12.119 Geochemical Analysis of Environmental Materials Spring 2004

Atomic Spectroscopy: Atomic Absorption, Atomic Emission and related optical techniques

I. Atomic spectroscopy techniques: their analytical role

A. The methods provide relatively rapid analysis (<1 minute for a single element; with multi-wavelength detectors, one can measure several elements simultaneously) of aqueous solutions at appropriate concentration levels (what is appropriate depends on the element and variant, but typically is micromolar, occasionally nanomolar). This pace makes it appropriate for routine monitoring and large-volume operations where detection of concentrations exceeding some critical level (e.g. chemical processing control; wastewater treatment plants, clinical labs). Optical methods are suitable for many elements (40-80), so they are versatile.

B. Sample size: milliliters for nebulized flame/plasma methods; tens of microliters for graphite furnace methods.

C. Sensitivity: typically ~10^{-6}M for flame methods; ~10^{-9}M for graphite furnace and recent plasma methods (for suitable elements). Concentration procedures (evaporation, coprecipitation, adsorption onto columns followed by elution,…) allow for analysis of lower levels while requiring larger samples.

D. Precision: 1-3% for typical effort; as good as 0.2% for some cases with special attention; 5% with very little effort.

E. Accuracy: depends on control of interferences; in a well-controlled analysis, accuracy is comparable to precision.

F. Range of elements: Most elements except upper right hand portion of the periodic table (e.g. halides, sulfur, carbon, phosphorus). Sensitivity varies with the absorption behavior of each element. Some refractory (difficult to atomize) elements are not sensitive for flame methods, although these elements usually are sensitive by plasma emission methods.

G. Low to moderate cost instrumentation ($10,000-$100,000). For atomic absorption, each element requires a separate light source (~$400). For plasma methods, the argon supply is a major cost ($5,000-$10,000 per year for an instrument in frequent operation)

H. Autosamplers can minimize the need for operator attention, once the instrument is set up and going smoothly.

II. Physics of atomic absorption and atomic emission

A. Electron energy states in an atom are characterized by discrete energy levels. Transitions of electrons to higher energy levels can be caused by (A) the absorption of photons or (B) thermal energy, and transitions to lower levels are accompanied by (C) the emission of photons. (A) is the phenomenon of atomic absorption whereas (C) is the phenomenon of atomic emission. The outer shell electron(s) are involved in this phenomenon. Transitions between these energy levels are discrete, resulting in sharp absorption and emission optical spectra in the visible and ultraviolet regions (approximately 180-800 nanometers wavelength).

B. History

1. Early 1800's: Wollaston observed dark bands in the spectrum of the sun; Fraunhofer designed instrumentation which recorded the position of ca. 500 absorption lines in solar spectrum.
3. 1860, 1861: Kirchoff and Bunsen established spectrochemical analysis. Kirchoff explains underlying basis of relation between emission and absorption.
4. Astronomers continue to use technique to establish stellar composition; chemists use emission for semi-quantitative analysis. Development of film recording spectrographs.
5. 1950's: Walsh develops atomic absorption spectroscopy (AAS).
6. 1960's: first commercial AAS instruments (Perkin-Elmer; Beckman; Jarrel-Ash).
7. 1970's: development and refinement of graphite furnace AAS.
6. late 1970's: inductively coupled plasma emission spectroscopy develops.

III. Absorption spectrophotometry concepts

A. Transmittance: the fraction of light which passes through an absorbing medium; commonly expressed as "percent absorption".

B. Beer's law: establishes relationship between concentration and the logarithm of the absorption in a medium of uniform concentration of absorbing materials

$$-\log\left(\frac{I}{I_o}\right) = \varepsilon C \Delta x$$

where I_o is the ingoing light intensity
I is the outgoing light intensity
ε is an extinction coefficient (a constant for a particular transition)
C is the concentration of the absorbing substance
Δx is the distance the light passes through the medium.

C. The atomic absorption extinction coefficient is a fundamental property of each atom, so <u>if</u> we could confine an exactly known number of atoms in a space and measure an absolute extinction coefficient, and <u>if</u> we could convert the elements within a sample to their atomic state in the same space, then we could then get an absolute analysis of the atomic concentration. <u>In practice</u>, it is too difficult to convert a sample into atoms confined within a known space, so most atomic absorption (and emission) measurements are made by proximate reference to a <u>standard</u> of known concentration, hence establishing an "f e Δx" term where f is a "fudge factor" which accounts for incomplete conversion of elements to the ground level atomic state. Hence these methods are <u>relative</u> (to standards), not absolute.

IV. Atomic absorption instrumentation

A. Light sources

1. <u>In principle</u>, a broadband continuum source of white light could be used as a light source and the absorption resolved by a spectrograph, much as the Fraunhofer lines are seen against the solar continuum. <u>In practice</u>, spectrographs which can resolve atomic lines are large, expensive and require narrow slits, and most light sources are as not bright as the sun! Hence we need to use a light source which aids our spectrograph at lower resolution.

2. John Walsh first suggested the use of a light emission source composed of a particular element (e.g. hollow cathode lamp). In this case, the light source is specific for the emission lines of the element, and the spectrograph does not have to have high resolution to take advantage of the narrowness of the atomic lines (the narrow line of correct wavelength being automatically supplied by the light source). For example, if two elements have nearby absorption lines, the spectrograph doesn't have to resolve these lines if the light source emits light at the wavelength of only one of these elements.

3. Hollow cathode light sources

   a. ~2 mm hole is drilled into a block of high purity metal; this block of metal is placed into a vacuum tube containing a noble gas (e.g. Ar) at moderately low pressures (a few milliatmospheres). This cavity is then maintained as the cathode at a few hundred volts potential relative to the anode. Under these conditions, argon is ionized, accelerated by the electrical potential gradient, and bombards the cathode with sufficient energy to sputter individual atoms of the metal into the hole. These atoms in turn collide with the energetic Ar ions, and their outer electrons are excited resulting in the emission of light at the characteristic wavelengths of the element.

b. Hence the ionized Ar gas is serving a dual purpose: sputtering and ionization. These functions work at cross purposes. In order to have more light emitted, you will want to have more atoms available and more energetic argon ions; these can both be achieved by turning up the electrical potential. Unfortunately, building up more atoms eventually leads to the phenomenon of <u>self-absorption</u>, where there are enough atoms in the tube to absorb the photons emitted by other atoms. Hence there is point of no-return beyond which turning up the potential results in *fewer* photons of the correct wavelength, so hollow cathode lamps have a natural maximum voltage (current) level for optimum absorption. You can physically run the lamp at higher currents (to a point) without destroying the lamp, but you then lose narrow-band light intensity.

4. Other light sources: for some elements, hollow cathode lamps do not provide a strong output, raising the noise level and degrading detection limit. Hence other light sources are needed for atomic absorption measurements of some elements.

   a. Electrodeless discharge lamp (radiofrequency excitation)

   b. "Superlamp" 4-electrode hollow cathode lamp.

C. Beam-splitting optics: allows for “double-beam” operation (comparison of reference and sample beams).

D. Atom sources

1. Nebulizers: need to have a small uniform droplet size; most require screening out larger droplets (90-99% of total solution)
2. Flames
   a. air-acetylene (good general-purpose; safety issues w/acetylene are significant but manageable).

   b. nitrous oxide-acetylene (higher temperature; better for refractory elements - note significantly higher explosion risk)

   c. air-hydrogen (lower temperature; less ionization of easily-ionized elements)

3. Graphite furnace

4. Hydride generators; cold vapor generators

E. Grating monochrometer and slits

F. Photon detection.

1. In most instruments, a cascade photomultiplier vacuum tube is used to detect the light. In the appropriate light intensity and amplification (voltage) range, the current of the photomultiplier is linear with the intensity of the incoming light. Hence the current coming out of the photomultiplier can be used to estimate I/I_o.

2. Almost as universally, the photomultiplier is used in an alternating current mode derived from an <u>emission chopper</u> or an <u>electrically pulsed hollow cathode lamp</u>. Almost all means for creating atoms involve heating sources (flame, plasma, hot graphite) that emit continuum light; hence we need to be able to distinguish between light emitted by the hollow cathode source and the

atomizing device. This can be done by pulsing the light source and putting a DC-blocking circuit on the detector.

3. Other light detection devices (e.g. charge coupled device) could be used as well, but the photomultiplier is cheap and rugged and well-understood, and hard to beat for general-purpose instrumentation. The CCD does allow for the possibility of some multiple-wavelength detection, however
4. Signal-to-noise ratio: relevant factors.

V. Calibration and interferences

A. It is easy to spray an element into an AAS instrument and have the instrument throw numbers back out at you. Without proper attention to calibration and interference control, these numbers can be almost meaningless.

B. Atomic spectroscopy methods are relative, so all concentrations are determined by reference to standards which are used to establish a <u>standard curve</u> (absorbance vs. concentration). This standard curve depends on the instrumentation and normally should be expected to <u>drift</u> slightly as the instrument warms up (both electronically and from the heat of the flame and lamp stabilization), so standards are typically run every few samples to monitor this drift.

1. Beyond a certain absorbance level, standard curves are non-linear. You must either dilute samples to be within the linear range, or use <u>curvature correction</u> algorithms to compute concentration from absorbance in the non-linear portion of the standard curve.
2. Curvature arises from:
   - a. <u>Stray light in the instrumentation.</u> Even at "infinite" concentration (complete absorption of light at the atomic wavelength), the detector will see this stray light and hence I/I_o will not be equal to zero. This is a problem common to all forms of UV/visible spectroscopy, but it is more of a problem in atomic spectroscopy methods because of light emission by the flame and graphite furnace sources. Note the importance of keeping the optics clean and masking out unwanted stray light.
   - b. <u>Overlapping spectral lines.</u> Sometimes a hollow cathode lamp will have two emission lines that are close enough together that the instrument cannot fully resolve them (e.g. Ni, Co). Of these two lines, one is the desired analytical line and the other is one that either absorbs significantly less (or not at all) than the desired line. In this case, then even at "infinite" concentration, the light from the secondary line will reach the detector and I/I_o will be greater than zero.
   - c. <u>Non-optimal light paths</u>: the shape of the light beam changes in transit between entering and leaving the flame, and it may be larger than the thickness of the flame. Light passing outside the flame or through non-absorbing parts of the flame cannot be absorbed.

C. Spectral interferences

1. <u>In the light source</u>: the source may emit a spectral line (e.g., from impurity) that falls within the spectral window of the monochromator. If that spectral line is an absorbing line of an element that occurs in your sample, then absorption will occur in the absence of the element you are trying to analyze (false positive).
2. <u>In the medium:</u> air absorbs strongly in the far-ultraviolet.
3. <u>In the atom source</u>: a flame contains species which absorb at certain wavelengths.

4. In the sample composition: The sample may contain elements which absorb the non-analytical spectral lines from the light source, or create molecular species and particulates ("smoke") which absorb light at particular wavelengths or in a continuum. The latter non-specific background absorption by "smoke" can be corrected for with the appropriate instrumentation (see later).

D. Atomization and Ionization interferences (flame spectroscopy)

1. The solution must be presented to the flame in the form of fine droplets that can be completely evaporated and converted to atoms in their short residence time in the flame. A poorly functioning nebulizer can prevent proper atom formation.

2. Even with a properly-functioning nebulizer, there are chemical effects may prevent conversion of the element of interest into atoms:

   a. a refractory element may need a temperature greater than that of the flame to convert to atoms.

   b. molecular species stable at high temperatures (e.g., $CaPO_4^-$) may form which resist conversion of the element to the atomic state.

   c. ionization interferences

      i. An easily ionized-element (e.g. Na) may be into an ionized form which does not absorb at the analytical wavelength.

      ii. The extent to which an easily-ionized element is ionized may depend on the presence of other easily-ionized elements (e.g., Na will ionize less in the presence of an excess of a more easily ionized element such as Cs).

3. To some extent, these interferences (2., above) can be controlled:

   a. change the fuel/air ratio of the flame (this alters the temperature and oxidizing/reducing characteristics of the flame).

   b. use a higher temperature flame (e.g. N_2O-acetylene) for refractory elements

   c. stable molecular species: add another element which out-competes the element of interest for the co-ion (e.g., La^{+++} will outcompete Ca for PO_4^{---}).

   d. add a more easily-ionized element (e.g. Cs) to suppress ionization, or use a cooler flame (e.g. H_2/air).

4. Even with these factors (3., above) taken into account, there are other subtle and poorly-understood interferences. For the most accurate analyses, it is important to exactly match the major element chemical matrix of the standards and samples. When you are analyzing samples of unknown composition, this matching can be accomplished best by the method of standard additions, where a small spike of the standard is added to a split of the sample solution.

E. Sensitivity and detection limits: definition and controlling factors. Factors limiting precision and accuracy in flame atomic absorption.

1. Different definitions of detection limit exist, but a typical version is that the detection limit is three times the standard deviation of samples near the detection limit.

2. Organic solvent signal enhancement.

VI. Flame emission spectroscopy: similar to AAS in many respects, except that you want the element to be ionized so that you can observed the emission of the photon. Difficulty stems from the many interferences that affect ionization efficiency, and this technique, while still valuable in a pinch, has largely been superseded by plasma atomic emission spectroscopy, where the much higher temperature of an argon plasma results in nearly complete ionization of most elements.

VII. Graphite furnace AAS analysis

A. Thermal energy of a hot graphite tube is used to dry the sample, followed by a higher temperature (red hot) char cycle that simplifies the chemical matrix and eliminates some interfering substances, followed by a high-temperature atomization cycle in which the tube becomes white-hot.

1. “Drying” is straightforward, but important. The sample should dry slowly with no visible "bumping" or boiling, so as to form a reproducible uniform film.
2. "Charring" is mysterious but important. It simplifies the sample matrix by decomposing some compounds (especially organics) and eliminating others entirely (through volatilization), and by chemical reactions that prepare the element of interest for atom formation and vaporization.
3. "Atomizing" is mysterious and very important. The element must be converted into atomic form and vaporized. The presence of other substances can affect the efficiency with which this is done and the rate at which these occur.
4. The gas flow path and heating history is important.

B. Graphite furnace AAS usually has a much lower detection limit than flame AAS (often 1000-fold) because there is no loss to nebulization (hence gaining a factor of 10-100) and because the sample is confined to a small space with a longer residence time of the atoms in the light path (thereby gaining another factor of 10-100). It is also suited for (in fact, it requires) much smaller samples, e.g. tens of microliters.

1. Note differences between concentration detection limit and absolute detection limit.

C. The principle difficulties of graphite furnace spectroscopy are:

1. Some elements are refractory, either inherently (e.g. Zr) or due to the formation of non-volatile carbides with the graphite at high temperatures (e.g. Ta). Very involatile and carbide-forming elements may show a "memory effect" (a signal from an earlier sample appears in subsequent atomization cycles).
2. The sample matrix (e.g. seawater) may alter the rate at which the atoms can move from the graphite furnace into the light path.
3. Graphite furnace atomization usually creates significant non-specific (continuum) background ("smoke") interferences. Other than for distilled water- or dilute-acid matrices, one shouldn't do GFAAS without background correction.

D. Effect of graphite surface (normal vs. pyrollitic graphite).

1. "Normal" graphite such as found in a pencil lead is very porous and has a large and rugged surface with a large surface area. This may be beneficial (e.g., more area available for reaction to reduce a metal, for example) or disadvantageous (e.g., metal diffuses into the graphite through the pores rather than into center of the tube; metal reacts with graphite to form carbides (e.g. Ba, W).

2. "Pyrollitic graphite" is formed by thermal decomposition of CH_4 at about 2000°C. Pyrollitic graphite is denser, less porous, and has a lower surface area than for normal graphite. Less carbide formation, more rapid atomization.

E. Stabilized temperature platform atomization: many of the flaws and interferences of graphite furnace AA are due to the rapidly changing temperature conditions within the graphite tube. As a way of minimizing this problem, a "stabilized temperature platform" is inserted into the tube with minimal contact with the graphite tube. The graphite tube heats up, the internal gas heats up, and then finally the platform heats up, letting the sample vaporize into a constant-temperature environment. The ultimate in this trend is the transversely-heated graphite tube, in which the current flows sideways through the tube rather than lengthwise, allowing for a more uniform temperature distribution through the length of the tube.

F. Peak height vs peak area measurement: One can derive a standard curve either from a measurement of peak height or peak area. It has been argued by some that peak area is superior because interferences that affect the rate at which the atoms come off the surface (but not the total number of atoms going into the center of the tube) will be compensated for in the area (e.g., broader peak as opposed to narrower, with same area for both). In some cases this has been shown to have merit, but it is not always true and in some cases peak area is an inferior method.

G. Note the particular importance of clean optics and furnace windows in GFAAS.

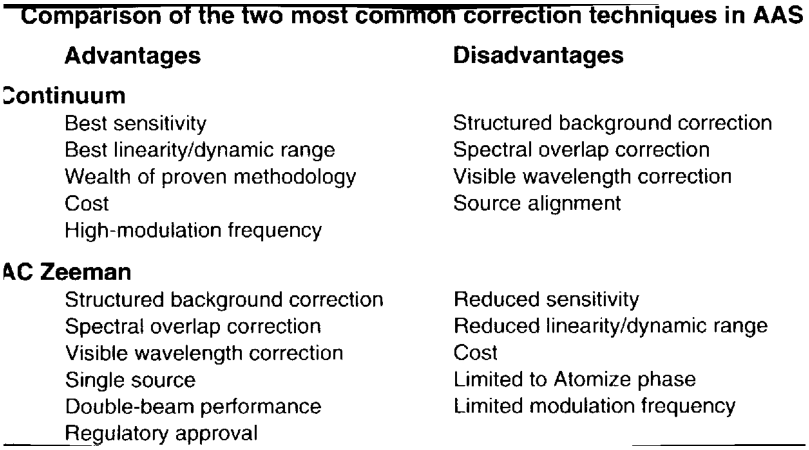
H. Controlling interferences in GFAAS.

1. Matrix modifiers
    a. NH_4NO_3 (helps minimize NaCl), $Mg(NO_3)_2$
    b. Organic acids (e.g. ascorbic acid, oxalic acid): helps make crystals smaller and more uniform; may help reduce metal; other mysterious effects.
    c. H_3PO_4, $MgPO_4$
    d. $PdNO_3$
2. Matrix matching: make sure standards have same major chemical composition as standards; compensate for slight variability in major chemical composition.
3. Method of standard additions: if you don't know what the major element composition is and if it is highly variable, then you should always use this method.

VII. Continuum background correction in AAS

A. Deuterium arc source

B. Zeeman background correction. Curvature in standard curves; issue of rollover.



Comparison of the two most common correction techniques in AAS

	Advantages	Disadvantages
Continuum	Best sensitivity	Structured background correction
	Best linearity/dynamic range	Spectral overlap correction
	Wealth of proven methodology	Visible wavelength correction
	Cost	Source alignment
	High-modulation frequency	
AC Zeeman	Structured background correction	Reduced sensitivity
	Spectral overlap correction	Reduced linearity/dynamic range
	Visible wavelength correction	Cost
	Single source	Limited to Atomize phase
	Double-beam performance	Limited modulation frequency
	Regulatory approval	

C. Smith-Heifje background correction.

VIII. Data Quality Control in an atomic absorption laboratory

A. Sensitivity and detection limits.

B. Standardization and quality control (consistency standards).