Guidelines for Troubleshooting and Maintenance of AA Systems

Presented by Eric Vanclay, Atomic Spectroscopy Consumables Product Manager

Common AA Problems Reported by Customers

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

High noise

- Can get the "right answers", but very noisy signal – this is also giving bad precision.

Accuracy

- Instrument does not give the "right" results.

Poor Sample Throughput

- The instrument throughput needs to improve
- Burner blocks too quickly

Causes of Poor Furnace AA Sensitivity

Furnace workhead

- Missed injection
- Aged (or damaged) tube in use
- Wrong electrodes fitted

Optimization

- Poor optimization – esp. drying conditions
- Workhead incorrectly aligned
- Optics setting – using right wavelength/slit?
- No modifier (or incorrect) modifier used
- Use of nitrogen as inert gas

Standard (& sample) preparation

- No acid in solution
- High blank level
- Standards prepared & stored correctly?
- Samples prepared correctly – digestion?

Causes of Poor Furnace AA Precision

Furnace workhead

- Missed injection
- Bubble formation in syringe
- Dirty dispensing capillary
- Using non-Agilent graphite tubes
- Graphite components excessively worn – poor electrical contact

Optimization

- Wrong dispensing height
- Poor optimization – esp. drying conditions
- Missing a cooldown step (esp. with platforms)
- Gas purity

Standard (& sample) preparation

- No acid or detergent in rinse (memory effects)
- No acid in solution
- Incomplete digestion – particles in solution

Causes of High Noise in Furnace AA

Furnace workead

- Dirty windows in workhead
- Use of platforms

Optimization

- High background levels
- High absorbance signals
- Wrong lamp operating current
- Workhead incorrectly aligned
- Poor optimization – especially the HC lamp

- Dirty optics
- Gas purity

Standard (& sample) preparation

- Incomplete digestion – particles in solution

Furnace AA System Tips

Do:

Check optimization each analysis

Check/monitor the dispensing height

Ensure the rinse solution has 10 drops conc. HNO_3 + 5 drops Triton X-100

Remove residue from the dispensing capillary

Check/monitor the graphite tube

Check the blank reading

Clean the workhead regularly

- Inspect condition of the graphite components

Follow analytical recommendations in “cookbook”

Don’t:

Assume system is still optimized

Assume dispensing height is the same

Use a simple water rinse

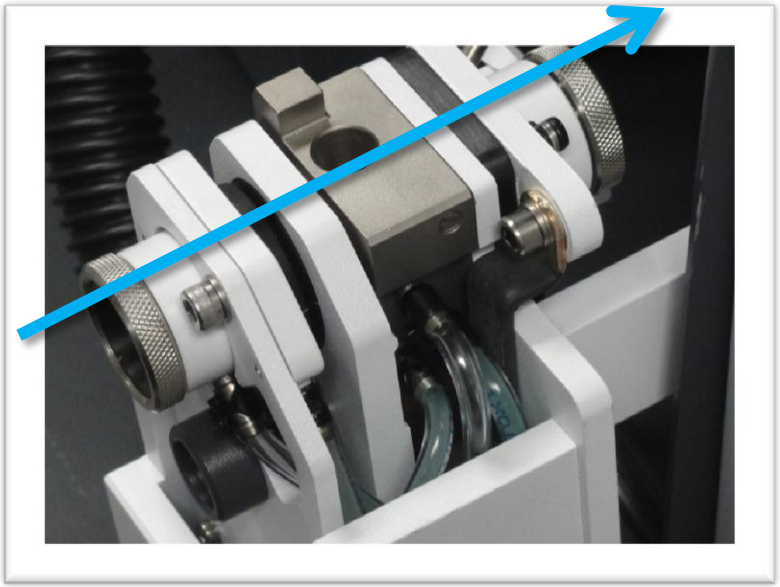
Start analysis with a dirty capillary tip

Start analysis with a tube near the end of it’s life

Furnace AA System Tips - Workhead Alignment

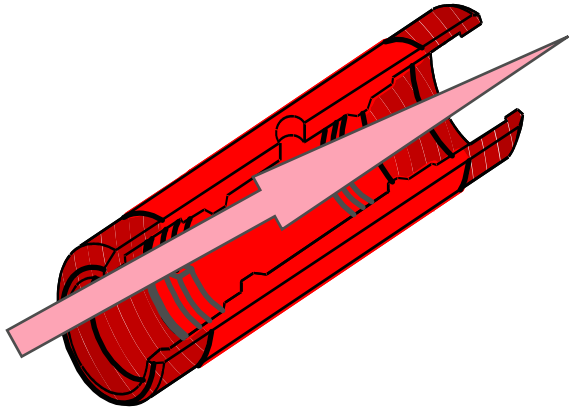
Furnace workhead

- Workhead position must be optimized (want light beam to pass through centre of graphite tube)
  - Align lamp first (no workhead), then place workhead in position and align

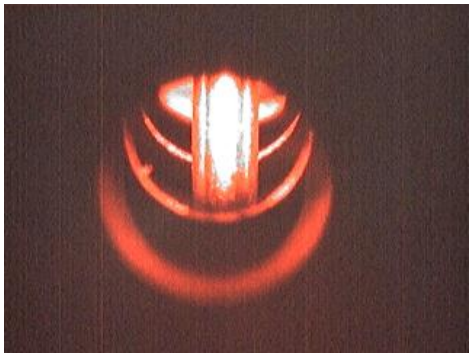


Sample Dispenser settings

- Carefully adjust injection depth – easy with the furnace camera



Light Beam Aligned Through Center of Graphite Tube



Furnace AA System Tips - Setting Injection Depth

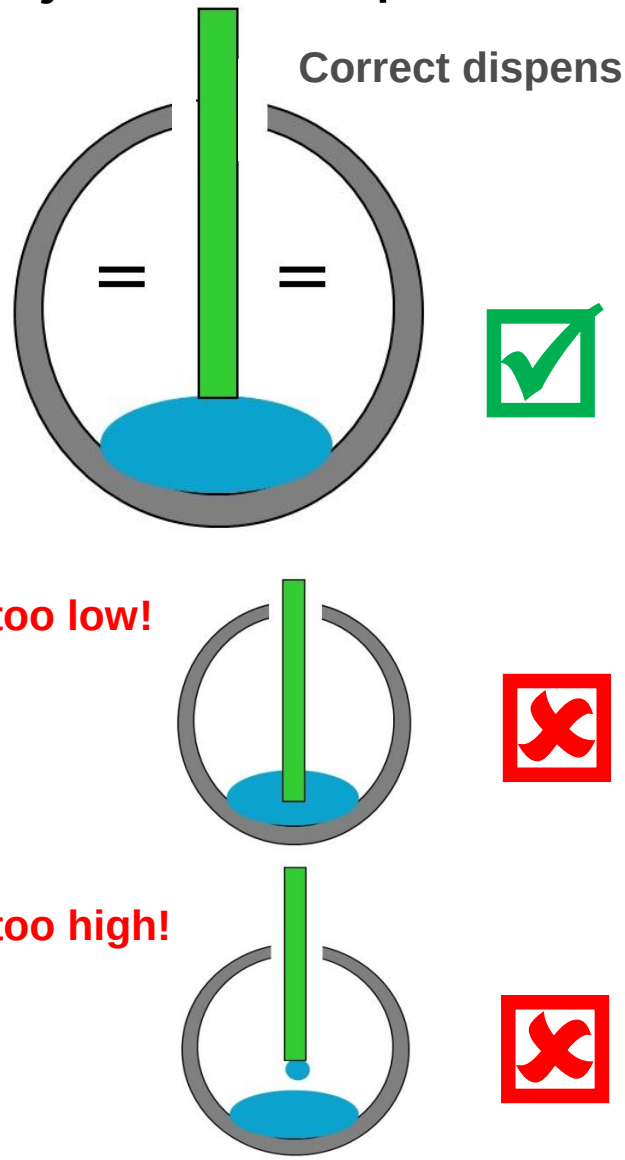
Capillary tip must remain in contact with solution during dispensing

Reduce dispensing height if sample spreads due to low surface tension

Ensure there is no liquid on the outside of the capillary after dispensing

Ensure there is no liquid inside the capillary tip after dispensing

Sample should remain as a drop in the centre of the tube



Furnace AA System Tips – Tube Conditioning

Why condition the tubes before use?

- Helps remove residual contamination
- Gently “beds” a new tube in
  - Important when determining concentrations near detection limit
  - Also important with some complex matrices
- Critical when using modifiers
  - Helps to build up coating inside the tube
  - Improves efficiency of the modifier
- Improves reproducibility

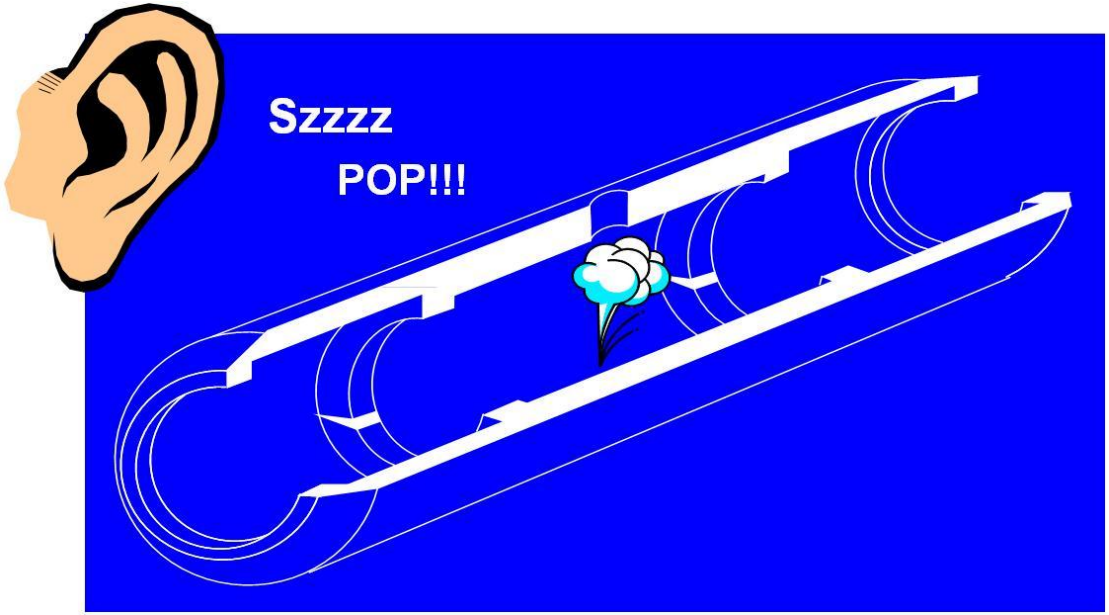
Recommended process

- Use “Tube Condition” facility (or otherwise, fire tube 5-10 times using either reagent blank or representative sample)

Furnace AA System Tips – Method Parameters

What to Check?

- Furnace parameters
  - Set appropriate drying temperature and time (2-3 sec/uL of solution injected)
  - Optimize ashing temperature using ashing study – use SRM optimization
  - Ensure inner gas flow “off” just prior to atomization

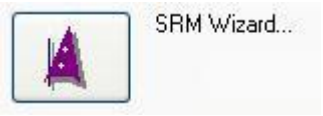


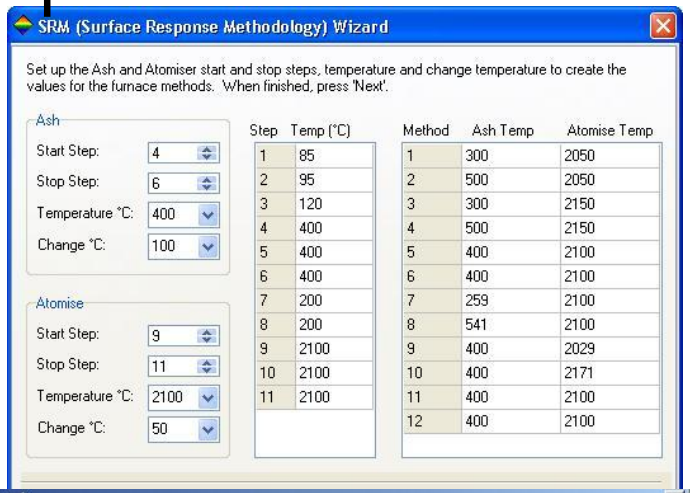
Does the sample sizzle or splatter during the dry stage?

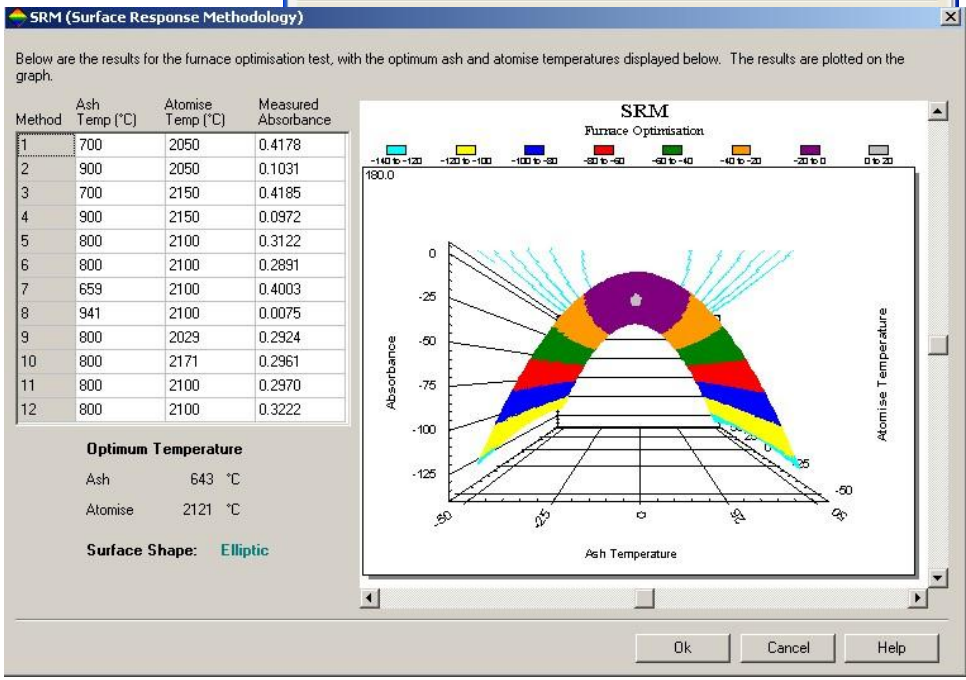
- Listen for the sound
- Use the mirror or furnace video to monitor the sample drying

Furnace AA System Tips – Method Optimization

- SRM “Wizard” automates furnace optimization
- Optimizes absorbance as a function of ashing and atomization temperature
- Automatically creates a method using recommended conditions
- Reduces training requirements for new users







Optimization results for Pb determination using phosphate modifier

Furnace AA System Tips – Reducing Sensitivity

May be required due to sensitivity of this technique:

- Switch to an alternate wavelength
  - Select a less sensitive wavelength (if available)
- Reduce sample volume
- Use slower ramp rate to atomization
  - Aim to broaden the peak during atomization
- Use low gas flow during the atomization step

Furnace AA System Tips – Factors Influencing Tube Lifetimes

Graphite components excessively worn – poor electrical contact

No tube preconditioning (or always using Tube Clean)

Sample matrix

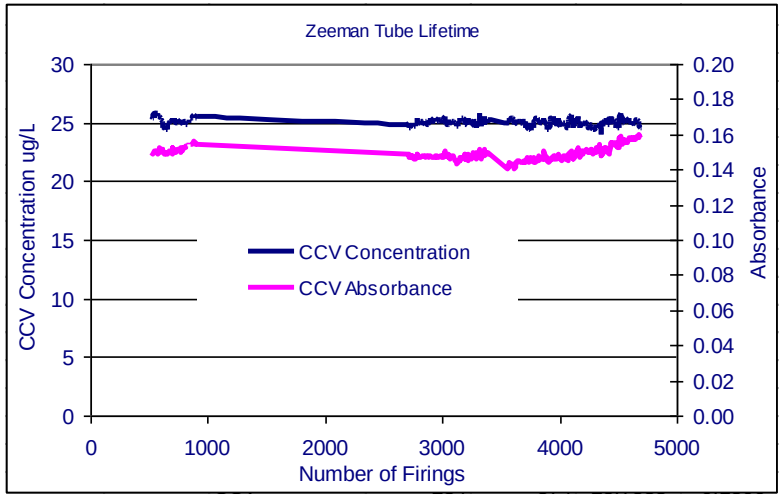
Inert gas used

- Argon gives longest life
- Nitrogen degrades tube faster due to oxygen presence

Temperature program used

Type of chemical modifiers used

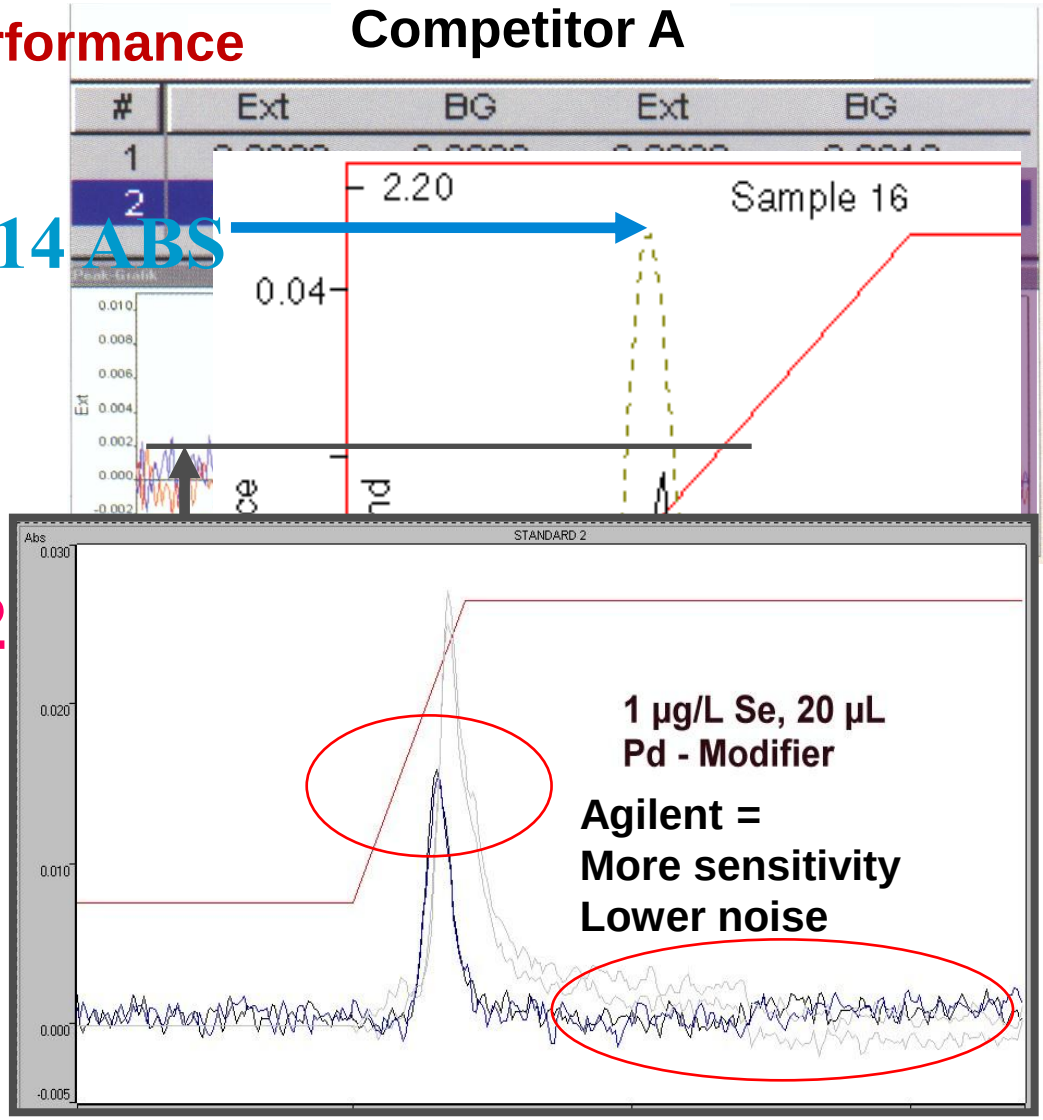
- Powerful oxidizing agents degrade tube faster
  - Perchloric acid
  - Perchlorates
  - Sodium nitrate



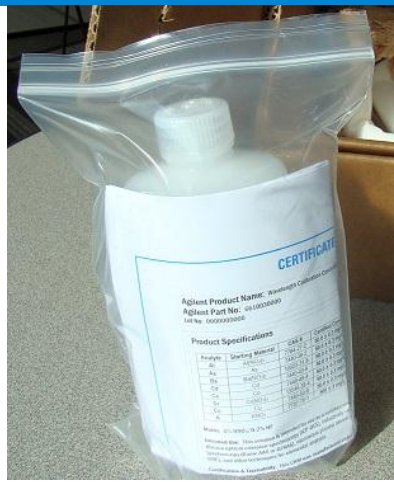
Agilent Furnace AA Systems – Benefits

Flexibility & Superior Furnace Performance

- Highest furnace sensitivity
- Best Zeeman correction capability:
  < 2 % error at > 2 Abs. b'ground
  - Polynomial interpolation of the background
  - 100/120 readings every second
- Best capability to handle difficult samples



Tips to Improve Standard Preparation



- How are they prepared?
  - Ensure purchased standards are still within “Use By” date
  - Use calibrated pipettes and class ‘A’ volumetric flasks for dilutions
    - Periodically, check accuracy & reproducibility of your pipettes
  - Use de-ionized water (Type I - conductivity $\geq$ 18 MΩ/cm^3)
    - Lower grades may have contamination
  - Use serial dilutions for preparing low concentrations from 1,000 ppm stock
    - Please don’t do large dilutions (> 1:10,000) in 1 step

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

- How are they stored?
  - Plastic vessels ensure better stability
  - Stabilize with acid – low pH ensures better stability

Tips to Reduce Contamination

Contamination can come from anything that comes into contact with your sample during storage, digestion (dilution) and analysis

- Check reagent purity
  - Always buy the best reagents
  - Always check the certificate of analysis for elevated levels
  - Caution if buying in large quantities
    - Worst case – can use contaminated acid for cleaning
    - Ensure still within “use by” date
  - Reseal immediately after use

CERTIFICATE OF ANALYSIS

BASELINE® Nitric Acid

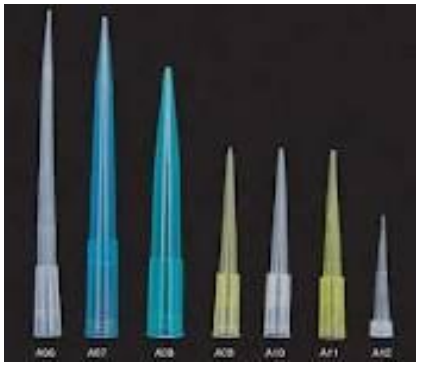
PRODUCT NUMBER: S020101 LOT NUMBER: 1211120 ASSAY (HNO_3, w/w): 68%

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)

- Other common contamination sources
  - Reagent water
  - Clean glassware?
  - Airborne dust in the lab.
  - Pipette tips
    - Don’t insert pipette tips into your acids
    - Use natural tips – colored tips may increase contamination (Cu, Fe, Zn, Cd)
  - Powdered gloves (esp. for Zn)



Tips to Improve Accuracy of Results

- 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

Tips for Cleaning Dirty Optics

Monitor the windows regularly

- Check lamp for fingerprints
- Check sample compartment windows for build-up of film/chemical residue

Smudges or chemical residue reduces light and increases noise

Cleaning the windows?

- Wipe clean with an optical tissue (as you would use to clean a camera lens)
- If necessary, use optical tissue moistened with ethanol

Cleaning end windows from furnace workhead

Furnace AA – Rec. Maintenance Schedule

Daily:

- Check the gas delivery pressures & cylinder contents
- Check exhaust system
- Check condition of the graphite tube – replace as necessary
  - When replacing the tube, check the condition of the electrodes
- Check dispensing capillary “free” and syringe
- Top up rinse reservoir as required
- Clean the workhead around the sample injection hole
- Empty waste container

Weekly:

- Check furnace workhead windows (clean if necessary)

Overview - Key Consumables for AA

All instruments:

- HC lamps
- AA standard solutions

Flame AA systems:

- Glass impact beads, burner cleaning strips, nebulizer components, capillary tubing, burners etc
- Ionization suppressant / buffer solutions
- With the SIPS dilution system – SIPS pump tubing and transfer tubing
- With an autosampler - sample tubes, racks, probes and transfer tubing

Graphite furnace AA systems:

- Graphite tubes
- Sample vials, dispensing capillary and syringe for autosampler
- Matrix modifiers

Vapor generation AA systems:

- Quartz atomization cells
- Peristaltic pump tubing
- Connecting tubing

Agilent AA Consumable Kits

Part Number	Description	Content
190034100	Flame AA operating supplies kit (for Mark 7 atomization system)	Nebulizer venturi, capillary kit, nebulizer block (excl. integral nebulizer), Glass impact beads Capillary tubing O ring kit Mixing paddles Burner cleaning strips
190065400	SPS 3 Flame Autosampler operating supplies kit	0.8 mm id inert probe 2 packs grey/grey 3 bridged pump tubing (12/pk) Connecting tubing, drain tubing and capillary tubing Rinse reservoir (10 L) 1 pack 16 mm od polypropylene tubes (1000/pk) 3 sample racks for 30 mm od tubes (21 positions) 1 pack 30 mm od polypropylene sample tubes (500/pk)
190067900 (for GTA 120); or 190068000 (for GTA 120 Zeeman)	Graphite Furnace AA operating supplies kits	2 sets graphite electrodes Graphite shroud 5 packs Omega tubes (each 10/pk) 100 µL syringe for PSD 1 pack of capillary assemblies for PSD (5/pk) 1 pack of plastic beakers (5/pk) 2 packs 2 mL furnace vials (1000/pk)
190025200	VGA 77 Vapor Generation AA operating supplies kit	2 sets tubing and connector kits 2 packs sample pump tubes (12/pk) 2 packs reagent pump tubes (12/pk) 1 set replacement pump beds 1 replacement AA gas-liquid separator 1 Hg Flow Through Cell (1/pk) 2 packs hydride absorption cell (2/pk) 1 spare AA hydride module
190025400	SIPS Flame Dilution System operating supplies kit	2 ea 500 mL constant pressure vessel 1 x 1L diluent bottle 1 x 3 way tee piece assembly 1 Pack SIPS pump tubing (6/pk) 1 Pack Pump Bands (10/pk) 1 SIPS tubing kit

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

Mark 7 Sample Introduction Spares

AA FAQs

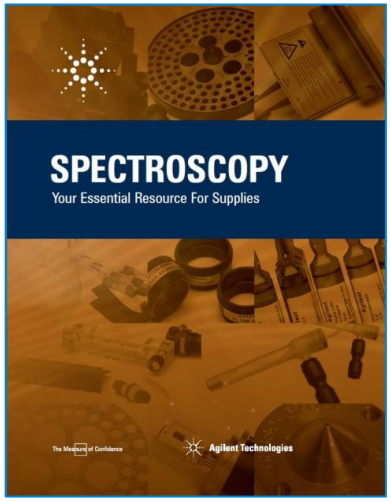
ICP-OES Parts & Supplies Portfolio

ICP-MS Supplies

Instrument Parts & Supplies

Atomic Spectroscopy Application Notes

Recorded Agilent e-Seminars



Agilent Quick Reference Guide for AA (pub. # 5990-9476EN)

Agilent Spectroscopy Supplies Catalogue (pub # 5991-1060EN)

Instrument User Manual for Agilent Graphite Tube Atomizer GTA 120 or Agilent 240/280 Series AA

Summary – To Achieve Quality Data

- Most “instrument” failures occur in the sample introduction area
  - Includes
    - Burner
    - 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 maintenance procedures can prevent problems