive pressure enclosure.

Vented enclosure. The addition of the optional flange, allows the fumes to be removed through a laboratory exhaust system (not supplied).

Dust cover. The WindTunnel can be used without the fan and filter to function as a convenient dust cover.

- Suitable for the Cetac 130, 260, 520 and 520HS autosamplers
- Shatter-proof polycarbonate construction
- Easy access through front and rear roll-up doors
- Optional fan maintains positive pressure
- Optional HEPA filter
- Optional exhaust port flange
- Multiple ports for tubing and power cords

Part No.	Description
70-803-1148	WindTunnel Autosampler Enclosure
70-803-1149	WindTunnel Fan Aus
70-803-1150	WindTunnel Fan Eur
70-803-1151	WindTunnel Fan USA
70-803-1152	WindTunnel Filter
70-803-1153	WindTunnel Flange

INSTRUMENT NEWS

From Agilent – Agilent Technologies Introduces Breakthrough ICP-MS and MP-AES Platforms

Agilent Technologies has introduced the **7900 ICP-MS** and the **4200 MP-AES**, the latest in a series of groundbreaking technologies featured in Agilent's portfolio of **spectroscopy solutions**.

The **7900 ICP-MS** features include:

- Unprecedented matrix tolerance – Ultra-high-matrix introduction technology enables laboratories to measure samples containing up to 25 percent brine.
- Enhanced trace-level detection – A new orthogonal detector system (ODS) reduces background and improves sensitivity, dramatically improving signal to noise by 10-fold.
- Redesigned **MassHunter software** features a simpler, more intuitive user interface along with powerful method automation capabilities.

The **4200 MP-AES** features a variety of unique capabilities:

- Safe and economical – Because flammable and oxidizing gas sources are not required for use, the system can be left unattended while performing overnight multi-element analysis.
- Robustness and reliability – Optimized high-performance waveguide and new torch design produces a robust nitrogen plasma.
- Advanced software platform – Newly released **MP Expert software** features advanced tools such as "FLIC" and IECs for assisting in eliminating spectral interferences.

From Spectro – New SPECTRO GENESIS ICP-OES Condition Monitoring System Offers Cost-Effective Analysis of Wear Metals in Oils

SPECTRO Analytical Instruments has introduced a condition monitoring system based on its SPECTRO GENESIS ICP-OES. The system sets new price, performance and productivity standards for condition monitoring laboratories and oil blenders. The GENESIS system swiftly, accurately, and cost-effectively assesses component wear trends by analyzing lubricating oils for the presence of metals and contaminants that may accelerate wear. This early detection allows users to prevent equipment failures and helps optimize maintenance programs.

Using the latest detector technology, the system's full-spectrum analysis covers the entire elemental range needed for additive, wear, and trace analysis of lubricating oils. In particular, it offers excellent sensitivity for critical light elements such as Na, Mg, Al, and Si, while offering high sensitivity for wear and trace elements. It also provides the speed of fully simultaneous analysis, achieving rapid sample cycle times of 90 seconds or less — independent of how many elements must be analyzed.

With a total condition monitoring package designed to ASTM and EN standards, the SPECTRO GENESIS offers a full complement of factory-installed methods and procedures, set up and ready for instant use. The package features high accuracy; excellent long-term stability; and easy, straightforward design and operation. Finally, with sturdy but lightweight (150 kg/330 lb) aluminum construction, the system fits standard laboratory benchtops.

The SPECTRO GENESIS condition monitoring system is available now, from SPECTRO dealers worldwide. For more information, visit **www.spectro.com/GENESIS**.

INSTRUMENT NEWS

From Teledyne Leeman Labs – Release of Prodigy7

Teledyne Leeman Labs, a leading manufacturer of analytical instrumentation for elemental analysis, announces the release of the Prodigy7 ICP spectrometer. The Prodigy7 reflects the combination of years of effort, a team of highly specialized engineers and application chemists to produce an ICP-OES instrument in which superior analytical performance does not have to be traded off for any reason including price. And while the Prodigy7 offers all of the advanced capabilities some laboratories require, none of them have to be purchased up front if not needed. They can be easily added later if needs change.

The Prodigy7 has distinct advantages over other ICPs:

- Large format, advanced CMOS Array Detector for true simultaneous measurement
- Full wavelength coverage from 135 nm - 1100 nm (with Halogen Detector option)
- 500 mm, Low Stray Light Optics
- Full Spectral Access (FSA) captures the entire wavelength spectrum in a single reading
- Available in Axial, Radial, and Dual-View configurations
- Twist-n-Lock, Auto-Aligning Sample Introduction System
- Compact benchtop design
- Designed for fast system startup and reduced gas consumption

For more information on this new instrument, please visit **http://web.teledyneleemanlabs.com/prodigy7**