Chapter 1

Elemental Analysis

1.1 Introduction to Elemental Analysis[1]

The purpose of elemental analysis is to determine the quantity of a particular element within a molecule or material. Elemental analysis can be subdivided in two ways:

- Qualitative: determining what elements are present or the presence of a particular element.
- Quantitative: determining how much of a particular or each element is present.

In either case elemental analysis is independent of structure unit or functional group, i.e., the determination of carbon content in toluene ($C_6H_5CH_3$) does not differentiate between the aromoatic sp^2 carbon atoms and the methyl sp^3 carbon.

Elemental analysis can be performed on a solid, liquid, or gas. However, depending on the technique employed the sample may have to be pre-reacted, e.g., by combustion or acid digestion. The amounts required for elemental analysis range from a few gram (g) to a few milligram (mg) or less.

Elemental analysis can also be subdivided into general categories related to the approach involved in determining quantities.

- Classical analysis relies on stoichiometry through a chemical reaction or by comparison with known reference sample.
- Modern methods rely on nuclear structure or size (mass) of a particular element and are generally limited to solid samples.

Many classical methods they can be further classified into the following categories:

- Gravimetric in which a sample is separated from solution as a solid as a precipitate and weighed. This is generally used for alloys, ceramics, and minerals.
- Volumetric is the most frequently employed involves determination of the volume of a substance that combines with another substance in known proportions. This is also called titrimetric analysis and is frequently employed using a visual end point or potentiometric measurement.
- Colorimetric (spectroscopic) analysis requires the addition of an organic complex agent. This is commonly used in medical laboratories as well as in the analysis of industrial wastewater treatment.

The biggest limitation in classical methods is most often due to sample manipulation rather than equipment error, i.e., operator error in weighing a sample or observing an end point. In contrast, the errors in modern analytical methods are almost entirely computer sourced and inherent in the software that analyzes and fits the data.

[1] This content is available online at <http://cnx.org/content/m48627/1.1/>.

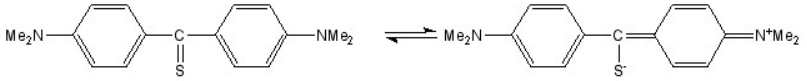
1.2 Spot Tests[2]

Spot tests (spot analysis) are simple chemical procedures that uniquely identify a substance. They can be performed on small samples, even microscopic samples of matter with no preliminary separation. The first report of a spot test was in 1859 by Hugo Shiff for the detection of uric acid.

In a typical spot test, a drop of chemical reagent is added to a drop of an unknown mixture. If the substance under study is present, it produces a chemical reaction characterized by one or more unique observables, e.g., a color change.

1.2.1 Detection of chlorine

A typical example of a spot test is the detection of chlorine in the gas phase by the exposure to paper impregnated with 0.1% 4-4'bis-dimethylamino-thiobenzophenone (thio-Michler's ketone) dissolved in benzene. In the presence of chlorine the paper will change from yellow to blue. The mechanism involves the Zwitter ionic form of the thioketone, (1.1), undergoing an oxidation reaction and subsequent disulfide coupling, (1.2).



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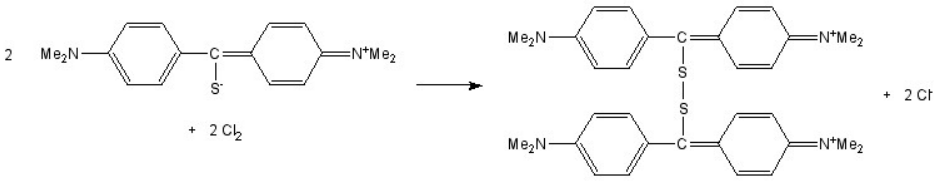

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1.2.2 Bibliography

- L. Ben-Dor and E. Jungreis, *Microchimica Acta*, 1964, **52**, 100.
- F. Feigl, *Spot Tests in Organic Analysis*, 7th Ed. Elsevier, New York, 2012
- N. MacInnes, A. R. Barron, R. S. Soman, and T. R. Gilbert, *J. Am. Ceram. Soc.*, 1990, **73**, 3696.
- H. Schiff, *Ann. Chim. Acta*, 1859, **109**, 67.

1.3 Introduction to Combustion Analysis[3]

1.3.1 Applications of combustion analysis

Combustion, or burning as it is more commonly known, is simply the mixing and exothermic reaction of a fuel and an oxidizer. It has been used since prehistoric times in a variety of ways, such as a source of direct heat, as in furnaces, boilers, stoves, and metal forming, or in piston engines, gas turbines, jet engines, rocket engines, guns, and explosives. Automobile engines use internal combustion in order to convert chemical into mechanical energy. Combustion is currently utilized in the production of large quantities of H_2. Coal or coke is combusted at 1000 °C in the presence of water in a two-step reaction. The first step shown in (1.3) involved the partial oxidation of carbon to carbon monoxide. The second step, (1.4), involves a mixture of

[2]This content is available online at <http://cnx.org/content/m48634/1.1/>.
[3]This content is available online at <http://cnx.org/content/m43578/1.1/>.

produced carbon monoxide with water to produce hydrogen and is commonly known as the water gas shift reaction.

$$C(g) + H_2O(g) \rightarrow CO(g) + H_2(g) \tag{1.3}$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \tag{1.4}$$

Although combustion provides a multitude of uses, it was not employed as a scientific analytical tool until the late 18th century.

1.3.2 History of combustion

In the 1780's, Antoine Lavoisier (Figure 1.1) was the first to analyze organic compounds with combustion using an extremely large and expensive apparatus (Figure 1.2) that required over 50 g of the organic sample and a team of operators.

Figure 1.1: French chemist and renowned "father of modern Chemistry" Antoine Lavoisier (1743-1794).

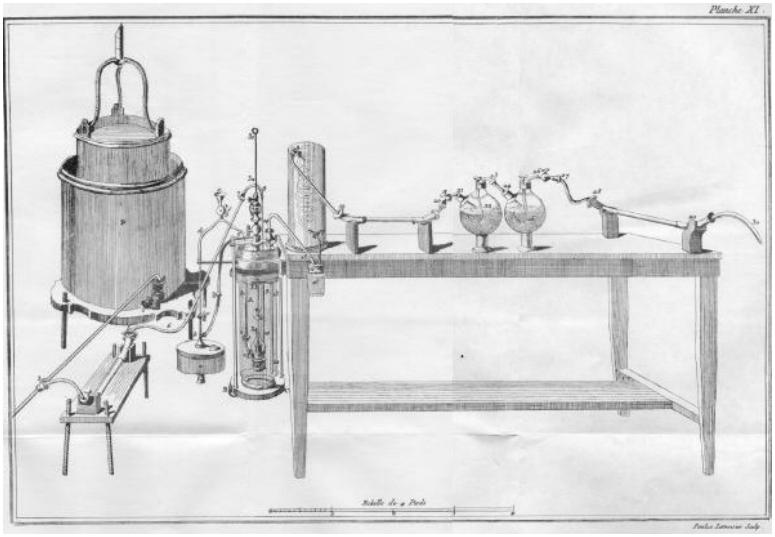

Figure 1.2: Lavoisier's combustion apparatus. A. Lavoisier, *Traité Élémentaire de Chimie*, 1789, **2**, 493-501.

The method was simplified and optimized throughout the 19^{th} and 20^{th} centuries, first by Joseph Gay-Lussac (Figure 1.3), who began to use copper oxide in 1815, which is still used as the standard catalyst.

Figure 1.3: French chemist Joseph Gay-Lussac (1778-1850).

William Prout (Figure 1.4) invented a new method of combustion analysis in 1827 by heating a mixture of the sample and CuO using a multiple-flame alcohol lamp (Figure 1.5) and measuring the change in gaseous volume.

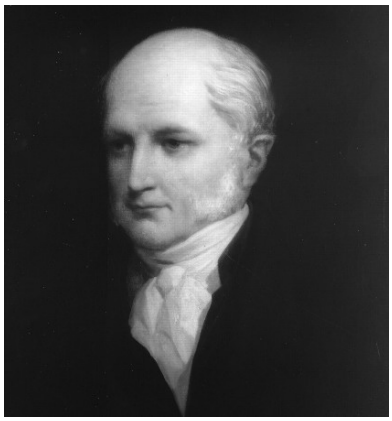

Figure 1.4: English chemist, physician, and natural theologian William Prout (1785-1850).

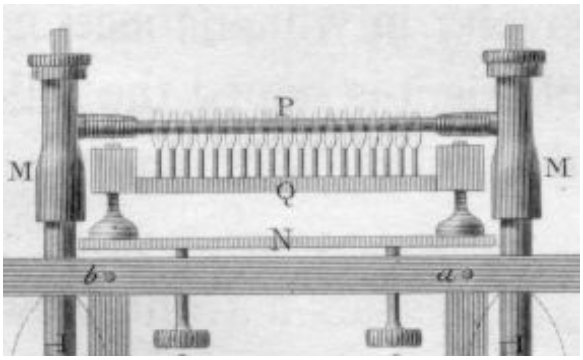

Figure 1.5: Prout's combustion apparatus. W. Prout, *Philos. T. R. Soc. Lond.*, 1827, **117**, 355.

In 1831, Justus von Liebig (Figure 1.6) simplified the method of combustion analysis into a "combustion train" system (Figure 1.7 and Figure 1.8) that linearly heated the sample using coal, absorbed water using calcium chloride, and absorbed carbon dioxide using potash (KOH). This new method only required 0.5 g of sample and a single operator, and Liebig moved the sample through the apparatus by sucking on an opening at the far right end of the apparatus.

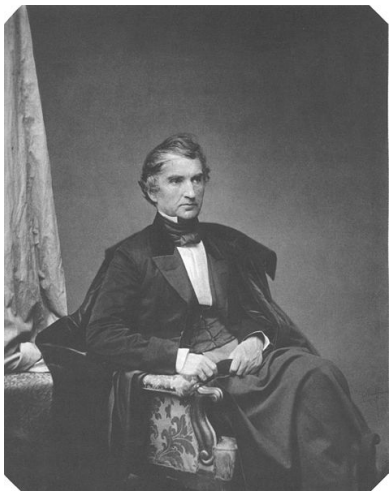

Figure 1.6: German chemist Justus von Liebig (1803-1873).

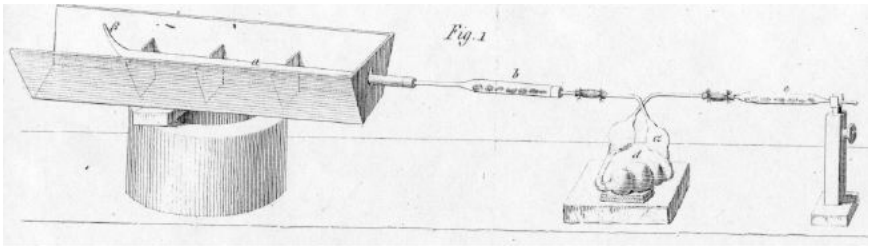

Figure 1.7: Print of von Liebig's "combustion train" apparatus for determining carbon and hydrogen composition. J. Von Liebig, *Annalen der Physik und Chemie*, 1831, **21**.

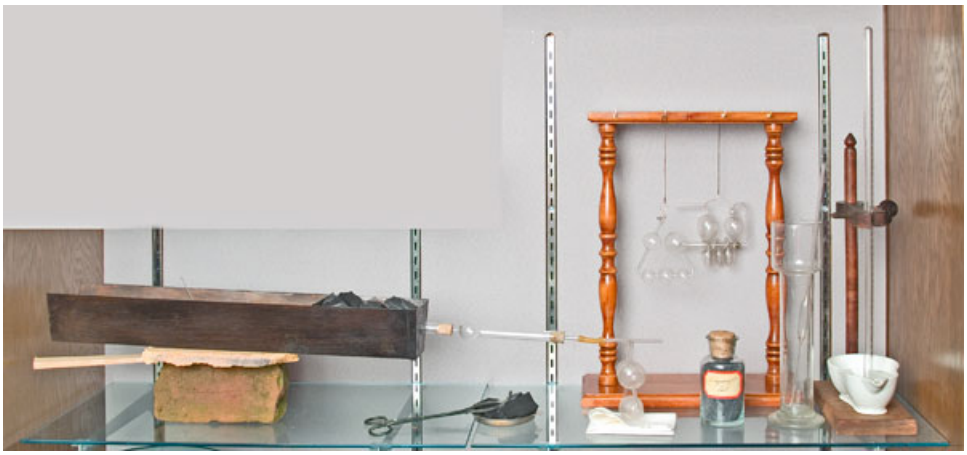

Figure 1.8: Photo of von Liebig's "combustion train apparatus" for determining carbon and hydrogen composition. The Oesper Collections in the History of Chemistry, Apparatus Museum, University of Cincinnati, Case 10, Combustion Analysis. For a 360° view of this apparatus, visit http://digitalprojects.libraries.uc.edu/oesper/museum/case10/shelf_02/CA0010/index.php[4].

Jean-Baptiste André Dumas (Figure 1.9) used a similar combustion train to Liebig. However, he added a U-shaped aspirator that prevented atmospheric moisture from entering the apparatus (Figure 1.10).

Figure 1.9: French chemist Jean-Baptiste André Dumas (1800-1844).

[4]http://digitalprojects.libraries.uc.edu/oesper/museum/case10/shelf_02/CA0010/index.php

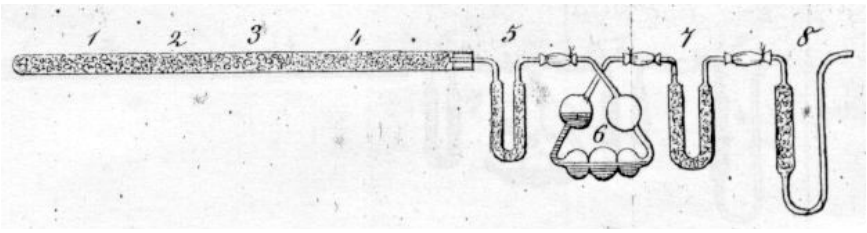

Figure 1.10: Dumas' apparatus; note the aspirator at 8. Sourced from J. A. Dumas, *Ann. der Chem. and Pharm.*, 1841, **38**, 141.

In 1923, Fritz Pregl (Figure 1.11) received the Nobel Prize for inventing a micro-analysis method of combustion. This method required only 5 mg or less, which is 0.01% of the amount required in Lavoisier's apparatus.

Figure 1.11: Austrian chemist and physician Fritz Pregl (1869-1930).

Today, combustion analysis of an organic or organometallic compound only requires about 2 mg of sample. Although this method of analysis destroys the sample and is not as sensitive as other techniques, it is still considered a necessity for characterizing an organic compound.

1.3.3 Categories of combustion

1.3.3.1 Basic flame types

There are several categories of combustion, which can be identified by their flame types (Table 1.1). At some point in the combustion process, the fuel and oxidant must be mixed together. If these are mixed before being burned, the flame type is referred to as a premixed flame, and if they are mixed simultaneously with combustion, it is referred to as a nonpremixed flame. In addition, the flow of the flame can be categorized as either laminar (streamlined) or turbulent (Figure 1.12).

Fuel/oxidizer mixing	**Fluid motion**	**Examples**
Premixed	Turbulent	Spark-ignited gasoline engine, low NO_x stationary gas turbine
Premixed	Laminar	Flat flame, Bunsen flame (followed by a nonpremixed candle for Φ>1)
Nonpremixed	Turbulent	Pulverized coal combustion, aircraft turbine, diesel engine, H_2/O_2 rocket motor
Nonpremixed	Laminar	Wood fire, radiant burners for heating, candle

Table 1.1: Types of combustion systems with examples. Adapted from J. Warnatz, U. Maas, and R. W. Dibble, *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*, 3rd Ed., Springer, Berlin (2001).

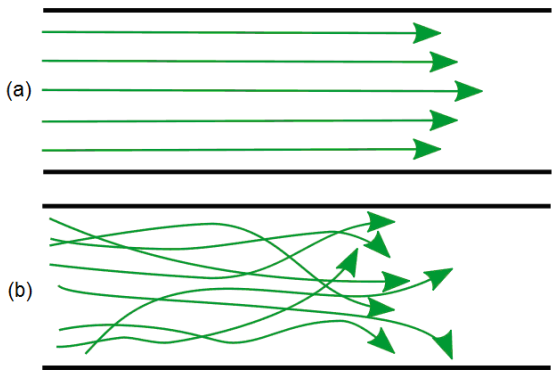

Figure 1.12: Schematic representation of (a) laminar flow and (b) turbulent flow.

The amount of oxygen in the combustion system can alter the flow of the flame and the appearance. As illustrated in Figure 1.13, a flame with no oxygen tends to have a very turbulent flow, while a flame with an excess of oxygen tends to have a laminar flow.

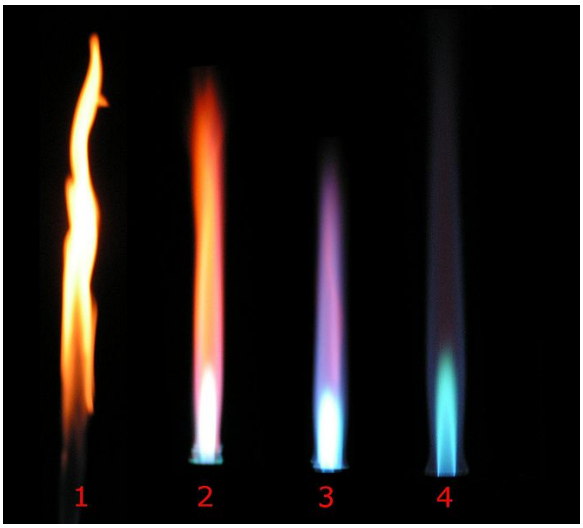

Figure 1.13: Bunsen burner flames with varying amounts of oxygen and constant amount of fuel. (1) air valve completely closed, (2) air valve slightly open, (3) air valve half open, (4) air valve completely open.

1.3.3.2 Stoichiometric combustion and calculations

A combustion system is referred to as stoichiometric when all of the fuel and oxidizer are consumed and only carbon dioxide and water are formed. On the other hand, a fuel-rich system has an excess of fuel, and a fuel-lean system has an excess of oxygen (Table 1.2).

Combustion type	Reaction example
Stoichiometric	$2H_2 + O_2 \rightarrow 2H_2O$
Fuel-rich (H_2 left over)	$3H_2 + O_2 \rightarrow 2H_2O + H_2$
Fuel-lean (O_2 left over)	$CH_4 + 3O_2 \rightarrow 2H_2O + CO_2 + O_2$

Table 1.2: Examples of stoichiometric, fuel-rich, and fuel-lean systems.

If the reaction of a stoichiometric mixture is written to describe the reaction of exactly 1 mol of fuel (H_2 in this case), then the mole fraction of the fuel content can be easily calculated as follows, where ν denotes the mole number of O_2 in the combustion reaction equation for a complete reaction to H_2O and CO_2, (1.5).

$$x_{\text{fuel,stoich.}} = \frac{1}{1+\nu} \tag{1.5}$$

For example, in the reaction (1.6), the stoichiometry is determined as shown in (1.7) and (1.8).

$$H_2 + {}^1/_2\, O_2 \rightarrow H_2O_2 + H_2 \tag{1.6}$$

$$\nu = 0.5 \tag{1.7}$$

$$x\mathrm{H_2,stoich.} = 2/3 \tag{1.8}$$

However, as calculated this reaction would be for the reaction in an environment of pure oxygen. On the other hand, air has only 21% oxygen (78% nitrogen, 1% noble gases). Therefore, if air is used as the oxidizer, this must be taken into account in the calculations, i.e., (1.9).

$$x\mathrm{N_2} = 3.762(x\mathrm{O_2}) \tag{1.9}$$

The mole fractions for a stoichiometric mixture in air are therefore calculated in following way: (1.10) - (1.12)).

$$x\mathrm{fuel,stoich} = \frac{1}{1 + \nu(4.762)} \tag{1.10}$$

$$x\mathrm{O_2,stoich} = \nu(x\mathrm{fuel,stoich}) \tag{1.11}$$

$$x\mathrm{N_2,stoich} = 3.762\,(x\mathrm{O_2,stoich}) \tag{1.12}$$

Example 1.1

Calculate the fuel mole fraction (xfuel) for the stoichiometric reaction:

$$\mathrm{CH_4} + 2\mathrm{O_2} + (2 \times 3.762)\mathrm{N_2} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O} + (2 \times 3.762)\mathrm{N_2} \tag{1.13}$$

In this reaction $\nu = 2$, as 2 moles of oxygen are needed to fully oxidize methane into H_2O and CO_2.

$$x\mathrm{fuel,stoich} = \frac{1}{1 + (2 \times 4.762)} = 0.09502 = 9.502\ \mathrm{mol\%} \tag{1.14}$$

Exercise 1.3.1 ***(Solution on p. 122.)***

Calculate the fuel mole fraction for the stoichiometric reaction

$$\mathrm{C_3H_8} + 5\mathrm{O_2} + (5 \times 3.762)\mathrm{N_2} \rightarrow 3\mathrm{CO_2} + 4\mathrm{H_2O} + (5 \times 3.762)\mathrm{N_2} \tag{1.15}$$

Premixed combustion reactions can also be characterized by the air equivalence ratio, λ, as shown in (1.16).

$$\lambda = \frac{x\mathrm{air}/x\mathrm{fuel}}{x\mathrm{air,stoich}/x\mathrm{fuel,stoich}} \tag{1.16}$$

The fuel equivalence ratio, Φ, is the reciprocal of this value (1.17).

$$\Phi = 1/\lambda \tag{1.17}$$

Rewriting (1.10) in terms of the fuel equivalence ratio gives: (1.18) - (1.21).

$$x\mathrm{fuel} = \frac{1}{1 + (\nu\, 4.672/\Phi)} \tag{1.18}$$

$$x\mathrm{air} = 1 - x\mathrm{fuel} \tag{1.19}$$

$$x\mathrm{O}_2 = x\text{air}/4.762 \tag{1.20}$$

$$x\mathrm{N}_2,\text{stoich} = 3.762(x\mathrm{O}_2) \tag{1.21}$$

The premixed combustion processes can also be identified by their air and fuel equivalence ratios (Table 1.3).

Type of combustion	Φ	λ
Rich	>1	<1
Stoichiometric	=1	=1
Lean	<1	>1

Table 1.3: Identification of combustion type by Φ and λ values.

With a premixed type of combustion, there is much greater control over the reaction. If performed at lean conditions, then high temperatures, the pollutant nitric oxide, and the production of soot can be minimized or even avoided, allowing the system to combust efficiently. However, a premixed system requires large volumes of premixed reactants, which pose a fire hazard. As a result, nonpremixed combusted, while not being efficient, is more commonly used.

1.3.4 Instrumentation

Though the instrumentation of combustion analysis has greatly improved, the basic components of the apparatus (Figure 1.14) have not changed much since the late 18th century.

Figure 1.14: Combustion apparatus from the 19$^{\text{th}}$ century. The Oesper Collections in the History of Chemistry, Apparatus Museum, University of Cincinnati, Case 10, Combustion Analysis. For a 360° view of this apparatus, visit http://digitalprojects.libraries.uc.edu/oesper/museum/case10/shelf_03/CA0012/index.php[5].

[5]http://digitalprojects.libraries.uc.edu/oesper/museum/case10/shelf_03/CA0012/index.php

The sample of an organic compound, such as a hydrocarbon, is contained within a furnace or exposed to a flame and burned in the presence of oxygen, creating water vapor and carbon dioxide gas (Figure 1.15). The sample moves first through the apparatus to a chamber in which H_2O is absorbed by a hydrophilic substance and second through a chamber in which CO_2 is absorbed. The change in weight of each chamber is determined to calculate the weight of H_2O and CO_2. After the masses of H_2O and CO_2 have been determined, they can be used to characterize and calculate the composition of the original sample.

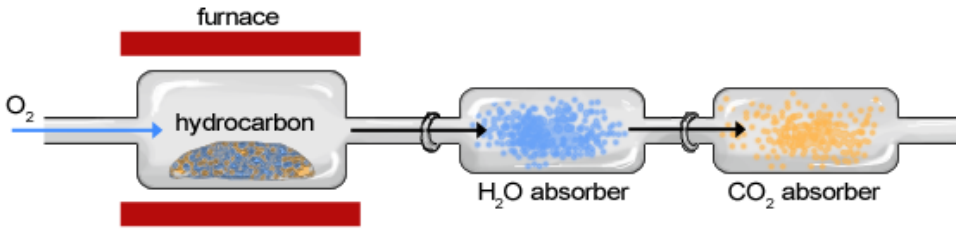

Figure 1.15: Typical modern combustion apparatus with a furnace.

1.3.5 Calculations and determining chemical formulas

1.3.5.1 Hydrocarbons

Combustion analysis is a standard method of determining a chemical formula of a substance that contains hydrogen and carbon. First, a sample is weighed and then burned in a furnace in the presence of excess oxygen. All of the carbon is converted to carbon dioxide, and the hydrogen is converted to water in this way. Each of these are absorbed in separate compartments, which are weighed before and after the reaction. From these measurements, the chemical formula can be determined.

Generally, the following reaction takes place in combustion analysis:

$$C_aH_b + O_2\,(xs) \rightarrow aCO_2 + {}^{b}/_{2}\,H_2O \tag{1.22}$$

Example 1.2

After burning 1.333 g of a hydrocarbon in a combustion analysis apparatus, 1.410 g of H_2O and 4.305 g of CO_2 were produced. Separately, the molar mass of this hydrocarbon was found to be 204.35 g/mol. Calculate the empirical and molecular formulas of this hydrocarbon.

Step 1: Using the molar masses of water and carbon dioxide, determine the moles of hydrogen and carbon that were produced.

$$1.410\text{g } H_2O \times \frac{1\text{ mol } H_2O}{18.015\text{ g } H_2O} \times \frac{2\text{ mol H}}{1\text{ mol } H_2O} = 0.1565\text{ mol H} \tag{1.23}$$

$$4.3051\text{ g } CO_2 \times \frac{1\text{ mol } CO_2}{44.010\text{ g } CO_2} \times \frac{1\text{ mol C}}{1\text{ mol } CO_2} = 0.09782\text{ mol C} \tag{1.24}$$

Step 2: Divide the larger molar amount by the smaller molar amount. In some cases, the ratio is not made up of two integers. Convert the numerator of the ratio to an improper fraction and

rewrite the ratio in whole numbers as shown.

$$\frac{0.1565 \text{ mol H}}{0.09782 \text{ mol C}} = \frac{1.600 \text{ mol H}}{1 \text{ mol C}} = \frac{13/5 \text{ mol H}}{1 \text{ mol C}} = \frac{8/5 \text{ mol H}}{1 \text{ mol C}} = \frac{8 \text{ mol H}}{5 \text{ mol C}} \tag{1.25}$$

Therefore, the empirical formula is C_5H_8.

Step 3: To get the molecular formula, divide the experimental molar mass of the unknown hydrocarbon by the empirical formula weight.

$$\frac{\text{Molar mass}}{\text{Empirical formula weight}} = \frac{204.35 \text{ g/mol}}{68.114 \text{ g/mol}} = 3 \tag{1.26}$$

Therefore, the molecular formula is $(C_5H_8)_3$ or $C_{15}H_{24}$.

Exercise 1.3.2 *(Solution on p. 122.)*

After burning 1.082 g of a hydrocarbon in a combustion analysis apparatus, 1.583 g of H_2O and 3.315 g of CO_2 were produced. Separately, the molar mass of this hydrocarbon was found to be 258.52 g/mol. Calculate the empirical and molecular formulas of this hydrocarbon.

1.3.5.2 Compounds containing carbon, hydrogen, and oxygen

Combustion analysis can also be utilized to determine the empiric and molecular formulas of compounds containing carbon, hydrogen, and oxygen. However, as the reaction is performed in an environment of excess oxygen, the amount of oxygen in the sample can be determined from the sample mass, rather than the combustion data (Example 1.3, Exercise 1.3.3).

Example 1.3

A 2.0714 g sample containing carbon, hydrogen, and oxygen was burned in a combustion analysis apparatus; 1.928 g of H_2O and 4.709 g of CO_2 were produced. Separately, the molar mass of the sample was found to be 116.16 g/mol. Determine the empirical formula, molecular formula, and identity of the sample.

Step 1: Using the molar masses of water and carbon dioxide, determine the moles of hydrogen and carbon that were produced.

$$1.928 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.015 \text{ g } H_2O} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 0.2140 \text{ mol H} \tag{1.27}$$

$$4.709 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.010 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 0.1070 \text{ mol C} \tag{1.28}$$

Step 2: Using the molar amounts of carbon and hydrogen, calculate the masses of each in the original sample.

$$0.2140 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.2157 \text{ g H} \tag{1.29}$$

$$0.1070 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 1.285 \text{ g C} \tag{1.30}$$

Step 3: Subtract the masses of carbon and hydrogen from the sample mass. Now that the mass of oxygen is known, use this to calculate the molar amount of oxygen in the sample.

$$2.0714 \text{ g sample} - 0.2157 \text{ g H} - 1.285 \text{ g C} = 0.5707 \text{ g O} \tag{1.31}$$

$$0.5707 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.03567 \text{ mol O} \tag{1.32}$$

Step 4: Divide each molar amount by the smallest molar amount in order to determine the ratio between the three elements.

$$\frac{0.03567 \text{ mol O}}{0.03567} = 1.00 \text{ mol O} = 1 \text{ mol O} \tag{1.33}$$

$$\frac{0.1070 \text{ mol C}}{0.03567} = 3.00 \text{ mol C} = 3 \text{ mol C} \tag{1.34}$$

$$\frac{0.2140 \text{ mol H}}{0.03567} = 5.999 \text{ mol H} = 6 \text{ mol H} \tag{1.35}$$

Therefore, the empirical formula is C_3H_6O.

Step 5: To get the molecular formula, divide the experimental molar mass of the unknown hydrocarbon by the empirical formula weight.

$$\frac{\text{Molar mass}}{\text{Empirical formula weight}} = \frac{116.16 \text{ g/mol}}{58.08 \text{ g/mol}} = 2 \tag{1.36}$$

Therefore, the molecular formula is $(C_3H_6O)_2$ or $C_6H_{12}O_2$. Possible compound with this molecular formula are shown in (Figure 1.16).

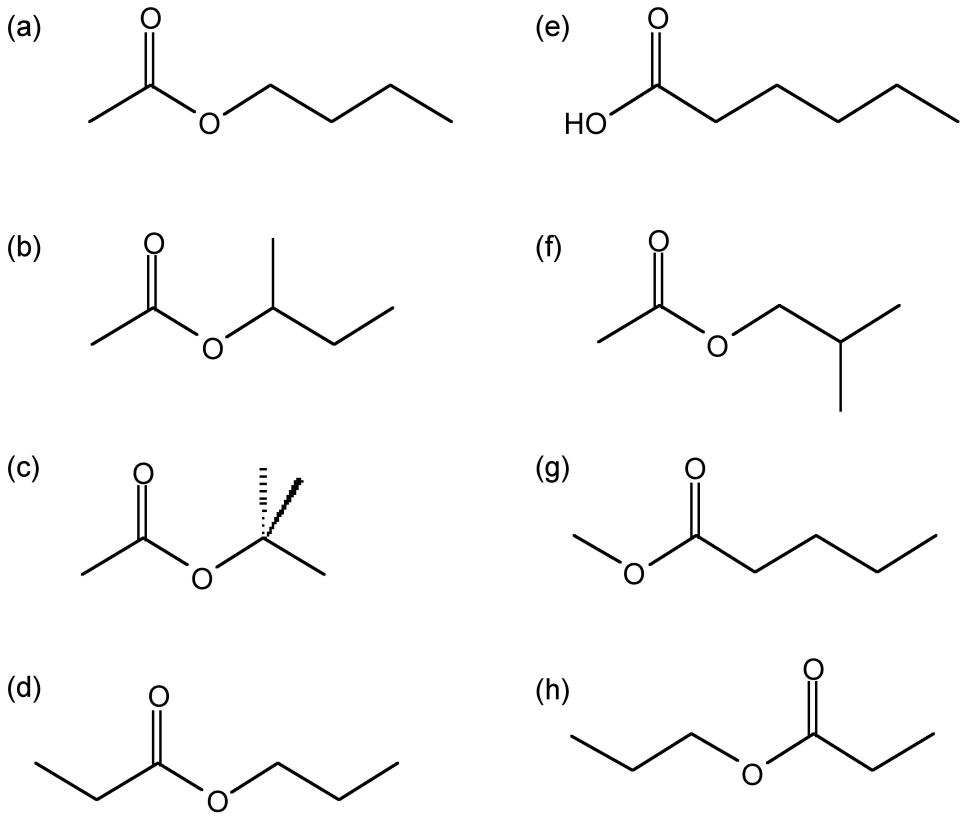

Figure 1.16: Structure of possible compounds with the molecular formula $C_6H_{12}O_2$: (a) butylacetate, (b) *sec*-butyl acetate, (c) *tert*-butyl acetate, (d) ethyl butyrate, (e) haxanoic acid, (f) isobutyl acetate, (g) methyl pentanoate, and (h) propyl proponoate.

Exercise 1.3.3 ***(Solution on p. 122.)***

A 4.846 g sample containing carbon, hydrogen, and oxygen was burned in a combustion analysis apparatus; 4.843 g of H_2O and 11.83 g of CO_2 were produced. Separately, the molar mass of the sample was found to be 144.22 g/mol. Determine the empirical formula, molecular formula, and identity of the sample.

1.3.5.3 Binary compounds

By using combustion analysis, the chemical formula of a binary compound containing oxygen can also be determined. This is particularly helpful in the case of combustion of a metal which can result in potential oxides of multiple oxidation states.

Example 1.4

A sample of iron weighing 1.7480 g is combusted in the presence of excess oxygen. A metal oxide ($Fe_x O_y$) is formed with a mass of 2.4982 g. Determine the chemical formula of the oxide product and the oxidation state of Fe.

Step 1: Subtract the mass of Fe from the mass of the oxide to determine the mass of oxygen in the product.

$$2.4982 \text{ g } Fe_xO_y \text{ - } 1.7480 \text{ g Fe} = 0.7502 \text{ g O} \tag{1.37}$$

Step 2: Using the molar masses of Fe and O, calculate the molar amounts of each element.

$$1.7480 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.845 \text{ g Fe}} = 0.031301 \text{ mol Fe} \tag{1.38}$$

$$0.7502 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.04689 \text{ mol O} \tag{1.39}$$

Step 3: Divide the larger molar amount by the smaller molar amount. In some cases, the ratio is not made up of two integers. Convert the numerator of the ratio to an improper fraction and rewrite the ratio in whole numbers as shown.

$$\frac{0.031301 \text{ mol Fe}}{0.04689 \text{ mol O}} = \frac{0.6675 \text{ mol Fe}}{1 \text{ mol O}} = \frac{{}^{2}/_{3} \text{ mol Fe}}{1 \text{ mol O}} = \frac{2 \text{ mol Fe}}{3 \text{ mol O}} \tag{1.40}$$

Therefore, the chemical formula of the oxide is Fe_2O_3, and Fe has a 3+ oxidation state.

Exercise 1.3.4 ***(Solution on p. 122.)***

A sample of copper weighing 7.295 g is combusted in the presence of excess oxygen. A metal oxide (Cu_xO_y) is formed with a mass of 8.2131 g. Determine the chemical formula of the oxide product and the oxidation state of Cu.

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1.4 Introduction to Atomic Absorption Spectroscopy[6]

1.4.1 Brief overview of atomic absorption spectroscopy

1.4.1.1 History of atomic absorption spectroscopy

The earliest spectroscopy was first described by Marcus Marci von Kronland in 1648 by analyzing sunlight as is passed through water droplets and thus creating a rainbow. Further analysis of sunlight by William

[6] This content is available online at <http://cnx.org/content/m38330/1.1/>.

Hyde Wollaston (Figure 1.17) led to the discovery of black lines in the spectrum, which in 1820 Sir David Brewster (Figure 1.18) explained as absorption of light in the sun's atmosphere.

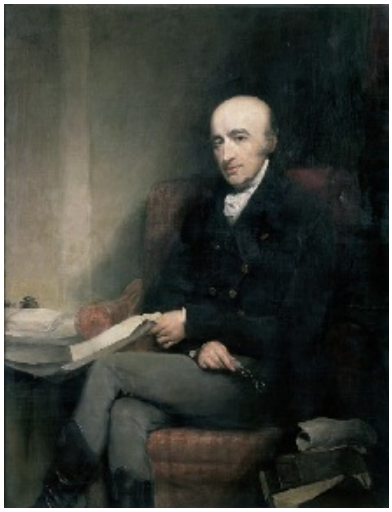

Figure 1.17: English chemist and physicist William Hyde Wollaston (1659 - 1724).

Figure 1.18: Scottish physicist, mathematician, astronomer, inventor, writer and university principal Sir David Brewster (1781 - 1868).

Robert Bunsen (Figure 1.19) and Gustav Kirchhoff (Figure 1.20) studied the sodium spectrum and came to the conclusion that every element has its own unique spectrum that can be used to identify elements in the

vapor phase. Kirchoff further explained the phenomenon by stating that if a material can emit radiation of a certain wavelength, that it may also absorb radiation of that wavelength. Although Bunsen and Kirchoff took a large step in defining the technique of atomic absorption spectroscopy (AAS), it was not widely utilized as an analytical technique except in the field of astronomy due to many practical difficulties.

Figure 1.19: German chemist Robert Bunsen (1811 - 1899).

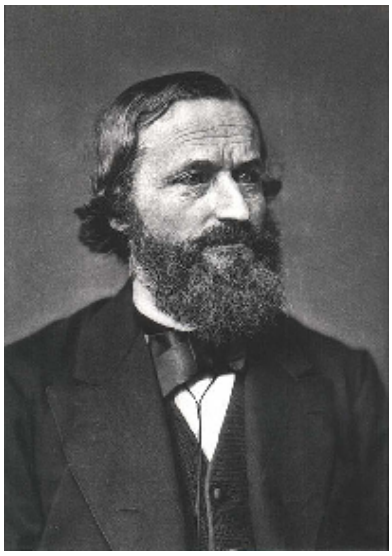

Figure 1.20: German physicist Gustav Robert Kirchhoff (1824 - 1887).

In 1953, Alan Walsh (Figure 1.21) drastically improved the AAS methods. He advocated AAS to many instrument manufacturers, but to no avail. Although he had improved the methods, he hadn't shown how it could be useful in any applications. In 1957, he discovered uses for AAS that convinced manufactures market the first commercial AAS spectrometers. Since that time, AAS's popularity has fluctuated as other analytical techniques and improvements to the methods are made.

Figure 1.21: British physicist Sir Alan Walsh (1916 - 1988).

1.4.1.2 Theory of atomic absorption spectroscopy

In order to understand how atomic absorption spectroscopy works, some background information is necessary. Atomic theory began with John Dalton (Figure 1.22) in the 18^{th} century when he proposed the concept of atoms, that all atoms of an element are identical, and that atoms of different elements can combine to form molecules. In 1913, Niels Bohr (Figure 1.23) revolutionized atomic theory by proposing quantum numbers, a positively charged nucleus, and electrons orbiting around the nucleus in the what became known as the *Bohr model of the atom*. Soon afterward, Louis deBroglie (Figure 1.24) proposed quantized energy of electrons, which is an extremely important concept in AAS. Wolfgang Pauli (Figure 1.25) then elaborated on deBroglie's theory by stating that no two electrons can share the same four quantum numbers. These landmark discoveries in atomic theory are necessary in understanding the mechanism of AAS.

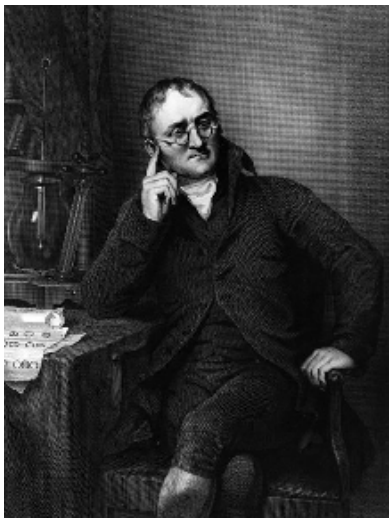

Figure 1.22: English chemist, physicist, and meteorologist John Dalton FRS (1766 - 1844).

Figure 1.23: Danish physicist Niels Henrik David Bohr (1885 - 1962).

Figure 1.24: French physicist and a Nobel laureate Louis de Broglie (1892 - 1987). Copyright: American Institute of Physics.

Figure 1.25: Austrian physicist Wolfgang Pauli (1900 - 1958).

Atoms have valence electrons, which are the outermost electrons of the atom. Atoms can be excited when irradiated, which creates an absorption spectrum. When an atom is excited, the valence electron moves up an energy level. The energies of the various stationary states, or restricted orbits, can then be determined

by these emission lines. The resonance line is then defined as the specific radiation absorbed to reach the excited state.

The Maxwell-Boltzmann equation gives the number of electrons in any given orbital. It relates the distribution to the thermal temperature of the system (as opposed to electronic temperature, vibrational temperature, or rotational temperature). Plank proposed radiation emitted energy in discrete packets (quanta) (1.41), which can be related to Einstein's equation, (1.42).

$$E = h\upsilon \tag{1.41}$$

$$E = mc^2 \tag{1.42}$$

Both atomic emission and atomic absorption spectroscopy can be used to analyze samples. Atomic emission spectroscopy measures the intensity of light emitted by the excited atoms, while atomic absorption spectroscopy measures the light absorbed by atomic absorption. This light is typically in the visible or ultraviolet region of the electromagnetic spectrum. The percentage is then compared to a calibration curve to determine the amount of material in the sample. The energy of the system can be used to find the frequency of the radiation, and thus the wavelength through the combination of equations (1.42) and (1.43).

$$\nu = c/\lambda \tag{1.43}$$

Because the energy levels are quantized, only certain wavelengths are allowed and each atom has a unique spectrum. There are many variables that can affect the system. For example, if the sample is changed in a way that increases the population of atoms, there will be an increase in both emission and absorption and *vice versa*. There are also variables that affect the ratio of excited to unexcited atoms such as an increase in temperature of the vapor.

1.4.2 Applications of atomic absorption spectroscopy

There are many applications of atomic absorption spectroscopy (AAS) due to its specificity. These can be divided into the broad categories of biological analysis, environmental and marine analysis, and geological analysis.

1.4.2.1 Biological analysis

Biological samples can include both human tissue samples and food samples. In human tissue samples, AAS can be used to determine the amount of various levels of metals and other electrolytes, within tissue samples. These tissue samples can be many things including but not limited to blood, bone marrow, urine, hair, and nails. Sample preparation is dependent upon the sample. This is extremely important in that many elements are toxic in certain concentrations in the body, and AAS can analyze what concentrations they are present in. Some examples of trace elements that samples are analyzed for are arsenic, mercury, and lead.

An example of an application of AAS to human tissue is the measurement of the electrolytes sodium and potassium in plasma. This measurement is important because the values can be indicative of various diseases when outside of the normal range. The typical method used for this analysis is atomization of a 1:50 dilution in strontium chloride ($SrCl_2$) using an air-hydrogen flame. The sodium is detected at its secondary line (330.2 nm) because detection at the first line would require further dilution of the sample due to signal intensity. The reason that strontium chloride is used is because it reduces ionization of the potassium and sodium ions, while eliminating phosphate's and calcium's interference.

In the food industry, AAS provides analysis of vegetables, animal products, and animal feeds. These kinds of analyses are some of the oldest application of AAS. An important consideration that needs to be taken into account in food analysis is sampling. The sample should be an accurate representation of what is being analyzed. Because of this, it must be homogenous, and many it is often needed that several samples are run. Food samples are most often run in order to determine mineral and trace element amounts so that

consumers know if they are consuming an adequate amount. Samples are also analyzed to determine heavy metals which can be detrimental to consumers.

1.4.2.2 Environmental and marine analysis

Environmental and marine analysis typically refers to water analysis of various types. Water analysis includes many things ranging from drinking water to waste water to sea water. Unlike biological samples, the preparation of water samples is governed more by laws than by the sample itself. The analytes that can be measured also vary greatly and can often include lead, copper, nickel, and mercury.

An example of water analysis is an analysis of leaching of lead and zinc from tin-lead solder into water. The solder is what binds the joints of copper pipes. In this particular experiment, soft water, acidic water, and chlorinated water were all analyzed. The sample preparation consisted of exposing the various water samples to copper plates with solder for various intervals of time. The samples were then analyzed for copper and zinc with air-acetylene flame AAS. A deuterium lamp was used. For the samples that had copper levels below 100 μg/L, the method was changed to graphite furnace electrothermal AAS due to its higher sensitivity.

1.4.2.3 Geological analysis

Geological analysis encompasses both mineral reserves and environmental research. When prospecting mineral reserves, the method of AAS used needs to be cheap, fast, and versatile because the majority of prospects end up being of no economic use. When studying rocks, preparation can include acid digestions or leaching. If the sample needs to have silicon content analyzed, acid digestion is not a suitable preparation method.

An example is the analysis of lake and river sediment for lead and cadmium. Because this experiment involves a solid sample, more preparation is needed than for the other examples. The sediment was first dried, then grounded into a powder, and then was decomposed in a bomb with nitric acid (HNO_3) and perchloric acid ($HClO_4$). Standards of lead and cadmium were prepared. Ammonium sulfate ($[NH_4][SO_4]$) and ammonium phosphate ($[NH_4][_3PO_4]$) were added to the samples to correct for the interferences caused by sodium and potassium that are present in the sample. The standards and samples were then analyzed with electrothermal AAS.

1.4.3 Instrumentation

1.4.3.1 Atomizer

In order for the sample to be analyzed, it must first be atomized. This is an extremely important step in AAS because it determines the sensitivity of the reading. The most effective atomizers create a large number of homogenous free atoms. There are many types of atomizers, but only two are commonly used: flame and electrothermal atomizers.

1.4.3.1.1 Flame atomizer

Flame atomizers Figure 1.26 are widely used for a multitude of reasons including their simplicity, low cost, and long length of time that they have been utilized. Flame atomizers accept an aerosol from a nebulizer into a flame that has enough energy to both volatilize and atomize the sample (Figure 1.26). When this happens, the sample is dried, vaporized, atomized, and ionized. Within this category of atomizers, there are many subcategories determined by the chemical composition of the flame. The composition of the flame is often determined based on the sample being analyzed. The flame itself should meet several requirements including sufficient energy, a long length, non-turbulent, and safe.

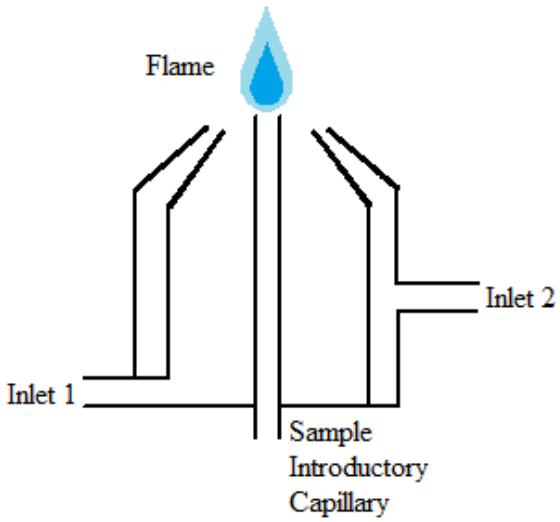

Figure 1.26: A schematic diagram of a flame atomizer shoing the oxidizer inlet (1) and fuel inlet (2).

1.4.3.1.2 Electrothermal atomizer

Although electrothermal atomizers were developed before flame atomizers, they did not become popular until more recently due to improvements made to the detection level. They employ graphite tubes that increase temperature in a stepwise manner (Figure 1.27). Electrothermal atomization first dries the sample and evaporates much of the solvent and impurities, then atomizes the sample, and then rises it to an extremely high temperature to clean the graphite tube. Some requirements for this form of atomization are the ability to maintain a constant temperature during atomization, have rapid atomization, hold a large volume of solution, and emit minimal radiation. Electrothermal atomization is much less harsh than the method of flame atomization.

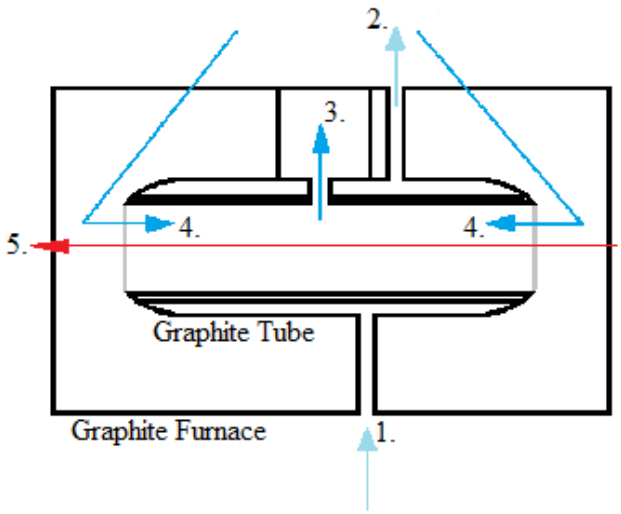

Figure 1.27: Schematic diagram of an electrothermal atomizer showing the external gas flow inlet (1), the external gas flow outlet (2), the internal gas flow outlet (3), the internal gas flow inlet (4), and the light beam (5).

1.4.3.2 Radiation source

The radiation source then irradiates the atomized sample. The sample absorbs some of the radiation, and the rest passes through the spectrometer to a detector. Radiation sources can be separated into two broad categories: line sources and continuum sources. Line sources excite the analyte and thus emit its own line spectrum. Hollow cathode lamps and electrodeless discharge lamps are the most commonly used examples of line sources. On the other hand, continuum sources have radiation that spreads out over a wider range of wavelengths. These sources are typically only used for background correction. Deuterium lamps and halogen lamps are often used for this purpose.

1.4.3.3 Spectrometer

Spectrometers are used to separate the different wavelengths of light before they pass to the detector. The spectrometer used in AAS can be either single-beam or double-beam. Single-beam spectrometers only require radiation that passes directly through the atomized sample, while double-beam spectrometers Figure 1.28, as implied by the name, require two beams of light; one that passes directly through the sample, and one that does not pass through the sample at all. (Insert diagrams) The single-beam spectrometers have less optical components and therefore suffer less radiation loss. Double-beam monochromators have more optical components, but they are also more stable over time because they can compensate for changes more readily.

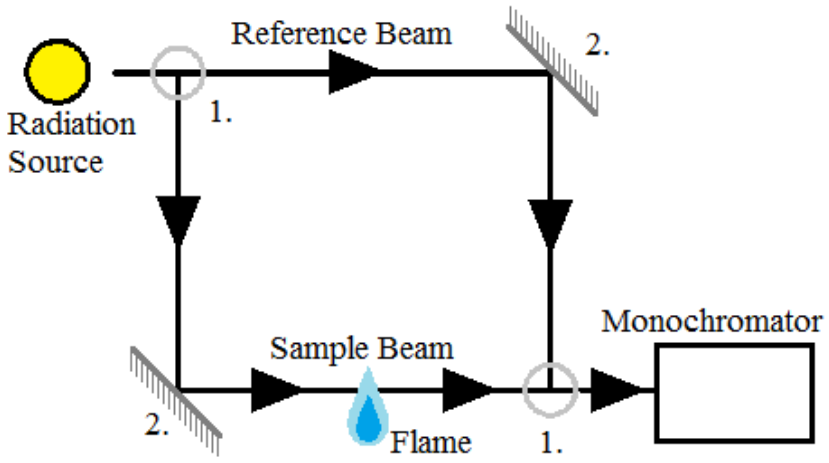

Figure 1.28: A schematic of a double-beam spectrometer showing the 50/50 beam splitters (1) and the mirrors (2).

1.4.4 Obtaining measurements

1.4.4.1 Sample preparation

Sample preparation is extremely varied because of the range of samples that can be analyzed. Regardless of the type of sample, certain considerations should be made. These include the laboratory environment, the vessel holding the sample, storage of the sample, and pretreatment of the sample.

Sample preparation begins with having a clean environment to work in. AAS is often used to measure trace elements, in which case contamination can lead to severe error. Possible equipment includes laminar flow hoods, clean rooms, and closed, clean vessels for transportation of the sample. Not only must the sample be kept clean, it also needs to be conserved in terms of pH, constituents, and any other properties that could alter the contents.

When trace elements are stored, the material of the vessel walls can adsorb some of the analyte leading to poor results. To correct for this, perfluoroalkoxy polymers (PFA), silica, glassy carbon, and other materials with inert surfaces are often used as the storage material. Acidifying the solution with hydrochloric or nitric acid can also help prevent ions from adhering to the walls of the vessel by competing for the space. The vessels should also contain a minimal surface area in order to minimize possible adsorption sites.

Pretreatment of the sample is dependent upon the nature of the sample. See Table 1.4 for sample pretreatment methods.

Sample	Examples	Pretreatment method
		continued on next page

Aqueous solutions	Water, beverages, urine, blood	Digestion if interference causing substituents are present
Suspensions	Water, beverages, urine, blood	Solid matter must either be removed by filtration, centrifugation or digestion, and then the methods for aqueous solutions can be followed
Organic liquids	Fuels, oils	Either direct measurement with AAS or diltion with organic material followed by measurement with AAS, standards must contain the analyte in the same form as the sample
Solids	Foodstuffs, rocks	Digestion followed by electrothermal AAS

Table 1.4: Sample pretreatment methods for AAS.

1.4.4.2 Calibration curve

In order to determine the concentration of the analyte in the solution, calibration curves can be employed. Using standards, a plot of concentration versus absorbance can be created. Three common methods used to make calibration curves are the standard calibration technique, the bracketing technique, and the analyte addition technique.

1.4.4.2.1 Standard calibration technique

This technique is the both the simplest and the most commonly used. The concentration of the sample is found by comparing its absorbance or integrated absorbance to a curve of the concentration of the standards versus the absorbances or integrated absorbances of the standards. In order for this method to be applied the following conditions must be met:

- Both the standards and the sample must have the same behavior when atomized. If they do not, the matrix of the standards should be altered to match that of the sample.
- The error in measuring the absorbance must be smaller than that of the preparation of the standards.
- The samples must be homogeneous.

The curve is typically linear and involves at least five points from five standards that are at equidistant concentrations from each other Figure 1.29. This ensures that the fit is acceptable. A least means squares calculation is used to linearly fit the line. In most cases, the curve is linear only up to absorbance values of 0.5 to 0.8. The absorbance values of the standards should have the absorbance value of a blank subtracted.

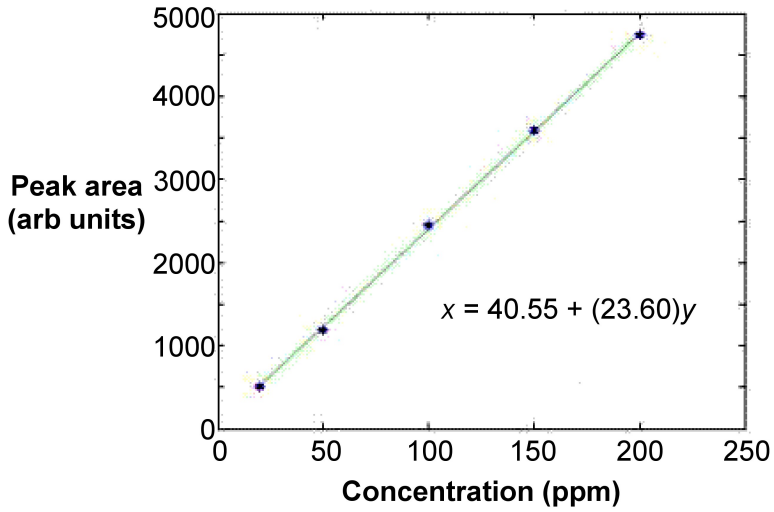

Figure 1.29: An example of a calibration curve made for the standard calibration technique.

1.4.4.2.2 Bracketing technique

The bracketing technique is a variation of the standard calibration technique. In this method, only two standards are necessary with concentrations c_1 and c_2. They bracket the approximate value of the sample concentration very closely. Applying (1.44) to determines the value for the sample, where c_x and A_x are the concentration and adsorbance of the unknown, and A_1 and A_2 are the adsorbance for c_1 and c_2, respectively.

$$c_x = \frac{(A_x - A_1)(c_1 - c_2)}{A_2 - A_1} + c_1 \tag{1.44}$$

This method is very useful when the concentration of the analyte in the sample is outside of the linear portion of the calibration curve because the bracket is so small that the portion of the curve being used can be portrayed as linear. Although this method can be used accurately for nonlinear curves, the further the curve is from linear the greater the error will be. To help reduce this error, the standards should bracket the sample very closely.

1.4.4.2.3 Analyte addition technique

The analyte addition technique is often used when the concomitants in the sample are expected to create many interferences and the composition of the sample is unknown. The previous two techniques both require that the standards have a similar matrix to that of the sample, but that is not possible when the matrix is unknown. To compensate for this, the analyte addition technique uses an aliquot of the sample itself as the matrix. The aliquots are then spiked with various amounts of the analyte. This technique must be used only within the linear range of the absorbances.

1.4.4.3 Measurement interference

Interference is caused by contaminants within the sample that absorb at the same wavelength as the analyte, and thus can cause inaccurate measurements. Corrections can be made through a variety of methods such

as background correction, addition of chemical additives, or addition of analyte Table 1.5.

Interference type	**Cause of interference**	**Result**	**Example**	**Correction measures**
Atomic line overlap	Spectral profile of two elements are within 0.01 nm of each other	Higher experimental absorption value than the real value	Very rare, with the only plausable problem being that of copper (324.754 nm) and europium (324.753 nm)	Typically doesn't occur in practical situations, so there is no established correction method
Molecular band and line overlap	Spectral profile of an element overlaps with molecular band	Higher experimental absorption value than the real value	Calcium hydroxide and barium at 553.6 nm in a air-acetylene flame	Background correction
Ionization (vapor-phase or cation enhancement)	atoms are ionized at the temperature of the flame/furnace, which decreases the amount of free atoms	Lower experimental absorption value than real value	Problems commonly occur with cesium, potassium, and sodium	Add an ionization suppressor (or buffer) to both the sample and the standards
Light scattering	Solid particles scatter the beam of light lowering the intensity of the beam entering the monochromater	Higher experimental absorption value than the real value	High in samples with many refractory elements, highest at UV wavelengths (add specific example)	Matrix modifaction and/or background correction
Chemical	The chemical being analyzed is contained withing a compound in the analyte that is not atomized	Lower experimental absorption value than real value	Calcium and phosphate ions form calcium phosphate which is then converted to calcium pyrophosphate which is stable in high heat	Increase the temperature of the flame if flame AAS is being used, use a releasing chemical, or standard addition for electrothermal AAS

continued on next page

Physical	If physical properties of the sample and the standards are different, atomization can be affected thus affecting the number of free atom population	Can vary in either direction depending upon the conditions	Viscosity differences, surface tension differences, etc	Alter the standards to have similar physical properties to the samples
Volitalization	In electrothermal atomization, interference will occur if the rate of volatilization is not the same for the sample as for the standard, which is often caused by a heavy matrix	Can vary in either direction depending upon the conditions	Chlorides are very volatile, so they need to be converted to a less volatile form. Often this is done by the addition of nitrate or slufate. Zinc and lead are also highly problamatic	Change the matrix by standard addition, or selectively volatileze components of the matrix

Table 1.5: Examples of interference in AAS.

1.4.5 Bibliography

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1.5 ICP-AES Analysis of Nanoparticles[7]

1.5.1 What is ICP-AES?

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is a spectral method used to determine very precisely the elemental composition of samples; it can also be used to quantify the elemental concentration with the sample. ICP-AES uses high-energy plasma from an inert gas like argon to burn analytes very rapidly. The color that is emitted from the analyte is indicative of the elements present, and the intensity of the spectral signal is indicative of the concentration of the elements that is present. A schematic view of a typical experimental set-up is shown in Figure 1.30.

[7] This content is available online at <http://cnx.org/content/m22058/1.19/>.

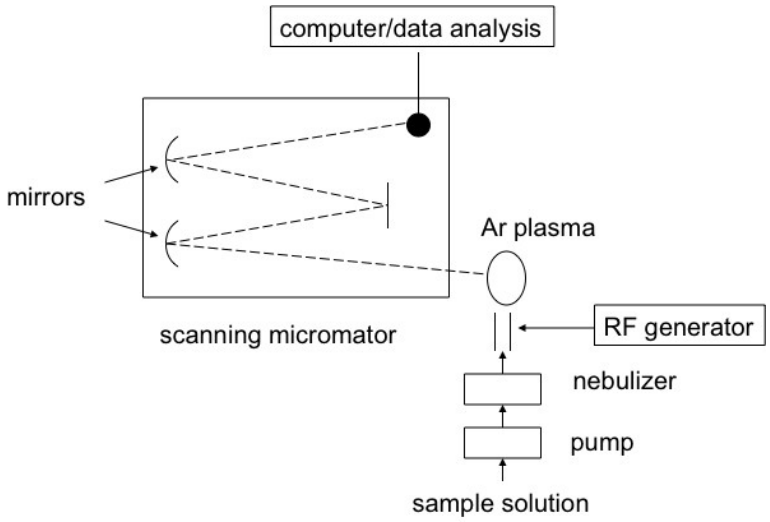

Figure 1.30: Schematic representation of an ICP-AES set-up.

1.5.2 How does ICP-AES work?

ICP-AES works by the emission of photons from analytes that are brought to an excited state by the use of high-energy plasma. The plasma source is induced when passing argon gas through an alternating electric field that is created by an inductively couple coil. When the analyte is excited the electrons try to dissipate the induced energy moving to a ground state of lower energy, in doing this they emit the excess energy in the form of light. The wavelength of light emitted depends on the energy gap between the excited energy level and the ground state. This is specific to the element based on the number of electrons the element has and electron orbital's are filled. In this way the wavelength of light can be used to determine what elements are present by detection of the light at specific wavelengths.

As a simple example consider the situation when placing a piece of copper wire into the flame of a candle. The flame turns green due to the emission of excited electrons within the copper metal, as the electrons try to dissipate the energy incurred from the flame, they move to a more stable state emitting energy in the form of light. The energy gap between the excited state to the ground state (ΔE) dictates the color of the light or wavelength of the light, (1.45), where h is Plank's constant (6.626×10^{-34} m^2kg/s), and ν is the frequency of the emitted light.

$$E = h\nu \tag{1.45}$$

The wavelength of light is indicative of the element present. If another metal is placed in the flame such as iron a different color flame will be emitted because the electronic structure of iron is different from that of copper. This is a very simple analogy for what is happening in ICP-AES and how it is used to determine what elements are present. By detecting the wavelength of light that is emitted from the analyte one can deduce what elements are be present.

Naturally if there is a lot of the material present then there will be an accumulative effect making the intensity of the signal large. However, if there were very little materials present the signal would be low. By this rationale one can create a calibration curve from analyte solutions of known concentrations, whereby the intensity of the signal changes as a function of the concentration of the material that is present. When

measuring the intensity from a sample of unknown concentration the intensity from this sample can be compared to that from the calibration curve, so this can be used to determine the concentration of the analytes within the sample.

1.5.3 ICP-AES of nanoparticles to determine elemental composition

As with any sample being studied by ICP-AES nanoparticles need to be digested so that all the atoms can be vaporized in the plasma equally. If a metal containing nanoparticle were not digested using a strong acid to bring the metals atoms into solution, the form of the particle could hinder some of the material being vaporized. The analyte would not be detected even though it is present in the sample and this would give an erroneous result. Nanoparticles are often covered with a protective layer of organic ligands and this must be removed also. Further to this the solvent used for the nanoparticles may also be an organic solution and this should be removed as it too will not be miscible in the aqueous medium.

Several organic solvents have low vapor pressures so it is relatively easy to remove the solvent by heating the samples, removing the solvent by evaporation. To remove the organic ligands that are present on the nanoparticle, choric acid can be used. This is a very strong acid and can break down the organic ligands readily. To digest the particles and get the metal into solution concentrated nitric acid is often used.

A typical protocol may use 0.5 mL of concentrated nanoparticle solution and digest this with 9.5 mL of concentrated nitric acid over the period of a few days. After which 0.5 mL of the digested solution is placed in 9.5 mL of nanopure water. The reason why nanopure water is used is because DI water or regular water will have some amount of metals ions present and these will be detected by the ICP-AES measurement and will lead to figures that are not truly representative of the analyte concentration alone. This is especially pertinent when there is a very a low concentration of metal analyte to be detected, and is even more a problem when the metal to be detected is commonly found in water such as iron. Once the nanopure water and digested solution are prepared then the sample is ready for analysis.

Another point to consider when doing ICP-AES on nanoparticles to determine chemical compositions, includes the potential for wavelength overlap. The energy that is released in the form of light is unique to each element, but elements that are very similar in atomic structure will have emission wavelengths that are very similar to one another. Consider the example of iron and cobalt, these are both transition metals and sit right beside each other on the periodic table. Iron has an emission wavelength at 238.204 nm and cobalt has an emission wavelength at 238.892 nm. So if you were to try determine the amount of each element in an alloy of the two you would have to select another wavelength that would be unique to that element, and not have any wavelength overlap to other analytes in solution. For this case of iron and cobalt it would be wiser to use a wavelength for iron detection of 259.940 nm and a wavelength detection of 228.616 nm. Bearing this in mind a good rule of thumb is to try use the wavelength of the analyte that affords the best detection primarily. But if this value leads to a possible wavelength overlap of within 15 nm wavelength with another analyte in the solution then another choice should be made of the detection wavelength to prevent wavelength overlap from occurring.

Some people have also used the ICP-AES technique to determine the size of nanoparticles. The signal that is detected is determined by the amount of the material that is present in solution. If very dilute solutions of nanoparticles are being analyzed, particles are being analyzed one at a time, i.e., there will be one nanoparticle per droplet in the nebulizer. The signal intensity would then differ according to the size of the particle. In this way the ICP-AES technique could be used to determine the concentration of the particles in the solution as well as the size of the particles.

1.5.4 Calculations for ICP concentrations

In order to performe ICP-AES stock solutions must be prepared in dilute nitric acid solutions. To do this a concentrated solution should be diluted with nanopure water to prepare 7 wt% nitric acid solutions. If the concentrated solution is 69.8 wt% (check the assay amount that is written on the side of the bottle) then the amount to dilute the solution will be as such:

- The density (d) of HNO_3 is 1.42 g/mL
- Molecular weight (M_W) of HNO_3 is 63.01

Concentrated percentage 69.8 wt% from assay. First you must determine the molarity of the concentrated solution, (1.46). For the present assay amount, the figure will be calculated from (1.47) and (1.48).

$$\text{Molarity} = [(\%)(d)/(M_W)] * 10 \tag{1.46}$$

$$M = [(69.8)(1.42) / (63.01)] * 10 \tag{1.47}$$

$$\therefore\ M = 15.73 \tag{1.48}$$

This is the initial concentration C_I. To determine the molarity of the 7% solution will be determined by (1.49), i.e., (1.50) is the final concentration C_F.

$$M = [(7)(1.42) / (63.01)] * 10 \tag{1.49}$$

$$\therefore M = 1.58 \tag{1.50}$$

We use these figures in (1.51) to determine the amount of dilution required to dilute the concentrated nitric acid to make it a 7% solution.

$$\text{mass}_I * \text{concentration}_I = \text{mass}_F * \text{concentration}_F \tag{1.51}$$

Now as we are talking about solutions the amount of mass will be measured in mL, and the concentration will be measured as a molarity, (1.52) and (1.53) where M_I and M_F have been calculated above. In addition, the amount of dilute solution will be dependent on the user and how much is required by the user to complete the ICP analysis, for the sake of argument let's say that we need 10 mL of dilute solution, this is mL_F, i.e., (1.54) and (1.55).

$$mL_I * C_I = mL_F * C_F \tag{1.52}$$

$$\therefore mL_I = [mL_F * C_F]/C_I \tag{1.53}$$

$$mL_I = [10 * 1.58] / 15.73 \tag{1.54}$$

$$\therefore mL_I = 10.03 \text{ mL} \tag{1.55}$$

This means that 10.03 mL of the concentrated nitric acid (69.8%) should be diluted up to a total of 100 mL with nanopure water.

Now that you have your stock solution with the correct percentage then you can use this solution to prepare your solutions of varying concentration. Let's take the example that the stock solution that you purchase from a supplier has a concentration of 100 ppm of analyte, which is equivalent to 1 μg/mL.

In order to make your calibration curve more accurate it is important to be aware of two issues. Firstly, as with all straight-line graphs, the more points that are used then the better the statistics is that the line is correct. But, secondly, the more measurements that are used means that more room for error is introduced to the system, to avoid these errors from occurring one should be very vigilant and skilled in the use of pipetting and diluting of solutions. Especially when working with very low concentration solutions a small

drop of material making the dilution above or below the exactly required amount can alter the concentration and hence affect the calibration deleteriously. The premise upon which the calculation is done is based on (1.52), whereby C refers to concentration in ppm, and mL refers to mass in mL.

The choice of concentrations to make will depend on the samples and the concentration of analyte within the samples that are being analyzed. For first time users it is wise to make a calibration curve with a large range to encompass all the possible outcomes. When the user is more aware of the kind of concentrations that they are producing in their synthesis then they can narrow down the range to fit the kind of concentrations that they are anticipating.

In this example we will make concentrations ranging from 10 ppm to 0.1 ppm, with a total of five samples. In a typical ICP-AES analysis about 3 mL of solution is used, however if you have situations with substantial wavelength overlap then you may have chosen to do two separate runs and so you will need approximately 6 mL solution. In general it is wise to have at least 10 mL of solution to prepare for any eventuality that may occur. There will also be some extra amount needed for samples that are being used for the quality control check. For this reason 10 mL should be a sufficient amount to prepare of each concentration.

We can define the unknowns in the equation as follows:

- C_I = concentration of concentrated solution (ppm)
- C_F = desired concentration (ppm)
- M_I = initial mass of material (mL)
- M_F = mass of material required for dilution (mL)

The methodology adopted works as follows. Make the high concentration solution then take from that solution and dilute further to the desired concentrations that are required.

Let's say the concentration of the stock solution from the supplier is 100 ppm of analyte. First we should dilute to a concentration of 10 ppm. To make 10 mL of 10 ppm solution we should take 1 mL of the 100 ppm solution and dilute it up to 10 mL with nanopure water, now the concentration of this solution is 10 ppm. Then we can take from the 10 ppm solution and dilute this down to get a solution with 5 ppm. To do this take 5 mL of the 10 ppm solution and dilute it to 10 mL with nanopure water, then you will have a solution of 10 mL that is 5 ppm concentration. And so you can do this successively taking aliquots from each solution working your way down at incremental steps until you have a series of solutions that have concentrations ranging from 10 ppm all the way down to 0.1 ppm or lower, as required.

1.5.5 ICP-AES at work

While ICP-AES is a useful method for quantifying the presence of a single metal in a given nanoparticle, another very important application comes from the ability to determine the ratio of metals within a sample of nanoparticles.

In the following examples we can consider the bi-metallic nanoparticles of iron with copper. In a typical synthesis 0.75 mmol of $Fe(acac)_3$ is used to prepare iron-oxide nanoparticle of the form Fe_3O_4. It is possible to replace a quantity of the Fe^{n+} ions with another metal of similar charge. In this manner bi-metallic particles were made with a precursor containing a suitable metal. In this example the additional metal precursor will be $Cu(acac)_2$.

Keep the total metal concentration in this example is 0.75 mmol. So if we want to see the effect of having 10% of the metal in the reaction as copper, then we will use 10% of 0.75 mmol, that is 0.075 mmol $Cu(acac)_2$, and the corresponding amount of iron is 0.675 mmol $Fe(acac)_3$. We can do this for successive increments of the metals until you make 100% copper oxide particles.

Subsequent Fe and Cu ICP-AES of the samples will allow the determination of Fe:Cu ratio that is present in the nanoparticle. This can be compared to the ratio of Fe and Cu that was applied as reactants. The graph Figure 1.31 shows how the percentage of Fe in the nanoparticle changes as a function of how much Fe is used as a reagent.

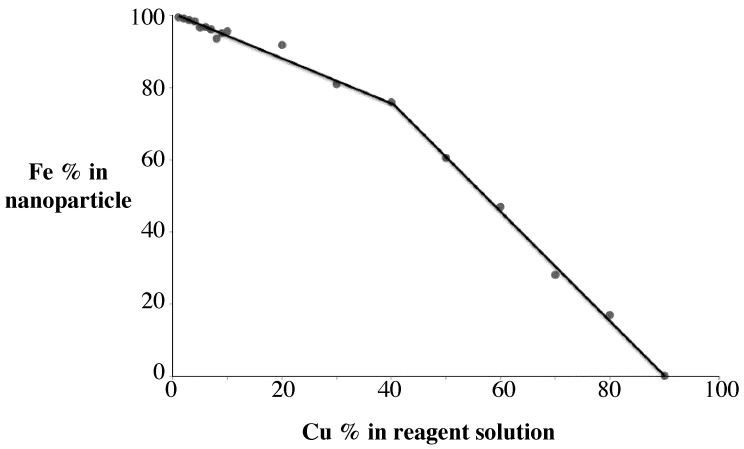

Figure 1.31: Change in iron percentage in the Fe-Cu-O nanoparticles as a function of how much iron precursor is used in the synthesis of the nanoparticles.

1.5.5.1 Determining analyte concentration

Once the nanoparticles are digested and the ICP-AES analysis has been completed you must turn the figures from the ICP-AES analysis into working numbers to determine the concentration of metals in the solution that was synthesized initially.

Let's first consider the nanoparticles that are of one metal alone. The figure given by the analysis in this case is given in units of mg/L, this is the value in ppm's. This figure was recorded for the solution that was analyzed, and this is of a dilute concentration compared to the initial synthesized solution because the particles had to be digested in acid first, then diluted further into nanopure water.

As mentioned above in the experimental 0.5 mL of the synthesized nanoparticles were first digested in 9.5 mL of concentrated nitric acid. Then when the digestion was complete 0.5 mL of this solution was dissolved in 9.5 mL of nanopure water. This was the final solution that was analyzed using ICP, and the concentration of metal in this solution will be far lower than that of the original solution. In this case the amount of analyte in the final solution being analyzed is $1/20^{th}$ that of the total amount of material in the solution that was originally synthesized.

1.5.5.2 Calculating concentration in ppm

Let us take an example that upon analysis by ICP-AES the amount of Fe detected is 6.38 mg/L. First convert the figure to mg/mL, using (1.56),

$$6.38 \text{ mg/L} * 1/1000 \text{ L/mL} = 6.38\text{x}10^{-3} \text{ mg/mL} \tag{1.56}$$

The amount of material was diluted to a total volume of 10 mL. Therefore we should multiply this value by 10 mL to see how much mass was in the whole container, (1.57).

$$6.38\text{x}10^{-3} \text{ mg/mL} * 10 \text{ mL} = 6.38\text{x}10^{-2} \text{ mg} \tag{1.57}$$

This is the total mass of iron that was present in the solution that was analyzed using the ICP device. To convert this amount to ppm we should take into consideration the fact that 0.5 mL was initially diluted to 10 mL, to do this we should divide the total mass of iron by this amount that it was diluted to, (1.58).

$$6.38 \times 10^{-2} \text{ mg} / 0.5 \text{ mL} = 0.1276 \text{ mg/mL} \tag{1.58}$$

This was the total amount of analyte in the 10 mL solution that was analyzed by the ICP device, to attain the value in ppm it should be mulitplied by a thousand, that is then 127.6 ppm of Fe.

1.5.5.3 Determining concentration of original solution

We now need to factor in the fact that there were several dilutions of the original solution first to digest the metals and then to dissolve them in nanopure water, in all there were two dilutions and each dilution was equivalent in mass. By diluting 0.5 mL to 10 mL , we are effectively diluting the solution by a factor of 20, and this was carried out twice, i.e., (1.59).

$$0.1276 \text{ mg/mL} * 20 = 2.552 \text{ mg/mL} \tag{1.59}$$

This is the amount of analyte in the solution of digested particles, to covert this to ppm we should multiply it by 1/1000 mL/L, in the following way:

$$2.552 \text{ mg/mL} * 1/1000 \text{ mL/L} = 2552 \text{ mg/L} \tag{1.60}$$

This is essentially your answer now as 2552 ppm. This is the amount of Fe in the solution of digested particles. This was made by diluting 0.5 mL of the original solution into 9.5 mL concentrated nitric acid, which is the same as diluting by a factor of 20. To calculate how much analyte was in the original batch that was synthesized we multiply the previous value by 20 again, i.e., (1.61). This is the final amount of Fe concentration of the original batch when it was synthesized and made soluble in hexanes.

$$2552 \text{ ppm} * 20 = 51040 \text{ ppm} \tag{1.61}$$

1.5.5.4 Calculating stoichiometric ratio

Moving from calculating the concentration of individual elements now we can concentrate on the calculation of stoichiometric ratios in the bi-metallic nanoparticles.

Consider the case when we have the iron and the copper elements in the nanoparticle. The amounts determined by ICP are:

- Iron = 1.429 mg/L.
- Copper = 1.837 mg/L.

We must account for the molecular weights of each element by dividing the ICP obtained value, by the molecular weight for that particular element. For iron this is calculated by (1.62), and thus this is molar ratio of iron. On the other hand the ICP returns a value for copper that is given by (1.63).

$$1.429 \text{ mg/L} / 55.85 = 0.0211 \tag{1.62}$$

$$1.837 \text{ mg/L} / 63.55 = 0.0289 \tag{1.63}$$

To determine the percentage iron we use (1.64), which gives a percentage value of 42.15% Fe.

$$\%\text{Fe} = [(\text{molar ratio of iron})/(\text{sum of molar ratios})] * 100 \tag{1.64}$$

To work out the copper percentage we calculate this amount using (1.65), which leads to an answer of 57.85% Cu.

$$\% \text{ Cu} = [(\text{molar ratio of copper})/(\text{sum of molar ratios})] * 100 \tag{1.65}$$

In this way the percentage iron in the nanoparticle can be determined as function of the reagent concentration prior to the synthesis (Figure 1.31).

1.5.5.5 Determining concentration of nanoparticles in solution

The previous examples have shown how to calculate both the concentration of one analyte and the effective shared concentration of metals in the solution. These figures pertain to the concentration of elemental atoms present in solution. To use this to determine the concentration of nanoparticles we must first consider how many atoms that are being detected are in a nanoparticle. Let us consider that the Fe_3O_4 nanoparticles are of 7 nm diameter. In a 7 nm particle we expect to find 20,000 atoms. However in this analysis we have only detected Fe atoms, so we must still account for the number of oxygen atoms that form the crystal lattice also.

For every 3 Fe atoms, there are 4 O atoms. But as iron is slightly larger than oxygen, it will make up for the fact there is one less Fe atom. This is an over simplification but at this time it serves the purpose to make the reader aware of the steps that are required to take when judging nanoparticles concentration. Let us consider that half of the nanoparticle size is attributed to iron atoms, and the other half of the size is attributed to oxygen atoms.

As there are 20,000 atoms total in a 7 nm particle, and then when considering the effect of the oxide state we will say that for every 10,000 atoms of Fe you will have a 7 nm particle. So now we must find out how many Fe atoms are present in the sample so we can divide by 10,000 to determine how many nanoparticles are present.

In the case from above, we found the solution when synthesized had a concentration 51,040 ppm Fe atoms in solution. To determine how how many atoms this equates to we will use the fact that 1 mole of material has the Avogadro number of atoms present, (1.66).

$$51040 \text{ ppm} = 51040 \text{ mg/L} = 51.040 \text{ g/L} \tag{1.66}$$

1 mole of iron weighs 55.847 g. To determine how many moles we now have, we divide the values like this:

$$(51.040 \text{ g/L}) / (55.847 \text{ g}) = 0.9139 \text{ moles/L} \tag{1.67}$$

The number of atoms is found by multiplying this by Avogadro's number (6.022×10^{23}):

$$(0.9139 \text{ moles/L}) * (6.022 \times 10^{23} \text{ atoms}) = 5.5 \times 10^{23} \text{ atoms/L} \tag{1.68}$$

For every 10,000 atoms we have a nanoparticle (NP) of 7 nm diameter, assuming all the particles are equivalent in size we can then divide the values, (1.69). This is the concentration of nanoparticles per liter of solution as synthesized.

$$(5.5 \times 10^{23} \text{ atoms/L}) / (10{,}000 \text{ atoms/NP}) = 5.5 \times 10^{19} \text{ NP/L} \tag{1.69}$$

1.5.5.6 Combined surface area

One very interesting thing about nanotechnology that nanoparticles can be used for is their incredible ratio between the surface areas compared with the volume. As the particles get smaller and smaller the surface area becomes more prominent. And as much of the chemistry is done on surfaces, nanoparticles are good contenders for future use where high aspect ratios are required.

In the example above we considered the particles to be of 7 nm diameters. The surface area of such a particle is 1.539 x10^{-16} m^2. So the combined surface area of all the particles is found by multiplying each particle by their individual surface areas.

$$(1.539 \times 10^{-16}\ m^2) * (5.5 \times 10^{19}\ NP/L) = 8465\ m^2/L \tag{1.70}$$

To put this into context, an American football field is approximately 5321 m^2. So a liter of this nanoparticle solution would have the same surface area of approximately 1.5 football fields. That is allot of area in one liter of solution when you consider how much material it would take to line the football field with thin layer of metallic iron. Remember there is only about 51 g/L of iron in this solution!

1.5.6 Bibliography

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1.6 ICP-MS for Trace Metal Analysis[9]

1.6.1 Introduction

Inductively coupled plasma mass spectroscopy (ICP-MS) is an analytical technique for determining trace multi-elemental and isotopic concentrations in liquid, solid, or gaseous samples. It combines an ion-generating argon plasma source with the sensitive detection limit of mass spectrometry detection. Although ICP-MS is used for many different types of elemental analysis, including pharmaceutical testing and reagent manufacturing, this module will focus on its applications in mineral and water studies. Although akin to ICP-AES (inductively coupled plasma atomic emission spectroscopy), ICP-MS has significant differences, which will be mentioned as well.

1.6.1.1 Basic instrumentation and operation

As shown in Figure 1.32 there are several basic components of an ICP-MS instrument, which consist of a sampling interface, a peristaltic pump leading to a nebulizer, a spray chamber, a plasma torch, a detector, an interface, and ion-focusing system, a mass-separation device, and a vacuum chamber, maintained by turbo molecular pumps. The basic operation works as follows: a liquid sample is pumped into the nebulizer to convert the sample into a spray. An internal standard, such as germanium, is pumped into a mixer along with the sample prior to nebulization to compensate for matrix effects. Large droplets are filtered out, and small droplets continue into the plasma torch, turning to ions. The mass separation device separates these ions based on their mass-to-charge ratio. An ion detector then converts these ions into an electrical signal, which is multiplied and read by computer software.

[8] http://www.ivstandards.com/extras/pertable/

[9] This content is available online at <http://cnx.org/content/m34666/1.1/>.

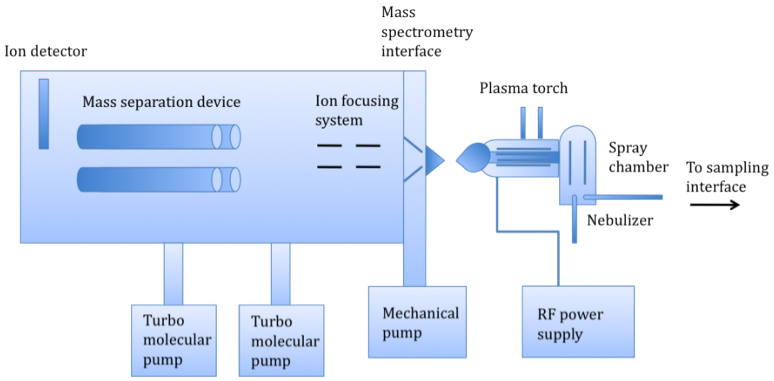

Figure 1.32: Scheme depicting the basic components of an ICP-MS system. Adapted from R. Thomas, *Practical Guide to ICP-MS: A Tutorial for Beginners*, CRC Press, Boca Raton, 2nd edn. (2008).

The main difference between ICP-MS and ICP-AES is the way in which the ions are generated and detected. In ICP-AES, the ions are excited by vertical plasma, emitting photons that are separated on the basis of their emission wavelengths. As implied by the name, ICP-MS separates the ions, generated by horizontal plasma, on the basis of their mass-to-charge ratios (m/z). In fact, caution is taken to *prevent* photons from reaching the detector and creating background noise. The difference in ion formation and detection methods has a significant impact on the relative sensitivities of the two techniques. While both methods are capable of very fast, high throughput multi-elemental analysis (~10 - 40 elements per minute per sample), ICP-MS has a detection limit of a few ppt to a few hundred ppm, compared to the ppb-ppm range (~1 ppb - 100 ppm) of ICP-AES. ICP-MS also works over eight orders of magnitude detection level compared to ICP-AES' six. As a result of its lower sensitivity, ICP-MS is a more expensive system. One other important difference is that only ICP-MS can distinguish between different isotopes of an element, as it segregates ions based on mass. A comparison of the two techniques is summarized in Table 1.6.

	ICP-MS	**ICP-AES**
Plasma	Horizontal: generates cations	Vertical: excites atoms, which emit photons
Ion detection	Mass-to-charge ratio	Wavelength of emitted light
Detection limit	1-10 ppt	1-10 ppb
Working range	8 orders of magnitude	6 orders of magnitude
Throughput	20-30 elements per minute	10-40 elements per minute
Isotope detection	Yes	No

continued on next page

Cost	~$150,000	~$50,000
Multi-element detection	Yes	Yes
Spectral interferences	Predictable, less than 300	Much greater in number and more complicated to correct
Routine accessories	Electrothermal vaporization, laser ablation, high-performance liquid chromatography, etc.	Rare

Table 1.6: Comparison of ICP-MS and ICP-AES.

1.6.1.2 Sample preparation

With such small sample sizes, care must be taken to ensure that collected samples are representative of the bulk material. This is especially relevant in rocks and minerals, which can vary widely in elemental content from region to region. Random, composite, and integrated sampling are each different approaches for obtaining representative samples.

Because ICP-MS can detect elements in concentrations as minute as a few nanograms per liter (parts per trillion), contamination is a very serious issue associated with collecting and storing samples prior to measurements. In general, use of glassware should be minimized, due to leaching impurities from the glass or absorption of analyte by the glass. If glass is used, it should be washed periodically with a strong oxidizing agent, such as chromic acid ($H_2Cr_2O_7$), or a commercial glass detergent. In terms of sample containers, plastic is usually better than glass, polytetrafluoroethylene (PTFE) and Teflon® being regarded as the cleanest plastics. However, even these materials can contain leachable contaminants, such as phosphorus or barium compounds. All containers, pipettes, pipette tips, and the like should be soaked in 1 - 2% HNO_3. Nitric acid is preferred over HCl, which can ionize in the plasma to form $^{35}Cl^{16}O^+$ and $^{40}Ar^{35}Cl^+$, which have the same mass-to-charge ratios as $^{51}V^+$ and $^{75}As^+$, respectively. If possible, samples should be prepared as close as possible to the ICP-MS instrument without being in the same room.

With the exception of solid samples analyzed by laser ablation ICP-MS, samples must be in liquid or solution form. Solids are ground into a fine powder with a mortar and pestle and passed through a mesh sieve. Often the first sample is discarded to prevent contamination from the mortar or sieve. Powders are then digested with ultrapure concentrated acids or oxidizing agents, like chloric acid ($HClO_3$), and diluted to the correct order of magnitude with 1 - 2% trace metal grade nitric acid.

Once in liquid or solution form, the samples must be diluted with 1 - 2% ultrapure HNO_3 to a low concentration to produce a signal intensity lower than about 10^6 counts. Not all elements have the same concentration to intensity correlation; therefore, it is safer to test unfamiliar samples on ICP-AES first. Once properly diluted, the sample should be filtered through a 0.25 - 0.45 μm membrane to remove particulates.

Gaseous samples can also be analyzed by direct injection into the instrument. Alternatively, gas chromatography equipment can be coupled to an ICP-MS machine for separation of multiple gases prior to sample introduction.

1.6.1.3 Standards

Multi- and single-element standards can be purchased commercially, and must be diluted further with 1 - 2% nitric acid to prepare different concentrations for the instrument to create a calibration curve, which will be read by the computer software to determine the unknown concentration of the sample. There should be several standards, encompassing the expected concentration of the sample. Completely unknown samples should be tested on less sensitive instruments, such as ICP-AES or EDXRF (energy dispersive X-ray fluorescence), before ICP-MS.

1.6.2 Limitations of ICP-MS

While ICP-MS is a powerful technique, users should be aware of its limitations. Firstly, the intensity of the signal varies with each isotope, and there is a large group of elements that cannot be detected by ICP-MS. This consists of H, He and most gaseous elements, C, and elements without naturally occurring isotopes, including most actinides.

There are many different kinds of interferences that can occur with ICP-MS, when plasma-formed species have the same mass as the ionized analyte species. These interferences are predictable and can be corrected with element correction equations or by evaluating isotopes with lower natural abundances. Using a mixed gas with the argon source can also alleviate the interference.

The accuracy of ICP-MS is highly dependent on the user's skill and technique. Standard and sample preparations require utmost care to prevent incorrect calibration curves and contamination. As exemplified below, a thorough understanding of chemistry is necessary to predict conflicting species that can be formed in the plasma and produce false positives. While an inexperienced user may be able to obtain results fairly easily, those results may not be trustworthy. Spectral interference and matrix effects are problems that the user must work diligently to correct.

1.6.3 Applications: analysis of mineral and water samples

In order to illustrate the capabilities of ICP-MS, various geochemical applications as described. The chosen examples are representative of the types of studies that rely heavily on ICP-MS, highlighting its unique capabilities.

1.6.3.1 Trace elemental analysis of minerals

With its high throughput, ICP-MS has made sensitive analysis of multi-element detection in rock and mineral samples feasible. Studies of trace components in rock can reveal information about the chemical evolution of the mantle and crust. For example, spinel peridotite xenoliths (Figure 1.33), which are igneous rock fragments derived from the mantle, were analyzed for 27 elements, including lithium, scandium and titanium at the parts per million level and yttrium, lutetium, tantalum, and hafnium in parts per billion. X-ray fluorescence was used to complement ICP-MS, detecting metals in bulk concentrations. Both liquid and solid samples were analyzed, the latter being performed using laser-ablation ICP-MS, which points out the flexibility of the technique for being used in tandem with others. In order to prepare the solution samples, optically pure minerals were sonicated in 3 M HCl, then 5% HF, then 3 M HCl again and dissolved in distilled water. The solid samples were converted into plasma by laser ablation prior to injection into the nebulizer of the LA-ICP-MS instrument. The results showed good agreement between the laser ablation and solution methods. Furthermore, this comprehensive study shed light on the partitioning behavior of incompatible elements, which, due to their size and charge, have difficulty entering cation sites in minerals. In the upper mantle, incompatible trace elements, especially barium, niobium and tantalum, were found to reside in glass pockets within the peridotite samples.

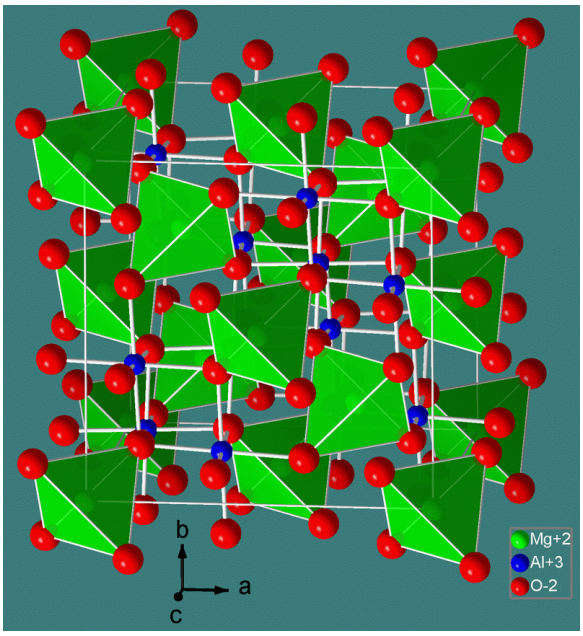

Figure 1.33: Crystal structure of a typical spinel, general formula $A^{2+}B_2{}^{3+}O_4{}^{2-}$.

1.6.3.2 Trace elemental analysis of water

Another important area of geology that requires knowledge of trace elemental compositions is water analysis. In order to demonstrate the full capability of ICP-MS as an analytical technique in this field, researchers aim to use the identification of trace metals present in groundwater to determine a fingerprint for a particular water source. In one study the analysis of four different Nevada springs determined trace metal analysis in parts per billion and even parts per trillion (ng/L). Because they were present is such low concentrations, samples containing rare earth elements lutetium, thulium, and terbium were preconcentrated by a cation exchange column to enable detection at 0.05 ppt. For some isotopes, special corrections necessary to account for false positives, which are produced by plasma-formed molecules with the same mass-to-charge ratio as the isotopic ions. For instance, false positives for Sc ($m/z = 45$) or Ti ($m/z = 47$) could result from CO_2H^+ ($m/z = 45$) or PO^+ ($m/z = 47$); and BaO^+ ($m/z = 151, 153$) conflicts with Eu-151 and Eu-153. In the latter case, barium has many isotopes (134, 135, 136, 137, 138) in various abundances, Ba-138 comprising 71.7% barium abundance. ICP-MS detects peaks corresponding to BaO^+ for all isotopes. Thus researchers were able to approximate a more accurate europium concentration by monitoring a non-interfering barium peak and extrapolating back to the concentration of barium in the system. This concentration was subtracted out to give a more realistic europium concentration. By employing such strategies, false positives could be taken into account and corrected. Additionally, 10 ppb internal standard was added to all samples to correct for changes in sample matrix, viscosity and salt buildup throughout collection. In total, 54 elements were detected at levels spanning seven orders of magnitude. This study demonstrates the incredible sensitivity and working range of ICP-MS.

1.6.3.3 Determination of arsenic content

Elemental analysis in water is also important for the health of aquatic species, which can ultimately affect the entire food chain, including people. With this in mind, arsenic content was determined in fresh water and aquatic organisms in Hayakawa River in Kanagawa, Japan, which has very high arsenic concentrations due to its hot spring source in Owakudani Valley. While water samples were simply filtered and prior to analysis, organisms required special preparation, in order to be compatible with the sampler. Organisms collected for this studied included water bug, green macroalga, fish, and crustaceans. For total As content determination, the samples were freeze-dried to remove all water from the sample in order to know the exact final volume upon resuspension. Next, the samples were ground into a powder, followed by soaking in nitric acid, heating at 110 °C. The sample then underwent heating with hydrogen peroxide, dilution, and filtering through a 0.45 μm membrane. This protocol served to oxidize the entire sample and remove large particles prior to introduction into the ICP-MS instrument. Samples that are not properly digested can build up on the plasma torch and cause expensive damage to the instrument. Since the plasma converts the sample into various ion constituents, it is unnecessary to know the exact oxidized products prior to sample introduction. In addition to total As content, the As concentration of different organic arsenic-containing compounds (arsenicals) produced in the organisms was measured by high performance liquid chromatography coupled to ICP-MS (HPLC/ICP-MS). The arsenicals were separated by HPLC before travelling into the ICP-MS instrument for As concentration determination. For this experiment, the organic compounds were extracted from biological samples by dissolving freeze-dried samples in methanol/water solutions, sonicating, and centrifuging. The extracts were dried under vacuum, redissolved in water, and filtered prior to loading. This did not account for all compounds, however, because over 50% arsenicals were nonsoluble in aqueous solution. One important plasma side product to account for was $ArCl^+$, which has the same mass-to-charge ratio ($m/z = 75$) as As. This was corrected by oxidizing the arsenic ions within the mass separation device in the ICP-MS vacuum chamber to generate AsO^+, with m/z 91. The total arsenic concentration of the samples ranged from 17 - 18 ppm.

1.6.4 Bibliography

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1.7 Ion Selective Electrode Analysis[10]

1.7.1 Introduction

Ion selective electrode (ISE) is an analytical technique used to determine the activity of ions in aqueous solution by measuring the electrical potential. ISE has many advantages compared to other techniques, including:

1. It is relatively inexpensive and easy to operate.
2. It has wide concentration measurement range.
3. As it measure the activity, instead of concentration, it is particularly useful in biological/medical application.
4. It is a real-time measurement, which means it can monitor the change of activity of ion with time.
5. It can determine both positively and negatively charged ions.

[10] This content is available online at <http://cnx.org/content/m43567/1.1/>.

Based on these advantages, ISE has wide variety of applications, which is reasonable considering the importance of measuring ion activity. For example, ISE finds its use in pollution monitoring in natural waters (CN^-, F^-, S^-, Cl^-, etc.), food processing (NO_3^-, NO_2^- in meat preservatives), Ca^{2+} in dairy products, and K^+ in fruit juices, etc.

1.7.2 Measurement setup

Before focusing on how ISE works, it would be good to get an idea what ISE setup looks like and the component of the ISE instrument. Figure 1.34 shows the basic components of ISE setup. It has an ion selective electrode, which allows measured ions to pass, but excludes the passage of the other ions. Within this ion selective electrode, there is an internal reference electrode (Figure 1.34), which is made of silver wire coated with solid silver chloride, embedded in concentrated potassium chloride solution (filling solution) saturated with silver chloride. This solution also contains the same ions as that to be measured. There is also a reference electrode similar to ion selective electrode, but there is no to-be-measured ion in the internal electrolyte and the selective membrane is replaced by porous frit, which allows the slow passage of the internal filling solution and forms the liquid junction with the external text solution. The ion selective electrode and reference electrode are connected by a milli-voltmeter. Measurment is accomplished simply by immersing the two electrodes in the same test solution.

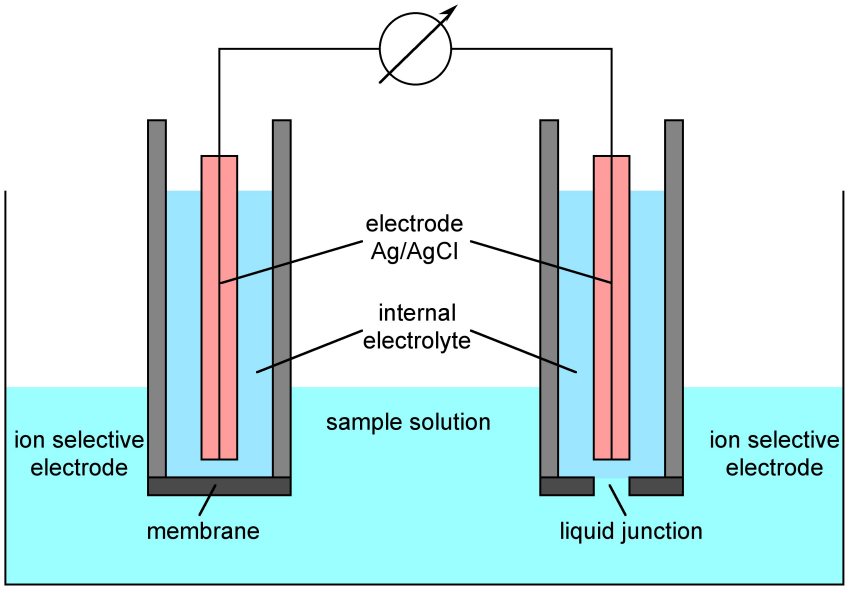

Figure 1.34: Measurement setup of ISE.

1.7.3 Theory of how ISE works

There are commonly more than one types of ions in solution. So how ISE manage to measure the concentration of certain ion in solution without being affected by other ions? This is done by applying a selective membrane at the ion selective electrode, which only allows the desired ion to go in and out. At equilibrium, there is potential difference existing between two sides of the membrane, and it is governed by the

concentration of the tested solution described by Nernst equation EQ, where E is potential, E^0 is a constant characteristic of a particular ISE, R is the gas constant (8.314 J/K.mol), T is the temperature (in K), n is the charge of the ion and F is Faraday constant (96,500 coulombs/mol). To make it relevant, the measured potential difference is proportional to the logarithm of ion concentration. Thus, the relationship between potential difference and ion concentration can be determined by measuring the potential of two solutions of already-known ion concentration and a plot based on the measured potential and logarithm of the ion concentration. Based on this plot, the ion concentration of an unknown solution can be known by measuring the potential and corresponding it to the plot.

$$E = E^0 + (2.030RT/nF)\log C \tag{1.71}$$

1.7.4 Example application: determination of fluoride ion

Fluoride is added into drinking water and toothpaste to prevent dental caries and thus the determination of its concentration is of great importance to human health. Here, we will give some data and calculations to show how the concentration of fluoride ion is determined and have a glance at how relevant ISE is to our daily life. According to Nernst equation, EQ ABOVE, in this case n = 1, T = 25 °C and E^0, R, F are constants and thus this equation can be simplied as EQ.

$$E = K + S \log C \tag{1.72}$$

The first step is to obtain a calibration curve for fluoride ion and this can be done by preparing several fluoride standard solution with known concentration (Table 1.7) and making a plot of E versus log C (Figure 1.35).

Concentration (mg/L)	log C	E (mV)
200.0	2.301	-35.6
100.0	2.000	-17.8
50.00	1.699	0.4
25.00	1.398	16.8
12.50	1.097	34.9
6.250	0.796	52.8
3.125	0.495	70.4
1.563	0.194	89.3
0.781	0.107	107.1
0.391	0.408	125.5
0.195	0.709	142.9

Table 1.7: Measurement results. Data from http://zimmer.csufresno.edu/~davidz/Chem102/FluorideISE/FluorideISE.html.

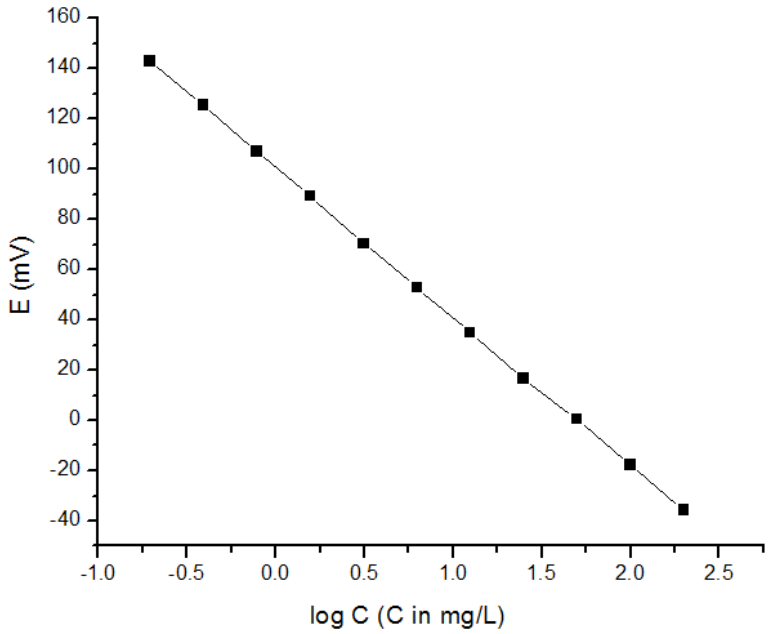

Figure 1.35: Plot of E versus log C. Based on data from http://zimmer.csufresno.edu/~davidz/Chem102/FluorideISE/FluorideISE.html.

From the plot in Figure 1.35, we can clearly identify the linear relationship between E versus log C with slope measeured at -59.4 mV, which is very closed to the theoretical value -59.2 mV at 25 °C. This plot can give the concentration of any solution containing fluoride ion within the range of 0.195 mg/L and 200 mg/L by measuring the potential of the unknown solution.

1.7.5 Limit of ISE

Though ISE is a cost-effective and useful technique, it has some drawbacks that cannot be avoided. The selective ion membrane only allows the measured ions to pass and thus the potential is only determined by this particular ion. However, the truth is there is no such membrane that only permits the passage of one ion, and so there are cases when there are more than one ions that can pass the membrane. As a result, the measured potential are affected by the passage of the "unwanted" ions. Also, because of its dependence on ion selective membrane, one ISE is only suitable for one ion and this may be inconvenient sometimes. Another problem worth noticing is that ion selective measures the concentration of ions in equilibrium at the surface of the membrane surface. This does matter much if the solution is dilute but at higher concentrations, the inter-ionic interactions between the ions in the solution tend to decrease the mobility of ions and thus the concentration near the membrane would be lower than that in the bulk. This is one source of inaccuracy of ISE. To better analyze the results of ISE, we have to be aware of these inherent limitations of it.

1.7.6 Bibliography

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1.8 A Practical Introduction to X-ray Absorption Spectroscopy[11]

1.8.1 Introduction

X-ray absorption spectroscopy (XAS) is a technique that uses synchrotron radiation to provide information about the electronic, structural, and magnetic properties of certain elements in materials. This information is obtained when X-rays are absorbed by an atom at energies near and above the core level binding energies of that atom. Therefore, a brief description about X-rays, synchrotron radiation and X-ray absorption is provided prior to a description of sample preparation for powdered materials.

1.8.1.1 X-rays and synchrotron radiation

X-rays were discovered by the Wilhelm Röntgen in 1895 (Figure 1.36). They are a form of electromagnetic radiation, in the same manner as visible light but with a very short wavelength, around 0.25 - 25 Å. As electromagnetic radiation, X-rays have a specific energy. The characteristic range is defined by *soft* versus *hard* X-rays. *Soft* X-rays cover the range from hundreds of eV to a few KeV, and the *hard* X-rays have an energy range from a few KeV up to around 100 KeV.

Figure 1.36: German physicist Wilhelm Conrad Röntgen (1845 –1923) who received the first Nobel Prize in Physics in 1901 for the production and use of X-rays.

[11] This content is available online at <http://cnx.org/content/m38333/1.1/>.

X-rays are commonly produced by X-ray tubes, when high-speed electrons strike a metal target. The electrons are accelerated by a high voltage towards the metal target; X-rays are produced when the electrons collide with the nuclei of the metal target.

Synchrotron radiation is generated when particles are moving at really high velocities and are deflected along a curved trajectory by a magnetic field. The charged particles are first accelerated by a linear accelerator (LINAC) (Figure 1.37); then, they are accelerated in a booster ring that injects the particles moving almost at the speed of light into the storage ring. There, the particles are accelerated toward the center of the ring each time their trajectory is changed so that they travel in a closed loop. X-rays with a broad spectrum of energies are generated and emitted tangential to the storage ring. Beamlines are placed tangential to the storage ring to use the intense X-ray beams at a wavelength that can be selected varying the set up of the beamlines. Those are well suited for XAS measurements because the X-ray energies produced span 1000 eV or more as needed for an XAS spectrum.

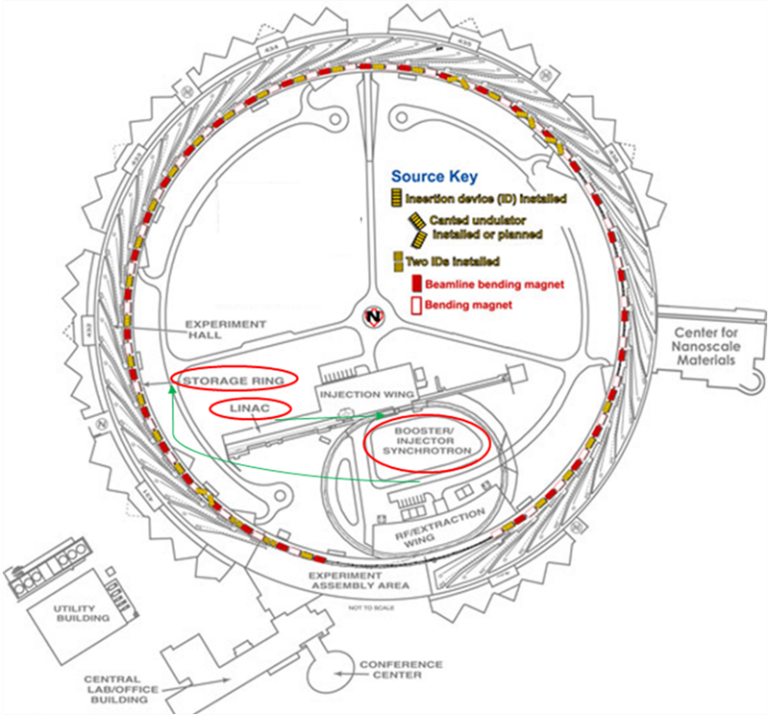

Figure 1.37: Scheme of a synchrotron and the particle trajectory inside it. Adapted from S. D. Kelly, D. Hesterberg, and B. Ravel in *Methods of Soil Analysis: Part 5, Mineralogical Methods*, Ed. A. L. Urely and R. Drees, Soil Science Society of America Book Series, Madison (2008).

1.8.1.2 X-ray absorption

Light is absorbed by matter through the photoelectric effect. It is observed when an X-ray photon is absorbed by an electron in a strongly bound core level (such as the $1s$ or $2p$ level) of an atom (Figure 1.38). In order for a particular electronic core level to participate in the absorption, the binding energy of this core level must be less than the energy of the incident X-ray. If the binding energy is greater than the energy of the

X-ray, the bound electron will not be perturbed and will not absorb the X-ray. If the binding energy of the electron is less than that of the X-ray, the electron may be removed from its quantum level. In this case, the X-ray is absorbed and any energy in excess of the electronic binding energy is given as kinetic energy to a photo-electron that is ejected from the atom.

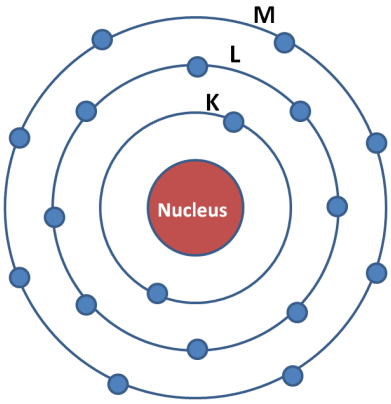

Figure 1.38: A schematic representation of the photoelectric effect when a photon with the right energy hits an electron, it is expelled.

When X-ray absorption is discussed, the primary concern is about the absorption coefficient, μ, which gives the probability that X-rays will be absorbed according to Beer's Law, (1.73), where I_0 is the X-ray intensity incident on a sample, t is the sample thickness, and I is the intensity transmitted through the sample.

$$I = I_0 e^{-\mu t} \tag{1.73}$$

The absorption coefficient, μ_E, is a smooth function of energy, with a value that depends on the sample density ρ, the atomic number Z, atomic mass A, and the X-ray energy E roughly as, (1.74).

$$\mu_E \approx \frac{\rho Z^4}{AE^3} \tag{1.74}$$

When the incident X-ray has energy equal to that of the binding energy of a core-level electron, there is a sharp rise in absorption: an absorption edge corresponding to the promotion of this core level to the continuum. For XAS, the main concern is the intensity of μ, as a function of energy, near and at energies just above these absorption edges. An XAS measurement is simply a measure of the energy dependence of μ at and above the binding energy of a known core level of a known atomic species. Since every atom has core-level electrons with well-defined binding energies, the element to probe can be selected by tuning the X-ray energy to an appropriate absorption edge. These absorption edge energies are well-known. Because the element of interest is chosen in the experiment, XAS is element-specific.

1.8.2 X-ray absorption fine structure

X-ray absorption fine structure (XAFS) spectroscopy, also named X-ray absorption spectroscopy, is a technique that can be applied for a wide variety of disciplines because the measurements can be performed on solids, gasses, or liquids, including moist or dry soils, glasses, films, membranes, suspensions or pastes, and

aqueous solutions. Despites its broad adaptability with the kind of material used, there are samples which limits the quality of an XAFS spectrum. Because of that, the sample requirements and sample preparation is reviewed in this section as well the experiment design which are vital factors in the collection of good data for further analysis.

1.8.2.1 Experiment design

The main information can be obtained using XAFS spectra consist in small changes in the absorption coefficient (E), which can be measured directly in a transmission mode or indirectly using a fluorescence mode. Therefore, a good signal to noise ratio is required (better than 10^3). In order to obtain this signal to noise ratio, an intense beam is required (on the order 10^{10} photons/second or better), with the energy bandwidth of 1 eV or less, and the capability of scanning the energy of the incident beam over a range of about 1 KeV above the edge in a time range of seconds or few minutes. As a result, synchrotron radiation is preferred further than other kind of X-ray sources previously mentioned.

1.8.2.1.1 Beamline setup

Despite the setup of a synchrotron beamline is mostly done by the assistance of specialist beamline scientists, nevertheless, it is useful to understand the system behind the measurement. The main components of a XAFS beamline, shown in Figure 1.39, are as follows:

- A harmonic rejection mirror to reduce the harmonic content of the X-ray beam.
- A monochromator to choose the X-ray energy.
- A series of slits which defines the X-ray profile.
- A sample positioning stage.
- The detectors, which can be a single ionization detector or a group of detectors to measure the X-ray intensity.

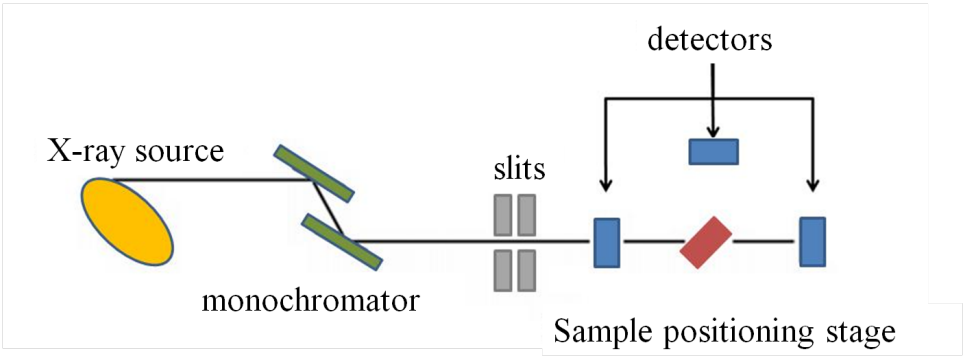

Figure 1.39: Schematic of the basic components of a XAFS beamline.

Slits are used to define the X-ray beam profile and to block unwanted X-rays. Slits can be used to increase the energy resolution of the X-ray incident on the sample at the expense of some loss in X-ray intensity. They are either fixed or adjustable slits. Fixed slits have a pre-cut opening of heights between 0.2 and 1.0 mm and a width of some centimeters. Adjustable slits use metal plates that move independently to define each edge of the X-ray beam.

1.8.2.1.1.1 Monochromator

The monochromator is used to select the X-ray energy incident on the sample. There are two main kinds of X-ray monochromators:

1) The double-crystal monochromator, which consists of two parallel crystals.
2) The channel-cut monochromator, which is a single crystal with a slot cut nearly through it.

Most monochromator crystals are made of silicon or germanium and are cut and polished such that a particular atomic plane of the crystal is parallel to the surface of the crystal as Si(111), Si(311), or Ge(111). The energy of X-rays diffracted by the crystal is controlled by rotating the crystals in the white beam.

1.8.2.1.1.2 Harmonic rejection mirrors

The harmonic X-ray intensity needs to be reduced, as these X-rays will adversely affect the XAS measurement. A common method for removing harmonic X-rays is using a harmonic rejection mirror. This mirror is usually made of Si for low energies, Rh for X-ray energies below the Rh absorption edge at 23 keV, or Pt for higher X-ray energies. The mirror is placed at a grazing angle in the beam such that the X-rays with fundamental energy are reflected toward the sample, while the harmonic X-rays are not.

1.8.2.1.1.3 Detectors

Most X-ray absorption measurements use ionization detectors. These contain two parallel plates separated by a gas-filled space that the X-rays travel through. Some of the X-rays ionize the gas particles. A voltage bias applied to the parallel plates separates the gas ions, creating a current. The applied voltage should give a linear detector response for a given change in the incident X-ray intensity. There are also other kinds as fluorescence and electron yield detectors.

1.8.2.1.2 Transmission and fluorescence modes

X-ray Absorption measurements can be performed in several modes: transmission, fluorescence and electron yield; where the two first are the most common. The choice of the most appropriate mode to use in one experiment is a crucial decision.

The transmission mode is the most used because it only implies the measure of the X-ray flux before and after the beam passes the sample. Therefore, the adsorption coefficient is defined as (1.75). Transmission experiments are standard for hard X-rays, because the use of soft X-rays implies the use the samples thinner than 1 μm. Also, this mode should be used for concentrated samples. The sample should have the right thickness and be uniform and free of pinholes.

$$\mu_E = \ln\left(\frac{I_0}{I}\right) \tag{1.75}$$

The fluorescence mode measures the incident flux I_0 and the fluorescence X-rays $I_f$that are emitted following the X-ray absorption event. Usually the fluorescent detector is placed at 90 ° to the incident beam in the horizontal plane, with the sample at an angles, commonly 45 °, with respect to the beam, because in that position there is not interference generated because of the initial X-ray flux (I_0). The use of fluorescence mode is preferred for thicker samples or lower concentrations, even ppm concentrations or lower. For a highly concentrated sample, the fluorescence X-rays are reabsorbed by the absorber atoms in the sample, causing an attenuation of the fluorescence signal, it effect is named as *self-absorption* and is one of the most important concerns in the use of this mode.

1.8.3 Sample preparation for XAS

1.8.3.1 Sample requirements

1.8.3.1.1 Uniformity

The samples should have a uniform distribution of the absorber atom, and have the correct absorption for the measurement. The X-ray beam typically probes a millimeter-size portion of the sample. This volume should be representative of the entire sample.

1.8.3.1.2 Thickness.

For transmission mode samples, the thickness of the sample is really important. It supposes to be a sample with a given thickness, t, where the total adsorption of the atoms is less than 2.5 adsorption lengths, $\mu Et \approx 2.5$; and the partial absorption due to the absorber atoms is around one absorption length $\Delta\ \mu Et \approx 1$, which corresponds to the step edge.

The thickness to give $\Delta\ \mu Et = 1$ is as (1.76). where ρ is the compound density, n is the elemental stoichiometry, M is the atomic mass, σE is the adsorption cross-section in barns/atom (1 barn = 10^{-24} cm^2) tabulated in McMaster tables, and $E+$and $E-$ are the just above and below the energy edge. This calculation can be accomplished using the free download software HEPHAESTUS.

$$t = \frac{1}{\Delta\mu} = \frac{1.66 \sum_i n_i M_i}{\rho \sum_i n_i \left[\sigma_i\left(E_+\right) - \sigma_i\left(E_-\right)\right]} \tag{1.76}$$

1.8.3.1.3 Total X-ray adsorption.

For non-concentrate samples, the total X-ray adsorption of the sample is the most important. It should be related to the area concentration of the sample (ρt, in g/cm^2). The area concentration of the sample multiplied by the difference of the mass adsorption coefficient $(\Delta\mu E/\rho)$give the edge step, where a desired value to obtain a good measure is a edge step equal to one, $(\Delta\mu E/\rho)\rho t \approx 1$.

The difference of the mass adsorption coefficient is given by (1.77), where $(\mu E/\rho)$iis the mass adsorption coefficient just above (E+) and below (E-) of the edge energy and fi is the mass fraction of the element i. Multiplying the area concentration, ρt, for the cross-sectional area of the sample holder, amount of sample needed is known.

$$\left(\frac{\Delta\mu_E}{\rho}\right) = \sum f_i \left[\left(\frac{\Delta\mu_E}{\rho}\right)_{i,(E_+)} - \left(\frac{\Delta\mu_E}{\rho}\right)_{i,(E_-)}\right] \tag{1.77}$$

1.8.3.2 Sample preparation

As was described in last section, there are diluted solid samples, which can be prepared onto big substrates or concentrate solid samples which have to be prepared in *thin films*. Both methods are following described.

Liquid and gases samples can also be measured, but the preparation of those kind of sample is not discussed in this paper because it depends in the specific requirements of each sample. Several designs can be used as long they avoid the escape of the sample and the material used as container does not absorb radiation at the energies used for the measure.

1.8.3.2.1 Method 1

Step 1. The materials needed are showed in Figure 1.40: Kapton tape and film, a thin spatula, tweezers, scissors, weigh paper, mortar and pestle, and a sample holder. The sample holder can be made from several materials, as polypropylene, polycarbonate or Teflon.

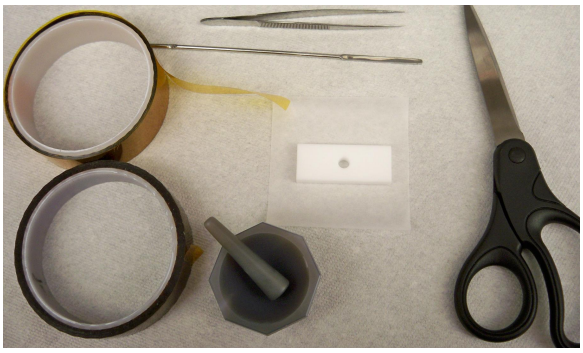

Figure 1.40: Several tools are needed for the sample preparation using Method 1.

Step 2. Two small squares of Kapton film are cut. One of them is placed onto the hole of the sample holder as shown Figure 1.41a. A piece of Kapton tape is placed onto the sample holder trying to minimize any air burble onto the surface and keeping the film as was previously placed Figure 1.41b. A side of the sample holder is now sealed in order to fill the hole (Figure 1.42).

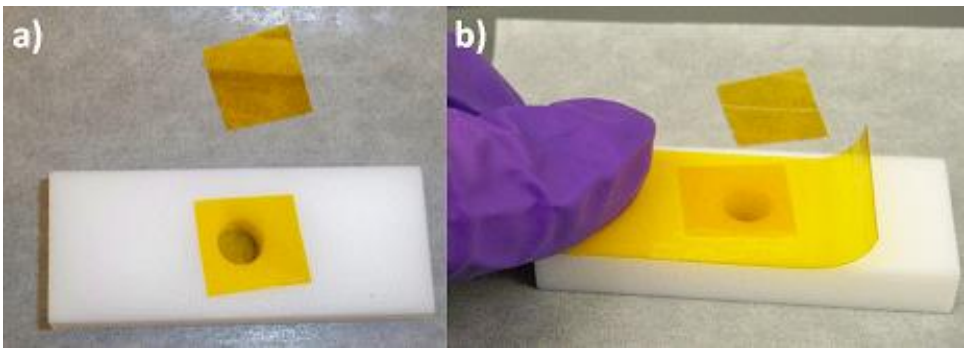

Figure 1.41: Preparing one face of the sample holder by (a) positioning a small piece of Kapton film onto the hole, which is held in place by Kapton tape (b).

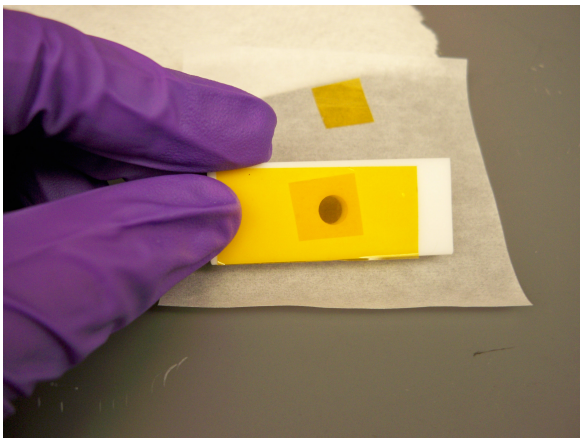

Figure 1.42: The side of the sample holder is closed.

Step 3. Before fill the sample holder, make sure your sample is a fine powder. Use the mortar to grind the sample (Figure 1.43).

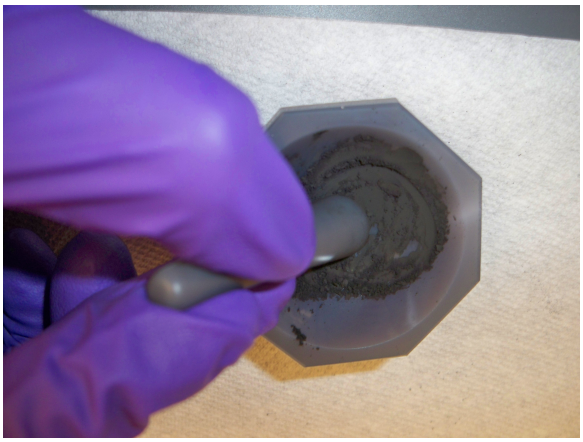

Figure 1.43: The sample is ground to be sure the grain size of the sample is homogeneous and small enough.

Step 4. Fill the hole with the powder. Make sure you have extra powder onto the hole (Figure 1.44a). With the spatula press the powder. The sample has to be as compact as possible (Figure 1.44b).

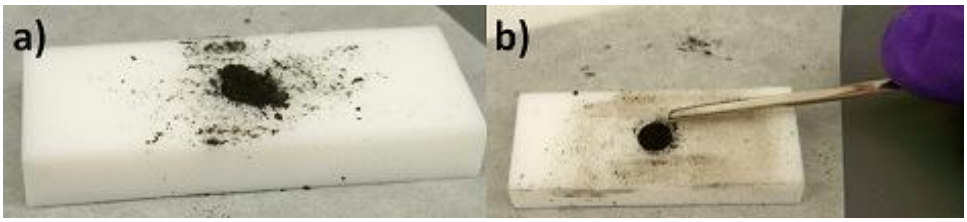

Figure 1.44: The sample holder is filled by (a) adding extra powder onto the hole then (b) compacting the sample with the spatula.

Step 5. Clean the surface of the slide. Repeat the step 2. Your sample loaded in the sample holder should look as Figure 1.45.

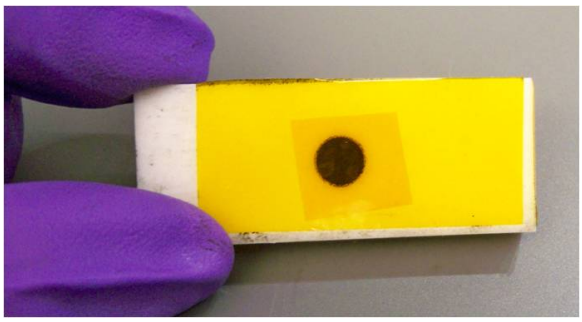

Figure 1.45: Sample loaded and sealed into the sample holder.

1.8.3.2.2 Method 2

Step 1. The materials needed are showed in Figure 1.46: Kapton tape, tweezers, scissors, weigh paper, mortar and pestle, tape and aluminum foil.

Figure 1.46: Several utensils are needed for the sample preparation using Method 2.

Step 2. Aluminum foil is placed as the work-area base. Kapton tape is place from one corner to the opposite one as shown Figure 1.47. Tape is put onto the extremes to fix it. In this case yellow tape was used in order to show where the tape should be placed but is better use Scotch invisible tape for the following steps.

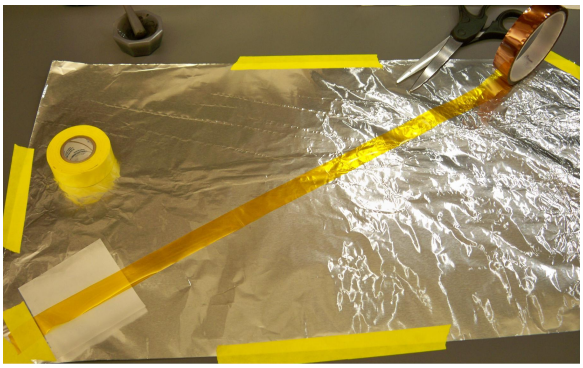

Figure 1.47: Preparation of the work-area.

Step 3. The weigh paper is placed under the Kapton tape in one of the extremes. Sample is added onto that Kapton tape extreme (Figure 1.48). The function of the weigh paper is further recuperation of extra sample.

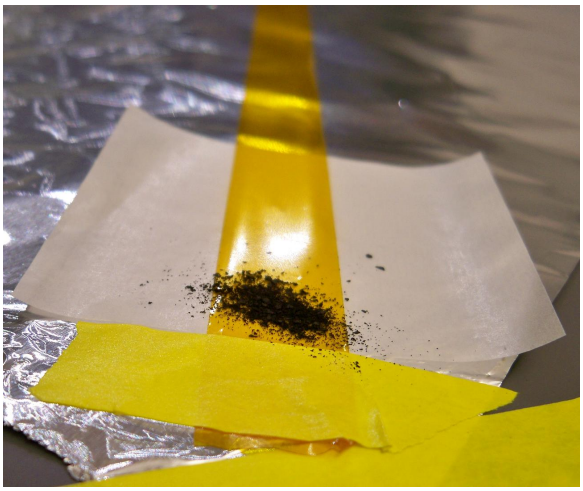

Figure 1.48: Add the sample onto an extreme of the Kapton tape.

Step 4. With one finger, the sample is dispersed along the Kapton tape, always in the same direction and taking care that the weigh paper is under the tape area is being used (Figure 1.49a). The finger should be slid several times making pressure in order to have a homogeneous and complete cover film (Figure 1.49b).

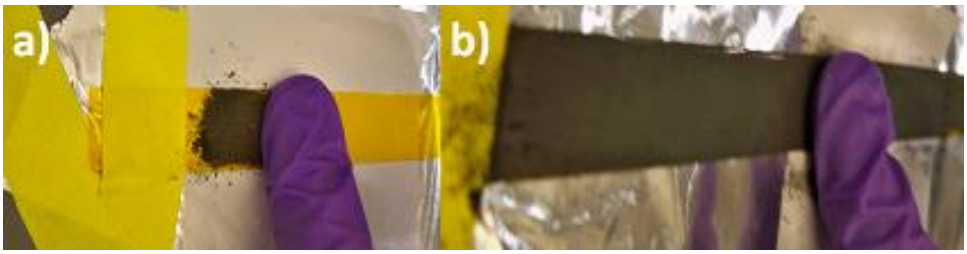

Figure 1.49: Making a thin film with a solid sample by (a) dispersing the solid along the Kapton tape and (b) repeated sliding several times to obtain a homogeneous film.

Step 5. The final sample covered Kapton tape should look like Figure 1.50. Cut the extremes in order to a further manipulation of the film.

Figure 1.50: A complete thin film.

Step 6. Using the tweezers, fold the film taking care that is well aligned and there fold is complete plane.

Figure 1.51a shows the first folding, generating a 2 layers film. Figure 1.51b and Figure 1.51c shows the second and third folding, obtaining a 4 and 8 layers film. Sometimes a 4 layers film is good enough. You always can fold again to obtain bigger signal intensity.

Figure 1.51: Folding of the thin film simple once results in a two layer film (a) and after a second and third folding four and eight layers films are obtained (b and c, respectively).

1.8.4 Bibliography

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1.9 Fluorescence Spectroscopy

1.9.1 Cold Vapor Atomic Fluorescence Spectroscopy[12]

1.9.1.1 Introduction

Atomic fluorescence spectroscopy (AFS) is a method that was invented by Winefordner and Vickers in 1964 as a means to analyze the chemical concentration of a sample. The idea is to excite a sample vapor with the appropriate UV radiation, and by measuring the emitting radiation, the amount of the specific element being measured could be quantified. In its most basic form, AFS consists of a UV light source to excite the sample, a monochromator, a detector and a readout device (Figure 1.52). Cold vapor atomic fluorescence spectroscopy (CVAFS) uses the same technique as AFS, but the preparation of the sample is adapted specifically to quantify the presence of heavy metals that are volatile, such as mercury, and allows for these elements to be measured at room temperature.

[12]This content is available online at <http://cnx.org/content/m38339/1.1/>.

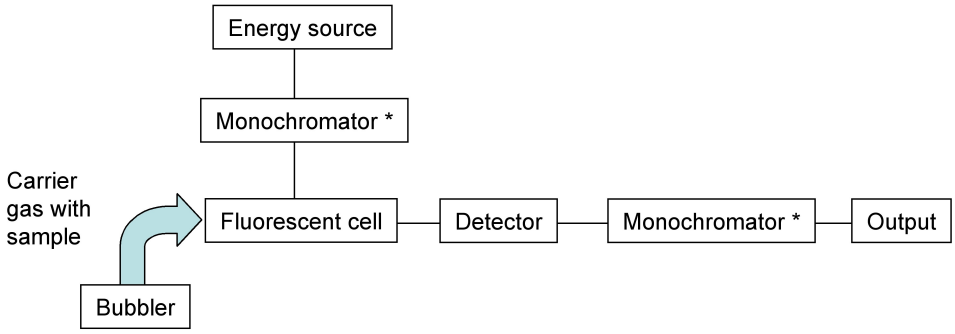

Figure 1.52: The basic setup for CVAFS. *The monochromator can be in either position in the scheme.

1.9.1.2 Theory

The theory behind CVAFS is that as the sample absorbs photons from the radiation source, it will enter an excited state. As the atom falls back into the ground state from its excited vibrational state(s), it will emit a photon, which can then be measured to determine the concentration. In its most basic sense, this process is represented by (1.78) where P_F is the power given off as photons from the sample, P_{abs} is the power of the radiation absorbed by the sample, and ϕ is the proportionality factor of the energy lost due to collisions and interactions between the atoms present, and not due to photon emission.

$$P_F = \varphi P_{abs} \tag{1.78}$$

1.9.1.3 Sample preparation

For CVAFS, the sample must be digested, usually with an acid to break down the compound being tested so that all metal atoms in the sample are accessible to be vaporized. The sample is put into a bubbler, usually with an agent that will convert the element to its gaseous species. An inert gas carrier such as argon is then passed through the bubbler to carry the metal vapors to the fluorescence cell. It is important that the gas carrier is inert, so that the signal will only be absorbed and emitted by the sample in question and not the carrier gas.

1.9.1.4 Atomic fluorescence spectroscopy

Once the sample is loaded into the cell, a collimated (almost parallel) UV light source passes through the sample so that it will fluoresce. A monochromator is often used, either between the light source and the sample, or between the sample and the detector. These two different setups are referred to as excitation or emission spectrum, respectively. In an excitation spectrum, the light source is kept at a constant wavelength via the monochromator, and multiple wavelengths of emitted light are gathered, whereas in the emission spectrum, only the specified wavelength of light emitted from the sample is measured, but the sample is exposed to multiple wavelengths of light from the excitatory source. The fluorescence will be detected by a photomultiplier tube, which is extremely light sensitive, and a photodiode is used to convert the light into voltage or current, which can then in turn be interpreted into the amount of the chemical present.