

Experiment 10

Determination of Trace Amounts of Metals by Atomic Absorption Spectrometry

Objective—The objective of this experiment is to introduce one of the most important methods of environmental chemistry, atomic absorption spectrometry. This instrumental method is used to detect metals and metalloids down to the ppb level. The method is fast and accurate and can be made to be essentially free of interferences.

Introduction—Free atoms cannot undergo rotational or vibrational energy transitions, as molecules can. Only electronic transitions can occur when energy is absorbed or emitted. Because electronic transitions are discrete (quantized), line spectra are observed.

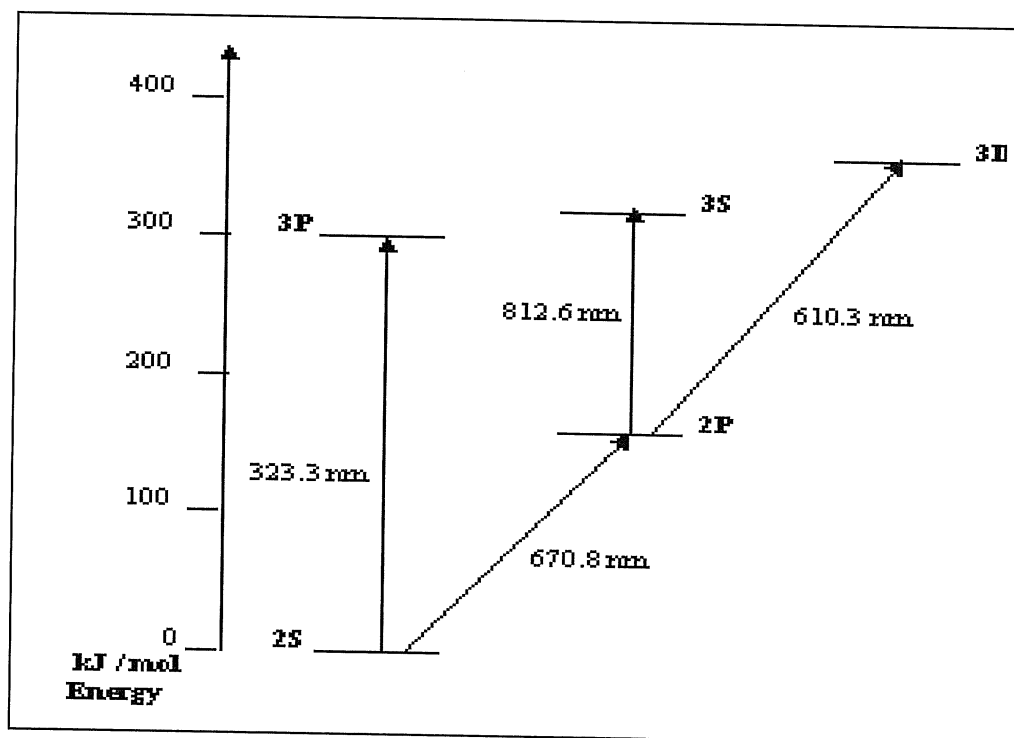
There are various ways of obtaining free atoms and measuring the radiation they absorb or emit. In flame spectrometry, a solution is aspirated into a flame and the compounds present are thermally dissociated into atomic vapor. The heat of the flame first causes the solvent to evaporate. The micro-crystals produced are partially (or wholly) dissociated into the elements in the gaseous state. Some of the atoms thus produced can absorb radiant energy of a particular wavelength and become excited to a higher electronic state. When these atoms fall back to lower energy levels and emit light, this provides the basis for a very sensitive analytical technique, **atomic emission spectroscopy**. In this method high-temperature electric arcs or plasmas are used to maximize the production of excited atoms.

The term “**atomic absorption**” refers to the absorption of energy from a light source, with a consequent decrease in the radiant power transmitted through the flame. The measurement of this absorption corresponds to **atomic absorption spectrometry**.

The majority of atoms in a flame are in the ground state; thus, most electronic transitions originate from this state. A partial energy-level diagram for lithium is shown in Figure 10-1. There are several possible transitions for lithium, but the primary line is at 670.890 nm.

More than 60 elements can be determined by atomic absorption spectrometry, many at the part per billion level. Only metals and metalloids can be determined directly by usual flame methods because the resonance lines for nonmetals occur in the vacuum ultraviolet region of the spectrum. Table 10-1 lists the atomic absorption detection limits and wavelengths used for several environmentally important elements. For analytical measurements, concentrations should be at least 10 times the detection limit since, by definition, the precision at the detection limit is no better than $\pm 50\%$.

Figure 10-1 Partial Energy Level Diagram for the Lithium Atom



Instrumentation

Atomic absorption uses essentially monochromatic radiation to excite vaporized atoms in their ground state. The instrument consists of a light source, a cell (consisting of the aspirated sample), a monochromator, and a detection system. The instrument is shown in Figure 10-2.

The source, usually a hollow cathode tube, emits essentially line radiation of the same wavelength as that being absorbed by the element under study. This is accomplished by making the source out of the sample element. Thus, if iron is to be determined, a lamp having an iron cathode is used.

The sample is nebulized into a premixed gas-air burner designed for a long path length. The radiation then passes into a monochromator and is measured at the detector. The amount of radiation absorbed is proportional to the concentration of the element in the sample. A calibration curve is obtained by measuring the absorbance of a series of standard solutions, as was done in Experiment 9.

Table 10-1 Wavelengths and Detection Limits for Various Elements

Element	Wavelength (nm)	Detection Limit (ppb)*
Ag	328.07	1
Ca	422.67	2
Cd	228.80	1
Co	240.72	2
Cr	357.87	2
Cu	324.75	4
Fe	248.33	4
Hg	253.65	500
K	766.49	3
Mg	285.21	3
Mn	279.48	0.8
Na	589.00	0.8
Ni	232.00	5
Pb	283.31	10
Sn	235.48	50
Sr	470.73	5
Zn	213.86	1

*Values in the table refer to an air-acetylene flame.

Source: *Analytical Methods for Atomic Absorption Spectrophotometry*,
Perkin Elmer Corporation, Norwalk, CT, 1982.

Experimental Methods

Atomic absorption spectrometry is used for the analysis of a great variety of substances, containing trace elements (ppb concentrations) as well as major (greater than 1%) inorganic constituents. Sample types include agricultural and biological samples, minerals, petroleum and its products, air, and water.

Some elements present in biological systems play an essential role when present in trace amounts. This is true for iron, zinc, boron, and manganese at levels of about 20 ppm, and for copper, cobalt, and molybdenum from 0.1 to about 5 ppm. Furthermore, some toxic elements can be bioaccumulated by animals and plants and include chromium, lead, mercury, arsenic, antimony, tellurium, and thallium.

Plants and other biological systems have an organic matrix. The digestion of these media can be accomplished by dry ashing at 450–500°C, followed by acid redissolution with 0.1 M HNO₃. Ashing methods run the risk of losing volatile elements, such as arsenic, antimony, selenium, tellurium, cadmium, mercury, and lead. In this case, a wet digestion with oxidizing acids is used. Wet acid digestion can be carried out using a combination of concentrated nitric and sulfuric acids.

Biological fluids (blood or urine) can usually be aspirated after a simple dilution. In a blood analysis, serum or plasma is generally used since this fraction contains significant amounts of metals. However, an analysis to detect lead poisoning uses red blood cells since they concentrate lead. The metals usually

measured in blood include potassium, zinc, iron, and magnesium.

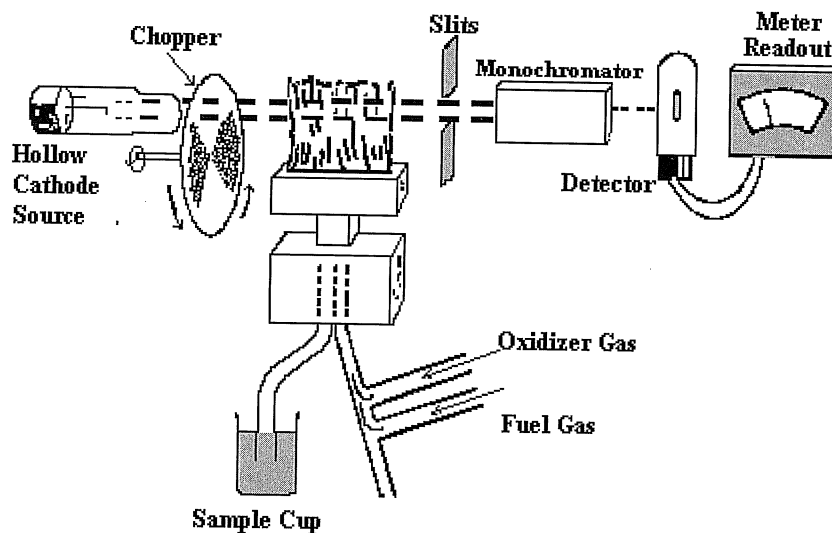
Atomic absorption is the method of choice for water analysis. Waters types frequently analyzed include spring and river waters, seawater, wastewaters, and industrial effluents. Elements frequently determined include cadmium, chromium, copper, arsenic, lead, mercury, selenium, and zinc.

Some precautions are necessary to obtain good results. Water samples require good filtration. In particular, river water can contain a colloidal suspension of clay and silica, the chemical constituents of which can interfere with the elements being measured. Also, if the anions in the sample are not known, the water should be acidified with an excess of 1% acid (such as HNO_3) to destroy carbonates and to create a uniform anionic matrix.

Glassware used to prepare samples for atomic absorption analysis should be thoroughly washed, after which it should be rinsed with concentrated, high-purity nitric acid. This is followed by rinsing with DI water and, if possible, nanopure water. Standard solutions should not be stored in glass containers because leaching will cause changes in the metal concentrations over time. Storing in plastic containers is recommended if the samples and standards are not going to be analyzed during the same lab period.

The sensitivity of atomic absorption is not always sufficient to measure concentration levels of ppb or less. In this case, separation or enrichment methods are used. By extracting organic complexes of the metal with a suitable solvent, it is possible to concentrate the trace element in a solution by a factor of 10–50. The extract can be analyzed directly.

Figure 10-2 A Basic Atomic Absorption Spectrometer



Source: G. H. Schenk, R. B. Hahn, and A. V. Hartkopf, *Introduction to Analytical Chemistry*, 2nd ed., Allyn and Bacon, Boston, 1981, p. 360. By permission.

Using the Atomic Absorption Spectrometer

The instrument consists of five main components, most of which are under microprocessor control on modern instruments. These are shown in Figure 10-2.

1. The hollow-cathode lamp power supply provides the controls for adjusting the current in the lamp. Each lamp has a maximum operating amperage which is indicated on the lamp. This current must not be exceeded or a very expensive lamp will be ruined.
2. The gas regulator panel controls and measures the flows of fuel and support (oxidant) gases. Each element requires a specific ratio of fuel to support gases, and specific conditions for each element are given in the methods manual for the instrument.
3. The burner assembly consists of the burner itself, the elevator for changing the burner height, and the aspiration system used to introduce the sample into the flame. The burner height is very important for each element.
4. The monochromator consists of the wavelength adjuster, a variable slit width, and controls used for zeroing the instrument and signal amplification.
5. The readout module provides a digital readout, a printer, or both.

Safety Issues

1. When heated sufficiently, nitric acid produces fumes of nitrogen dioxide. These attractive red-brown fumes are exceptionally toxic; 100 ppm levels are considered dangerous for even a short exposure and 200 ppm may be fatal. (See *The Merck Index*, [3], for further information on nitrogen dioxide.)
2. Safety glasses must be worn at all times in the chemistry laboratory.
3. When using the atomic absorption spectrometer, an instructor must be present.
4. Since air/acetylene mixtures can be explosive in certain ratios, it is essential that there be sufficient air and acetylene in the cylinders. Also, do not exceed the red line pressure on the reduction gauge of the acetylene regulator.
5. Before using the instrument, obtain instructions for shutting the instrument down quickly in the event of an emergency. Most modern instruments have built-in safety features, including a button or switch that shuts off the flow of gases immediately.

Locate the shut-off valve on the acetylene cylinder. This should be closed immediately in case of a fire.

6. The hood above the instrument must be on when aspirating samples. Otherwise vapors of metals and acid will be inhaled.

7. Biological samples, including foods, fish, plants, and even soils and sediments can be decomposed by dry ashing (followed by acid treatment, including perchloric acid) or by wet digestion with acids, including perchloric acid. However, it is highly recommended that any procedure calling for the use of perchloric acid **not be used!!** When dry, the resulting residue can be highly explosive. The authors have found that most samples can be digested, at least to the extent of freeing the desired metals, with concentrated nitric acid or with a mixture of nitric and sulfuric acids, and extensive heating.
8. Concentrated nitric acid is strongly oxidizing and should be kept away from organic matter (except for the sample, of course). In contact with some organic matter, it can be explosive. It is corrosive to the skin, and all contact with it should be avoided. Also, inhaling its fumes can cause severe respiratory distress. Fumes from the heating of nitric acid contain nitrogen dioxide, which is exceptionally toxic and is discussed in Safety Precaution Number 1.
9. Concentrated sulfuric acid at room temperature is not oxidizing. However, it is exceedingly hygroscopic, absorbing rapidly any water it comes in contact with. On the skin it rapidly absorbs water and can cause permanent damage in seconds. Use the utmost care in handling it!
10. The metals from the environment that are frequently analyzed include mercury, lead, cadmium, and many other heavy metals that are extremely toxic. In making up standard solutions of these and other toxic materials, use gloves and work on paper towels or other protective material so that if there is spillage, it will not get on the lab desk top. Most of these metals can cause serious problems even at the low part per million level, or even lower in the case of mercury.
11. Make sure that there is a loop in the drain tube and follow the instructions in the instrument manual on whether the drain tube in the waste vessel should be submerged or not.

Procedure—This experiment is intended to illustrate the basic procedures used to analyze real samples for metals at the low part per million level. Metals found in quantity in river sediments include iron, manganese, lead, and strontium. Samples taken near shipyards are often rich in chromium, cadmium, lead, titanium, and other metals. Seashells also provide interesting samples as they accumulate significant amounts of lead, strontium, and other metals.

1. Prepare a sediment sample by first decanting off excess water.
2. Tare a labeled 150 mL beaker on an analytical balance and scoop in 9–11 g of wet sediment. Weigh the sample to the nearest 0.1 mg. Repeat for a different environmental sample. (Instead of using a wet sample, a sample can be dried (time-consuming) or a dry weight of the sample can be determined as described in Experiments 2 and 9. Also, the core segments prepared in Experiment 2 can be used in this experiment.)
3. In a fume hood, add 10 mL DI water and 10 mL of high-purity (for trace metal analysis) concentrated nitric acid to each sample. Add the acid slowly if there is frothing.
4. Prepare a blank by adding 10 mL of DI water and 10 mL of high-purity concentrated nitric acid to another 150 mL beaker. Treat the blank identically to the samples.

5. Cover the beakers with watch glasses and gently swirl to mix. Heat on a hot plate to just below the boiling point and continue heating for 30 minutes. If necessary, add an additional 10 mL of acid if it appears that organic matter has not decomposed. Also, add additional water if there is much evaporative loss. (As mentioned in Experiment 9, the NO_2 fumes given off by decomposing nitric acid are extremely toxic. Avoid breathing in any of these fumes. Refer to Safety Issues 1.)

6. Remove the beakers from the hot plate, add 10 mL DI water to each sample, and allow to cool for 5 min. Filter each sample, including the blank, using medium speed filter paper, catching the filtrate in a 100 mL volumetric flask (see Note 1). Rinse the beaker twice with small portions of DI water, adding the rinses to the funnel. Finally, rinse the funnel twice, using small amounts of DI water from a squeeze bottle. Bring the volume in the flask up to the mark, stopper, and mix thoroughly. The solution should be clear and devoid of any particulates. Transfer the samples and blank to plastic bottles if they are not going to be immediately analyzed.

7. Prepare four standard solutions having concentrations of 1, 2, 4, and 8 ppm of the metal under study. They are made by diluting a 100 ppm (0.1 mg/mL) stock solution using pipets and volumetric flasks. Prepare 100 mL of each standard and transfer to plastic containers for storage if samples and standards are not going to be immediately analyzed. (**Note to the instructor:** It is convenient to have different groups make up standards of different metals and the entire class can use the complete sets of standards. That way each group can determine several metals in their sample.)

8. Familiarize yourself with the instrument by locating the various components, referring to Figure 10-2 and the instrument itself. The instructor should give an introductory presentation on the adjustments that must be made and on using the instrument's software.

9. Zero the instrument before making readings on samples or standards. Then measure the absorbance of the blank. If the blank does not read zero, aspirate more water and read the blank again.

10. Determine the absorbance of the standards and then the absorbance of the samples (see Note 2). If the absorbance of a sample is higher than the absorbance of the most concentrated standard, dilute the sample to bring it into the range of the standards. If standards from other groups are used, switch to the next lamp, and run the blank, followed by the standards and samples as before.

11. After samples have been measured, again measure the absorbances of some standards for each metal analyzed to check the stability of the instrument.

12. Aspirate DI water into the flame for 5 minutes after running your last sample to clean the burner assembly.

Waste Minimization and Disposal

1. Sediment or soil samples from previous experiments can be used. If new samples are collected, do not collect more than 100 g to minimize disposal efforts and costs.

2. Standard solutions of toxic metals must be poured into an appropriate waste receptacle, and the waste will be properly treated or disposed of (a commercial hazardous waste contractor, for example).

Data Analysis

1. Prepare a calibration plot of A (ordinate) versus concentration of the metal for the standards (if the instrument's computer does not generate one). This assumes a zero absorbance for the blank. If this is not the case, the net absorbance is used. Repeat for each metal tested.

2. If the instrument's computer does not calculate the ppm of the analyte, use the calibration plots to calculate ppm of the metal. Repeat for each sample and then repeat for the other metals. Alternatively, use computer software to carry out a least-squares analysis of the data for the standards. The results of the analysis can then be used to write an equation for the straight line, and this in turn can be used to calculate the sample solution concentrations. The product of this concentration times the volume of the solution gives the total amount of extracted metal (see Step 3).

3. Calculate the (mg of metal)/(kg of sediment) for each metal and for each sample. The amount of analyte, X , in the sediment (soil) is obtained by first multiplying the measured extract concentration (mg/L) of X times the volume, V of the extract solution, in liters:

$$\text{mg } X = (\text{mg/L}) \times V \quad (10-1)$$

Then the mg of X per kg of sample is

$$(\text{mg/L}) (V) / \text{kg sample} = \text{ppm } X \quad (10-2)$$

4. Discuss the significance of your results. Do your values fall within expected values, or are they much higher than normal background levels? Remember to cite your sources for "normal" levels.

Supplemental Activity

1. If time allows, the student can observe the effect of changing the following parameters by aspirating a concentrated standard: changing the lamp alignment, changing the burner height, increasing the flow of acetylene, increasing the flow of air.

2. After aspirating a concentrated sample of a metal and determining its absorbance, add 1–3 drops of 85% phosphoric acid to about 10 mL of the sample and reaspirate it to observe the effect of complexation.

3. Because of similar size, Pb^{2+} is often found associated with Ca^{2+} . Elevated lead levels have been found in calcium-based antacids and calcium supplements. A possible small project is the determination of the lead content of those products. The authors have also found strontium to be at substantial levels in these products.

Questions and Further Thoughts

1. In dilute aqueous solution, why is the numerical value of ppm the same as mg/L?
2. Why do sediment samples taken near shipyards usually have elevated levels of many metals, especially lead, cadmium, and chromium?

Notes

1. Particulates must be scrupulously eliminated from samples before aspirating them into the burner. Otherwise, the aspirator becomes clogged. Medium porosity filter paper is sufficient for this purpose (Whatman Number 1, for example).
2. If absorbances fluctuate, the most likely cause is poor aspiration due to a clog. See the instructor about this problem. The use of a wire supplied with the instrument can be used to dislodge the obstacle.
3. There must be a good, fully functional hood over the flame. **The hood can get very hot!**
4. Some metals should not be studied at all by beginning students or even advanced students. One such metal is beryllium, which can cause serious lung disease even at extremely low concentrations.
5. The final results of this experiment are mg/kg wet sediment. Many literature results are given in this form, but mg/kg dry sediment is preferable since the water content of samples can be quite variable. The dry weight basis can be determined by either:
 - a) Drying the sample before digesting. This can be lengthy.
 - b) Taking a 1 g sample of wet sediment and drying to constant weight at 110°C. This takes less than 1 hour. Letting the ratio, $(\text{dry weight})/(\text{wet weight}) = f$, the dry weight equivalent of a sample is $\text{dry weight} = f(\text{sample wet weight})$, and then,

$$\text{mg/kg dry weight} = (\text{mg/L}) / f \text{ kg dry sample} \quad (10-3)$$

Literature Cited

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