

## Chapter 9 Atomic Absorption and Fluorescence Spectrometry

Problems: 1, 3, 6, 8, 10, 12, 14, 16, 20, 21

### 9A Sample Atomization

Start with 2 Common methods, then 3 specialized methods

#### 9A-1 Flame Atomization

Method used in our machine!

Solution is nebulized by flow of a gas

Gas is mixed with a fuel so it can be burned

Gas mixture carried to flame where atomization occurs

**In the flame lots of other things happen (figure 9-1)**

Desolvation (solvent evaporated)

So now have molecular aerosol

Molecules dissociate into atoms

Some atoms ionize to electrons and cations

Some atoms and some ions raised to excited states

Other stuff going on in the burning of the fuel as well

With so much going on this process is key to the method

#### Types of Flames

##### Table 9-1

can vary oxidant or fuel

can vary temp from 1700°C to 3100°C

#### Flame rate

If gas flow rate < burning velocity, flame can burn back inside burner and make 'flashback'

If gas flow rate > burning velocity, flame rises off burner and blows out

So gas flow rate needs to be close to burning rate

#### Flame Structure

Figure 9-2

Appearance of these zones varied from mixture to mixture

##### Primary Combustion Zone

In a Bunsen burner the typical light blue inner cone

Band spectra of C<sub>2</sub>, CH and other radicals

Not at thermal equilibrium so not used in spectroscopy

##### Interzonal region

Usually small in Bunsen burner flame

Can be very large in fuel rich oxy/acetylene

Lots of free atoms, so this zone is used for most work  
 Secondary combustion Zone  
 Products of inner cone getting converted to stable oxides  
 Oxides getting dispersed into air

### Temperature Profiles Figure 9-3

Max temp about 1cm above primary combustion  
 This is where you want to be for emission so need to focus here

### Flame Absorbance Profiles Figure 9-4

Sweet spot for each metal is different, so example:  
 Mg as go higher get more atoms due to higher T  
 But when get too high get into secondary oxidation where  
 oxides are produced and oxidized do not absorb at same  
 wavelength  
 Ag doesn't oxidize so can go much higher into secondary  
 combustion region  
 Cr oxidizes easily so need to keep low

### Flame atomizers Figure 9-5

Again, this is what we have  
 Use either a concentric tube nebulizer  
 Gets mixed with oxidizer and fuel gas  
 Baffles to remove larger particles  
 Pushed into a 10 cm slotted burner  
 This burner has pressure relief vents is flame has flashback inside  
 burner, ours is simply on a rubber O ring and it will blow off.  
 It has wires to keep it from blowing too far

### Fuel and Oxidant regulators

Need to be able to control flow of both fuel and oxidant  
 Usually roughly stoichiometric ratios  
 For Metals that form stable oxides you burn extra fuel so  
 make reducing, and oxides don't form as easily  
 Flow rated controlled by regulators on the tanks  
 Followed by a needle valve on the machine  
 Monitored by **rotameter** a tapers gas tube with a light weight  
 inside, height of the weigh is proportional to gas flow

### Performance characteristics

Flame atomizer best for reproducibility  
 However not the most efficient so not the most sensitive  
 Why?  
 1. most of the liquid isn't turned into a vapor, so it is  
 discarded

2. Sample only spends about .0001 sec where it can be detected

### 9A-2 Electrothermal Atomization

More sensitive because atoms in light for 1 sec or more  
Used in absorption and fluorescence, but not much in emission  
we don't have one

#### Figure 9-6

few microliters of solution on a platform in a graphite tube  
Graphite used because conducts electricity  
evaporated at low temp (run a little current through tube)  
then taken to higher temp to turn into ash (run a little more current through tube)  
then run several hundred amp through the tube  
The tube soars to 2000-3000 in a few seconds  
atomized particles found over the platform

### Electrothermal Atomizers

Same figure

Tube is open at both ends

a hole in the middle so you can put your sample in  
tube about 5 cm long and diameter about 1 cm

Need 2 streams of inert gas

1 through the inside so you can ash the sample without oxidizing it

1 around outside so graphite tube itself won't oxidize (burn) in the air  
when it gets hot

A L'vov platform is sometimes added

sample placed on platform inside tube

doesn't get hot as fast

usually a little more reproducible

Plain graphite tubes sometimes give poor reproducibility

apparently some of the atoms are getting absorbed into the graphite

Must coat tube with pyrolytic graphite to seal it up and get better results

### Output Signal

Max absorption or fluorescence occurs a few seconds after ignition

then rapidly disappears

Need fast electronics to follow the signal

quantitate usually based on peak height during the pulse

Typical output Figure 9-7

### Performance Characteristics

sample volumes 0.5 to 10  $\mu$ l

Absolute amount of substance in this volume is  $10^{-10}$  to  $10^{-13}$ g  
 relative precision only 5-10%

(Was 1% or less with flame or plasma atomization)

Low range, only 10-100 so have to have the sample at just the right concentration

### **Analysis of Solids with Electrothermal Atomizers**

Most other methods can only be used for solutions  
 this can use a slurry  
 or can even try a finely ground up solid powder

### **9A-3 Specialized Atomization Techniques**

I think we'll skip

## **9B Atomic Absorption Instrumentation**

Box diagram for AA figure 7-1a (page 144)

Radiation source, sample holder, wavelength selector, detector, readout

### **9B-1 Radiation Sources**

Absorption bands are very narrow (.002 to .005 nm)

For Beer's law to work, bandwidth of spectrometer must be *narrower* than absorption width

Most monochrometers using a continuous source can't get that narrow

Even the ones that can, allow very little light through because you are using such a small fraction of the sources light so S/N is lousy

Need to use line sources

Lamps containing the metal you are trying to analyze!

Lamp uses emission of metal as source

set up emission lamp so Doppler broadening is < broadening that occurs in the atomizer

Do this by keeping source temp < flame temp

Thus source is narrower than absorbance

Most metals have other emission lines, can get rid of these other lines with a cheap monochromator

Nice, simple, only problem is that you need a separate lamp for each element!

### **Hollow Cathode Lamps**

What we have

Figure 9-11

Tungsten anode (+)  
 Cylindrical cathode (-)  
 Tube is filled with 1-5 torr (.001-.005 atm) Ne or Ar  
 Window at end transparent to  $\lambda$  desired

Key is cylindrical cathode  
 cathode is either the metal you want to emit  
 Or supports a layer of that metal

Ionize the inert gas with a potential of about 300V  
 Electrons migrate to anode  
 +ion migrate to cathode

Ions hitting cathode dislodge atoms of the metal  
 Make an atomic cloud around cathode  
 Process called *sputtering*  
 These atoms are in excited state, so spontaneously emit light  
 Then in ground state, diffuse back to anode, or to glass  
 walls of tube

Hollow cylinder serves 2 purposes  
 Concentrates radiation in one area so focused  
 Maximizes probability that atoms will diffuse back to cathode and  
 not leak off onto glass

Efficiency depends on geometry and potential  
 As an experimentalist you can't mess with the geometry, but you  
 can with the voltage

High potential, higher current greater intensity - MAYBE  
 Increased Doppler broadening so may become non linear  
 Also more unexcited atoms, so more *self-absorption* of light

Bottom line, lamp comes with a factory optimum, use it  
 You can try varying this a bit to find a better value  
 Don't try too high, you can blow out the lamp

Many lamps made with one element  
 Can also make with several elements for more flexibility

### **Electrodeless Discharge Lamps (EDL)**

**Fig 9-12**

Intensity 10 to 100x better than hollow cathode tube lamps  
 but not as reliable

sealed quartz tube  
 filled with a few torr of inert gas  
 small quantity of metal or metal salt  
 NO ELECTRODE!

Have a coil of wire  
 use coil to make radio frequency or microwave radiation inside tube  
 this radiation makes inert gas ionize  
 The process the same

### Source Modulation

Flame will always have some emission at the wavelength you are looking at, giving you some signal when you shouldn't have one  
 So detector will always have light from source that is being absorbed by sample + added light from flame to throw reading off  
 If can turn source on and off then can look at signal from flame, and from flame + lamp, and filter one signal from the other  
 Either use a chopper on the lamp to cut light on and off  
 or use a pulsing power supply to licker lamp on and off

(I don't see a chopper on our machine, and I don't know about its power supply)

### 9B-2 Spectrophotometers

lots of designs, cheap and expensive, single and double beam, simple and sophisticated

Simplest design, several lamps and several interchangeable filters to remove interfering lines

Most common design includes good-quality UV/Vis monochromator with bandwidth of 1Å (Emission lines themselves much narrower, this is just used to filter out closely spaced lines)

Most use PM tubes for transducers  
 Most have microcomputers for instrument control and signal processing

Common designs, Figure 9-13

### Single Beam

(I think this is ours because I don't see a chopper)  
 Several different lamps  
 Source with a physical chopper or a pulsed power supply  
 Atomizer

Monochromator  
PM tube transducer

Chopper or power supply switches lamp on and off so see flame  
signal and flame+lamp signal  
Use a blank sample for 100% transmittance signal

### **Double Beam**

Have lamp on continuously  
But use chopper to send light around flame  $\frac{1}{2}$  the time  
Use electronics to turn into an absorbance signal

Technically alternate light path is not a true blank or 100% sample because it doesn't pass through the flame so doesn't include extra light from the flame or scattering of the light beam caused by the flame. Special techniques are used to correct for this. SEE NEXT SECTION

## **9C Interferences in AA**

2 types of interference

1. Spectral Interference
  - absorption or emission lines of other species in sample lie so close to sample absorption line that they can't be filtered by monochromator so measured absorption is off
2. Chemical Interference
  - Chemical reactions occur in the sample, during atomization, or in the flame that change the absorption characteristics of the analyte

### **9C-1 Spectral Interference**

Lines from hollow cathode tubes are very narrow, so interference due to having two overlapping lines is rare  
On occasions where it does occur, you can sometimes look at a different line

More common problem combustion products in flame exhibit broadband absorption that adds to your signal's absorption  
Or particulates in flame scatter light, again making light passing through flame lower than it should be

If this is caused by the flame alone, then a water blank aspirated through flame makes this correction

If it is caused by some other chemical in the sample itself you have a more difficult problem. Called a *Matrix Effect*

Sometimes can eliminate by changing flame temp to change chemistry that is going on in the flame

Other times need to use method of standard addition to properly analyze signal in presence of interfering compound

Scattering artifacts typically seen in Ti, Zr, or W samples  
 oxides are forming that clump together to form particles  
 Also seen in organic solvents or when have organics added to sample  
 due to incomplete combustion of organics

Above effect are fairly rare  
 often avoided by changing the flame  
 sometimes use a blank containing the interfering compound

Interference effect seen more often in electrothermal atomization

Corrections used for Electrothermal Atomization

The book now talks about 4 different methods used to correct for problems in electrothermal atomization. Since we don't have that kind of instrument lets skip

### **9C-2 Chemical Interferences**

Chemical interferences more common than spectral interferences

Effect often minimized by proper conditions

Can regard flame as a solvent can treat chemical reaction and equilibria  
 reactions to shift to more favorable conditions

Three major reaction will look at  
 Formation of low volatility compounds  
 Dissociation Equilib  
 Ionization

#### **Formation of low volatility compounds**

Most common form is anions that form compounds with analyte to make compounds with low volatility, hence fewer atoms of analyte get atomized

Example Ca

Interfered by either  $\text{PO}_4^{-3}$  or  $\text{SO}_4^{-2}$

If hold Ca constant, amount seen in AA will decrease as increase conc of either of these two anions, up to anion:Ca ration of .5, then levels off

Cation interference also occurs

$\text{Al}^{+3}$  will bind to Mg and lower its response

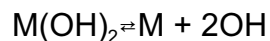
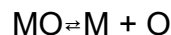
Interferences due to formation of low volatility compounds often mediated

1. use of higher flame temp
2. use of releasing agents
  - Preferentially bind to interfering ion, so it can't bind to analyte
  - Excess of Sr or La - binds Phosphate so doesn't bind Ca
3. use of protective agent
  - Binds to analyte to form stable but volatile species
  - Examples EDTA, 8-hydroxyquinoline, etc

### Dissociation Equilibria

in flame lots of different dissociation/association events take place between metal and other compounds

Some reaction reversible so can treat like equilibria



would be 2 reaction that would allow a free metal to form from an oxide or a hydroxide

Don't understand these reactions well so treat empirically

Alkaline earth (Group 2) oxides are relatively stable

Molecular bands from these compounds are large

Need high temp for enough E to dissociate

So Molecular bands prominent and may be larger than atomic spectra except at high T

Alkali metals (group 1) oxides and hydroxide more easily dissociated

Atomic spectra dominate even at lower T

Dissociation of ions other than O may be important

Na lines weaker in presence of HCl

$\text{Cl}^-$  in flame makes  $\text{Cl}^0$



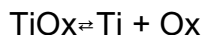
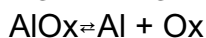
Also indirect effects

Determination of V

Al or Ti interfere in fuel rich flames

Don't interfere in lean (fuel poor flames)

Several metal/oxide/hydroxide equilibria going on



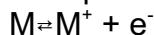
Fuel rich, oxy poor flame, little  $\text{O}_x$ , equilib with Al and Ti use up most of  $\text{O}_x$ , so  $\text{O}_x \downarrow$  and  $\text{V} \uparrow$  so V signal is better

In lean (fuel poor/Oxy rich) flame,  $\text{O}_x$  high so Al and Ti conc don't effect, and  $\text{Vox} \uparrow$  so V signal  $\downarrow$

### Ionization Equilibria

When using air as the oxidant the oxidation of metals to their ions by oxygen is usually small and can be neglected

In hotter flames when using  $\text{O}_2$  or  $\text{NO}_2$  oxidation becomes important and have equilib



Can estimate a K for this reaction  
from K can estimate a % ionization

% ionization for different T's and P shown in table 9-2

Can see why alkali metals especially Cs, Rb, and K are done at low T, because at High T get ionized

Can also push this equilib the other way!

If have a second compound that is ionizing, it increases the  $[\text{e}^-]$

And that can push the equilib between the metal and the ion toward the metal!

Called *Ion suppression*

Figure 9-17

As add K response to Sr increase!

## 9D AA Analytical techniques

Practical details of AA

### 9D-1 Sample Preparation

Most atomization system designed around introduction of a clean aqueous solution

What do you do with interesting samples like soil, plants, tissues, and petroleum products?

Usually extensive decomposition preparation steps  
often more difficult than running the machine!  
Often add more error as well

Decomposition usually involves rigorous treatment at high T  
potential loss of analyte as volatile or as smoke  
reagents used may add trace amount of what you are looking for, or may  
add interfering compounds

Often if doing trace analysis the bulk of the analyte is coming from your  
reagents! Net result error, even if you do a blank

Common decomposition methods

1. Treat with hot mineral acid
2. Oxidation with liquid reagent(sulfuric, nitric or perchloric acids)  
Also called wet ashing
3. Combustion in an O<sub>2</sub> bomb
4. Ashing at high T
5. High T fusion - boric acid, Sodium Carbonate, sodium peroxide,  
potassium pyrosulfate

One advantage of electrothermal atomization is that many solids like tissue, plant  
leaves, blood or petroleum byproduct can be placed directly in oven and ashed  
and atomized directly with out all the above manipulation. However proper blank  
or control can be difficult

### 9D-2 Organic Solvents

can get enhanced AA signals for samples in low molecular weight alcohols, ester  
or ketones

lower surface tension - smaller drop size- better atomization  
solvent also evaporates out of drop more quickly

To offset organic material in flame, need to run leaner (less fuel)

This makes temp lower, and increases chance of chemical interference

Some metal chelators are soluble in organic solvent

Makes a nice system

add chelator

extract chelator in small volume of organic solvent

Get a concentration increase

May also be able to leave behind some interfering compounds!

### 9D-3 Calibration Curves

AA should obey Beer's law, but often doesn't  
 so shouldn't assume a linear relationship so always need to make a  
 calibration curve

one major variable is atomization of sample, this can vary day to day, hour to  
 hour. Always need to run at least 1 standard every day  
 prefer to run standard both before and after sample  
 even better is one has lower conc than sample and the other has a higher  
 conc

#### **9D-4 Standard Addition Method**

Use frequently in AA since can eliminate matrix interferences

#### **9D-5 Applications of AA**

sensitive measure for 60+ metals and metalloids  
 lines for most nonmetals are  $<200$  so can't be done (vacuum UV, Gases in air,  
 mostly  $O_2$  absorb so need to work in vacuum. How do you make flame in  
 vacuum? )

#### **Detection limits**

Table 9-3 detection limits for some elements

AA with flame atomization about 1-20ng/ml (.001-.02 ppm)  
 with electrothermal .002-.02ng (.00001-.000002 ppm)  
 At least 1000x better

#### **Accuracy**

Flame - ordinary conditions 1-2%, special care .2%  
 Electrothermal - 5-10%, special care, 2%

#### **9E Atomic Fluorescence**

Don't have, fairly specialized so will skip.

### **10 Intro to Atomic Emission**

In AA the flame is used primarily to atomize that sample and suspend the  
 sample in the light beam. so you can see detect that amount of light that is  
 absorbed as you raise the electrons in the atoms from ground state orbital to  
 higher E level orbitals

If you get the flame hot enough, you can use the T of the flame to actually put  
 kick the electrons into higher E state as well,. And then you can look for light  
 being emitted from the sample as the electrons fall back down to lower E levels

This is the basis of Atomic Emission Spectroscopy

Originally this technique was developed for use in flame AA spectrometers. In fact it is simpler to do an emission determination than an absorbance measurement because you don't need a light source!

What make this technique a little harder to do, is that you need to heat the sample to as high a temperature as possible, so you can get as many molecules excited as possible.

In early machines this was accomplished by switching from the air/acetylene flame to a nitrous oxide/acetylene flame (T about 2300 to T about 2700C, 2600-3000K) See problem 8-9 chapter 8 for suitable calculation)

While this temp rise was only moderate it is enough to make many metals doable on a Flame AA type apparatus. And, in fact, many atoms were self complementary, if they were hard to do in AA, the Emission was usually OK, or if they were hard to get with emission, the AA work.

As you will see in the lab, we will try to do an emission experiment on our Flame AA by simply pulling out the lamp, and resetting the electronics for an emission signal instead of an absorbance signal.

Today this kind of emission spectroscopy had been surpassed by fancy new technology so the book only mentions this kind of emission spectroscopy in the very last section of chapter 10. Since we don't have one of the newer machines we will bypass the bulk of this chapter

The one part of chapter 10 I want you to look at is section 10A-1 Inductively coupled Plasma sources, because this is the key to the newer technique

The new machines use one of several different methods to elevate the analyte atoms to temperature in the +6000-8000K range, easily 2-3time higher than the flames we use in the AA, Since the ICP (inductively coupled plasma is the most common, that is the one I want to introduce you to)

First, what is a plasma?

A gas that contains enough ions that it can conduct electricity

It is interesting, but the way we get a gas as hot as 6000-8000K will not be to burn anything! We will actually be using Argon, an inert gas

### Figure 10-1

What you do first is to strike a spark in the Ar gas, and this gives you some Ar<sup>+</sup> and some

$e^-$  ions

I in the diagram represents an induction coil around the tip of what we will call the ICP torch

Induction coil means that we will run a high AC current through the wires at 27 or 41 MHz frequency (radio) The current running in the wire sets up a magnetic field around the wire (Ellipsoids with arrows, H on diagram) When the ions see this alternating magnetic field what do they do? They start oscillating around the annular region shown in dark gray. +'s are going 1 way. -'s the other, then as the AC goes from + to -, they spin back the other way. This heats this region up into the 1,000's K range! At this T the bulk of the Ar atoms that weren't ionized become ionized, and with more ions, things just keep getting hotter until the whole region is at about 10,000K. Now this is more than enough heat to melt the glass tubing and the induction coil, so the induction coil has to be water cooled, and the blow fresh, Rt AR around the inside of the tube to keep it cooled. This starts sucking Ar gas at the rate of 5-20 L/min, and can get pretty spendy.

Now in the center of all this we add a sample vaporizer similar to the one used in the AA, only using Ar gas to suspend and atomize the sample in. This jet of atoms is blown into the 10,000 plasma region, and then the hot atom rise just as they do in any flame and quickly cool as they rise. All we need to do now is rig up a monochromator to look at the light that is emitted as the atoms fall back to their ground states as they rise and cool.

Actually a very good technique. This is so hot that there are very few interferences, and with high end monochromator and electronics, you can actually analyze for many different atoms simultaneously.

For a comparison of detection limits all methods, see table 10-3