Guidelines for Trouble Shooting and Maintenance of ICP-OES Systems

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Today’s Agilent: Atomic Spectroscopy
World’s best, most complete atomic spectroscopy portfolio!

ICP-OES
Flame AAS

ICP-MS
Graphite Furnace AAS

ICP-QQQ
4100 MP-AES
Agilent’s Atomic Spectroscopy Portfolio - Features

**Flame AA**
- Lowest price
- Single element
- DLs typically ~100’s ppb
- Fast (for 1 element)
- Good elemental coverage
- Low running cost

**MP-AES**
- Lowest running cost
- Multi element
- DLs typically single to 10’s ppb
- Faster
- Broader elemental coverage
- Lowest running cost

**Furnace AA**
- Trace levels at lowest price
- Single element
- DLs typically 10’s to 100’s ppt
- Very slow
- Limited elemental coverage
- Moderate running cost

**ICP-OES**
- Fastest measurement
- Multi element
- DLs typically single ppb
- Very fast
- Can measure most elements
- High running cost

**ICP-MS**
- Broadest coverage
- Multi element
- DLs typically single or sub-ppt
- Fast
- Can measure almost all elements
- Highest running cost
Common ICP-OES Problems Reported by Users

Sensitivity:
- Sensitivity is worse than it used to be
- I have a new application and I can’t get the sensitivity I need
- How come I can’t get the instrument to meet published detection limits?

Precision
- Sensitivity is acceptable but precision is terrible

Accuracy
- Instrument does not give the “right” results.

Poor Sample Throughput
- The instrument throughput needs to improve
- Nebulizer and/or Injector of the Torch blocks too quickly
ICP-OES Sensitivity - What Impacts This?

4 areas of the instrument can affect sensitivity:

- **Sample introduction system**
- **Method parameters**
- **Cleanliness**
- **Quality of standards used for calibration**

Remember – **SMCQ**

Or

“**System Must Create Quality**”
Sensitivity – Quality of Standards

– What concentration are they?
  • Low concentration standards have a finite life
    – Prepare ppb (ug/L) concentration standards daily from high conc. stock
    – Prepare low ppm (mg/L) concentration standards weekly

– How are they prepared?
  • Ensure purchased standards are still within “Use By” date when used
  • Use calibrated pipettes and class ‘A’ volumetric flasks for dilutions
  • Use de-ionized water (Type I - conductivity ≥ 18 MΩ/cm³) – lower grades may have contamination
    • Please don’t do that 1:100,000 dilution

– How are they stored?
  • Plastic vessels ensure better stability
  • Stabilize with acid – low pH ensures better stability
Sensitivity – Contamination Sources

Anything that touches sample during prep., dilution, transfer, analysis and storage

- **Acid purity**
  - Buy only what you need to do the job
  - Check the certificate of analysis
  - Don’t insert pipette tips into your acids
  - Use contaminated acid for cleaning

- **Pipette tips**
  - Colors add interest – but increase contamination (Cu, Fe, Zn, Cd)

- **Gloves**
  - Powder free, unless you like Zn
ICP-OES Sensitivity – Sample Intro.

What to Check?

– Torch type and alignment
  • Torch alignment required after removing/replacing the torch
  • Ensures optics viewing highest emission signal from the plasma
  • Can also provide a quick performance check – monitor max. sensitivity

– Spray chamber
  • Spray chamber type changes sensitivity
    – Single pass gives best sensitivity (not suitable for all samples)
    – Double pass gives best precision (best for organics & high % TDS samples)
  • Features an internal baffle to ensure a finer aerosol
It’s a good idea to keep a log of the intensities whenever you run the Torch Alignment routine.
Low ICP-OES Sensitivity

What to Check?

– Standards prepared correctly and fresh
– Check for blockage of nebulizer (easier with the glass cyclonic s/chamber)
  • If required, remove nebulizer and check liquid flow/aerosol formation
– Check for blockage in the injector of the torch
  • Aspirate a Y solution
  • Check the position of “bullet” in the plasma
  • Should be stable
– Check the pump tubing (see tips on later slide)
– Check your method conditions (see tips on later slide)
– Check gas left in argon cylinder – low nebulizer gas flow
ICP-OES Sensitivity - Peristaltic Pump Tubing

- Selection of tubing used for an application based on 2 key factors
  - Resistance to the solvent in use
  - ID of the tubing required (indicated by the coloured tabs)
- Users’ usually know what size they need
  - Axial ICP – white/white for sample and blue/blue for drain
  - Radial ICP – grey/grey for sample and blue/blue for drain
- Smaller sizes used when application demands it
  - Black/black tubing used for organics/high %TDS samples
  - Orange/orange used for Int. Standard/Ionization Suppressant

<table>
<thead>
<tr>
<th>Tubing</th>
<th>Recommendations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard PVC tubes</td>
<td>Suitable for all aqueous solutions, medium-concentrated acids and bases</td>
</tr>
<tr>
<td>Solvent Flexible (Solvaflex)</td>
<td>Suitable for kerosene, white spirit, alcohols, medium-highly concentrated acids and bases</td>
</tr>
<tr>
<td>Viton</td>
<td>Suitable for gasoline, naptha, toluene, xylene (aromatic hydrocarbons), highly concentrated acids and bases</td>
</tr>
<tr>
<td>Marprene</td>
<td>Suitable for ketone-based solvents including MIBK and DIBK</td>
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</table>
Potential Pump Tube Problems

What to Check?

– Tubing diameters
  • Want tubing used for waste to be larger ID than sample ID

– Chemical compatibility
  • Ensure tubing is resistant to the solvent being used

– Tube lifetime
  • Typical lifetime is 1-2 weeks based on normal 8 hour working day
    – Detach from tube holder after use – allows tube to “relax”
  • Check 2 key things on pump tubing
    – Roundness of tube – should not be any “flat” spots
    – Tubing should still be elastic – replace if obviously stretched
  • Using “old” tubing can lead to problems with precision and stability
  • Installation and tensioning critical
    – Don’t overtighten – just need smooth and even sample flow

– Remember to check other tubing for wear, leaks and crimps
ICP Sensitivity – Method Parameters

What to Check?

– Wavelength selection
  • Using the most sensitive line?

– Pump speed
  • Use the default speed as guide – 12-15 rpm recommended for most samples
  • Change pump tubing to give resistance to the solvent – and to control sensitivity (by changing tubing ID)

– Interferences?
  • Check for spectral interferences – change wavelength first! (if required)
    – Otherwise, use FACT or IEC correction
  • Physical interferences can affect aerosol formation
    – Use internal standard, matched standards or standard additions
  • Chemical interferences can reduce atom formation
    – Use higher RF power, optimize neb. flow + appropriate matrix modifiers
• **Automatic optimization** of power, nebulizer flow and if applicable, viewing height (on Radial ICP models only)
ICP Sensitivity – System Cleanliness

What to Check?

– Sample Introduction System
  • Deposits in nebulizer can reduce sample uptake rate
    – Soak in aqua regia or use a nebulizer cleaning tool to back flush
  • Solid material in torch injector affects aerosol introduction into plasma and increases noise
  • Contamination in spray chamber impacts on aerosol formation – increases noise
  • If beading in spray chamber
    – Soak in 25% detergent solution overnight (preferably for 24 hours)
Precision - Why is This Important?

What does “Precision” mean?

- Ability to get the same result for the same sample when measured multiple times
- Usually measured as % RSD or sometimes, SD
  \[
  \text{% RSD} = \left( \frac{\text{SD}}{\text{Mean Result}} \right) \times 100
  \]
- Low values indicate good precision
  - For ICP-OES, expect 1-2% RSD

Why is this important?

- User loses confidence in the system

What impacts on precision?

- Nebulizer/plasma stability
- Sample introduction system
- Method parameters
ICP-OES Precision – What to Check?

- System stabilized?
  - Allow 10 mins. for plasma warm-up before analysis
  - Optics purge stabilized – only required when measuring < 190 nm
    - Allow > 20 mins purge before analysis (from stand-by mode)

- Plasma status
  - “Bullet” in the plasma should be stable
  - Check for deposits in the injector of the torch

- Method parameters
  - Appropriate times set for sample uptake delay and stabilization times?
ICP-OES Precision – Sample Intro.

What to Check? – Nebulizer

• Nebulizer type used can impact on sensitivity and precision
  – **Inert OneNeb gives the best precision and handles all sample types**
  – Glass concentric best for aqueous samples
  – K style nebulizer (concentric type) best for organics
  – V-groove gives poorer precision - best for aggressive acids (HF) and high %TDS samples

• Check nebulizer condition regularly
  – Chips in the nebulizer tip impact on aerosol formation – poor precision (use a magnifying glass if necessary)
  – Check for deposits or blockage in the tip

• Sample uptake or flow rate
  – Lower pump speed or using narrow bore pump tubing will reduce uptake rate
    - better for high %TDS samples
ICP-OES Precision – What to Check?

- Sample Introduction
  - Contamination in the spray chamber:
    - Any visible droplet formation?
  - Any blockages in the nebulizer injector?
    - Check for stable aerosol formation
  - Air leaks in connecting tubes
    - Are they in good condition with tight connections?
  - Damaged pump tubes?
    - When did you check the pump tubes?
  - Is the pump speed too slow?
    - Low pump speeds may cause signal pulsation
    - If required, use narrower bore pump tube and increase pump speed
  - Samples have a high %TDS content
  - Measuring at an appropriate concentration
    - Close to the detection limit, noise is high and precision/accuracy is impacted
ICP-OES Precision – What to Check?

– Memory effects?
  • Can occur when measuring high concentrations of selected analytes
  • Usually see high intensity for first replicate – subsequent replicates are more consistent
  • Common culprits:
    – Ag, Au, B, Hg, Mo, Si, Sn, W, Zn, Zr
ICP-OES Precision – What to Check?

– Memory effects?
  • If possible, avoid running high concentrations of these analytes
    – Maybe necessary to pre-dilute samples
      (if known to be high in concentration)
  
  • Ensure an adequate rinse time
    – Should be at least equal to the sample uptake delay
      (30-40 seconds typical)

  • May require an acidified rinse solution between samples
    (2 % HNO₃)

  • Other strategies to minimize memory effects
    – Use a spray chamber with small internal volume (smallest surface area)
    – Use a Switching Valve to improve wash-out characteristics
    – Use “SmartRinse” to optimize rinse time, based on actual intensity
Accuracy - Why is This Important?

What does “Accuracy” mean?
- Ability to get the “right” answer for the sample
- Heavily dependent on operator’s skill

Why is this important?
- User loses confidence in the system
- Your reputation…
  - Customer’s question the results
  - Poor performance in “round robin” comparisons

How do You Confirm Accuracy?
- Check the result for a prepared standard
- Measure a certified reference material
- Use other quality control checks to check analysis
Accuracy – What to Check?

– Calibration standards properly prepared?
  • See earlier recommendations – important to match to samples, prepare accurately and use them “fresh”

– Any interferences impacting on results?
  – Use matched standards or standard additions
  – Ensure wavelength selected has no spectral interferences

– Precision optimized
  • Optimum signal to noise performance improves accuracy
  • Measuring at an appropriate concentration
    – Close to the detection limit, noise is high and precision/accuracy is impacted

ICP-OES Maintenance & Trouble Shooting
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Accuracy – What to Check?

– Sample preparation
  • Is the most appropriate digestion being used?
  • Are all of the analytes being quantitatively (and reproducibly) extracted and dissolved?
  – Many digestions are only partial extracts – efficiency will vary with the sample matrix
  – Some volatile analytes may be “lost” during digestion
    • Confirm by taking a solid certified reference material through your preparation and analysis procedure
  • Is the digest stable – or are you seeing any precipitates or a suspension?
  • Do you see any potential contamination from either reagents or the digestion equipment? e.g. especially with Si, B or Ca
    • Include a “Reagent Blank” with every sample batch to monitor
ICP-OES – Potential Autosampler Issues

– More customers use autosamplers with ICP for automation

– Issues to consider:
  • Long transfer tube between sampler and ICP-OES
    – May need to program a longer sample uptake delay
    – May exacerbate problems with memory effects
    – Use “Fast Pump” during sample uptake delay
  
  • Caution! – not always possible. Not recommended with high %TDS samples and organics
  
  • Ensure probe diameter is appropriate for sample matrix
    – Use wider bore for high % TDS or viscous samples
  
  • Sample stability - potential for sample changes while uncovered in racks – impacts accuracy
    – Dust ingress can introduce contamination
    – Sample evaporation may occur during long unattended runs
    – Sediment in the sample may settle out, esp. with wear metals or suspensions
  
  • Ensure transfer line to ICP-OES is in good condition
    – Kinks in the line may cause poor uptake, or pulsing in the sample
    – Impacts on precision and accuracy
Laboratory Environment

Laboratory environment can have direct impact on quality of results

- Clean, uncluttered work area
- Proper ventilation
- Safety considerations
- Instrument lifetime consideration
Sample Throughput – What to Check?

– Samples fully digested?
  • No excess particulates in the sample that may cause blockage

– Sample Introduction System optimized?
  – Capable of handling the %TDS levels in the sample
  – Torch/Nebulizer cleaned and ready for analysis?

– Method parameters optimized
  • Sample uptake delay and stabilization times are appropriate – optimized
  • Integration time is appropriate for the expected concentration
    – Use a longer integration time at low concentrations
  • Rinse time is appropriate
    – Use “Smart Rinse” or Switching Valve for faster washout
**Agilent ICP-OES Performance - Benefits**

**Robust, stable analysis**

- Copes easily with difficult sample matrices such as organic solvents
- Continuous wavelength coverage ensures flexibility and gives you confidence in your results:
  - Extend the linear range by using $\lambda$ of different sensitivities (in the same run) – no time penalty
  - Eliminate interferences
- One view, one step measurement of major, minor and trace elements for highest productivity
  - Fastest warm-up time
  - Fastest measurement speed

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**Superb Long Term Stability**

Agilent 720 ICP-OES Long-term precision over 8 hours: < 1 % RSD Max.
ICP-OES – Recommended Maintenance Schedule

Daily:

• Inspect torch for injector blockage/other damage
• Check nebulizer for blockage/pulsation
• Inspect peristaltic pump tubing for stretching or flatness
• Check exhaust system operating (smoke test?)
• After analysis is complete:
  – Aspirate rinse solution for 5-10 mins. before shutting down
    • Minimizes sample deposits in spray chamber, nebulizer tip and torch injector
  – Release pressure bar and detach peristaltic pump tubes from holder
  – Empty waste vessel
  – Wipe down exterior surfaces of your ICP-OES (esp. sample compartment)
  – Leave ICP-OES in stand-by mode (gas and power on; software shutdown)
ICP-OES – Recommended Maintenance Schedule

Weekly:

- Clean torch (or earlier if required)
- Check the other sample introduction tubing and O-rings
  - Look for excessive wear, poor sealing or kinks and replace as necessary
  - Especially look at the transfer tube from spray chamber to torch and the spray chamber waste outlet
- Inspect cone (axial ICP) or snout (radial ICP)
  - If cleaning required, sonicate in dilute detergent solution, rinse and dry
- Inspect torch bonnet (radial ICP) for cracks or sample deposition
ICP-OES – Recommended Maintenance Schedule

Monthly:

- Clean spray chamber (or earlier if “beading” visible)
- Clean nebulizer
- Inspect the state of the induction coil
- Clean/check the air filter for the cooling air inlet (behind chimney)
- Clean/check air filter on the water chiller/recirculator
- Check the water level in the water chiller/recirculator
  - Top up with water if required
  - Do not add any more algaecide without flushing the circulator
ICP-OES – Recommended Maintenance Schedule

6 Monthly:

- Clean the water particulate filter on back of instrument
- Replace the water in the water chiller/recirculator
  - Dose with algaecide as recommended by chiller manufacturer
- Change argon filters on argon gas inlet (if using gas cylinders for argon supply)

These functions (and more!) are completed as part of a Preventative Maintenance program by an Agilent Field Service Engineer.
Overview – Key Consumables for ICP-OES

Sample introduction:
- Peristaltic pump tubing
- Torches
- Nebulizers
- Spray chambers
- Transfer and drain tubing
- Application kits (adapt your instrument to a new application)
- ICP standard solutions
- Ionization suppressant / buffer solutions

Autosampling:
- Sample tubes, racks, probes and transfer tubing

Vapor generation systems:
- Peristaltic pump tubing
- Connecting tubing
ICP Sample Introduction

Key consumable items requiring frequent replacement:

- Pump tubing
- Transfer & connecting tubing
- Torches
- Nebulizers
- Spray chambers

Where can customers find ordering details?

- On-line help in the ICP Expert S/W
- Agilent Spectroscopy Supplies Catalogue
- Agilent website – dedicated webpage. Use this link:

SPS 3 Autosampler Consumables

- Peristaltic pump tubing
- Sample racks
- Sample tubes
- Spare probes
- Standard racks
- Connecting tubing

**Where to find ordering details?**

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- Agilent Spectroscopy Supplies Catalogue
- Agilent website – dedicated webpage. Use this link:

Where to Find the Right Consumable?

Analytical Consumables: Consumables & Supplies

1-800-227-9770 (Option 1,1)
www.agilent.com/chem/contactus

Agilent Assist: Instrument Sales & Services

1-800-227-9770 (Option 1,3)
www.agilent.com/chem/contactus

On-Line resources:

Atomic Absorption Supplies
ICP-OES Parts & Supplies Portfolio
ICP-MS Supplies
Instrument Parts & Supplies
Atomic Spec. Application Notes

Agilent Quick Reference Guide for Axial ICP (pub. # 5990-9475EN)
Agilent Quick Reference Guide for Radial ICP (pub. # 5990-9474EN)
Agilent Atomic Spec. Supplies Catalogue (pub. # 5990-8767EN)
Agilent Consumables Catalogue (pub. # 5990-6674EN)
Instrument User Manuals
Other Support Resources for Agilent ICP-OES Users

• Are you a member of Agilent’s PlasmaNet email forum?
  – This is a direct email link to other Agilent ICP-OES users worldwide

• PlasmaNet allows you to:
  – Ask a question and get responses from other users doing the same application and/or Agilent Specialists worldwide
  – Share your knowledge and experience with other users

• To register, use this link to the registration form on the Agilent website (or ask your Agilent representative):
Summary – To Achieve Quality Data

- Most “instrument” failures occur in the sample introduction area
  - Includes
    - Torch
    - Spray chamber
    - Nebulizer
    - All tubing
    - Drain Assembly

- Improper maintenance of this area can result in poor data quality

- Frequently less experienced analysts can fail to recognize problems resulting in productivity losses

- Establishing routine maintenance procedures can prevent problems before they occur
Questions?

The Market Leaders in Atomic Spectroscopy

Agilent MP-AES

Agilent AAS

Agilent ICP-OES

Agilent ICP-MS