**Laboratory #3**

**Chem 6614 Instrumental Methods of Chemistry**

**SUNY Alfred State College**

***Determination of the Concentration of Ni(II) and Cu(II) in an Unknown Mixture***

***via Atomic Absorption Spectroscopy and Standard Addition***

**Lab notebook due Thursday 13 February**

**3.1. Background**

In the UV-VIS lab (Lab #2) you deduced the concentration of two unknown species (Cu(II) and Ni(II) ) in solution by creating a total of 4 calibration plots. If you had to carry out a similar analysis with **n** unknowns in a solution, you’d need to make **n2** calibration plots. This is because each of the species contributes an absorption at each of the **n** wavelengths of analysis necessary to solve the **n** unknown system. Thus, if 6 unknown metals are in a sample solution of waste water sample, a daunting total of **62= 36** calibrations need to be carried out.

An even more worrisome problem not broached in Lab #2 is that unknown samples are rarely found in a solution of 1% nitric acid/distilled water. Rather, a typical field sample may contain indeterminate quantities of interfering `muck’. The ‘muck’ problem, more politely called the *matrix problem*  is very common. Imagine for example sampling water from a shallow dairy farm pond, preparatory to doing a water analysis for Cu and Ni. It must be expected that the water will be full of mud, cow poop, bugs and a host of other inorganic and organic chemicals. Even if you filter out the bugs, poop and mud, there will always be an unknown set of materials in your sample which can interfere with analysis. Duplicating this background *matrix* in your calibration standards is basically impossible. Hence, even if you do make up the n2 calibration solutions in 1% nitric acid, they will not reflect the real sample conditions ,making the reliability of any unknown concentration estimated from them unreliable.

Thus, while the UV-VIS technique is the most common one introduced to beginning students of chemistry, it is rarely used in practice for elemental analysis. To circumvent the difficulty of each element contributing to each absorbance in UV-VIS spectroscopy it is common the employ some version of Atomic spectroscopy.

In this lab you will use a traditional flame atomic absorption method (**Atomic Absorption Spectroscopy** or AAS) to determine the concentration of Ni(II) and Cu(II) in an unknown solution. 1 As discussed in lecture, AAS uses a single element **Hollow Cathode Lamp** (HCL) in conjunction with a flame atomization of the sample so that each element can be examined without worrying about signal contributions from other elements. Even if the unknown mixture contains n elements to be analyzed, AAS allows you to analyze the mixture as if any selected single element is the only one present. This reduces the number of calibrations required for an AAS analysis of **n** unknown elements to **n**, not **n2** as is required in UV-VIS spectroscopy.

1 Most modern labs now prefer emission atomic absorption methods, notably **Ion Coupled Plasma (ICP)** spectroscopy since this method allows simultaneous analysis of up to 40 elements while AAS requires a serial analysis of each element separately.

The second problem- that of an undefined background matrix -is easily and efficiently addressed using the ***method of standard additions***. This method consists of adding the same **standard** volume, **Vs** of your *unknown* solution to each of several identical volumetric flasks and then adding to each individual flask, **Vs** , 2 **V­s** ...**.**N **Vs** standard volumes containing a *known* **concentration,** Cs, composed of each of the elements to be analyzed. All the flasks are then diluted to the same volume with 1% nitric acid and the resulting set of standard addition solutions are analyzed serially for absorbances **A** of each element or compound. A plot of **Absorbance** vs the number of standard volumes added, the concentration within **Vs** of the original unknown solution can be ascertained as we will discuss below in **Calculations.**

The charm of the foregoing is that whatever `muck’ is in the sample, it is also automatically present in the calibration solutions and in identical concentrations. Because of this preparative trick, the target element is seeing the same level of `muck’ in each calibration flask.

**3.2. Purpose**

The concentration of Cu(II) and Ni(II) in a diluted version of the original unknown mixture from Experiment 2 will be determined by Flame AAS using the standard addition samples prepared in Experiment 1. The original unknown concentrations of Cu(II) and Ni(II), **CCu** and **CNi**  in moles/L will then be extracted based on the dilution procedure described in Experiment 1 and compared with the values obtained by UV-VIS methods in experiment #2.

**3.3. Procedure**

* + 1. **Setting up and Tuning the Perkin-Elmer (PE) Analyst 100 AAS**

The instructor will demonstrate how to install the **Ni** HCL lamp and access the operating system of the PE Analyst 100 AAS. He will also demonstrate how to select the correct operating conditions, light and tune the acetylene-air burner flame , tune the **Ni** signal for the selected wavelength and adjust the solution flow to the burner to optimize analysis. You are responsible for mastering this process since you will need to reproduce it when the **Cu** lamp is installed. The procedure will be part of the final practicum. Record all instrument conditions in **Observations/Data.**

* + 1. **AAS Analysis of the Standard Addition Solutions for Ni(II)**

Insert the capillary tube used to sample standard solutions in the tuning process into the *least* concentrated standard addition solution (flask #1) and record the average **A** for the **Ni(II)** in the flask after c.a. five 1 second individual measurements. Repeat this process for next 4 standard solutions in order from lowest to highest. Make sure to re-establish the instrument `zero’ with 1 % nitric acid blanks between each flask sampling. Record your **Data** in a table similar to that below. A total of 5 measurements are expected.

**Table 1: Observed Ni(II) Absorbances, A(Ni), for Standard Solutions #1-5**

|  |  |  |
| --- | --- | --- |
| Standard solution flask # | *Standard addition #* = **x** | Observed A(Ni) |
| 1 | 0 |  |
| 2 | 1 |  |
| 3 | 2 |  |
| 4 | 3 |  |
| 5 | 4 |  |

* + 1. **AAS Analysis of the Standard Addition Solutions for Cu(II)**

Turn off the AAS and replace the Ni HCL lamp with the **Cu** HCL lamp. Set up and tune the **Cu** HCL lamp and the spectrometer as demonstrated in 3.3.1. If you are unsure which set of **Cu** analysis conditions to use, you may consult the instructor. Once the AAS is tuned again, repeat the analysis procedure you carried out above in 3.3.2 for **Ni** with the **Cu** lamp. Record your data in a table like that shown below:

**Table 2: Observed Cu(II) Absorbances, A(Cu), for Standard Solutions #1-5**

|  |  |  |
| --- | --- | --- |
| Standard solution flask # | *Standard addition #*=**x** | Observed **A(Cu)** |
| 1 |  |  |
| 2 |  |  |
| 3 |  |  |
| 4 |  |  |
| 5 |  |  |

* 1. **Calculations**

**3.4.1. Graphical Analysis**

Using Excel or graph paper, plot **x**, the *standard addition #*, vs **A(Ni)** from Table 1 Make sure to allow the x axes to extend to the left (negative) side of the plot as sketched below. Draw your best straight line through the points and measure **Nu(Ni)** the point on the x axis where the extrapolation of the best straight line falls.



Repeat this analysis for the **A(Cu)**

Data from Table 2 on a separate

Graph and extract a **Nu (Cu)** for the

copper data.

**Nu(Ni)**

**3.4.2. Alternative least square fit Graphical analysis**

Instead of drawing the `eyeball estimate’ of the best line, fit the **A** and **x** to the straight line function

**1**  **A = mx +b**

for both the Ni and Cu data. Plot this fitted version of the line on each graph instead of the eyeball estimated line. This allows a more accurate estimate of **Nu** since:

**2** -**b = Nu**

**m**

* + 1. **Computing the Unknown Concentrations of Ni and Cu in Standard Addition flasks**

**Let C­Ni(dilute**) = the concentration of the unknown Ni(II) standard addition in each flask

**Let CCu(dilute)** = the concentration of the unknown Cu(II) standard addition in each flask

As will be explained in lecture:

**3 CNi(dilute) = Nu(Ni) \* CNio**  ***in ppm***

**4 CCu(dilute) = Nu(Cu) \* CCuo** ***in ppm***

Where **CNio** and **CCuo** are the values you reported in the **Results** of **Experiment 1.**

**3.4.4. Computing the Concentrations of Ni and Cu in the Original Unknown Mixture**

Explain and compute here, the dilution factor, **F**, applied to the unknown mixture in Experiment #1 in section 1.3.4 of that experiment.

Let **CNi** = the concentration of the original unknown Ni

Let **CCu** = the concentration of the original unknown Cu

**5** **CCu** = **F**\* CCu(dilute) in ppm

**6** **CNi**  = **F**\*CNi(dilute) in ppm

Convert both **CCu** and **CNi** in **ppm** to their equivalent **molar** (**moles cation/L**) concentrations (show calculations) and report these in Results as shown along with UV-VIS results for comparison.

* 1. **Results**

*method*

|  |  |  |
| --- | --- | --- |
| **Unknown concentration** | **From current experiment via AAS** | **From previous experiment: via UV-VIS** |
| **CCu (moles Cu2+ /L)** |  |  |
| **CNi (moles Ni2+ /L)** |  |  |