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

Flame AAS

ICP-OES

ICP-MS

MP-AES

Graphite Furnace AAS

AAS instruments can be flame only, furnace only, or combined (switchable)
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

AA Maintenance & Trouble Shooting
Apr. 2012
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

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

Poor Sample Throughput
• The instrument throughput needs to improve
• Burner blocks too quickly
AA Sensitivity - What Impacts This?

4 areas of the instrument can affect sensitivity:

– **S**ample introduction system (and AA lamp optimization)
– **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 within “Use By” date
  • 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

– How are they stored?
  • Plastic vessels ensure better stability
  • Stabilize with acid – low pH ensures better stability
AA Sensitivity – Sample Introduction

What to Check?

– Lamp type and alignment
  • Alignment should be checked – gain setting should be consistent
  • Lamp type can improve performance e.g. using high intensity UltrAA lamp

– Burner
  • Burner position must be optimized (vertical, horizontal & rotational positioning)
  • Burner type changes path length (for air/acetylene elements)

Optimum viewing height for Ca
AA Sensitivity Compromise

Higher Sensitivity: $N_2O/C_2H_2$

Lower Noise: $Air/C_2H_2$
What to Check?

– Nebulizer settings
  • Nebulizer uptake rate
    – low flow rates better for high %TDS samples

– Impact bead position

– Acetylene cylinder contents remaining (acetone can “mask” any signal)
AA Sensitivity – Method Parameters

What to Check?

– Gas flows
  • Flame stoichiometry affects sensitivity (oxidizing vs reducing flame)

– Wavelength/Slit selection and Lamp current
  • Using the most sensitive line?
  • Check you’re using the rec. lamp current and slit width (different for multi-element lamps)

– Interferences?
  • Physical interferences can affect aerosol formation
    – Use matched standards or standard additions
  • Chemical interferences can reduce atom formation
    – Use high temperature N$_2$O/acetylene flame + appropriate matrix modifiers
Nitrous Oxide/Acetylene Flame Stoichiometry

Lean

Stoichiometric

Rich
AA Sensitivity – System Cleanliness

What to Check?

– Clean windows?
  • Check lamp and sample compartment windows
  • Smudges or chemical residue reduces light throughput and increases noise

– Sample Introduction System
  • Deposits in nebulizer can reduce sample uptake rate
  • Solid material on burner slot reduces path length and increases noise
  • Contamination in spray chamber impacts on aerosol formation – increases noise
AA Sensitivity – Rec. Settings

For most flame AA applications:
- Fit the mixing paddles
- Optimize the impact bead for best sensitivity
- Use narrow bore capillary tubing

For highest flame AA sensitivity:
- Remove mixing paddles
- Adjust impact bead further away from the nebulizer
- Use wide bore capillary tubing (highest uptake rate)

For high TDS samples:
- Fit the mixing paddles
- Adjust impact bead ½ to 1 turn clockwise (towards nebulizer) from optimum sensitivity position
- Use wide bore capillary tubing (to reduce chance of blockage)
Agilent Flame AA Performance – Benefits

Tunable performance means…

- Highest flame sensitivity: > 0.9 Abs. for 5 mg/L Cu
- Best precision: < 0.5 % RSD using 10 x 5 s readings
- Extended operation with difficult samples
- No loose gas hoses and no tools required for gas connection
- Fast change-over to furnace operation (manual - < 30 s)

100 mg/L Al in Cola
GFAA Sensitivity – Sample Introduction

What to Check?

– Lamp type and alignment
  • Alignment should be checked – gain setting should be consistent
  • Lamp type can improve performance e.g. using high intensity UltrAA lamp

– 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

Light Beam Aligned Through Center of Graphite Tube
GFAA Sensitivity – Sample Introduction

What to Check?

– Sample Dispenser settings
  • Carefully adjust injection depth – easy with the furnace camera

– Autosampler rinse
  • Acidify rinse with 0.01 % (v/v) HNO₃ plus a few drops of Triton X-100

– Choice of inert gas impacts sensitivity
  • Argon gas preferred – ensures optimum sensitivity and best tube life
  • Nitrogen gas reduces sensitivity by up to 20 % and decreases tube life
GFAA Sensitivity – Correct Capillary Alignment

- 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
GFAA Sensitivity – 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
Automated Furnace 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
GFAA Sensitivity – Method Parameters

What to Check?

– Wavelength/Slit selection and Lamp current
  • Using the most sensitive line?
  • Check you’re using the rec. lamp current and slit width (different for multi-element lamps)

– Interferences?
  • Physical interferences can affect sample spreading in the tube
    – Maintain constant volume; use matched standards and partitioned tube
  • Chemical interferences can reduce atom formation
    – Use modifiers with temp. programming, matrix match & standard additions
GFAA Sensitivity – Cleanliness

What to Check?

– Clean windows?
  • Check lamp and sample compartment windows
  • Smudges or chemical residue reduces light throughput and increases noise

– Sample Introduction System
  • Deposits on capillary tip can affect sample dispensing
  • Ensure no bubbles in dispensing syringe (current design is bubble free)
  • Residues in graphite tube impacts on sensitivity – may cause contamination, high noise or high background
    – Condition tube before use (even if starting with a new tube)
    – Helps to “bed” the tube in
Agilent Furnace AA Performance – Benefits

Flexibility & Superior Furnace Performance

- Highest furnace sensitivity
- Best correction capability: < 2 % error at > 2 Abs. b’ground
  - High speed correction
- Best capability to handle difficult samples

Competitor

Agilent =
More sensitivity
Lower noise
Hydride AA Sensitivity – Sample Introduction

What to Check?

– Sample and reductant pump rates
  • Check the pressure bar - only apply enough pressure to ensure uniform flow
  • Check pumping rates

– Quartz cell positioning
  • Quartz cell position must be optimized (want light beam to pass through centre of the cell)
    – Align lamp first (no cell), then place the cell into position and align

Light Beam Aligned Through Center of Quartz Cell
Hydride AA Sensitivity – Sample Introduction

What to Check?

– Was the cell conditioned before use?
  • If required, recondition the cell again

– Allow longer pre-read delay time (Hg needs a longer time)

– Use an acid rinse between solutions

– Check acid tubing for deterioration

– Check/clean absorption cell
Hydride AA Sensitivity – Sample Introduction

• Low Signal with As:
  – Check As$\text{III}$ stable – not being oxidized back to As$^\text{V}$

• Low Signal with Se:
  – Ensure KI not added before analysis

• Low Signal with Hg:
  – Check that Hg is stabilized in solution
  – Avoid presence of KI – clean system thoroughly with 1% sodium thiosulfate (or swap reagent modules)
Agilent Hydride AA Performance – Benefits

• Faster than graphite furnace technique
  – 50 – 70 analyses per hour
  – Relative easy to automate

• Analyte is removed from matrix
  – Eliminating matrix interferences
  – Minimizing background
  – Can easily analyze matrices that are difficult to run by graphite furnace

• 100 % sampling efficiency
  – Detection limits in the sub-ppb range
  – Extremely sensitive for ultra-trace Hg

• Excellent in run precision
  – Typically 1 – 2 % RSD
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
  \[ \text{RSD} = \frac{\text{SD}}{\text{Mean Result}} \times 100 \]
- Low values indicate good precision
  - For flame AA, expect < 1% RSD (Hydride AA < 2% RSD)
  - For GFAAS, expect < 4% RSD

Why is this important?
- User loses confidence in the system

What impacts on precision?
- Lamp and burner/plasma stability
- Sample introduction system
- Method parameters
AA Precision – What to Check?

– Lamp properly aligned?

– System stabilized?
  • Allow 5-10 mins. warm-up for lamp/burner before analysis

– Sample Introduction
  • Nebulizer uptake rate adjusted
    – High uptake rate means great sensitivity and worse precision
  • Impact bead adjusted correctly
  • Burner position optimized?
  • Mixing paddles fitted?
  • Measuring at an appropriate concentration
    – Close to the detection limit, noise is high and precision/accuracy is impacted
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
  – For AA - use high temperature N\textsubscript{2}O/acetylene flame + appropriate matrix modifiers

– 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
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
  – Burner cleaned and ready for analysis?

– Method parameters optimized
  • Pre-read delay time is appropriate – optimized
  • Read time is appropriate for the expected concentration
    – Use a longer measurement time at low concentrations
  • Rinse time is appropriate
  • Use a faster measurement technique – like Fast Sequential AA
Flame AA – Recommended Maintenance Schedule

Daily:
- Empty waste container
- Check exhaust system
- Clean burner compartment & instrument
- Check the gas delivery pressures & cylinder contents (esp. acetylene)
- Check the nebulizer uptake rate and burner condition

Weekly:
- Clean burner (or earlier if required)
  - Check condition of O rings and impact bead (no pitting)

Monthly:
- Clean windows in sample compartment
Furnace AA – Rec. Maintenance Schedule

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

Weekly:
• Check and clean furnace workhead windows (if required)
Hydride AA – Rec. Maintenance Schedule

Daily:
- Empty waste container
- Check pump tubing for stretching, deformation or severe discoloration
  - Release after each analysis
- Check connections to the reaction coil
- Clean the absorption cell (soak in nitric acid)
- Clean any spills and wipe the pump unit

Weekly:
- Replace and condition the absorption cell (or earlier as required)
- Check the rollers rotate freely
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 suppresant / 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
Flame Atomizer - Mark 7 Design

Key consumable items requiring frequent replacement:

• O rings
• Glass impact beads
• Burner cleaning strips
• Nebulizer capillary kit
• Nebulizer venturi kit
• Capillary tubing
• Nebulizer cleaning wire
• Liquid trap assy
• Mixing paddles
• Burners

Where to find ordering details?

• On-line help in the SpectrAA S/W
• Agilent website – dedicated webpage: Mark 7 Spares
• Agilent Quick Reference Guide for AA
• Agilent Atomic Spectroscopy Supplies Catalogue
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
ICP-OES Parts & Supplies Portfolio
ICP-MS Supplies
Instrument Parts & Supplies
FAQs
Atomic Spec. Application Notes

Agilent Quick Reference Guide for AA (pub. # 5990-9476EN)
Agilent Atomic Spec. Supplies Catalogue (pub. # 5990-8767EN)
Agilent Consumables Catalogue (pub. # 5990-6674EN)
Instrument User Manuals
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
Questions?

The Market Leaders in Atomic Spectroscopy