# 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**

**ICP-MS**

**ICP-QQQ**

**Flame AAS**

**Graphite Furnace AAS**

**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

**Lowest** ← **Selling Price** → **Highest**

# 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:

- **S**ample introduction system
- **M**ethod parameters
- **C**leanliness
- **Q**uality of standards used for calibration

Remember – **SMCQ**

Or

"**S**ystem **M**ust **C**reate **Q**uality"

# 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

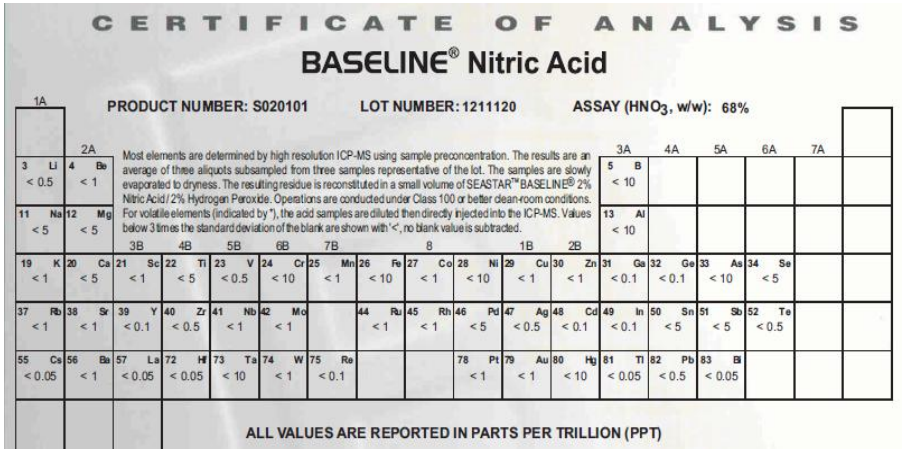
- How are they prepared?
  - Ensure purchased standards are still within “Use By” date when used
  - Use calibrated pipettes and class ‘A’ volumetric flasks for dilutions
  - Use de-ionized water (Type I - conductivity $\geq$ 18 M$\Omega$/cm$^3$) – lower grades may have contamination
  - Please don’t 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



CERTIFICATE OF ANALYSIS

BASELINE® Nitric Acid

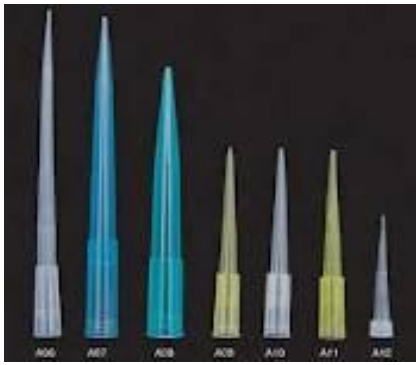
PRODUCT NUMBER: S020101 LOT NUMBER: 1211120 ASSAY ($HNO_3$, w/w): 68%

Most elements are determined by high resolution ICP-MS using sample preconcentration. The results are an average of three aliquots subsampled from three samples representative of the lot. The samples are slowly evaporated to dryness. The resulting residue is reconstituted in a small volume of SEASTAR™ BASELINE® 2% Nitric Acid / 2% Hydrogen Peroxide. Operations are conducted under Class 100 or better clean-room conditions. For volatile elements (indicated by *), the acid samples are diluted then directly injected into the ICP-MS. Values below 3 times the standard deviation of the blank are shown with '<', no blank value is subtracted.

| 1A | 2A | 3B | 4B | 5B | 6B | 7B | 8 | | | 1B | 2B | 3A | 4A | 5A | 6A | 7A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 Li < 0.5 | 4 Be < 1 | | | | | | | | | | | 5 B < 10 | | | | |
| 11 Na < 5 | 12 Mg < 5 | | | | | | | | | | | 13 Al < 10 | | | | |
| 19 K < 1 | 20 Ca < 5 | 21 Sc < 1 | 22 Ti < 5 | 23 V < 0.5 | 24 Cr < 10 | 25 Mn < 1 | 26 Fe < 10 | 27 Co < 1 | 28 Ni < 10 | 29 Cu < 1 | 30 Zn < 1 | 31 Ga < 0.1 | 32 Ge < 0.1 | 33 As < 10 | 34 Se < 5 | |
| 37 Rb < 1 | 38 Sr < 1 | 39 Y < 0.1 | 40 Zr < 0.5 | 41 Nb < 1 | 42 Mo < 1 | | 44 Ru < 1 | 45 Rh < 1 | 46 Pd < 5 | 47 Ag < 0.5 | 48 Cd < 0.1 | 49 In < 0.1 | 50 Sn < 5 | 51 Sb < 5 | 52 Te < 0.5 | |
| 55 Cs < 0.05 | 56 Ba < 1 | 57 La < 0.05 | 72 Hf < 0.05 | 73 Ta < 10 | 74 W < 1 | 75 Re < 0.1 | | | 78 Pt < 1 | 79 Au < 1 | 80 Hg < 10 | 81 Tl < 0.05 | 82 Pb < 0.5 | 83 Bi < 0.05 | | |

ALL VALUES ARE REPORTED IN PARTS PER TRILLION (PPT)

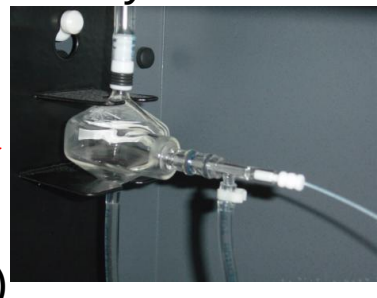
- Pipette tips
  - Colors add interest – but increase contamination (Cu, Fe, Zn, Cd)
- Gloves
  - Powder free, unless you like Zn



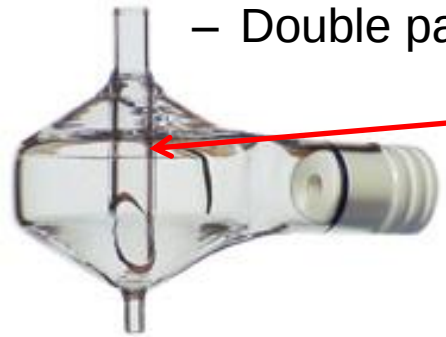
# ICP-OES Sensitivity – Sample Intro.

## 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



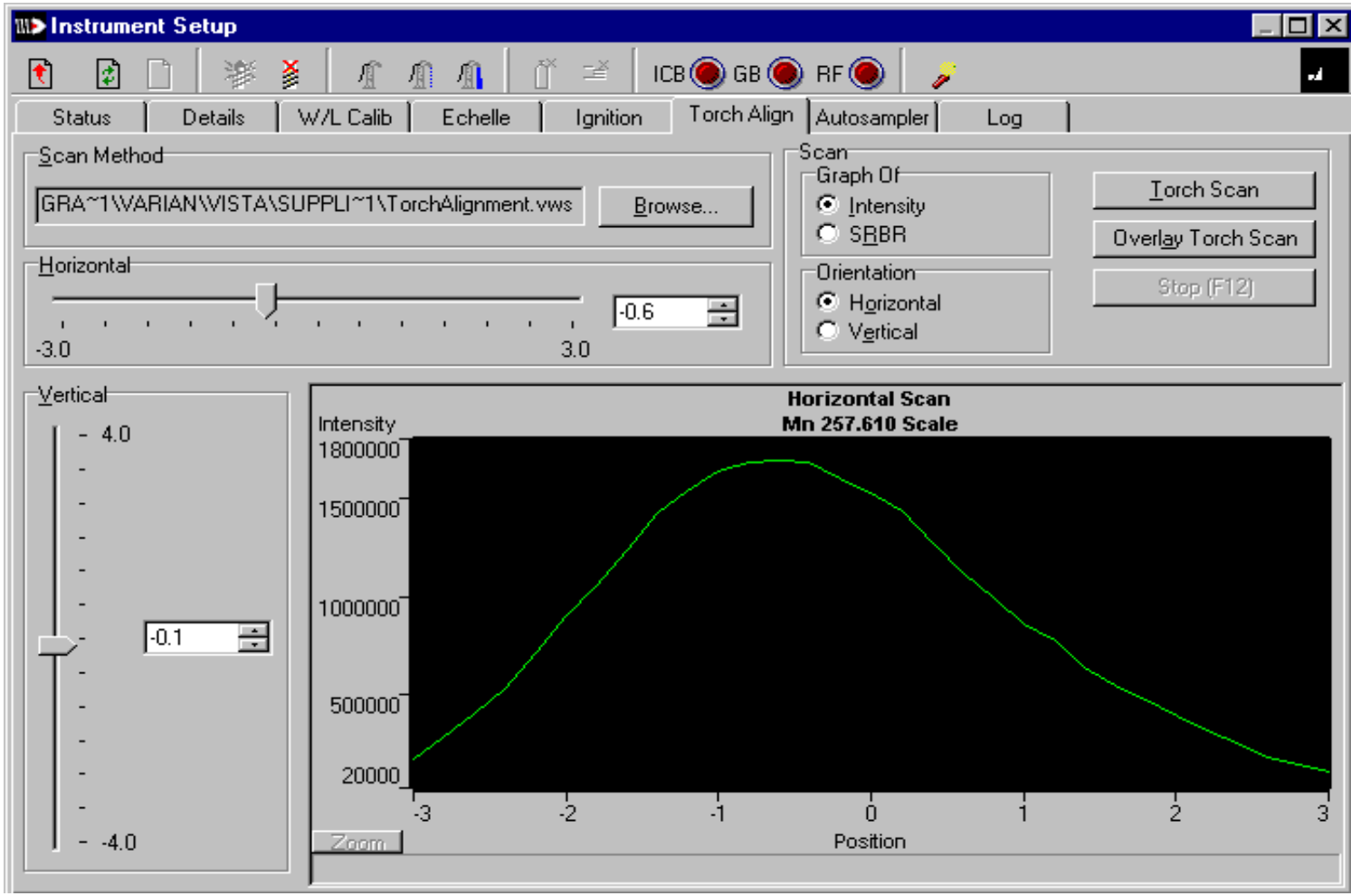
- Spray chamber
  - Spray chamber type changes sensitivity
    - Single pass gives best sensitivity (not suitable for all samples)
    - Double pass gives best precision (best for organics & high % TDS samples)



- Features an internal baffle to ensure a finer aerosol

# ICP-OES Sensitivity – Torch Alignment

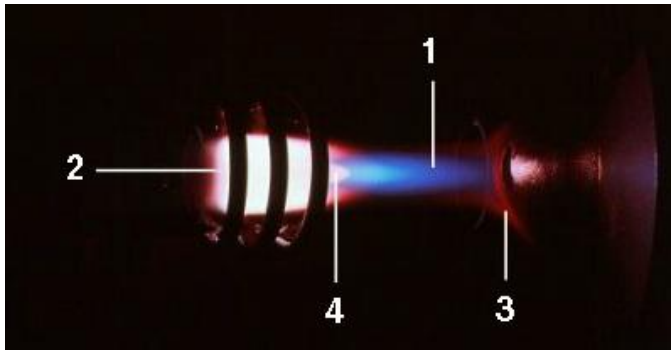
It's a good idea to keep a log of the intensities whenever you run the Torch Alignment routine



# 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

**Peristaltic Pump Tubing Chemical Compatibility**

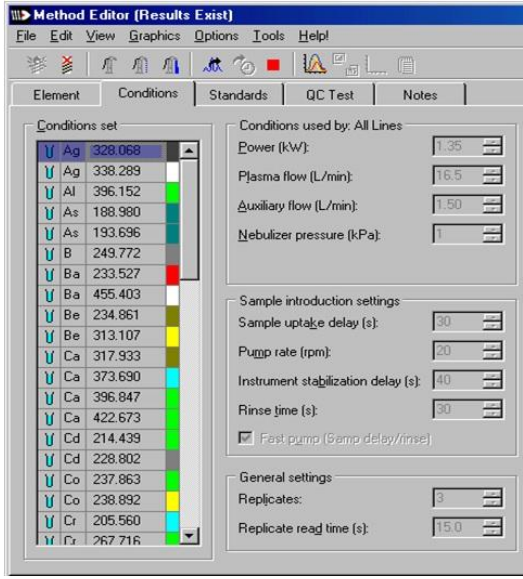
| Tubing | Recommendations |
|---|---|
| Standard PVC tubes | Suitable for all aqueous solutions, medium-concentrated acids and bases |
| Solvent Flexible (Solvaflex) | Suitable for kerosene, white spirit, alcohols, medium-highly concentrated acids and bases |
| Viton | Suitable for gasoline, naptha, toluene, xylene (aromatic hydrocarbons), highly concentrated acids and bases |
| Marprene | Suitable for ketone-based solvents including MIBK and DIBK |

# 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

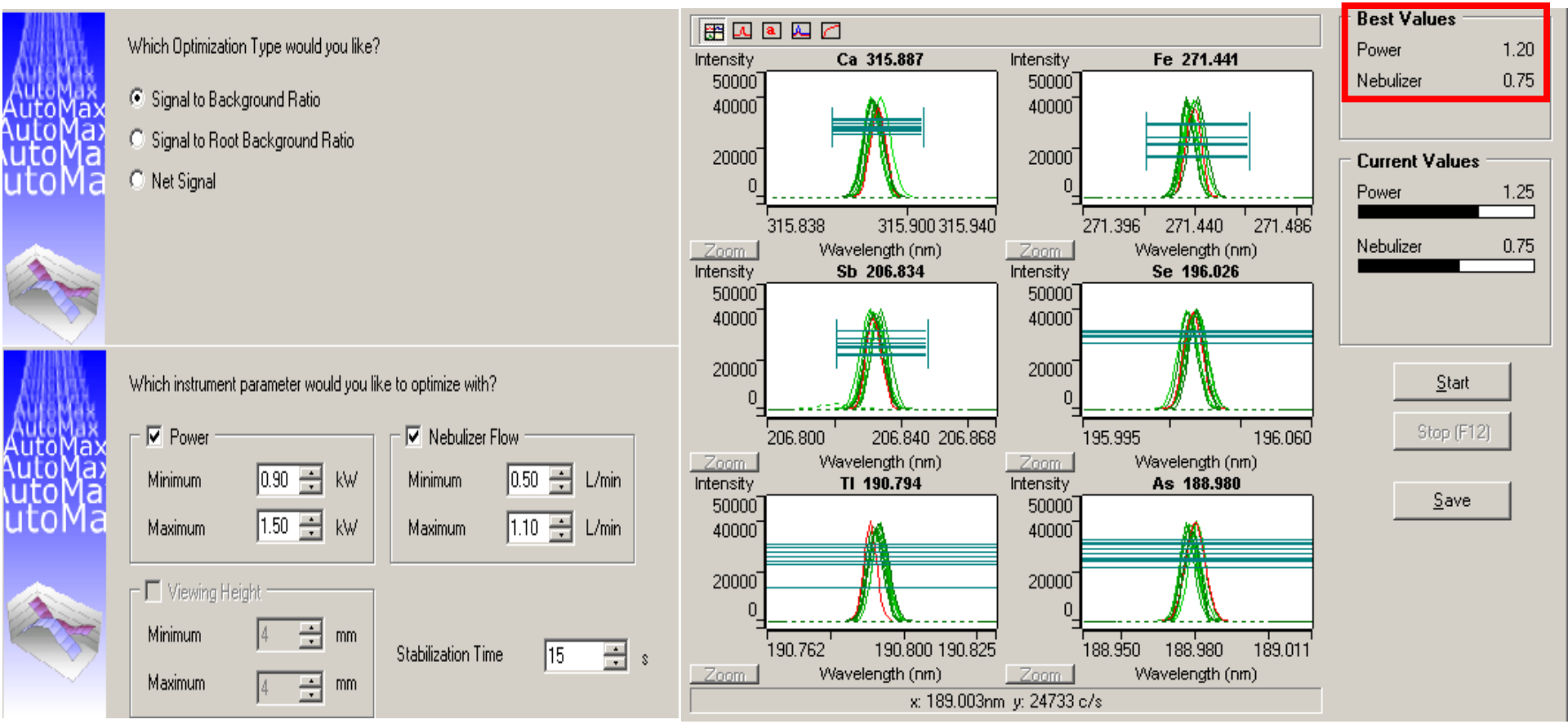
# ICP Sensitivity – Method Parameters




## 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

# Automated ICP Method Optimization - Automax



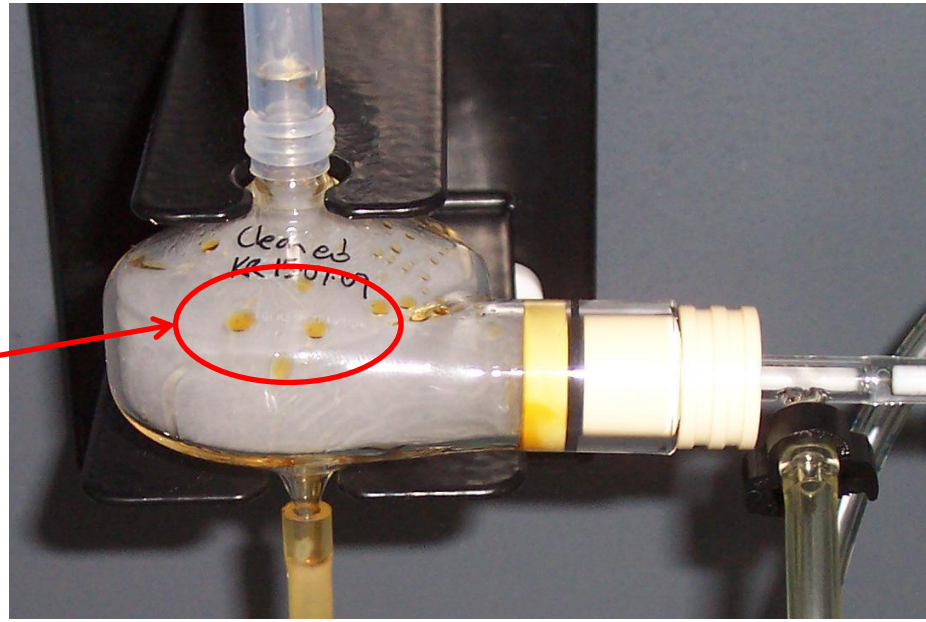

- Automatic optimization of power, nebulizer flow and if applicable, viewing height (on Radial ICP models only)

# 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)

Nebulizer cleaner
Agilent P/N G3266-80020



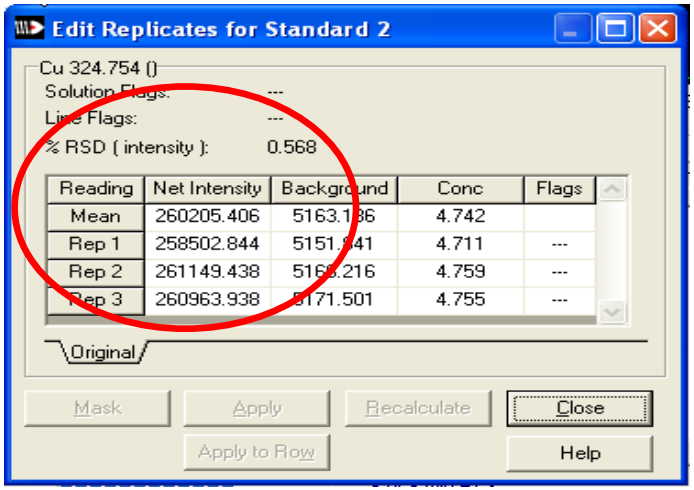
# Precision - Why is This Important?

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
  % RSD = (SD / Mean Result) * 100
- Low values indicate good precision
  - For ICP-OES, expect 1-2% RSD

Why is this important?

- User loses confidence in the system

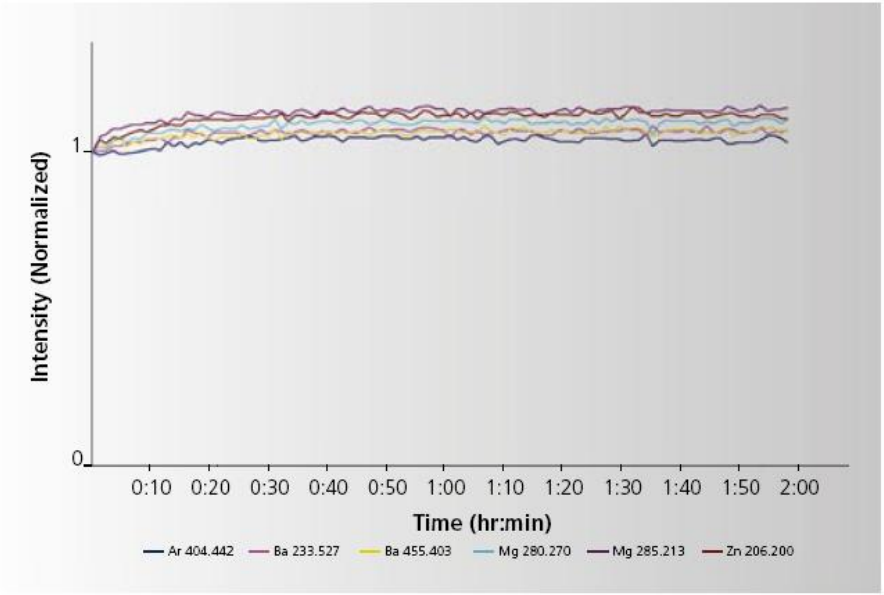



What impacts on precision?

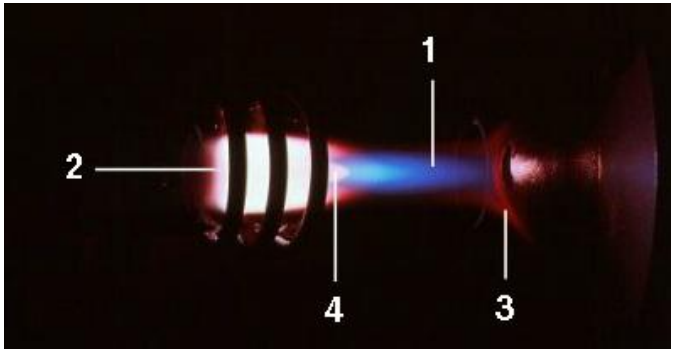
- Nebulizer/plasma stability
- Sample introduction system
- Method parameters

# 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?




Start analyzing samples in less than 10 minutes. Shown is the rapid stabilization of Ar, Ba, Mg and Zn (Mermet lines) following plasma ignition.



# ICP-OES Precision – Sample Intro.

## What to Check? – Nebulizer

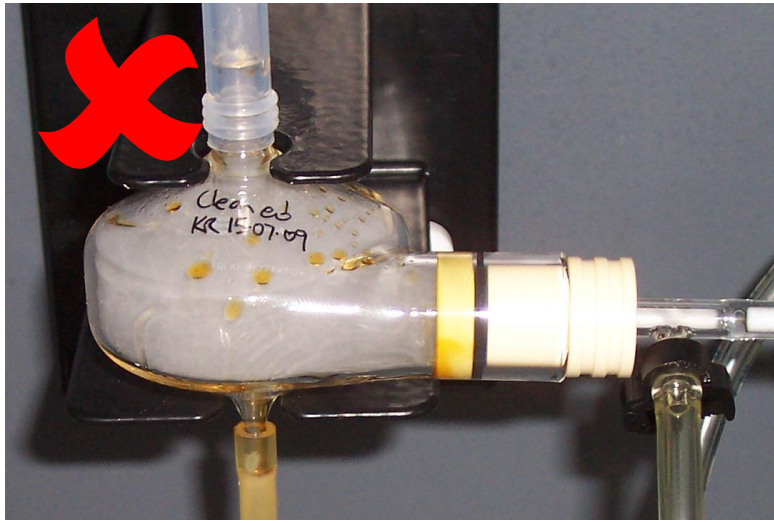
- Nebulizer type used can impact on sensitivity and precision
  - Inert OneNeb gives the best precision and handles all sample types
  - Glass concentric best for aqueous samples
  - K style nebulizer (concentric type) best for organics
  - V-groove gives poorer precision - best for aggressive acids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

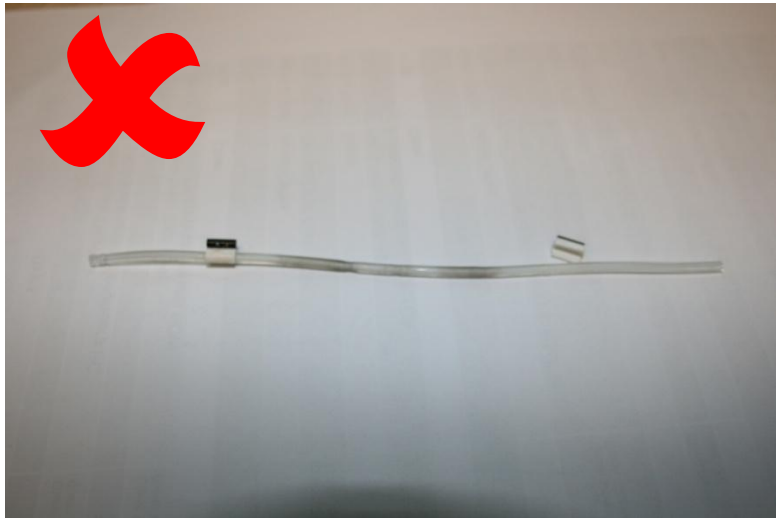
- Check nebulizer condition regularly
  - Chips in the nebulizer tip impact on aerosol formation – poor precision (use a magnifying glass if necessary)
  - Check for deposits or blockage in the tip
- Sample uptake or flow rate
  - Lower pump speed or using narrow bore pump tubing will reduce uptake rate - better for high %TDS samples

# ICP-OES Precision – What to Check?

– Sample Introduction

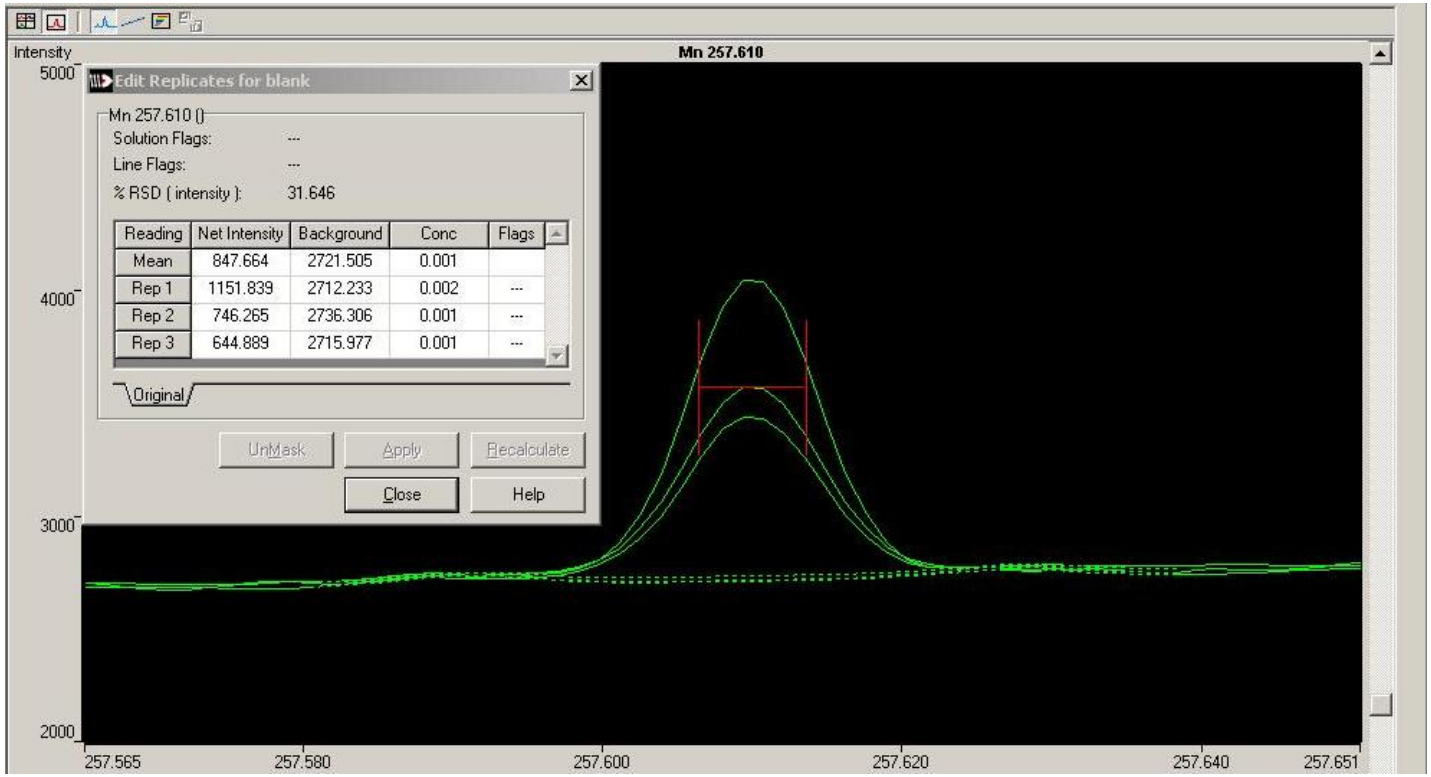
- Contamination in the spray chamber:
  - Any visible droplet formation?
- Any blockages in the nebulizer injector?
  - Check for stable aerosol formation
- Air leaks in connecting tubes
  - Are they in good condition with tight connections?
- Damaged pump tubes?
  - When did you check the pump tubes?
- 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





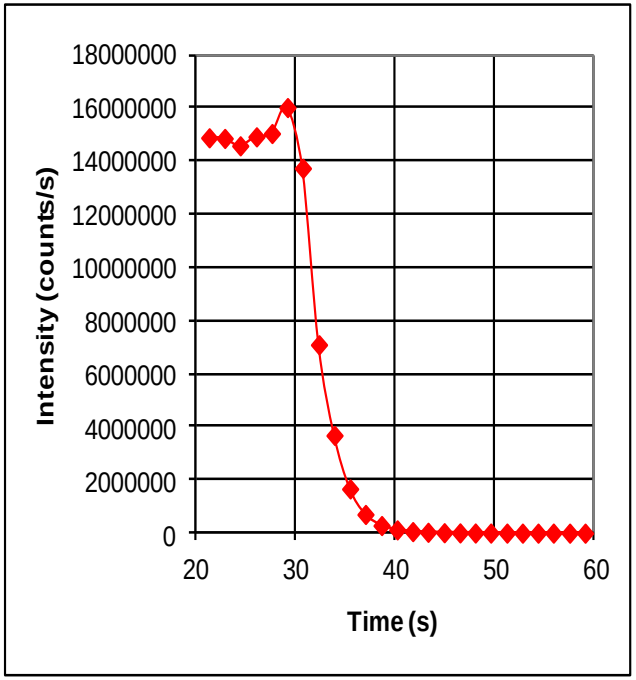
# ICP-OES Precision – What to Check?

- 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

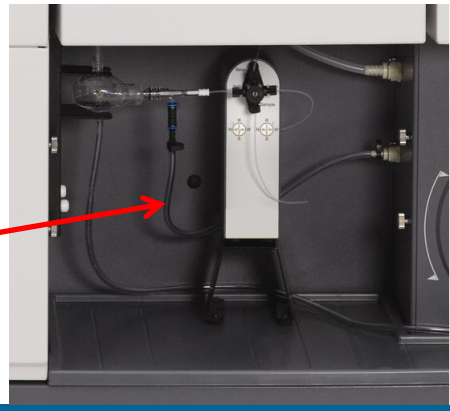


# ICP-OES Precision – What to Check?

- 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 % $HNO_3$)
  - 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




Wash-out for 1000 ppm Mn



# 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

# 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

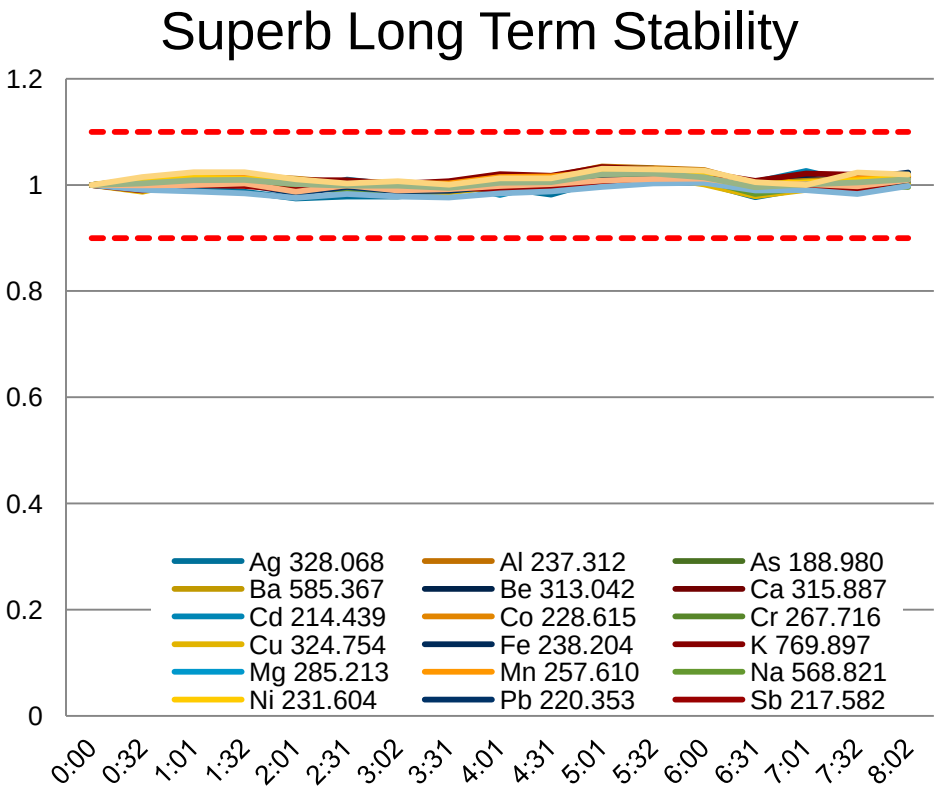
# Sample Throughput – What to Check?

- 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 λ 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




**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:

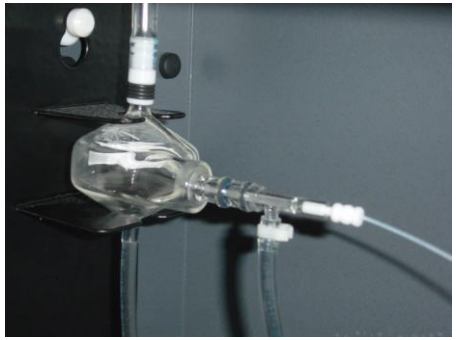
- Clean the water particulate filter on back of instrument
- Replace the water in the water chiller/recirculator
  - Dose with algaecide as recommended by chiller manufacturer
- Change argon filters on argon gas inlet (if using gas cylinders for argon supply)

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:
- http://www.chem.agilent.com/en-US/Products/columns-supplies/instrumentparts/icp-oes/Pages/default.aspx

# SPS 3 Autosampler Consumables

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

***Agilent's fast spectroscopy autosampler meets the diverse requirements of high-throughput analytical laboratories.***

## Where to find ordering details?

- On-line help in the ICP Expert S/W
- Agilent Spectroscopy Supplies Catalogue
- Agilent website – dedicated webpage. Use this link:
  http://www.chem.agilent.com/en-US/Store/_layouts/Agilent/Commerce/SubcategoryListing.aspx?cat=SubCat1ECS_22701(Agilent)&pcat=CatECS_22675(Agilent)&rcat=ClassECS_22674(Agilent)

# 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:

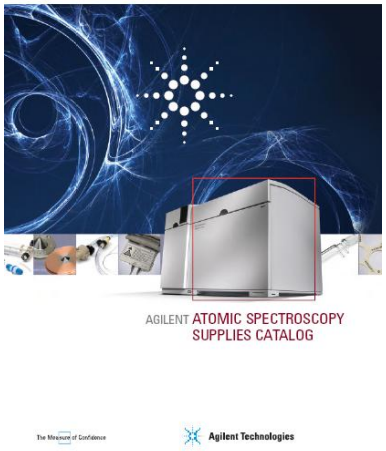
Atomic Absorption Supplies

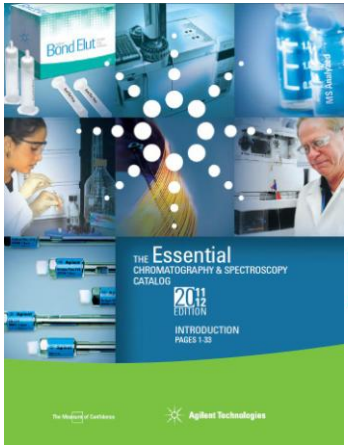
ICP-OES Parts & Supplies Portfolio

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):

  http://www.chem.agilent.com/en-US/Support/Pages/plasmanetwemailforum.aspx

PlasmaNet

# 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?

Agilent MP-AES

Agilent AAS

Agilent ICP-OES

Agilent ICP-MS

## The Market Leaders in Atomic Spectroscopy