Lab I
GRAVIMETRIC ANALYSIS OF SILVER IN PRE-1964 DIMES

1. Introduction

A gravimetric analysis is one which determines the composition of a material by directly weighing one or more of the separated components. Accurate analytical balances were developed well over 100 years ago, so that gravimetric methods played a major role, historically, in the analysis of rock and metal samples and in accurate determination of atomic weights for most elements. They are the most accurate and straightforward traditional methods available to the analyst.

Gravimetric techniques have tended to disappear from the modern analytical laboratory, where the emphasis (for most clinical, industrial, and environmental analyses) is usually on rapidity and sensitivity, rather than on 3- or 4-significant-figure accuracy. Great ingenuity has gone into the development of techniques which are capable of automation and which lessen the need for manipulative skill and special care on the part of the analyst. Nevertheless, one of the purposes of general chemistry laboratory is to provide experience in the traditional methods of "wet chemistry" and to develop the carefulness and thoughtfulness that permits execution of highly reproducable experiments in any field. This ability, required of all scientists, is best cultivated by experience and is of particular importance when one becomes involved in research.

In this experiment you are to carry out a gravimetric analysis for the amount of silver in dimes minted before 1965 (at which time a Ni-Cu alloy was substituted). The object is to achieve reasonable precision (agreement between results for the two samples you analyze) and accuracy (agreement with the actual Ag content of the material analyzed). While the bulk of the experimental work will take place in the four-hour regularly scheduled lab period, some extra short visits will be necessary both before and after.

2. Theory

The first step in any quantitative analysis involves the complete separation of the element or compound of interest. In an alloy of metallic elements this is most easily accomplished by oxidizing the metal atoms with a sufficiently strong oxidizing agent and then using a specific procedure for separating the metal ions. As is seen in the following list of standard reduction potentials, the nitrate ion is thermodynamically capable of oxidizing both Ag and Cu, the two major components of the alloy used in making the older dimes.

<u>Standard Reduction Potential in Acid Solution at 298 K</u>

Half reaction (couple)	**ε°(volts)**
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99
$NO_3^- + 4H^+ + 3e^- \rightarrow NO(g) + H_2O$	0.96
$Ag^+ + e^- \rightarrow Ag(s)$	0.80
$Cu^+ + e^- \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	0.22
$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$2H^+ + 2e^- \rightarrow H_2(g)$	0.00

Nitric acid is used to dissolve noble metals. The highly toxic NO(g) which is formed immediately reacts with dioxygen: $2NO + O_2 \rightarrow 2NO_2(g)$ (brown).

Looking at the same table of reduction potentials we notice that Ag^+ is a stronger oxidizing agent than Cu^{+2}; this leads to a procedure for separating the silver ions from the copper ions in the aqueous acidic solution. If we are not interested in quantifying the copper in the dime alloy, a redox reaction with a piece of copper wire leads to precipitation of silver metal and the silver metal can then be gravimetrically quantified. By determining the amount of copper wire dissolved, we in fact have another complementary way to determine the amount of silver present. Note, however, that the NO_3^- must be removed or it too will oxidize the copper wire and lead to erroneous results. Qualitative tests are used to monitor completion of the redox reactions and washing of the precipitated silver crystals.

3. Procedure

A) The first step in the procedure is to bring two clean filter crucibles to "constant weight" by drying them in a 120°C oven. To prepare the crucibles for filtering, place <u>one</u> glass fiber filter mat (rough side up) in each crucible and wash the assembly with water and then with 0.02M HNO_3 . (Prepare this rinse solution from the stock 6 M HNO_3; 1 drop = ~1/20 mL.) The washing is facilitated by mounting the crucible on a suction flask and connecting the flask to the aspirator at the sink. Wipe the crucibles dry, put them in a 600 mL beaker and place the beaker in one of the ovens around the lab. Be sure to record the identifying mark that appears on each crucible . Also place a slip of paper with your name on it in the beaker so that the name can be read from the outside.

After at least three hours at 120°C, remove the beaker (with desiccator tongs!) and transfer the crucibles to a desiccator. Nest the crucibles in 30 mL beakers within the desiccator and securely slide the top to keep moisture from condensing inside as the crucibles cool.

It will take about an hour for the crucibles to cool to room temperature, and only then is it possible to make an accurate weighing because convection currents within the weighing chamber will make a warm object appear lighter. (On the balance, an object that is still cooling will appear to be gaining weight; one that is still drying will appear to be losing weight.) Handle the crucibles with a Kimwipe or tongs to avoid leaving fingerprints (which often have significant weight!). <u>Use the same balance for each weighing in this experiment</u> and make sure it is properly leveled and zeroed before <u>each</u> use. Consider that "constant weight" has been achieved when consecutive weighings differ by no more than 0.0003 g. This usually takes no more than three oven dryings (and obviously takes a least two).

B) Obtain two "samples", accurately weigh the coins and place them in individual 250 mL beakers. <u>**IN THE HOOD, CAREFULLY**</u> dissolve the coins in 10 mL 6M HNO_3. This acid is quite corrosive and upon reaction will produce a red-brown gas; it may be necessary to heat the solution gently to completely dissolve the coin. You are advised to use the disposable gloves.

It is now necessary to replace the nitrate ion with the sulfate ion: $NO_3^- + H_2SO_4 \rightarrow HNO_3 + SO_4^{2-} + H^+$. Add 25 mL 3M H_2SO_4 and boil down the solution to about 2 mL or until dense white fumes begin to evolve. At this point all the HNO_3 has been evaporated and the H_2SO_4 itself begins to decompose: $H_2SO_4 \rightarrow H_2O + SO_3$ (choking fumes). Is any precipitate observed during this procedure? What might it be? Cool the solution and then <u>**CAUTIOUSLY**</u> add 125 mL water. Heat almost to boiling, with stirring, until any solid dissolves. At this point the solution should contain Cu^{2+}, H^+, Ag^+ and SO_4^{2-}.

The silver is now precipitated through a redox reaction with copper metal. Accurately weigh a piece of copper wire which has been coiled as shown at the right. Place it in the 250 mL beaker
solution so that part of the wire emerges from the solution. Let the silver deposit for ~half hour in the hot but not boiling solution; scrape the "mossy" silver off the Cu wire as it is deposited, using a rubber policeman.

The completeness of this reaction is determined by performing a qualitative test for Ag^+. On a watch glass, mix a few drops of the solution with a drop of 1 M HCl; a precipitate (AgCl) indicates the presence of Ag^+ and an incomplete redox reaction. In the event of positive test continue the reaction for another 10 minutes and then repeat the test. When the silver has completely deposited on the copper, scrape loose all the remaining solid from the wire with a policeman. Decant the cooled solution through the weighed filter crucible and wash the solid silver five times with 10 mL water while crushing it. Decant each rinse through the crucible to catch any small flakes. Test the sixth wash for Cu^{+2}: to ~l mL of this wash in a small test tube, add a drop of the 0.1M potassium ferrocyanide solution; a brown precipitate ($Cu_2Fe(CN)_6$) indicates the presence of cupric ion. If a positive test results, wash the solid silver three more times.

Quantitatively transfer the remaining silver precipitate to the filter crucible. Apply suction to remove as much of the water as possible. Wipe off the outsides of the crucibles and place them in a beaker in the 120°C oven. Dry them as before until constant weight is achieved; determine the weight percent silver in the dimes. After drying the copper wire, accurately weigh it to determine the amount of copper lost and compare this value to the direct determination of Ag [(loss in weight of Cu)/(predicted loss based on Ag recovered)].

4. Report

The lab report should center about a calculation of the weight percent silver in the coins. The data sheet at the end of this manual is all that is required as a lab report. Assuming the alloy used in minting all dimes is identical, to the limits of detection in this experiment, report an average of your two results (unless you have good reason for discarding one of them) and report the average deviation from the true value (90%). This is a measure of your accuracy. In addition, find the average deviation of your two results from your mean value, an exercise to replace the standard deviation which has little meaning with only two measurements. This is a measure of your precision. Discuss the different sources of error and their relative importance, comment upon your own precision (relative to the known sources of random error) and speculate about whether there might be any systematic error which would make your results too high or too low. Include balanced chemical reactions that are important to various stages of the analysis, as noted on the data sheet.

5. Questions

These two questions should be answered before coming to lab.

1. A sample containing Cu weighs 0.4976 g. It is dissolved in HNO_3; H_2SO_4 is added and the nitric acid is boiled off. The solution is diluted, and sulfurous acid and ammonium thiocyanate are added. Cuprous thiocyanate, Cu(SCN), quantitatively precipitates, is filtered, washed and dried. This precipitate weighs 0.6898 g. What is the weight percent Cu in the sample?

2. A solid solution with the composition $Ni_x\ Mg_{1-x}\ (NH_4)_2\ (SO_4)_2 \bullet 6H_2O$ is analyzed and found to contain 11.58% Ni by weight. Find the value of x, retaining the proper number of significant figures.

Laboratory Report Sheet--Gravimetric Analysis

Weight percent Silver ...Sample 1________________

Weight percent Silver ...Sample 2________________

Average weight percent Silver_____________

Average Deviation from expected value (accuracy)________________

Precision, expressed in %_________________

Average change in weight of copper wire_________________

Expected change in copper wire weight based on Ag analysis_________________

Precision, expressed in %________________

Balanced reaction for the electrochemical precipitation of silver

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Brief notation on possible systematic errors (approx. one paragraph)