**Laboratory #2**

**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 UV-VIS Spectrophotometry***

***(lab notebook due Thursday 15 Feb)***

**Figure 1: Beer’s law plot**

* 1. **Background**

***k=slope***

At modest concentrations, a pure, single material

Ax(**λ1**)

absorbs light of a given wavelength **λ1** in direct

proportion to its concentration **C** (mol/L).

The linear relationship is often referred to as

**Beer’s Law:**

*Beer’s Law equation with one absorbing species*

**1** **A**1 **= kC Cx**

**A1**, is called the ***absorbance*** of wavelength λ1 by the absorbing species and the constant **k** is called the ***extinction coefficient*** . The value of **k**, which also varies with wavelength, is determined by measuring the slope of the line illustrated in **Figure 1.**

Absorbance is not measured directly. Typically, a spectrophotometer records

% transmittance, **%T1** , which is the amount the light, **Iout** that manages to pass through the sample at **λ1** vs the initial input light at **λ1** incident to the sample, **Iin**  e.g:

**%T1 =100\* Iout**

**2**

**Iin**

**A1** is then calculated from **%T1** using equation **3**:

**3** A1 = 2 – log10 (%T1 ).

The above relationship reflects the fundamental exponential relationship between the relative intensities **I­out/Iin**  and the concentration C of the absorbing species,

**I­out/Iin** = 10-kC

Beer’s law is commonly introduced in freshmen chemistry labs as a way to determine concentrations of a single unknown in solution, since it is easy to create a calibration curve from standards and then use the unknown **Ax** to read the corresponding **Cx** from the abscissa of the calibration plot as illustrated in Figure 1.

When more than one absorbing species is present, however, Beer’s law is no longer as simple to use . This is because each species present can contribute to the absorbance at any wavelength. Hence, if two species, **x** and **y**, are present **A1** is the sum of **two** absorbances-one from **x**  (**Ax1**) and one from **y** (**Ay1**) as shown below in **4:**

**4** **A1 = Ax1  + Ay1**

Since **x** and **y** absorb light at **λ1** independently of each other, they each have their own independent extinction coefficients**, kx1**and **ky1** and if observed calibration data is used to fit for A vs concentrations, an additional intercept constant, b, is also necessary since fitting is usually done to the general form:

**A = kC +b**

Thus, **4** can be re-written to show the connection between **x** and **y** concentrations and the total absorbance **A1** as in **5**:

*Beer’s Law equation*

*with two absorbing species*

**5 A1 = (kx1Cx + bx1) + (ky1Cy + by1)**

Where kx1 refers to the extinction coefficient determined by linear regression of a calibration curve for species x at wavelength 1 and bx1is that fit’s intercept constant.

While straightforward, the *two species* Beer’s equation presents a dilemma.

*Even given values fo*r **kx1** **bx1** , **ky1** and **by1** *and a value for* **A1,** *it is*  *impossible to determine* ***C­x*** *and* ***Cy*** *from* ***5*** *alone since we have one equation but two unknowns* **(Cx** *and* **Cy)**

In order to find **Cx** and **Cy**, we thus need a second absorbance sum, **A2** measured at a different wavelength **λ2** :

**6** **A2 = Ax2 + Ay2 .**

This requires two more pairs of extinction coefficients and intercepts (**kx2 ,** **bx1)** , (**ky1** , **by2)**as shown in **7:**

**7 A2  = (kx2Cx + bx2) + ( ky2Cy + by2)**

Thus, to find the concentrations **Cx** and **Cy**of a mixture of two absorbing species **x** and **y** it is necessary to measure two absorbances **A1, A2** for the unknown mixture and determine four different extinction coefficients **kx1,** **kx2, ky1 and ky2**  from standard solutions of pure **x** or **y.** The resulting two equation/two unknown linear system is then solved for **Cx** and **Cy** by routine algebraic manipulation or through the use of determinants.

***2 equations/ 2 unknowns***

***system for determination of Cx and Cy***

**5 A1 = (kx1Cx + bx1) + (ky1Cy + by1)**

**7 A2  = (kx2Cx + bx2) + ( ky2Cy + by2)**

The general solution for **Cx** and **Cy** are expressed in **8 :**

**8a C­x**  = [**A1-( bx1 + by1)] \*ky2 –(A2-bx2-by2)\*ky1**  **kx1\*ky2 –kx2\*ky1**

**8b** **Cy** = [**A1-( bx1+ by1)]\*kx2 – (A2-bx2-by2)kx1**

**kx2\*ky1 –kx1\*ky2**

Note that 8a and 8b are the result of solving **5** and **7** as a pair of simultaneous equations in two variables (**C**x and **Cy)**. Programs exist on EXCEL and in calculators that can simplify this computation.

**2.2. Purpose**

Determination of the molar concentration of Cu(II) and Ni(II) in an unknown mixture of these species in 1% nitric acid.

**2.3. Procedure**

**2.3.1 Determination of analysis wavelengths λ1 and λ2**

Use the double beam Lambda 35,or 25 Perkin Elmer UV-VIS, or (if you are brave) the Lambda 4B UV-VIS as demonstrated by your instructor to scan the full uv-vis range (180-900 nm) of your 0.10 M Cu(II) molar reference operated in absorbance mode and from the scan select the wavelength at which the absorbance is highest and reasonably broad. Call that wavelength **λ1.**

Repeat this process with your 0.10 M Ni(II) molar reference and identify the wavelength of highest absorbance for the Ni(II) solution. Call that wavelength **λ2**.

**2.3.2. Calibration Plots**

Using either the Lambda 4b or Lambda 25, record the absorbance of each of your molar standard solutions at **λ1** and then at **λ2** in nm. (It is probably most convenient to do all the solutions at a single wavelength and then switch to the second one. )

You should end up with 4 sets of data composed of 6 measurements ( a total of 24 data points similar to to the example tables below: (your concentrations may be different)

**Table 1: Observed Absorbances of Cu(II) Molar references at λ1(nm)and λ2 (nm)**

|  |  |  |
| --- | --- | --- |
| Cu(II) concentration,M | ACu at **λ1(nm)** | ACu at **λ2(nm)** |
| 0.000 | 0 | 0 |
| 0.010 |  |  |
| 0.020 |  |  |
| 0.030 |  |  |
| 0.040 |  |  |
| 0.050 |  |  |

**Table 2: Observed Absorbances of Ni(II) Molar references at λ1 (nm) and λ2 (nm)**

|  |  |  |
| --- | --- | --- |
| Ni(II) concentration,M | ANi at **λ1(nm)** | ANi at **λ2(nm)** |
| 0.000 | 0 | 0 |
| 0.010 |  |  |
| 0.020 |  |  |
| 0.030 |  |  |
| 0.040 |  |  |
| 0.050 |  |  |

**2.3.3. Unknown Mixture Absorbances**

Using the same spectrophotometer and cuvettes as employed above, record the absorbances A1 at **λ1**and A2 at **λ2** for the unknown mixture of Cu(II) and Ni(II) using the same procedure as employed for the calibrations.

**Table 3: Observed Absorbances of unknown Mixture at λ1(nm) and λ2(nm)**

|  |  |
| --- | --- |
| Wavelength of analysis | Observed absorbance of unknown mixture |
| **λ1(nm)** | A1 = |
| **Λ2(nm)** | A2 = |

**2.4. Calculations**

**2.4.1. Calibration plots of Cu(II) and Ni(II) Molar standard absorbances**

Using Excel or a carefully drawn graph in ink, plot the 4 calibration curves you collected in **Tables 1** and **2** above . Let **A** be the `y**’** axis and molar concentration, **C,** be **`x’** axis. You should include a point at `zero’ concentration where the A value is assume = 0.

Using Excel or a hand calculator, l*east square fit the curves* to find the ***slopes*** of each of the 4 plots. With reference to the equations **5**-**8:**

**kX1** = slope for Cu standards at **λ1**

**kx2** = slope for Cu standards at **λ2**

**ky1 =** slope for Ni standards at **λ1**

**ky2** = slope for Ni standards at **λ2**

* + 1. **Determination of Cx =[Cu(II)] unknown and Cy= [Ni(II)] unknown**

Formally substitute the numeric values for the k values into the equations **5** and **7** along with the measured values of **A1** and **A2** from table 3 :

*Put in numeric values for k ,b and A*

**5 A1 = kx1Cx + ky1Cy +(bx1+by1)**

**7 A2  = kx2Cx + ky2Cy + (bx2 + by2)**

Solve for **Cx** (= **CCu** unknown Cu concentration) and **Cy** (= **CNi** unknown Ni concentration) using your own algebraic methodology, a hand calculator capable of matrix operations , an EXCEL routine1 or using the derived results in **8a** and **8b.**

**Indicate explicitly what tool or approach you used**

**8a C­x**  = [**A1-( bx1 + by1)] \*ky2 –A2\*ky1 +ky1(bx2 +by2)**  **kx1\*ky2 –kx2\*ky1**

**8b** **Cy** = [**A2-( bx2+ by2)]\*kx1 – A2\*kx2 + kx2(bx1 +bx2)**

**kx1\*ky2 –kx2\*ky1**

**2.5. Results**

**a)analysis wavelengths**

**b) table of k values**

**c) CCu = … CNi =…. In moles/L**

1The instructor will illustrate an example of how to use EXCEL to do this in class.