Elemental Analyses by ICP-AES

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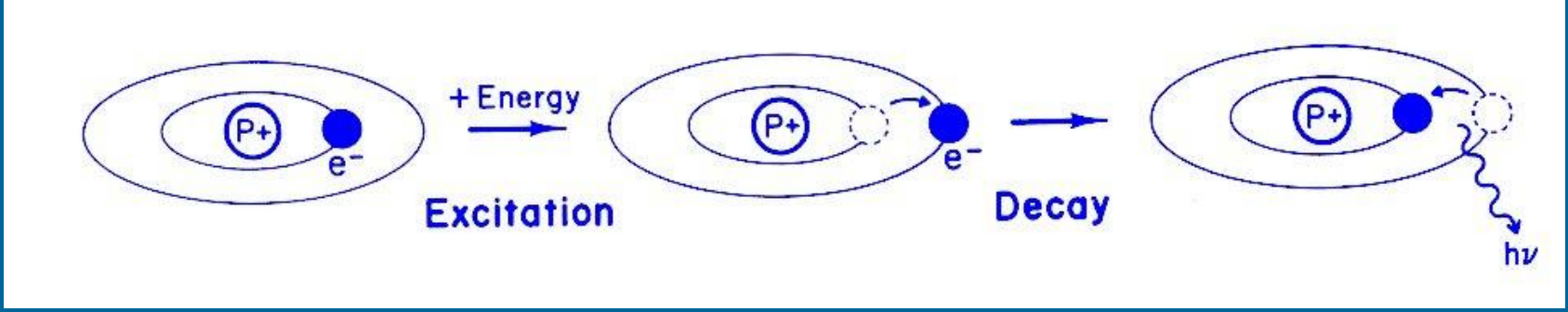
ICP-AES – inductively coupled plasma atomic emission spectrophotometry



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.

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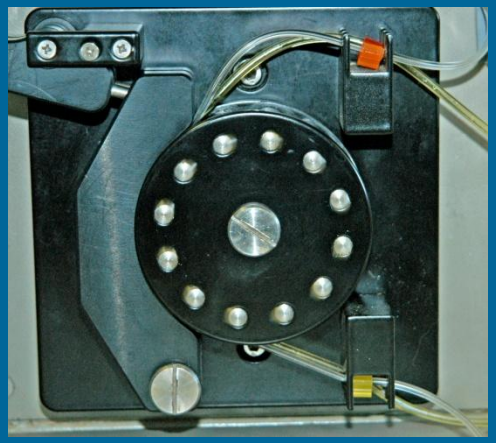
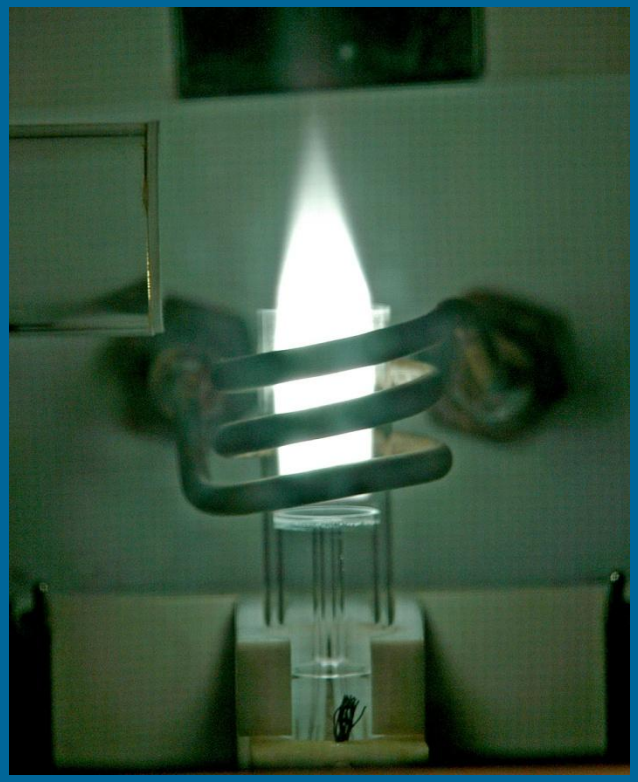
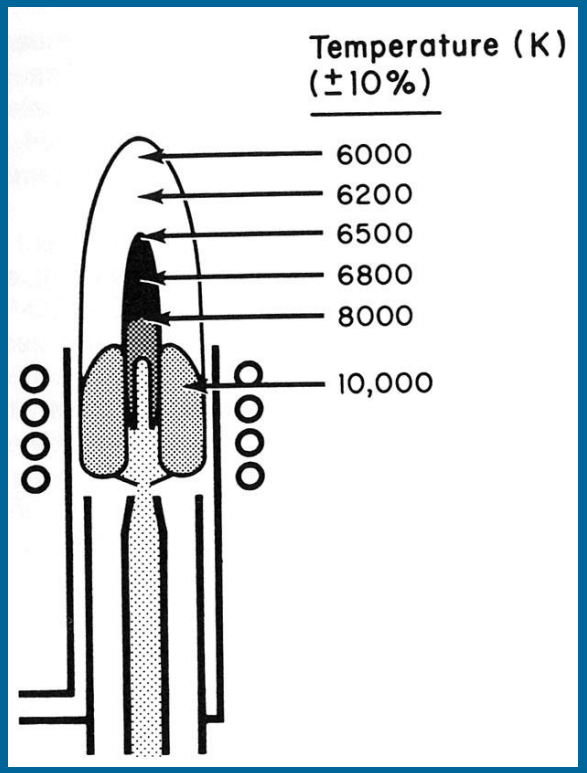
Sample Introduction

- 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



Plasma Torch





Ionized argon stream carrying current is roughly the surface temperature of the sun.

Only a small portion of the plasma is sampled

Optical Path in an ICP-AES

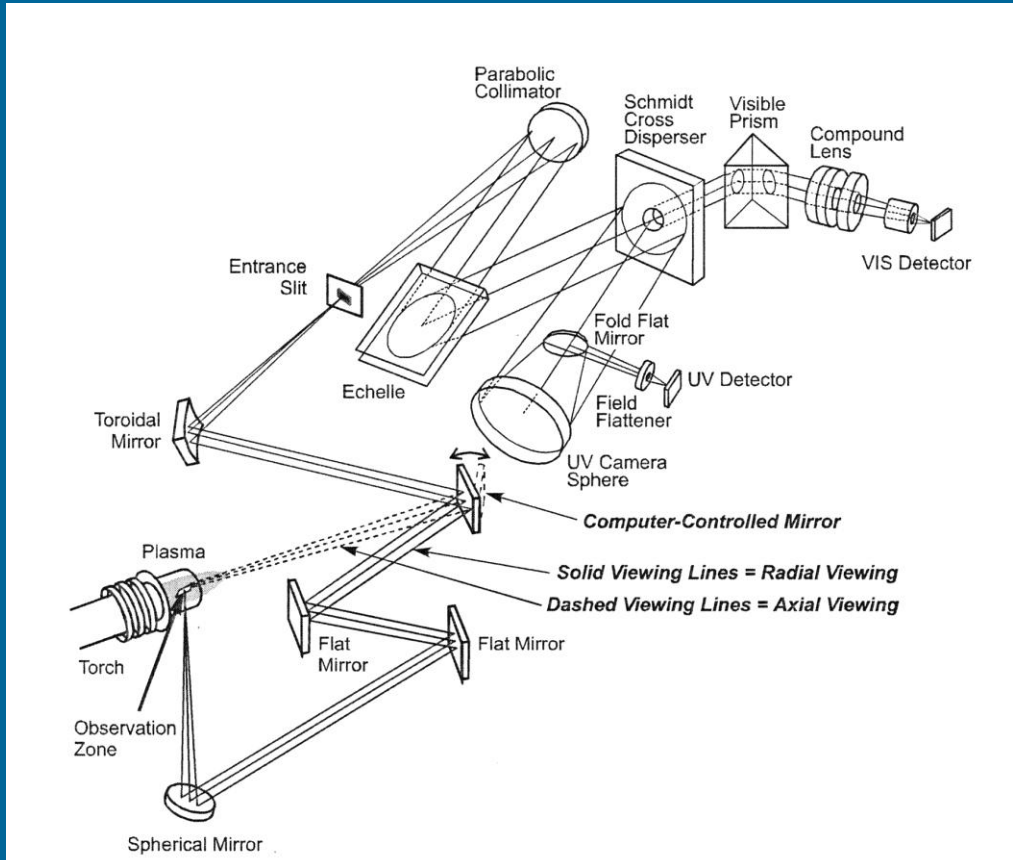
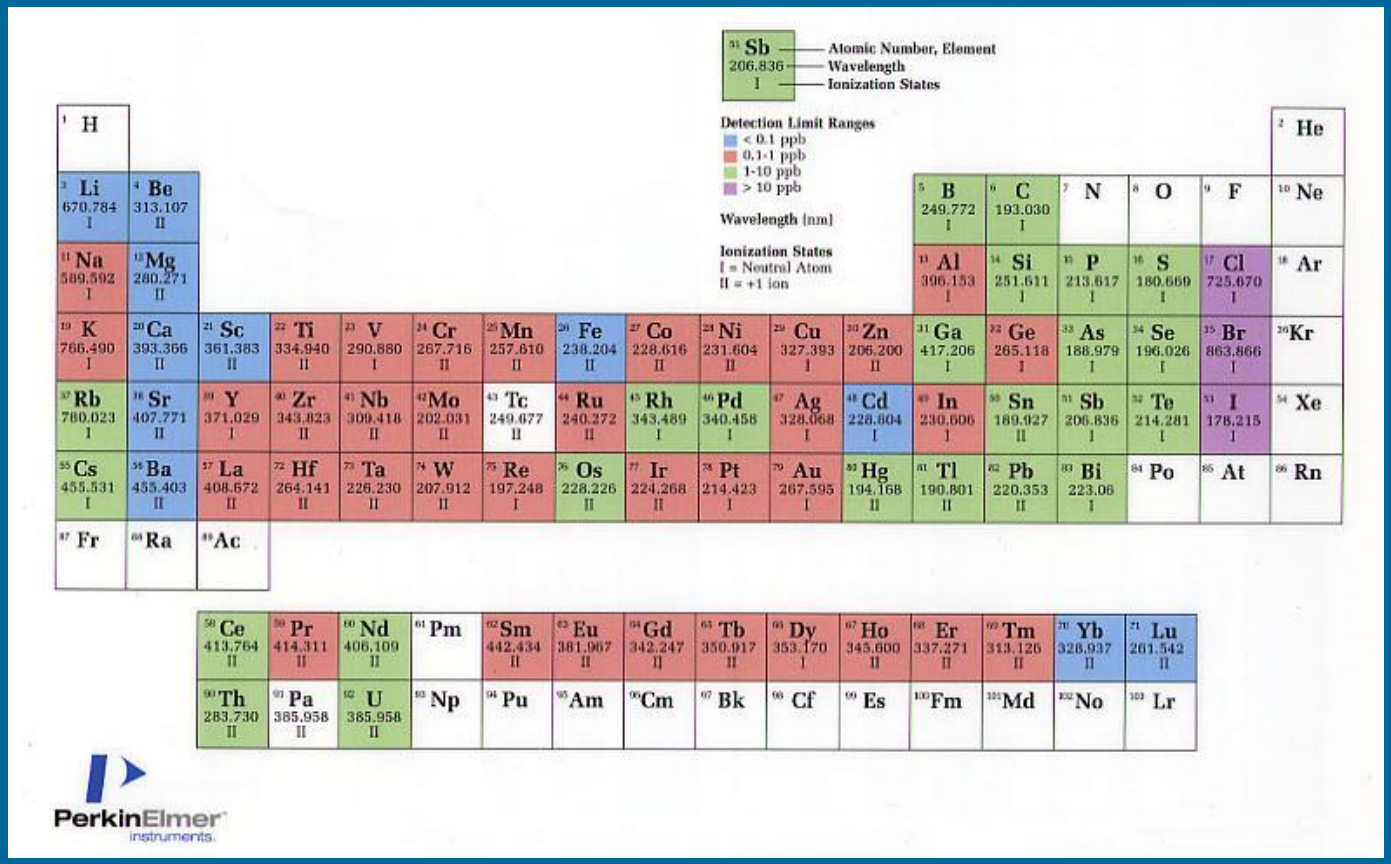


Figure 3-15. Schematic diagram of the Optima 5300 DV optical system.

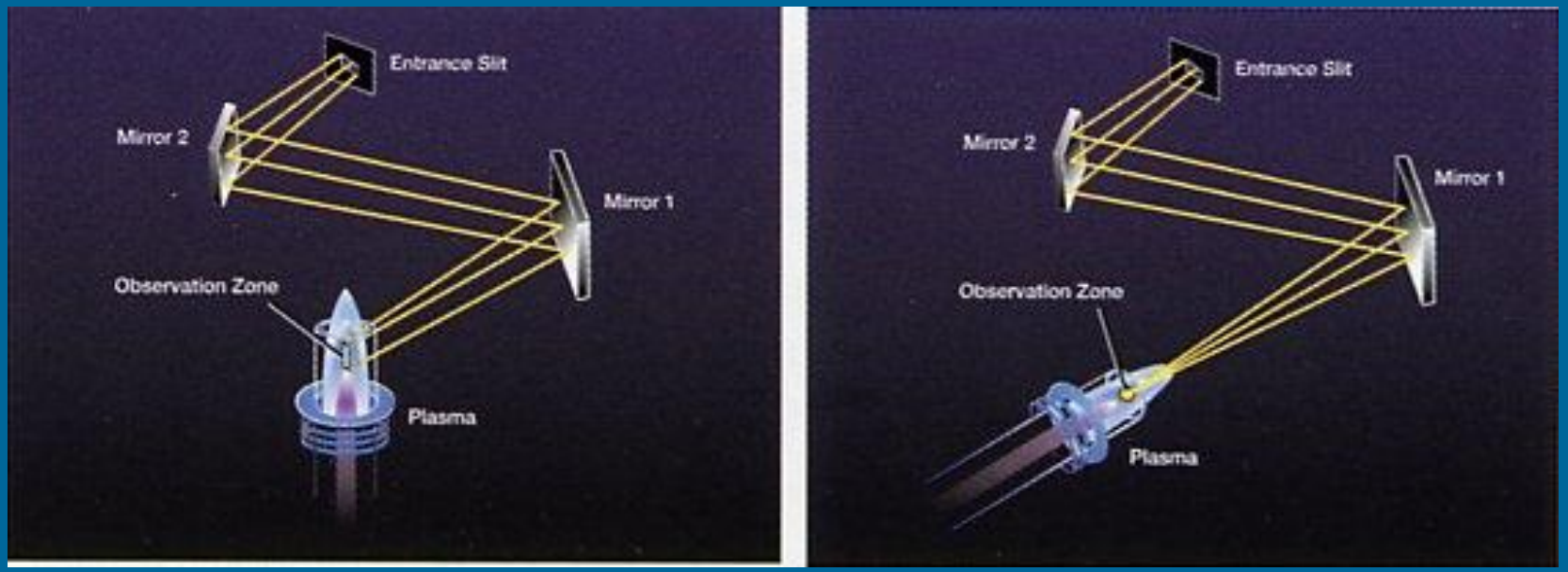
Prisms and echelle grating separate out (disperse) the wavelengths of emitted radiation into distinct, measurable, emission lines.

Elements by ICP-AES



Different elements have different emission intensities. Alkalis (Na, K, Rb, Cs) are weakly emitting. Alkaline Earths (Be, Mg, Ca, Sr, Ba) are strongly emitting.

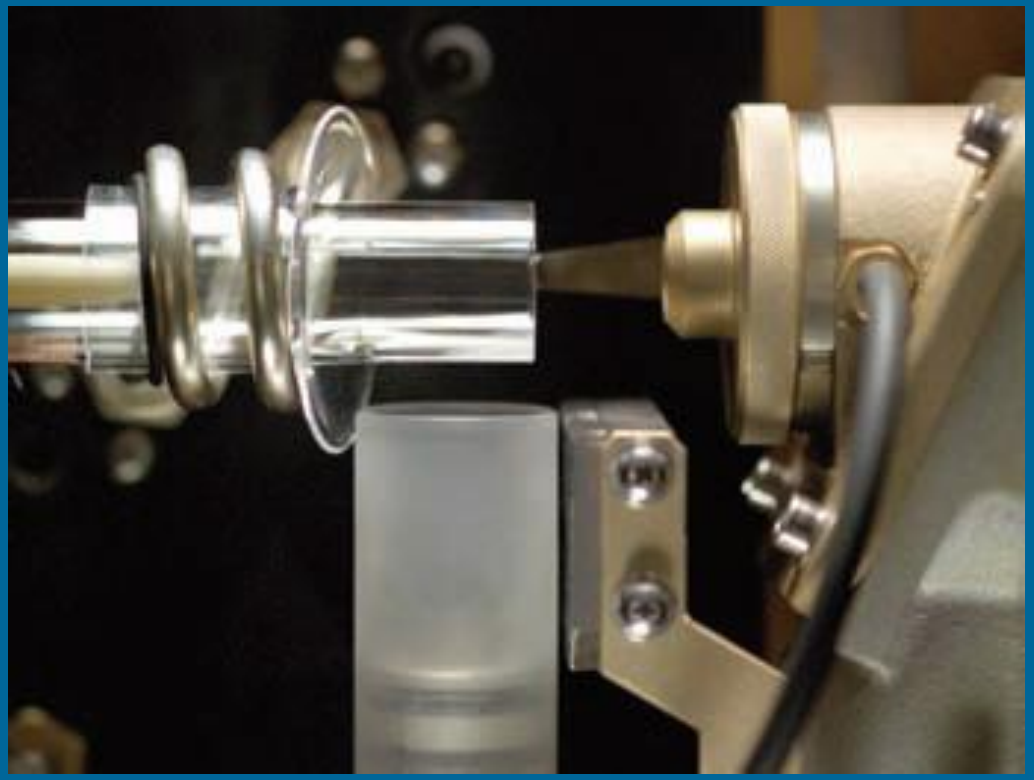
Radial vs. Axial Viewing



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

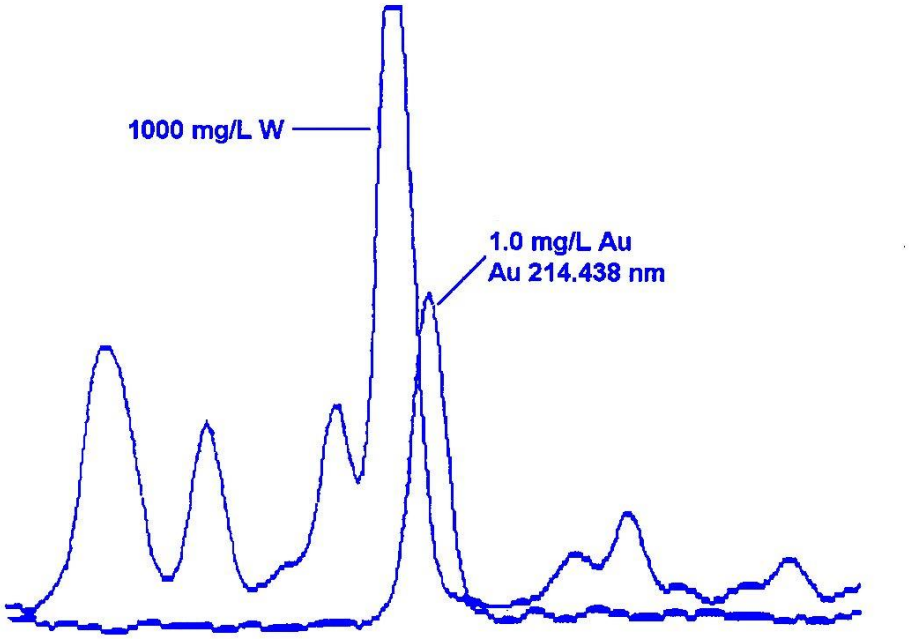


Figure 4-10. Tungsten matrix spectrum causing a complex background shift at the gold 267.595 nm line.

Some elemental lines may interfere with others.

Best solution is to find another spectral line.

Samples should be scanned for possible problems

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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

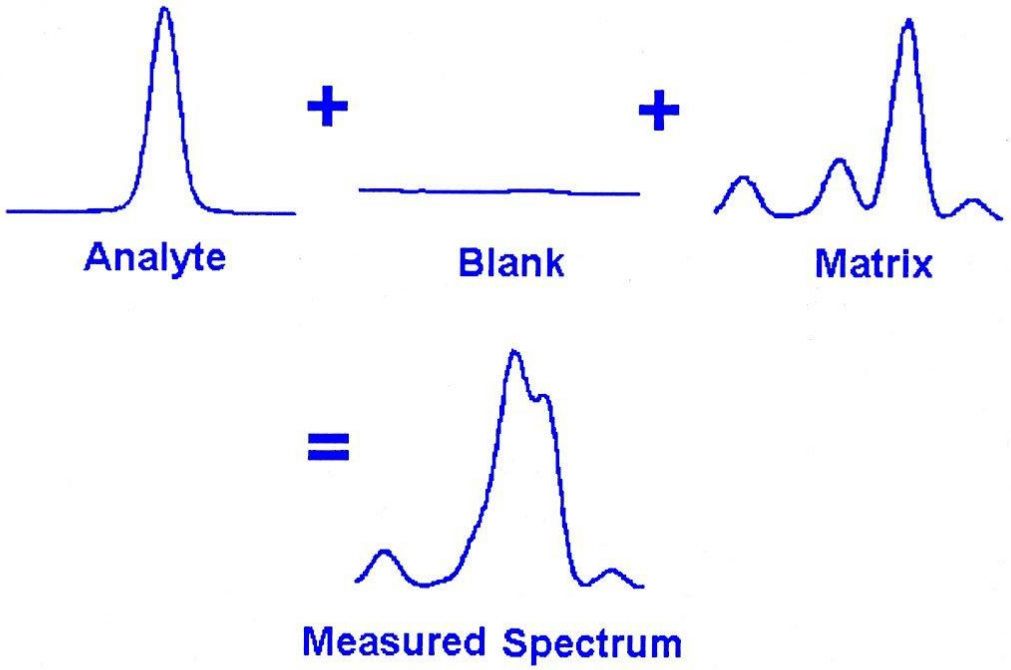

Figure 4-11. Components of the emission spectrum.

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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

Basic Analytical Scheme

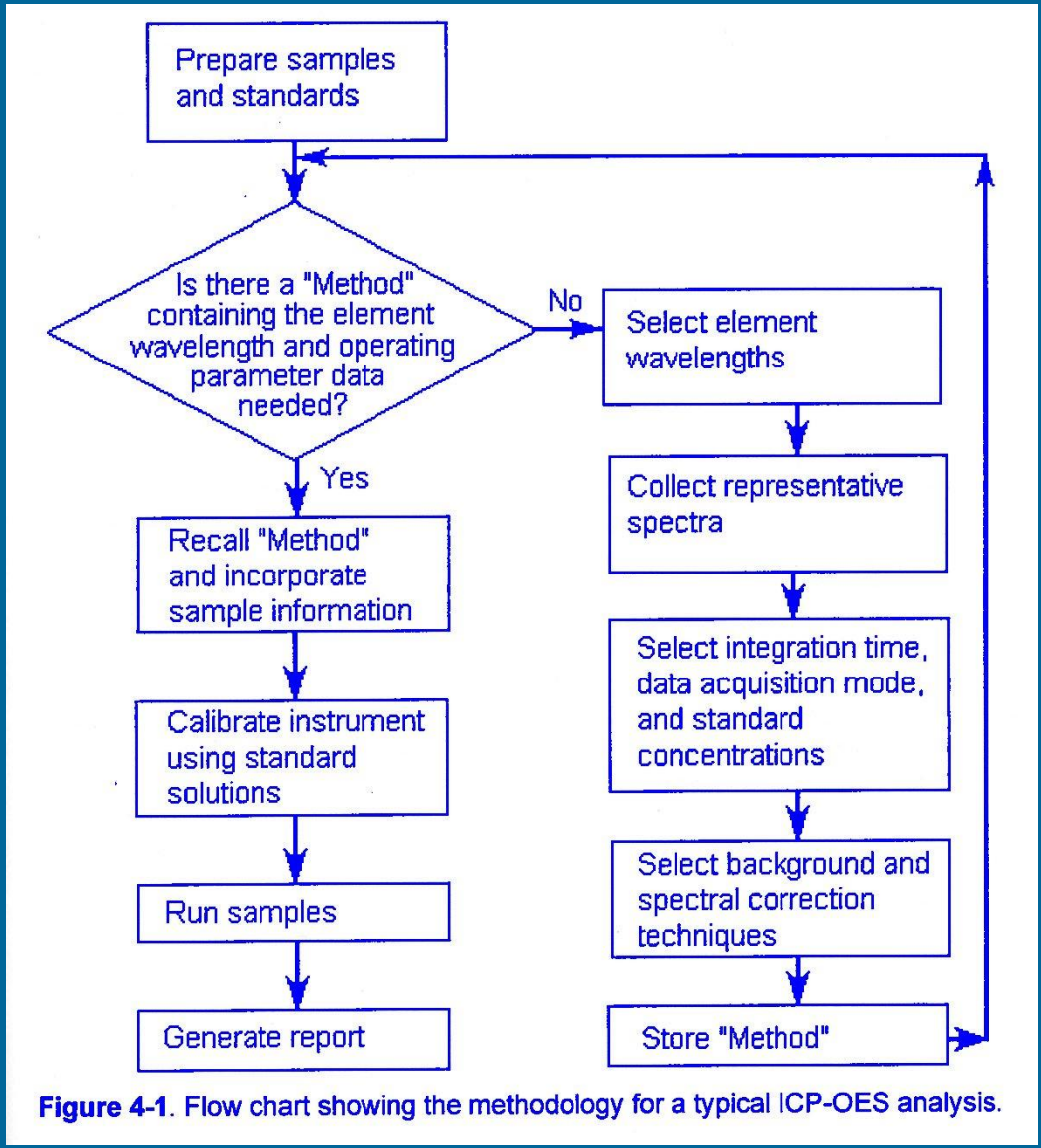

Figure 4-1. Flow chart showing the methodology for a typical ICP-OES analysis.

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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 900C and dissolved in a nitric acid solution

Pros:

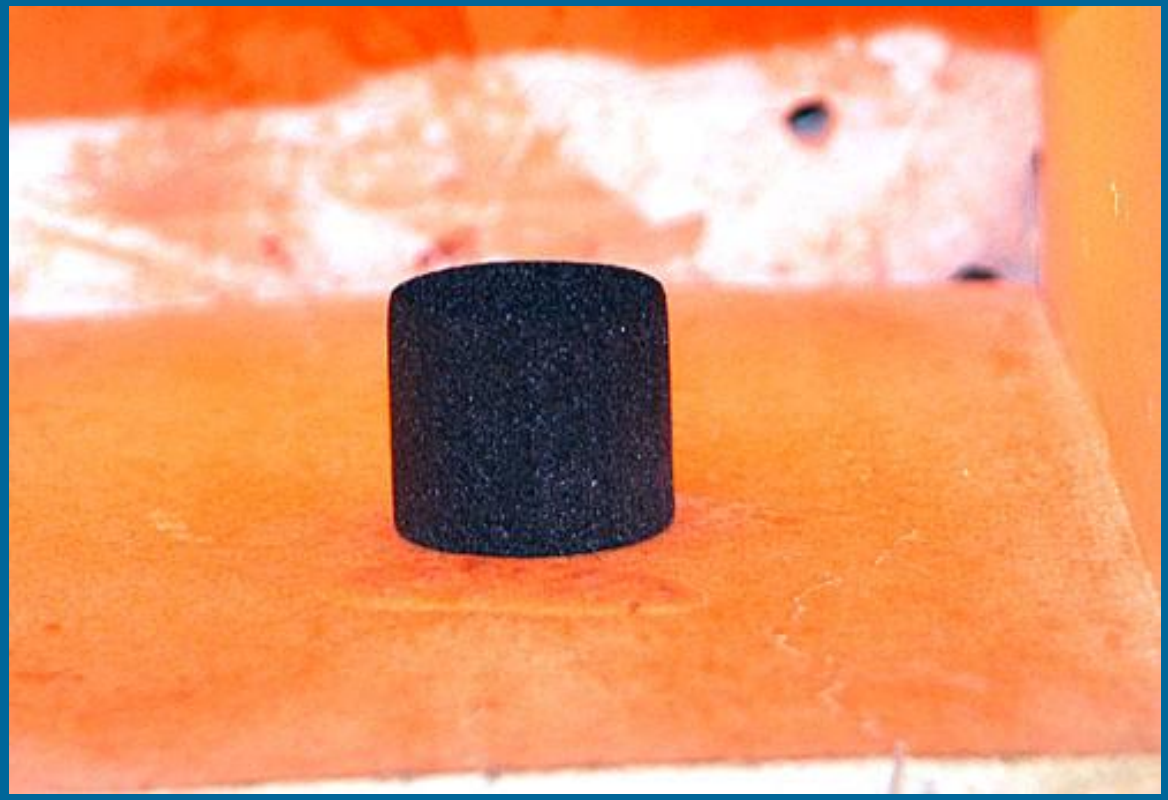
Attacks geologicals and most ceramics

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:

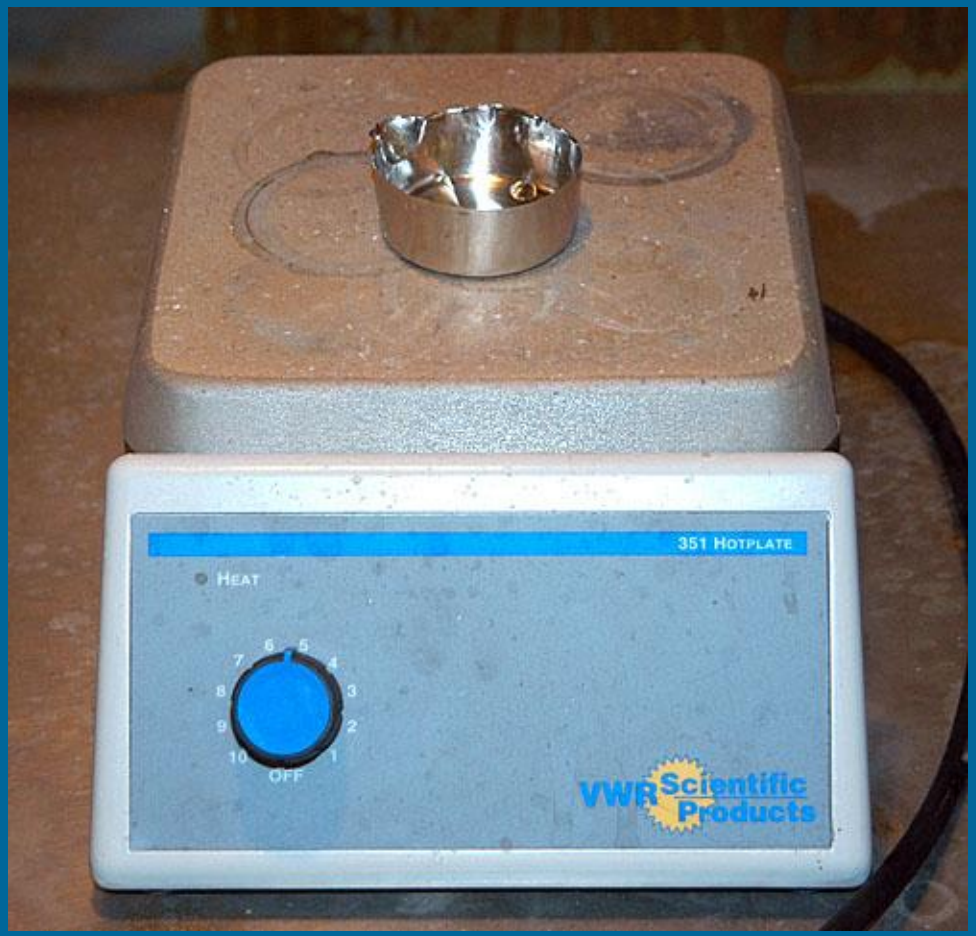
Most direct dissolution, minimizing possible introduction of contaminants

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

MARS 5
Microwave
Digestion System

Data Reduction

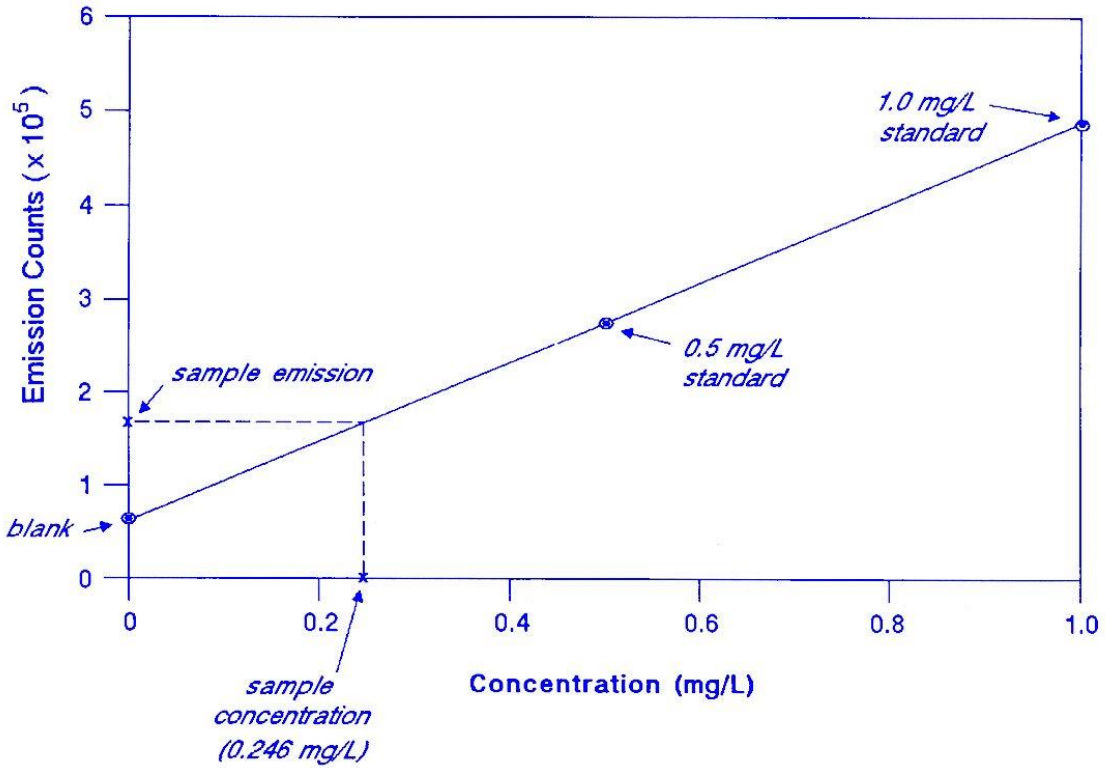


Figure 2-6. Calibration curve used for ICP-OES.

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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

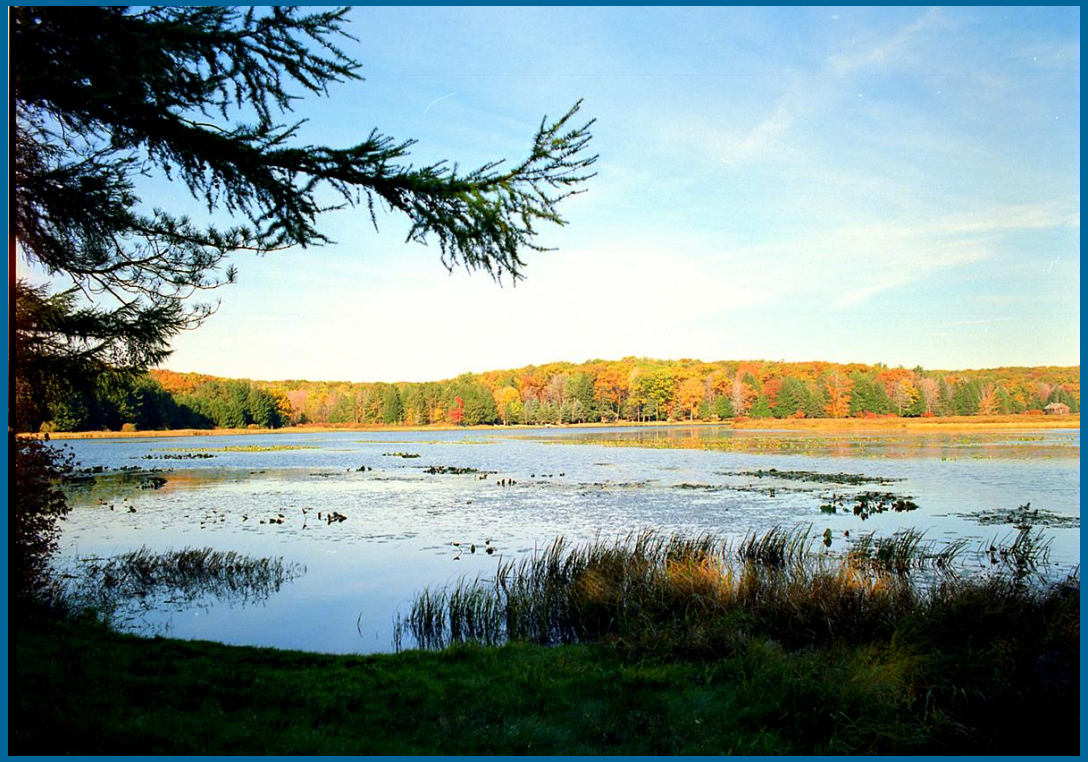
- Precision is generally on the order of 2 to 5 relative weight percent
- Precision will vary from sample type to sample type depending on a number of factors

Typical Analytical Data

Sample	1st	2nd	3rd	Mean	Extrapolated
04-1141	2.788	2.728	2.739	2.743	**2.76**
04-1152	.279	.269	.268	.272	**.27**
04-1160	1.112	1.112	1.118	1.114	**1.12**
blank	-.0005	-.0004	-.0003	-.0004	**-.01**

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

Concentration Level (ppm or mg/L)	Technique
>1	ICP-AES
.01-1	ICP-AES, ICP-MS
< .01	ICP-MS

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

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