**Supplement #2:**   **Method of Standard Additions**

  *6614 Chemical Instrumentation*

**1. Reason For Using Standard Additions Method (see also: text 1D-3 pp. 13-14 )**

Often samples are not neat, clean dilutions in distilled water, but contain indeterminate quantities of interfering `muck’. Imagine for example sampling water from a shallow farm pond, preparatory to doing a water analysis for Cu. The water will be full of mud, bugs and a host of other chemicals. While you can filter bugs and mud, there will always be an unknown set of materials in your sample which can interfere with you quantitative analysis. This interference is not accounted for in the calibration curves you have constructed so far since you don’t know the `muck’s’ composition. Hence, your calibration solutions may not faithfully reflect the sample conditions. To circumvent this sticky problem, the method of standard additions has been developed.

**2. The Method of Standard Additions**

The basic method consists of adding an identical, **`standard’** volume, Vs, of your unknown solution to a volumetric flask and adding to each individual flask, 0, 1 Vs , 2 V­s ....N Vs standard volumes containing a known concentration, Cs, of the element or compound to be analyzed. All the flasks are then diluted to the same volume and the resulting set of standard addition solutions analyzed serially for absorbances A of that element or compound. By extrapolating backwards on a plot of A vs # standard volumes added, the concentration in Vs of the original unknown solution can be ascertained. (See Figure below)

Note that in the foregoing, whatever `muck’ is in the sample, is also automatically present in the calibration solutions and in

identical concentrations.

**3. An Example**

**Standard addition volume, Vs = 5.00 mL. Volumetric flask volume= 50.00 mL Known Cu Solution, Cs = 10 ppm**

**TABLE OF SOLUTION VOLUMES AND OBSERVED ABSORBANCES FOR AQUEOUS Cu2+** **AT 679 nm**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **standard solution #** | **Volume of** **unknown added** | **# standard**  **additions of Cs** | **volume of standard addition, mL** | **A(observed) of 50 mL****of standard solution** |
| **1** | **5.00** | **0** | **0.00** | **0.302** |
| **2** | **5.00** | **1** | **5.00** | **0.404** |
| **3** | **5.00** | **2** | **10.0** | **0.501** |
| **4** | **5.00** | **3** | **15.0** | **0.610** |
| **5** | **5.00** | **4** | **20.0** | **0.748** |

**FIND THE ORIGINAL Cu CONCENTRATION OF THE 5 mL UNKNOWN SOLUTION\_\_\_\_\_\_\_\_\_\_\_**



~-2.67

**4. SOLUTION TO PROBLEM:**

Extrapolating back to `0’ absorbance requires `subtracting’ the copper added from ~2.67 hypothetical standard addition volumes of 10 ppm solution from the 50 mL flask. This is the same as saying the original 5 mL volume of unknown present in all the flasks contained

 2.67\*5 mL \*10 ppm Cu = 13.35 mL \* 10 ug Cu/mL = 133.5 ug Cu=>

 **Cu**= Cu concentration of original 5 mL unknown = 133.5 ug / 5 mL **= 26.7 ppm Cu**

Note that since the standard addition volume=the volume of the unknown aliquot:

 **Cu = Nu \*Cs (Vu = Vs)**

**5. EXTENSIONS**

The standard addition volume, Vs of known solution of concentration Cs need not be identical in volume to the unknown aliquot, Vu.

Given that Vtotal is the final, common diluted volume of all solutions, then if the number of standard additions required to

extrapolate the standard addition curve to A= 0, is Nu, then the concentration of the unknown solution added to Vu, Cu is:

 **Cu = Nu \* Cs\*Vs/Vu**  **(Vu ≠ Vs)**

Further, if a linear regression analysis of the standard addition plot is carried out to yield a relation between the number

of standard additions, N, and A, e.g:

 **A = m\*N +b**

Then:

  **Nu =** **b/m**

So:

 **Cu = b\* Cs\*Vs/m\*Vu**  **(Vu ≠ Vs)**

If V­u =Vss then the above reduces to:

 **Cu = b\* Cs/m** **(Vu=V2)**

A linear regression fit of the above data yields : m= 0.110, b= 0.293 so

 **Cu  = 0.293\*10/0.11 = 26.6 ppm**