

## Chapter 16

### Advanced Instrumentation

Advanced instrumentation is used primarily for analysis of trace contaminants such as metals or hydrocarbons. Most smaller municipalities don't have the need for this expensive equipment unless there is an industrial component to the waste stream. It is usually more cost effective for municipalities to send the occasional sludge sample or industrial pretreatment sample to larger labs that are accustomed to handling trace analysis.

#### Units

Up to now, the unit of measure has been primarily mg/L or ppm. When measuring trace contaminants, the concentration in mg/L is too low, for example 0.015 mg/L. To avoid reporting such small numbers, the units are often changed to micrograms/liter (ug/L) or parts per billion (ppb). There are 1000 micrograms in 1 milligram. For example, 0.015 mg/l would be converted to 15 ug/L. For extremely low levels of contaminants, the concentration is reported as nanograms/liter (ng/L) or parts per trillion (ppt). There is a 1,000,000 nanograms in 1 milligram.

#### Metals

Metals are analyzed by a variety of instruments. The 3 most common instruments used are:

- Atomic absorption Spectrophotometry (AA)
- Flame photometry
- Inductively Coupled Plasma (ICP)

Metals follow the same definitions as solids.

a. Total metals are defined as the concentration of the metal in an unfiltered sample after vigorous digestion.

b. Dissolved metals are defined as the metals in an unacidified sample that pass through a 0.45u filter.

c. Suspended metals are defined as the metals in an unacidified sample that are retained on a 0.45u filter.

#### Sample Collection and Preservation

The laboratory technician must know what type of metal sample is going to be analyzed prior to collection of the sample. If dissolved metals are needed, the sample should not be preserved with acid as the acid will cause particulate metals to dissolve. Because of the low concentrations of metals being measured, every effort must be made to minimize contamination. Significant sample contamination can come from

- Sample containers
- Sample caps
- Sample collection devices
- Preservative acid
- Filters and filtration equipment

All sample collection materials must be acid washed. A typical cleaning procedure could be:

1. clean with a non-ionic detergent
2. rinse with tap water
3. soak in 1+1 HNO<sub>3</sub> or 1+1 HCl for 24 hours
4. rinse with metal free deionized water

The best sample containers, least likely to contain leachable metals, are quartz and Teflon. These containers are expensive and used primarily for critical analysis. Routine samples are usually collected in dedicated polypropylene (PP) or linear polyethylene (LPE).

Preservation for total metals consists of adding concentrated nitric acid to pH <2. If

dissolved metals are to be measured, filter the sample prior to adding nitric acid.

### **Preliminary Treatment**

The amount of pretreatment needed will depend upon the type of metals tested and the method used. Consideration must be given not to introduce contaminants into the sample during any pretreatment steps.

Because of the trace levels being measured, contamination from reagents, laboratory water, laboratory equipment, and laboratory air can introduce significant error. Blanks should be run to determine background contamination levels. Pretreatment includes:

- Filtration
- Digestion
- Extraction

### **Filtration**

Filtration using a preconditioned 0.45µ filter is used to separate dissolved and suspended metals. Acidify the filtrate after filtration to preserve the sample.

### **Digestion**

Digestion is used to prepare samples for total metals. Organically and inorganically bound metal complexes need to be broken down to release the free metals. There are a variety of different digestion methods. The most common method is nitric acid digestion. The procedure involves measuring 100 ml of well-mixed, preserved sample into a beaker. Five milliliters of nitric acid is added, the beaker covered with a watch glass, then heated to a gentle boil in the fume hood. Evaporate the sample until a precipitate forms or a light-colored clear solution forms. Do not heat to dryness. Wash down the beaker walls with metal free water to recover any metals splashed on the side, filter if necessary, then transfer to a 100 ml volumetric flask. Rinse the beaker

with additional metal-free water and add to the volumetric flask. Fill to the mark.

### **Microwave Digestion**

The microwave digestion method is recommended for metals analysis using ICP. The microwave digestion method is a closed digestion method,

### **Extraction**

Extraction is a process used to concentrate trace levels of materials, in this case metals. Some metals are able to be complexed with an organic chelating agent. The organic chelating agent, most commonly, Ammonium pyrrolidine dithiocarbamate (APDC), chemically binds the metals in the water. APDC is easily dissolved in the non-polar organic solvent, methyl isobutyl ketone (MIBK). Because MIBK is non-polar, it will not dissolve in water and will separate from the water like oil and water. Only small volumes of MIBK are used, so the extracted metals that were in perhaps 200 ml of sample are now concentrated in 10 ml of MIBK. This results in a concentration of metals 20 times. The MIBK is aspirated into the atomic absorption spectrophotometer and the absorbance measured.

### **Atomic Absorption Spectrophotometry**

Atomic absorption requires the presence of ground state metal atoms ( $Me^0$ ). The initial process which takes place in an atomic absorption spectrophotometer is to create a population of ground state atoms. This is accomplished in a variety of ways, usually classified as flame and non-flame. The simplest and most common method uses a flame to produce these atoms. This atomization process involves 5 steps:

1. nebulization
2. droplet precipitation
3. mixing

4. desolvation

5. compound decomposition

The atomization process begins when a sample that has been pretreated is "sucked" into the machine by an oxidizing gas (air). The liquid sample is converted in a spray of fine mist using a nebulizer. Different manufacturers have different methods for this atomization process. The nebulization process breaks the large droplets of sample into a fine mist. The droplets of water that don't shatter sufficiently precipitate out and go to drain. The smaller "mist" droplets then mix with the fuel in a spray chamber. Changes in direction of flow within the spray chamber, create turbulence which ensures a smooth quiet, well-mixing flow into the burner head. The heat of the flame within the burner now desolvates (dries) the remaining water from the sample particles and decomposes the particles into their constituent ground state atoms. Thus somewhere within the flame is a pocket of ground state atoms which can now be measured. The effectiveness of each step influences the number of ground state atoms produced.

### **Nebulizers**

Each manufacturer has their own nebulizer design. The design influences the effectiveness of the spray reaching the flame. The most effective nebulizer will create a mist of small drops of uniform particle size. The smaller and more uniform the droplets, the steadier the absorption result will be. Large droplets will be difficult to desolvate and will produce chemical interferences with light passing through the flame.

### **Flames**

Different gas mixtures produce different flame temperatures. The most common flame is the air-acetylene flame. The air-

acetylene flame produces a flame temperature hot enough to desolvate and decompose most particles into ground state atoms. Some compounds do not decompose as easily or as readily as others, therefore a higher temperature flames (nitrous oxide-acetylene) may be needed to decompose the compound. Likewise, the flame fuel to oxidant ratio can be adjusted. If more fuel is added and less oxidant (air), the flame is called a reducing flame. If more oxidant is added and less fuel is used, the flame is called an oxidizing flame. The procedure usually indicates what the best fuel-oxidant ratio should be, but changing the mixture can affect the number of ground state atoms produced.

### **Light absorption**

Once the ground state atoms ( $Me^0$ ) have been produced in the flame, they can be energized by a specific wavelength of light. Each different ground state atom has a number of very specific wavelengths which can react with the ground state electrons and send them to a different electronic states. For example, a ground state sodium atom has one electron in its outer ground state orbital (3s). That ground state electron can be excited by light energy at a wavelength of 589.0 nm. This wavelength is called its resonance line. Only sodium will be able absorb light at 589.0 nm. The resulting electron is now "excited" and is in a different orbital (say 3p). Other atoms work the same way, thus by choosing specific resonance lines different metals can be measured, ie  $Co^0$  at 324.7 nm,  $Ni^0$  at 232.0 nm, and  $Fe^0$  at 248.3 nm. Every atom will have a series of spectral lines specific for its excitation patterns.

### **Hollow Cathode Lamps**

Hollow cathode lamps are "lights" that are composed of the element being measured. These lamps emit only the specific

resonance wavelengths of interest. The lamp is energized and the light beam is directed through the flame. The lamp and burner are adjusted up/down, left/right, until the ground state atom cloud is maximized. The instrument now follows the Beer-Lambert Law as before. Blanks, reagent blanks, calibration curves can be run as before.

### Monochromator

The light from the hollow cathode lamp passes through the sample and the optical system focuses the light on the entrance slit to the grating monochromator. The monochromator is used to select only the specific resonance line emitted by the hollow cathode lamp. For instance, copper may have 10 resonance lines, but only the one at 324.7 nm is desired. The monochromator directs the incoming light through the exit slit, minimizing stray light. The light now passes through to the detector which converts the light energy into electrical energy. The electrical energy is now converted by the detector system into an answer on the display.

Because the number of ground state atoms energized is very low in direct flame AA, the sensitivity of the flame AA methods is not very high. Newer methods increase the ground state atom density which improves the sensitivity and detection limits significantly. The most common are

1. Electrochemical AA, also called graphite furnace
2. Hydride generation
3. Cold Vapor Mercury

All of these methods work off the same atomic absorption theory using the same instrument. However, the method of generating the atoms differs. The graphite furnace uses high electrical current to heat the sample and create ground state atoms.

The sample is usually placed in a carbon cup or tube, taken through a drying, ashing, and atomizing stage, then measured using light absorbance as before. No flame or burner is used.

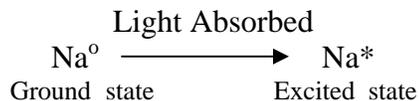
The Hydride method uses chemical reactions with sodium borohydride to create large clouds of gaseous hydrides. The gaseous hydride, representing a large amount of sample, can then be swept into the flame very quickly rather than slow aspiration through the nebulizer. This increases the number of ground state atoms and improves sensitivity and detection limit.

The Cold Vapor Mercury method again used chemical reactions to create atomic mercury vapor. Because the mercury is already in its ground state, the mercury vapor is passed through a tube aligned in the light path. No flame is needed. Because the mercury is concentrated within the tube, the sensitivity and detection limit are also improved.

All methods are subject to the same alignment problems

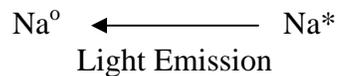
### Flame Emission Photometry

Flame emission photometry works on the same similar principle as atomic absorption spectrophotometry. This method is limited to metals that are easily excited such as sodium, potassium, and lithium. In AA, the amount of light absorbed by the ground state atom being excited to a different energy level was measured.



In Flame emission photometry, standards and solutions are aspirated into the flame. The hot flame evaporates the solvent, atomizes the metal, and excites a valence electron to an upper state. Light is emitted at

characteristic wavelengths for each metal as the electron returns to the ground state. The light emitted by these excited ground state atoms is measured.



Optical filters are used to select the emission wavelength monitored for the analyte species. Comparison of emission intensities of unknowns to either that of standard solutions, or to those of an internal standard, allows quantitative analysis of the analyte metal in the sample solution.

Follow the instrument manufacturer's operating instruction.

### **Interferences**

The flame emission photometer is susceptible to the same problems as AA. Alignment, sample viscosity, fuel and oxidant flow rates, reagent water purity, and solids all can effect the emission readout.

