Atomic Spectroscopy
AA/ICP/ICPMS:
A Comparison of Techniques
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AA/ICP/ICPMS: A Comparison of Techniques

Topics of Discussion

• Atomic Absorption Spectrometry (AA, FAA, GFAA)
• Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)
• Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS)
• Compare techniques Detection Limits and Measurement Range
• Compare Analysis Speed & Limit for each techniques
• Compare the Performance vs. Investment of each Technique
Atomic Absorption Spectrophotometry

Atomic spectroscopy is the determination of elemental composition by its electromagnetic (light) spectrum.

(185 nm to 900 nm)
Atomic Absorption

- Sample is reduced to **Atomic State**
- Elements Absorb light of a **specific wavelength** from Hollow Cathode Lamp
- The drop in the amount of light reaching the detector is measured
- One element at a time
Hollow Cathode Lamp

3 primary components:

- **Cathode**: which is made of or coated with the specific element
- **Anode**: which is a simple copper wire
- **Neon Gas**: what the lamp is filled with

Cathode Lamp

- Electrons are boiled off the anode and accelerated cathode where they collide
- Excited atoms emit light specific to the element in the cathode
- Lamps come as single element lamps or multi element lamps.
Flame AA
- ppm level sensitivity
- Sample is aspirated in the nebulizer where the liquid is converted into an aerosol.
- Larger droplets are broken up by an impact bead before entering the flame
- Some element require Modifiers

Flame Types
- Air-Acetylene & Nitrous-Acetylene
- Air-Acetylene reaches temperatures of 2300 °C
- Nitrous-Acetylene reaches temperatures of 3000 °C
Autosampler can reduce analysis workload

**Autosampler Considerations**

- How many samples do you need to analyze?
- Does it work with other accessories?
- Do you need dilutions capabilities?
- Do you need Modifiers added?

**Micro-Sampling Capabilities**

- Small sample volumes 50 to 90 μL
- Calibration from a single standard
- Automatic addition of Modifiers
- Auto-dilution for over range measurements
- Automation of standard addition method
- No blockage of burner slot with high salts
Furnace Atomic Absorption Method (Electro thermal Heating)

- Tubes are held between the cap and holder and the tube acts a resister and heats as electricity is applied.
- During the heating process the water and organics are removed by an argon sweep gas.
- The sweep gas is shut off prior to atomization to increase the sensitivity.
- Sensitivity is in the parts per billion (ppb) range.
- Analysis time is 2-3 minutes per replicate per element.
Graphite tubes: Which to use

Graphite Tubes

- Tubes come as High-Density, Pyro-coated and Platform

- The stages of a furnace heating program is drying, ashing, atomization, cleaning and cool down

- Platform tubes have a different heating scheme and are better for complex matrix

- Pyro-coated tubes prevent carbides from forming
Atomic Absorption: Flame

**Benefits of Flame AA**

- Cost ($)
- Ease of use
- Fast analysis
- LDR > GFAAS

**Drawbacks of Flame AA**

- Requires gases (can get expensive)
- Open-flame source (limits throughput → must have analyst present)
  - Combustible gases
- Requires large amounts of sample (7 mL/min) → Micro-sampling is an option
- Flame must be adjusted for sample viscosity
- Ionization interferences (requires use of matrix modifier → adds to sample prep)
- Sensitivity
- One element at a time
- Requires ventilation
## Atomic Absorption: Furnace

<table>
<thead>
<tr>
<th>Benefits of Furnace AA</th>
<th>Drawbacks of Furnace AA</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Cost (compared to ICP/ICP-MS)</td>
<td>• Analysis time (several minutes → heating stages)</td>
</tr>
<tr>
<td>• Excellent detection limits (can be better than ICP)</td>
<td>• Furnace program can be complex (five stages)</td>
</tr>
<tr>
<td>• Uses small amounts of sample (uL)</td>
<td>• Droplet must be optimized for viscosity</td>
</tr>
<tr>
<td>• Does not require excessive use of expensive gases (uses argon)</td>
<td>• Consumables (tubes, cap and holder, tips)</td>
</tr>
<tr>
<td>• Can be completely automated and is safe to operate overnight (argon is inert)</td>
<td>• One element at a time</td>
</tr>
<tr>
<td>• High long-term precision (no drift)</td>
<td>• Requires ventilation</td>
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</tbody>
</table>
ICP

**Inductively Coupled Plasma**

Apply an RF

Add some Argon
ICP-OES/MS Principle

- Samples are prepared in a liquid solution.
- Sample is introduced and reduced to Atoms/Ions by plasma.
- Elements in the sample are excited in ICP, and emit light and produce ions.
- A monochromator separates the spectral lines and intensities are measured or ions directed to a mass detector for counting.
Plasma: a gaseous phase of matter containing charged ions

Generation of Plasma
• RF is applied to a coil generating a magnetic field that causes collision with electrons and argon atoms that generate argon ions.
• Argon reaches a temp of 10,000 K

Application of Plasma
• Energy source
• break bonds of molecules to atomize sample
• introduce energy for electron promotion

Sample Progression
• Sample is desolvated, atomized and ionized in the plasma
ICPs are Spectrometers

ICP-OES

- Spectrometer comprised of a Source, Optics, and Detector
- Two types of systems, simultaneous and sequential
  - Simultaneous systems measure all elements at the same time*
  - Sequential have scanning gratings and have high resolution and measure one wavelength at a time
- Most common detectors are Solid State or Photomultiplier Tube (PMT)
Sample Introduction/Glassware

Sample Introduction System

- Solution is introduced to **nebulizer** where it is converted to an aerosol; ~1% is converted or 99% goes to waste*

- The **spray chamber** separates the size of the aerosol particles

- These particles flow into **torch** then into the plasma

Considerations –

**Overflow Style drain:**

- Does not use a peristaltic pump to drain spray chamber

- No deterioration of pump tubing, or troubles caused by improper draining.

- Improper drainage deforms and damages the torch

**Low flow Torches**

- Use less argon 8-10 L/min compared to 20 L/min with conventional systems

- Can generate considerable saving
ICP-OES Spectra and Quantitation

Spectra and Quantitation

- Example of Spectra from an ICP-OES
- The overlaps represent different concentrations
- Standards are measured and a calibration curve is generated by plotting intensity vs. concentration
- Other quantitation models include standard addition method
Optical Bench – Vacuum or Purged Optics

- \(\text{O}_2\) absorbs light in the UV region (\(<200\ \text{nm}\))
- Can remove by Purging or Vacuum systems
- Strong Resonance lines for Al, P, S

Vacuum vs. Purge

- Reduces Gas consumption
- No consumption of gas when not operating
- Pumps require Maintenance (oil)
- Purge systems require cylinders
Autosamplers

Autosampler considerations

• How many samples do you have?
• Do you need an enclosure?
• Do you need express throughput?
Torch Orientation

Orientation

- Two configurations: Vertical & Horizontal
- Vertical orientation can handle more difficult matrix and has less carryover than horizontal
- Horizontal configurations cannot handle salt as well and are more prone to clogging

View

- Axial or Radial
- Axial has 20x better sensitivity
- Radial has larger dynamic range
- 9 orders of magnitude analysis range
Gas Reducing Features

**Reduced Operating Gas**

The Mini-torch design, operating at half the flow rate of conventional torches, improves excitation efficiency and therefore higher sensitivity by reducing cross sectional area of the plasma. The result is a higher energy density plasma with reduced flow rates.

**Reduced Standby Gas**

Eco Mode saves energy and reduces costs by lowering the RF power to 0.5 kW and flow rates to 5 L/min during idle times. Analysis modes restart smoothly having no effect on sample intensity ensuring stable analyses.

**Reduced Startup Gas**

Reduce operating gases by employing a vacuum pump to evacuate atmosphere in the optical bench and enables measurements in the vacuum UV region (below 290 nm). This eliminates the need for purge gases and facilitates a faster startup.

**Cone**

Reduces operating gases by employing a cooling cone instead of sheer gas. This reduces operating cost.
ICP-OES

**Benefits of ICP-OES**

- Sample throughput
  - Can run overnight
  - Simultaneous measurement of all elements at all wavelengths
- Good detection limits
  - Especially when considering speed compared to GFAAS
- Excellent precision
- Excellent LDR
- Can handle complex matrices (e.g. high TDS)
  - Variety of sample introduction glassware
- Uses inert gas (Ar)
- Easy routine operation

**Drawbacks of ICP-OES**

- Sample introduction techniques can add to analysis time (and cost)
- Requires large amounts of sample
- Prone to interferences
  - Physical (e.g. acid concentration)
  - Spectral (110,000 lines...there will be overlap)
    - Correction can get complex
- Requires ventilation
- Plasma must be optimized for organics/petrochemical products
  - Can be difficult to maintain
ICPM Systems

ICPMS Information

• Most sensitive of all the atomic spectroscopy techniques

• Some elements are sub ppt

• In addition to elemental information, ICPMS can also provide isotopic information

• These systems can all be combined with HPLC or GC systems to give speciation information
Plasma: a gaseous phase of matter containing charged ions

Generation of Plasma
• RF is applied to a coil generating a magnetic field that causes collision with electrons and argon atoms that generate argon ions.
• Argon reaches a temp of 10,000 K

Application of Plasma
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Sample Progression
• Sample is desolvated, atomized and ionized in the plasma
Types of Spectral Interference

Detected intensity = Target element’s ion intensity + Interference

Interferences that can be formed in the plasma
- Isobar ions
- Polyatomic ions
- Doubly charged ions

Mass Interference
- Differing from ICP-OES, ICPMS has different types of interferences that were not a concern previously
- Isobaric – same mass
- Polyatomic – two or more atoms/ions together
- Doubly charged – mass-to-charge, if +2 mass appears at half mass number
ICPMS Schematic

Vacuum System

- 3rd (~0.0001Pa)
- 2nd (~0.1Pa)
- 1st (~100Pa)

Turbo Pump (Split Flow)

Rotary Pump

Collision gas (He)

27 MHz RF Generator

Mini Torch

Sample Introduction

Interface Cones

Octopole Collision Cell

Ion Lens

Off-Axis Lens

Q-MS Filter

Detector

Pump

Sample
ICPMS Parts and Function

- Mini-torch
- Sampling & Skimmer Cones
- Mass Filter Quad
- Spray Chamber
- Nebulizer
- Collision Cell
- Detector (EMT)
Autosample considerations

- How many samples do you have?
- Do you need an enclosure?
- Do you need express throughput?

Autosamplers
ICPMS Spectrum: Cd analysis

Actual sample

Cd Isotope

<table>
<thead>
<tr>
<th>Mass</th>
<th>Ratio</th>
<th>BEC</th>
<th>Isobar</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>1.25</td>
<td>0.00</td>
<td>Pd: 27.38</td>
</tr>
<tr>
<td>108</td>
<td>0.89</td>
<td>0.00</td>
<td>Pd: 26.46</td>
</tr>
<tr>
<td>110</td>
<td>12.49</td>
<td>0.00</td>
<td>Pd: 11.72</td>
</tr>
<tr>
<td>111</td>
<td>12.80</td>
<td>0.00</td>
<td>---</td>
</tr>
<tr>
<td>112</td>
<td>24.13</td>
<td>0.00</td>
<td>Sn: 0.97</td>
</tr>
<tr>
<td>113</td>
<td>12.22</td>
<td>0.00</td>
<td>In: 4.30</td>
</tr>
<tr>
<td>114</td>
<td>28.73</td>
<td>0.00</td>
<td>Sn: 0.65</td>
</tr>
<tr>
<td>116</td>
<td>7.40</td>
<td>0.00</td>
<td>Sn: 14.53</td>
</tr>
</tbody>
</table>
Determining Optimal Mass Number

- $^{114}\text{Cd}$: Abundance (sensitivity) is the highest but exist isobaric interference of Sn.
- $^{111}\text{Cd}$: No isobaric interference but exist molybdenum oxide (poly atomic ion).
- $^{106}\text{Cd}$: No interference of isobaric and poly atomic ion but abundance (sensitivity) is low.

- Picking the mass number requires experience and knowledge.
- To do this you must know the coexistence element is necessary.
Method Development of ICP-MS analysis

Conventional

1. Prepare sample
2. Qualitative analysis (all elements)
3. Determine optimal masses for target elements
   - Confirm
     ① Isobaric ion
     ② Oxide ion (~16 mass of measurement mass)
     ③ Doubly charged ion (twice mass of measurement mass)
4. Select internal standard elements and masses
   - Internal standard element and mass
     1. Amount contained in sample no more than 1/100 of added amount
     2. Ionization energy close to that of target element
     3. Not subject to spectral interference
     4. No spectral interference with target element
     5. Sufficient sensitivity
5. Setting of calibration samples
6. Method completed in 10 min. or more

Development Assistant

1. Prepare samples
2. Perform qualitative analysis (all elements)
3. Select elements
   - Measurement masses, internal standard element (mass) and calibration standard concentration are set automatically using the database.
4. Method completed in 2 min.
Checking Data – Post Processing

Checking data Conventionally

* If only target elements are measured, then information about other elements is not obtained, which means the presence of interference cannot be determined.

* When analyte element and other elemental spectra were measured, interference can be determined

If 100 samples are measured, then basically checks the above for all samples.

If there are problems, it is necessary revise the method.

Checking process completed in 30min. or more

Diagnosis Assistant function

Checking Data using Diagnosis Assistant function

Diagnosis assistant function automatically checks for any spectra interference based on all elements and all mass data for all measured samples

All element and all mass profiles

If a problem is founded, Assistant function shows what kind of problem occurs in each sample.

Checking process completed in 3 min.
Collision Cell

- He gas in the collision cell collides with polyatomic ion and measurement ion.
- The measurement ion overcomes the energy barrier (KED: kinetic energy discrimination).
- Polyatomic ion have a higher energy loss because it has a larger cross section.
- The energy loss of the polyatomic ion increases and is separated by the energy barrier (KED).
Mass Spectrum using a Collision Cell

56Fe, Interference by ArO
40Ar+16O=56

75As, Interference by ArCl
40Ar+35Cl=75
Cost Reducing Features for ICPMS

- 40% reduction of argon consumption by Mini torch
- 70% reduction of argon consumption in standby mode
- Ar gas of 99.95% or greater purity is enough

![Graph showing argon consumption](chart.png)
## Benefits of ICP-MS

- Excellent detection limits
- **Sample throughput**
  - Can run overnight
  - "Simultaneous" measurement of all elements
- Excellent LDR
- Capable of isotopic analysis
- Uses small amounts of sample
- Uses inert gas

## Drawbacks of ICP-MS

- Cost
  - Capital
  - Operating
    - Consumables (e.g. cones)
- Prone to chemical interferences
- Cannot handle high TDS (<0.1%)
- Skilled analyst generally required
- Environmental considerations
  - Clean lab
- Plasma must be optimized
  - Can be difficult to sustain
- Not common in petrochemical industry
  - Industry methods usually AA, ICP-OES
Detection Limits and Measurement Range

Why the difference Range?
The analysis range is related the technique

Atomic Absorption
• Techniques have different ranges based on flame or graphite furnace
• Flame: few hundreds ppb to a few hundred ppm
• Furnace: mid ppt range to few hundred ppb range

ICP-OES
• Two different observation modes: Axial and Radial
• 20x difference between Axial and Radial
• High ppt to mid % level concentrations

ICPMS
• Most sensitive and widest range
• Range is a few 10s of ppq to a few hundred ppm
Why the difference in speed?
The analysis speed is related to the technique

Atomic Absorption
- Liquid samples are desolvated, vaporized, and atomized by a flame or a graphite furnace.
- The gaseous atoms pass through a beam of light emitted from a radiation source like Hollow Cathode.
- The element absorbs an amount of light that is proportional to its concentration. The process repeats for each element

ICP-OES
- Liquid samples are desolvated, vaporized, atomized and excited in an argon plasma
- Excited atoms relax back to ground state and emit characteristic wavelengths of light whose intensity is proportional to its concentration
- A detector collects all the emitted wavelength of light

ICP-MS
- Liquid samples are desolvated, vaporized, atomized and ionized in an argon plasma
- Elements have different mass once ionized, each element forms its own characteristic mass spectrum
- A ion counting detector counts the ions at each mass-to-charge ratio which is proportional to the concentration of each element
Performance vs. Investment of each Technique

Economics of Ownership

Atomic Absorption
- Flame uses Lamps, Gasses & O-rings
- Furnace in addition need Graphite tube and Caps & Holders

ICP-OES
- Argon gas (Purge Gas: Argon or Nitrogen)
- Glassware: torches, spray chambers, nebulizers

ICPMS
- Argon gas (Purge Gas: Argon or Nitrogen)
- Glassware: torches, spray chambers, nebulizers
- Cones: Skimmer and Sampling
Thank you for your time!

Any Questions?