Elemental Analyses by ICP-AES

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Electrons of an atom absorb energy and jump to higher energy levels. When they return to normal states, they emit characteristic photons of energy. By isolating these photon wavelengths, we can determine the types and concentrations of the elements present.
Sample Introduction

- Solution is drawn up by means of a peristaltic pump
- Solution is turned into a fine aerosol by a nebulizer
- Aerosol is introduced into a plasma which excites the atomic species in the aerosol
Ionized argon stream carrying current is roughly the surface temperature of the sun.

Only a small portion of the plasma is sampled.
Prisms and echelle grating separate out (disperse) the wavelengths of emitted radiation into distinct, measurable, emission lines.
Different elements have different emission intensities. Alkalis (Na, K, Rb, Cs) are weakly emitting. Alkaline Earths (Be, Mg, Ca, Sr, Ba) are strongly emitting.
Radial vs. Axial Viewing

Radial - traditional side view, better for concentrated samples.
Axial - direct view into plasma, lower sensitivity, shifts detection range lower.
Radial AND Axial Viewing
Common Problems in ICP-AES

Sampling and Sample Preparation
Spectral Interference
Matrix Effects
Instrumental Drift
Sampling and Sample Preparation

Are the samples representative of what you are trying to measure?
What steps should MCL take to make your samples representative?
Will any elements volatilize during sample preparation?
How much contamination can the sample tolerate during preparation?
Spectral Interference

Some elemental lines may interfere with others.

Best solution is to find another spectral line.

Samples should be scanned for possible problems.

**Figure 4-10.** Tungsten matrix spectrum causing a complex background shift at the gold 267.595 nm line.
Matrix Effects

Differing viscosities can affect amount of sample uptake

Matrices can change nature of plasma

Certain matrices (HF) can attack torch

Matrices can contain interfering spectral components
Combined Effects

Figure 4-11. Components of the emission spectrum.

Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, Boss and Freeden, Perkin Elmer
Instrumental Drift

Instrument reading can drift over a period of time due to physical changes in the optical system, or the configuration of the plasma.

Standards need to be run at the beginning and end of each run in order to estimate and correct for this drift.

Internal standards are used to compensate for differing matrices from sample to sample.
Compensation

Standards run with every sample run

Drift Correction or internal standardization is taken with every sample run

Matrix of standards should be closely matched with that of the samples

Preliminary scans are taken to see if any spectral overlaps occur
Figure 4-1. Flow chart showing the methodology for a typical ICP-OES analysis.
Sample Dissolution for Solid Samples

Salt Fusions - typically lithium metaborate and sodium peroxide

Acid Digestions - nitric, hydrochloric, perchloric and hydrofluoric

Microwave Digestion - basically acid digestion in controlled temperature and pressure vessels.

Samples are typically dried, ashed if necessary, and ground to <74 microns prior to dissolution procedures
Salt Fusion

Sample is mixed with lithium metaborate in a 1:9 ratio.
Mix is melted at 900°C and dissolved in a nitric acid solution.

Pros:
Attacks geologicals and most ceramics.
Provides a high concentration salt environment which dampens any intersample matrix differences.

Cons:
Easily volatilized elements cannot be determined.
High metal contents may prove difficult.
Graphite crucible with lithium metaborate in furnace
Acid Digestion

Sample is allowed to dissolve in an acid mix.
Sample is typically heated to speed dissolution.

Pros:
Most direct dissolution, minimizing possible introduction of contaminants
Usually best for metals

Cons:
Ineffective against geologicals and ceramics, especially if Si is to be determined
Can be time consuming
Acid digestion in a Pt dish
Microwave Digestion

Sample is allowed under controlled temperature and pressure conditions in a pressure vessel.

Pros:

Effective for a wide range of materials, especially those containing organics

Direct method of dissolution, minimizing introduction of contaminants

Cons:

Time consuming method development

Labor intensive
Data Reduction

Figure 2-6. Calibration curve used for ICP-OES.

Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, Boss and Freeden, Perkin Elmer
What do the data mean?

Precision and accuracy

• Precision is how well the instrument replicates data over time

• Accuracy is how close to the true value the observed results will be

• Precision is generally on the order of 2 to 5 relative weight percent

• Precision will vary from sample type to sample type depending on a number of factors
## Typical Analytical Data

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<th>Sample</th>
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<th>2nd</th>
<th>3rd</th>
<th>Mean</th>
<th>Extrapolated</th>
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Typical applications of ICP-AES/ICP-MS

- Natural Waters
- Saline Brines
- Geological Materials
- Ceramics and glasses
- Coals and Paper Products
- Leachates
Natural Waters

• Leaching from mine sites
• Geochemical prospecting
• Sediment analyses
More Sample Types

Discarded candy wrappers

Glass and geologicals
Strengths of ICP-AES

- Can detect most cations and some anions
- Detection Limits down to parts per trillion for some elements
- Rapid simultaneous determination of selected elements
- Selective determination of other elements in sequential mode
- Good linear range - up to hundreds of ppms for alkalis
- Suitable for routine analyses of multiple samples
- Dependable work horse type of instrument
Weaknesses of ICP-AES

- Not effective for low levels of alkalis (less than 1-5 ppm)
- Subject to matrix problems
- Suitable standards required on every run
- Only elemental data is provided - no direct structural information
- Does not provide, in most cases, parts per billion or parts per trillion data – Go to ICP-MS
MCL capabilities:

Perkin-Elmer Optima 5300 ICP-AES

Lithium Metaborate and Sodium Peroxide Fusion capabilities.

Acid Digestion Facilities

MARS Microwave Digestion Capabilities
Acceptable sample forms:

- Solutions, preferably aqueous based with minimal or no HF
- Minimal solution volume is 3-4 ml or more depending on analyses
- Solids, can usually be dissolved using various techniques
Characterization Techniques for Solutions

<table>
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<th>Concentration Level (ppm or mg/L)</th>
<th>Technique</th>
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<tr>
<td>&gt;1</td>
<td>ICP-AES</td>
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<tr>
<td>.01-1</td>
<td>ICP-AES, ICP-MS</td>
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<tr>
<td>&lt; .01</td>
<td>ICP-MS</td>
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</table>

For unknown solutions, characterize with ICP-AES THEN use ICP-MS to determine lower concentrations of interest.
ICP-AES vs. ICP-MS

ICP-AES is an atomic emission technique - the inductively coupled plasma (ICP) serves as a means of exciting atoms and ions so that they emit characteristic wavelengths of energy.

ICP-MS is a mass spectrometric technique - the ICP serves only as a means of generating ions for the mass spectrometer.
ICP-AES

Robust and cheap
Dependable
Student Proof (sort of)
Good for routine analyses

ICP-MS

Delicate and expensive
Finicky
Student phobic
Capable of extraordinary performances