

Experiments

To Accompany
Quantitative Chemical Analysis, 6th Edition (2002)
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1. Calibration of Volumetric Glassware	2
2. Gravimetric Determination of Calcium as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	3
3. Gravimetric Determination of Iron as Fe_2O_3	5
4. Penny Statistics	8
5. Statistical Evaluation of Acid-Base Indicators	15
6. Preparing Standard Acid and Base	18
7. Using a pH Electrode for an Acid-Base Titration	19
8. Analysis of a Mixture of Carbonate and Bicarbonate	22
9. Analysis of an Acid-Base Titration Curve: The Gran Plot	24
10. Kjeldahl Nitrogen Analysis	26
11. EDTA Titration of Ca^{2+} and Mg^{2+} in Natural Waters	29
12. Synthesis and Analysis of Ammonium Decavanadate	31
13. Iodimetric Titration of Vitamin C	35
14. Preparation and Iodometric Analysis of High-Temperature Superconductor	36
15. Potentiometric Halide Titration with Ag^+	40
16. Electrogravimetric Analysis of Copper	43
17. Polarographic Measurement of an Equilibrium Constant	44
18. Coulometric Titration of Cyclohexene with Bromine	46
19. Spectrophotometric Determination of Iron in Vitamin Tablets	48
20. Microscale Spectrophotometric Measurement of Iron in Foods by Standard Addition	50
21. Spectrophotometric Measurement of an Equilibrium Constant	52
22. Spectrophotometric Analysis of a Mixture: Caffeine and Benzoic Acid in Soft Drink	54
23. Mn^{2+} Standardization by EDTA Titration	57
24. Measuring Manganese in Steel by Spectrophotometry with Standard Addition	59
25. Measuring Manganese in Steel by Atomic Absorption Using a Calibration Curve	63
26. Properties of an Ion-Exchange Resin	66
27. Analysis of Sulfur in Coal by Ion Chromatography	69
28. Measuring Carbon Monoxide in Automobile Exhaust by Gas Chromatography	71
29. Amino Acid Analysis by Capillary Electrophoresis	73
30. DNA Composition by High-Performance Liquid Chromatography	77
31. Analysis of Analgesic Tablets by High-Performance Liquid Chromatography	80
32. Anion Content of Drinking Water by Capillary Electrophoresis	82

Experiments

Experiments described here illustrate major analytical techniques described in the textbook, *Quantitative Chemical Analysis*. Procedures are organized roughly in the same order as topics in the text. You are invited to download these instructions and reproduce them freely for use in your laboratory. References to many additional experiments published in recent years in the *Journal of Chemical Education* are listed at the ends of many chapters in the textbook.¹ Some of the experiments refer to the availability of standards or unknowns from Thorn Smith.²

Although these procedures are safe when carried out with reasonable care, *all chemical experiments are potentially hazardous*. Any solution that fumes (such as concentrated HCl), and all nonaqueous solvents, should be handled in a fume hood. Pipetting should never be done by mouth. Spills on your body should be flooded immediately with water and washed with soap and water; your instructor should be notified for possible further action. Spills on the benchtop should be cleaned immediately. Toxic chemicals should not be flushed down the drain. Your instructor should establish a procedure for disposing of each chemical that you use.

1. Calibration of Volumetric Glassware

An important trait of good analysts is the ability to extract the best possible data from their equipment. For this purpose, it is desirable to calibrate your own volumetric glassware (burets, pipets, flasks, etc.) to measure the exact volumes delivered or contained. This experiment also promotes improved technique in handling volumetric glassware. The procedure for calibrating a 50-mL buret is described at the end of Chapter 2 of the textbook.

Other volumetric glassware can also be calibrated by measuring the mass of water they contain or deliver. Glass transfer pipets and plastic micropipets can be calibrated by weighing the water delivered from them. A volumetric flask can be calibrated by weighing it empty and then weighing it filled to the mark with distilled water. Perform each procedure at least twice. Compare your results with the tolerances listed in tables in Chapter 2 of the textbook.

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1. You can search for experiments by key words in the index of the *Journal of Chemical Education*, at <http://jchemed.chem.wisc.edu/> on the Internet.
 2. Thorn Smith Inc., 7755 Narrow Gauge Road, Beulah, MI 49617. Phone: 231-882-4672; e-mail: www.thornsmithlabs.com. The following analyzed unknowns are available: Al-Mg alloy (for Al, Mg), Al-Zn alloy (for Al, Zn), Sb ore (for Sb), brasses (for Sn, Cu, Pb, Zn), calcium carbonate (for Ca), cast iron (for P, Mn, S, Si, C), cement (for Si, Fe, Al, Ca, Mg, S, ignition loss), Cr ore (for Cr), Cu ore (for Cu), copper oxide (for Cu), ferrous ammonium sulfate (for Fe), Fe ore (for Fe), iron oxide (for Fe), limestone (for Ca, Mg, Si, ignition loss), magnesium sulfate (for Mg), Mn ore (for Mn), Monel metal (for Si, Cu, Ni), nickel silver (for Cu, Ni, Zn), nickel oxide (for Ni), phosphate rock (for P), potassium hydrogen phthalate (for H⁺), silver alloys (for Ag, Cu, Zn, Ni), soda ash (for Na₂CO₃), soluble antimony (for Sb), soluble chloride, soluble oxalate, soluble phosphate, soluble sulfate, steels (for C, Mn, P, S, Si, Ni, Cr, Mo), Zn ore (for Zn). Primary standards are also available: potassium hydrogen phthalate (to standardize NaOH), As₂O₃ (to standardize I₂), CaCO₃ (to standardize EDTA), Fe(NH₄)₂(SO₄)₂ (to standardize dichromate or permanganate), K₂Cr₂O₇ (to standardize thiosulfate), AgNO₃, Na₂CO₃ (to standardize acid), NaCl (to standardize AgNO₃), Na₂C₂O₄ (to standardize KMnO₄).

2. Gravimetric Determination of Calcium as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ¹

Calcium ion can be analyzed by precipitation with oxalate in basic solution to form $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The precipitate is soluble in acidic solution because the oxalate anion is a weak base. Large, easily filtered, relatively pure crystals of product will be obtained if the precipitation is carried out slowly. This can be done by dissolving Ca^{2+} and $\text{C}_2\text{O}_4^{2-}$ in acidic solution and gradually raising the pH by thermal decomposition of urea (Reaction 27-2 in the textbook).

REAGENTS

Ammonium oxalate solution: Make 1 L of solution containing 40 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ plus 25 mL of 12 M HCl. Each student will need 80 mL of this solution.

Unknowns: Prepare 1 L of solution containing 15-18 g of CaCO_3 plus 38 mL of 12 M HCl. Each student will need 100 mL of this solution. Alternatively, solid unknowns are available from Thorn Smith.²

PROCEDURE

1. Dry three medium-porosity, sintered-glass funnels for 1–2 h at 105° C; cool them in a desiccator for 30 min and weigh them. Repeat the procedure with 30-min heating periods until successive weighings agree to within 0.3 mg. Use a paper towel or tongs, not your fingers, to handle the funnels. An alternative method of drying the crucible and precipitate is with a microwave oven.³ A 900-W kitchen microwave oven dries the crucible to constant mass in two heating periods of 4 min and 2 min (with 15 min allowed for cooldown after each cycle). You will need to experiment with your oven to find appropriate heating times.
2. Use a few small portions of unknown to rinse a 25-mL transfer pipet, and discard the washings. *Use a rubber bulb, not your mouth, to provide suction.* Transfer exactly 25 mL of unknown to each of three 250- to 400-mL beakers, and dilute each with ~75 mL of 0.1 M HCl. Add 5 drops of methyl red indicator solution (Table 12-4 in the textbook) to each beaker. This indicator is red below pH 4.8 and yellow above pH 6.0.
3. Add ~25 mL of ammonium oxalate solution to each beaker while stirring with a glass rod. Remove the rod and rinse it into the beaker. Add ~15 g of solid urea to each sample, cover it with a watchglass, and boil gently for ~30 min until the indicator turns yellow.
4. Filter each hot solution through a weighed funnel, using suction (Figure 2-15 in the textbook). Add ~3 mL of ice-cold water to the beaker, and use a rubber policeman to help transfer the remaining solid to the funnel. Repeat this procedure with small portions of ice-cold water until all of the precipitate has been transferred. Finally, use two 10-mL portions of ice-cold water to rinse each beaker, and pour the washings over the precipitate.
5. Dry the precipitate, first with aspirator suction for 1 min, then in an oven at 105° C for 1-2 h. Bring each filter to constant mass. The product is somewhat hygroscopic, so only one filter

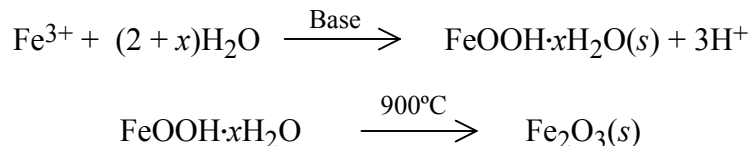
at a time should be removed from the desiccator, and weighings should be done rapidly. Alternatively, the precipitate can be dried in a microwave oven once for 4 min, followed by several 2-min periods, with cooling for 15 min before weighing. The water of crystallization is not lost.

6. Calculate the molarity of Ca^{2+} in the unknown solution or the weight percent of Ca in the unknown solid. Report the standard deviation and relative standard deviation (s/\bar{x} = standard deviation/average).

-
1. C. H. Hendrickson and P. R. Robinson, *J. Chem. Ed.* **1979**, *56*, 341.
 2. Thorn Smith Inc., 7755 Narrow Gauge Road, Beulah, MI 49617. Phone: 231-882-4672; e-mail: www.thornsmithlabs.com.
 3. R. Q. Thompson and M. Ghadiali, *J. Chem. Ed.* **1993**, *70*, 170.

3. Gravimetric Determination of Iron as Fe₂O₃¹

A sample containing iron can be analyzed by precipitation of the hydrous oxide from basic solution, followed by ignition to produce Fe₂O₃:



The gelatinous hydrous oxide can occlude impurities. Therefore, the initial precipitate is dissolved in acid and reprecipitated. Because the concentration of impurities is lower during the second precipitation, occlusion is diminished. Solid unknowns can be prepared from reagent ferrous ammonium sulfate or purchased from Thorn Smith.²

PROCEDURE

1. Bring three porcelain crucibles and caps to constant mass by heating to redness for 15 min over a burner (Figure 1). Cool for 30 min in a desiccator and weigh each crucible. Repeat this procedure until successive weighings agree within 0.3 mg. Be sure that all oxidizable substances on the entire surface of each crucible have burned off.

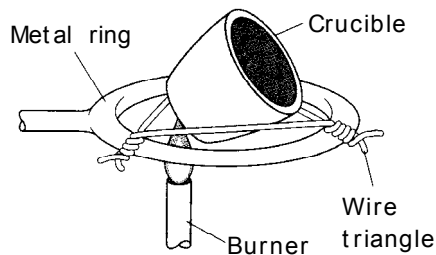


Figure 1. Positioning a crucible above a burner.

2. Accurately weigh three samples of unknown containing enough Fe to produce ~0.3 g of Fe₂O₃. Dissolve each sample in 10 mL of 3 M HCl (with heating, if necessary). If there are insoluble impurities, filter through qualitative filter paper and wash the filter very well with distilled water. Add 5 mL of 6 M HNO₃ to the filtrate, and boil for a few minutes to ensure that all iron is oxidized to Fe(III).
3. Dilute the sample to 200 mL with distilled water and add 3 M ammonia[†] with constant stirring until the solution is basic (as determined with litmus paper or pH indicator paper). Digest the precipitate by boiling for 5 min and allow the precipitate to settle. ([†] Basic reagents should not be stored in glass bottles because they will slowly dissolve the glass. If ammonia from a glass bottle is used, it may contain silica particles and should be freshly filtered.)

- Decant the supernatant liquid through coarse, ashless filter paper (Whatman 41 or Schleicher and Schnell Black Ribbon, as in Figures 2-16 and 2-17 in the textbook). Do not pour liquid higher than 1 cm from the top of the funnel. Proceed to Step 5 if a reprecipitation is desired. Wash the precipitate repeatedly with hot 1% NH_4NO_3 until little or no Cl^- is detected in the filtered supernate. (Test for Cl^- by acidifying a few milliliters of filtrate with 1 mL of dilute HNO_3 and adding a few drops of 0.1 M AgNO_3 .) Finally, transfer the solid to the filter with the aid of a rubber policeman and more hot liquid. Proceed to Step 6 if a reprecipitation is not used.
- Wash the gelatinous mass twice with 30 mL of boiling 1% aqueous NH_4NO_3 , decanting the supernate through the filter. Then put the filter paper back into the beaker with the precipitate, add 5 mL of 12 M HCl to dissolve the iron, and tear the filter paper into small pieces with a glass rod. Add ammonia with stirring and reprecipitate the iron. Decant through a funnel fitted with a fresh sheet of ashless filter paper. Wash the solid repeatedly with hot 1% NH_4NO_3 until little or no Cl^- is detected in the filtered supernate. Then transfer all the solid to the filter with the aid of a rubber policeman and more hot liquid.
- Allow the filter to drain overnight, if possible, protected from dust. Carefully lift the paper out of the funnel, fold it (Figure 2), and transfer it to a porcelain crucible that has been brought to constant mass.

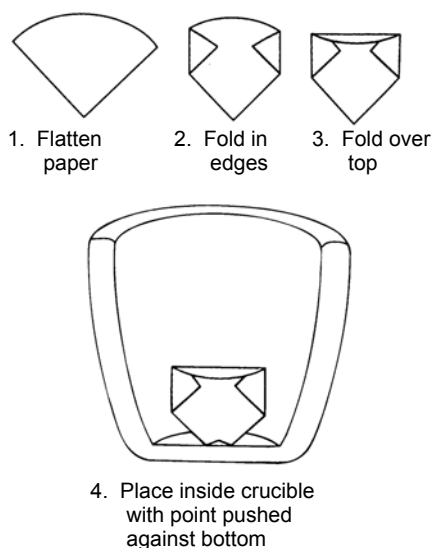


Figure 2. Folding filter paper and placing it inside a crucible for ignition. Continue folding paper so entire package fits at the bottom of the crucible. Be careful not to puncture the paper.

- Dry the crucible cautiously with a small flame, as shown in Figure 1. The flame should be directed at the top of the container, and the lid should be off. Avoid spattering. After it is dry, *char* the filter paper by increasing the flame temperature. The crucible should have free access to air to avoid reduction of iron by carbon. (The lid should be kept handy to smother the crucible if the paper inflames.) Any carbon left on the crucible or lid should be burned away by directing the burner flame at it. Use tongs to manipulate the crucible. Finally, *ignite* the product for 15 min with the full heat of the burner.

8. Cool the crucible briefly in air and then in a desiccator for 30 min. Weigh the crucible and the lid, reignite, and bring to constant mass (within 0.3 mg) with repeated heatings.
9. Calculate the weight percent of iron in each sample, the average, the standard deviation, and the relative standard deviation (s/\bar{x}).

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1. D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, 3d ed. (New York: Holt, Rinehart and Winston, 1976).
 2. Thorn Smith Inc., 7755 Narrow Gauge Road, Beulah, MI 49617. Phone: 231-882-4672; e-mail: www.thornsmithlabs.com.

4. Penny Stastics¹

U.S. pennies minted after 1982 have a Zn core with a Cu overlayer. Prior to 1982, pennies were made of brass, with a uniform composition (95 wt % Cu / 5 wt % Zn). In 1982, both the heavier brass coins and the lighter zinc coins were made. In this experiment, your class will weigh many coins and pool the data to answer the following questions: (1) Do pennies from different years have the same mass? (2) Do pennies from different mints have the same mass? (3) Do the masses follow a Gaussian distribution?

Gathering Data

Each student should collect and weigh enough pennies to the nearest milligram to provide a total set that contains 300 to 500 brass coins and a similar number of zinc coins. Instructions are given for a spreadsheet, but the same operations can be carried out with a calculator. Compile all the class data in a spreadsheet. Each column should list the masses of pennies from only one calendar year. Use the spreadsheet "sort" function to sort each column so that the lightest mass is at the top of the column and the heaviest is at the bottom. (To sort a column, click on the column heading to select the entire column, go to the DATA menu, select the SORT tool, and follow the directions that come up.) There will be two columns for 1982, in which both types of coins were made. Select a year other than 1982 for which you have many coins and divide the coins into those made in Denver (with a "D" beneath the year) and those minted in Philadelphia (with no mark beneath the year).

Discrepant Data

At the bottom of each column, compute the mean and standard deviation. Retain at least one extra digit beyond the milligram place to avoid round-off errors in your calculations.

Damaged or corroded coins may have masses different from those of the general population. Discard grossly discrepant masses lying ≥ 4 standard deviations from the mean in any one year. (For example, if one column has an average mass of 3.000 g and a standard deviation of 0.030 g, the 4-standard-deviation limit is $\pm(4 \times 0.030) = \pm 0.120$ g. A mass that is ≤ 2.880 or ≥ 3.120 g should be discarded.) After rejecting discrepant data, recompute the average and standard deviation for each column.

Confidence Intervals and t Test

Select the two years (≥ 1982) in which the zinc coins have the highest and lowest average masses. For each of the two years, compute the 95% confidence interval. Use the t test to compare the two mean values at the 95% confidence level. Are the two average masses significantly different? Try the same for two years of brass coins (≤ 1982). Try the same for the one year whose coins you segregated into those from Philadelphia and those from Denver. Do the two mints produce coins with the same mass?

Distribution of Masses

List the masses of all pennies made in or after 1983 in a single column, sorted from lowest to highest mass. There should be at least 300 masses listed. Divide the data into 0.01-g intervals

(e.g., 2.480 to 2.489 g) and prepare a bar graph, like that shown in Figure 1. Find the mean \bar{x} , median, and standard deviation (s) for all coins in the graph. For random (Gaussian) data, only 3 out of 1 000 measurements should lie outside of $\bar{x} \pm 3s$. Indicate which bars (if any) lie beyond $\pm 3s$. In Figure 1 two bars at the right are outside of $\bar{x} \pm 3s$.

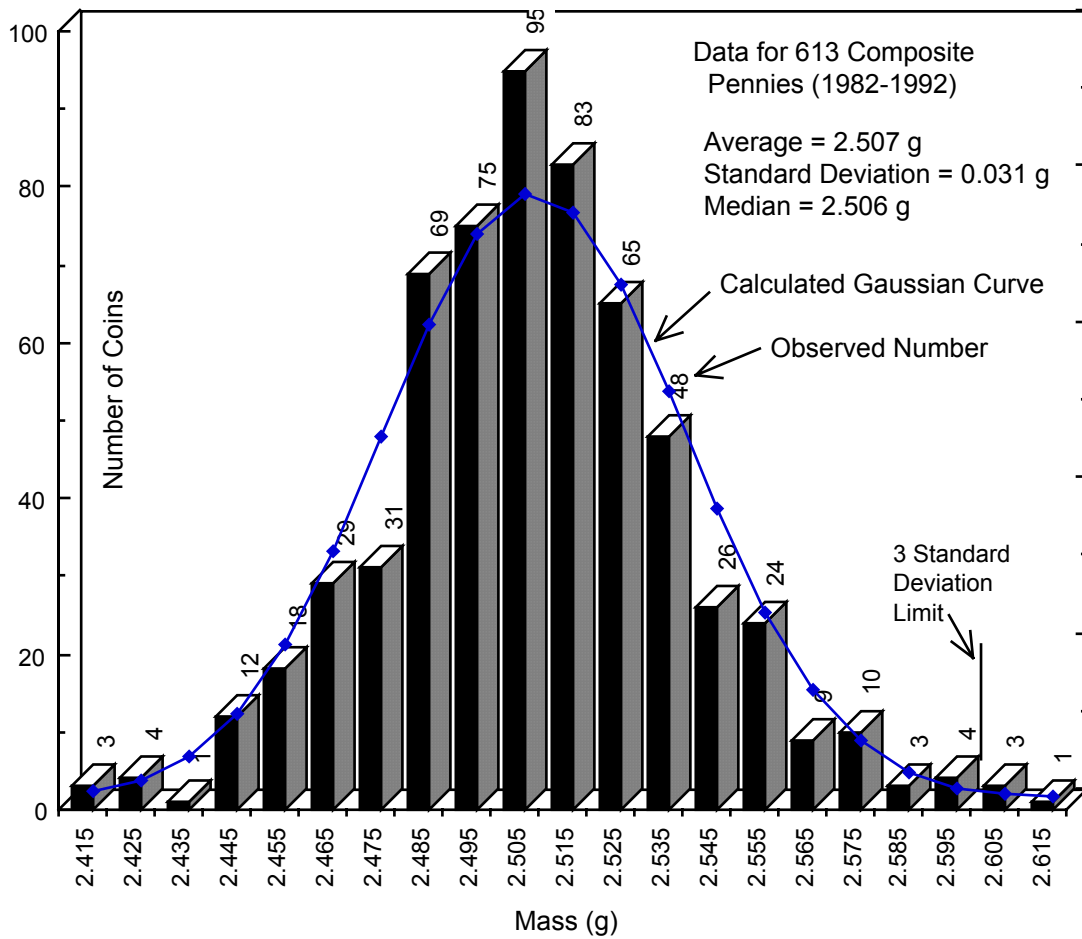


Figure 1. Distribution of penny masses from the years 1982 to 1992 measured in Dan's house by Jimmy Kusznir and Doug Harris in December 1992.

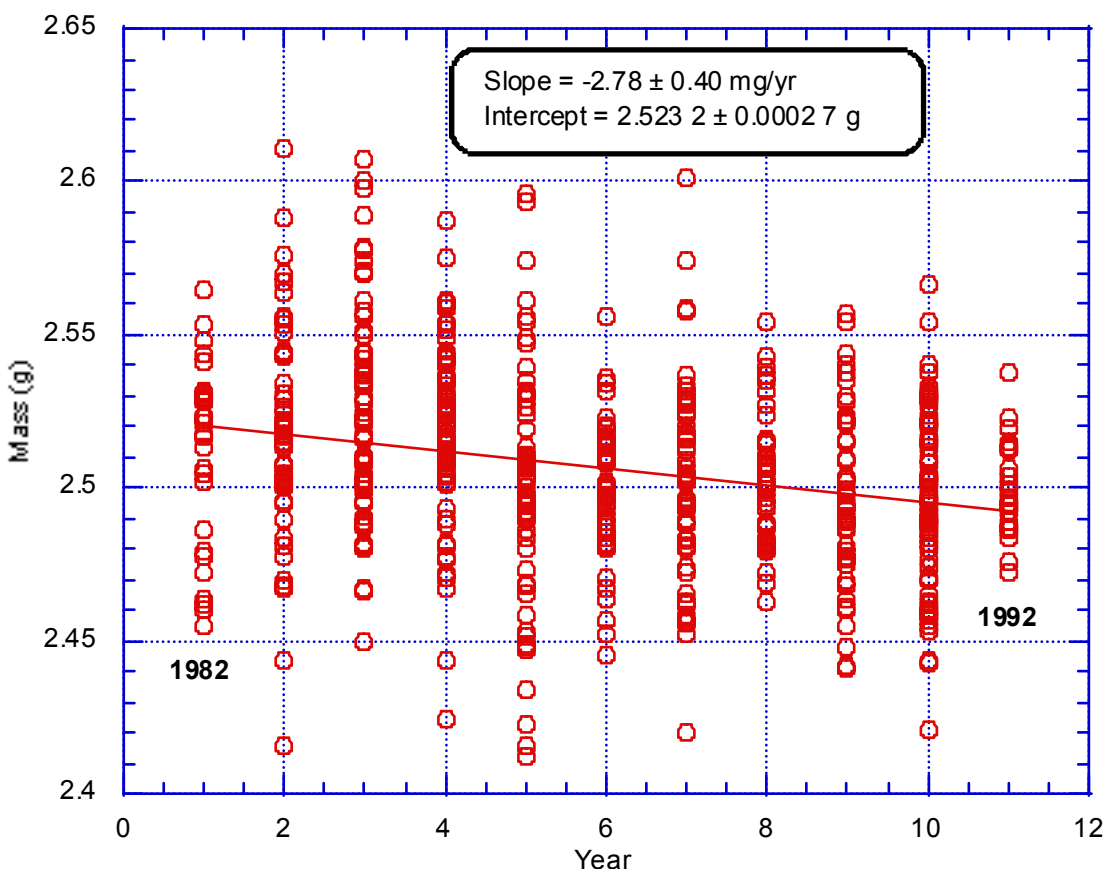


Figure 2. Penny mass versus year for 612 coins. Because the slope of the least-squares line is *significantly* less than 0, we conclude that the average mass of older pennies is greater than the average mass of newer pennies.

Least-Squares Analysis: Do Pennies Have the Same Mass Each Year?

Prepare a graph like Figure 2 in which the ordinate (y -axis) is the mass of zinc pennies minted each year since 1982 and the abscissa (x -axis) is the year. For simplicity, let 1982 be year 1, 1983 be year 2, and so on. If the mass of a penny increases systematically from year to year, then the least-squares line through the data will have a positive slope. If the mass decreases, the slope will be negative. If the mass is constant, the slope will be 0. Even if the mass is really constant, your selection of coins is random and the slope is not exactly 0.

We want to know whether the slope is *significantly* different from zero. Suppose that you have data for 14 years. Enter all of the data into two columns of the least-squares spreadsheet in Figure 5-9 in the textbook. Column B (x_i) is the year (1 to 14) and column C (y_i) is the mass of each penny. Your table will have several hundred entries. (If you are not using a spreadsheet, just tabulate the average mass for each year. Your table will have only 14 entries.) Calculate the slope (m) and intercept (b) of the best straight line through all points and find the uncertainties in slope (s_m) and intercept (s_b).

Use Student's t to find the 95% confidence interval for the slope:

$$\text{confidence interval for slope} = m \pm ts_m \quad (1)$$

where Student's t is for $n-2$ degrees of freedom. For example, if you have $n = 300$ pennies, $n-2 = 298$, and it would be reasonable to use the value of $t (= 1.960)$ at the bottom of the table for $n = \infty$. If the least-squares slope is $m \pm s_m = -2.78 \pm 0.40$ mg/year, then the 95% confidence interval is $m \pm ts_m = -2.78 \pm (1.960)(0.40) = -2.78 \pm 0.78$ mg/year.

The 95% confidence interval is $-2.78 \pm 0.78 = -3.56$ to -2.00 mg/year. We are 95% confident that the true slope is in this range and is, therefore, *not* 0. We conclude that older zinc pennies are heavier than newer zinc pennies.

Does the Distribution of Masses Follow a Gaussian Distribution?

The smooth Gaussian curve superimposed on the data in Figure 1 was calculated from the formula

$$y_{\text{calc}} = \frac{\text{number of coins}/100}{s \sqrt{2\pi}} e^{-(x-\bar{x})^2/2s^2} \quad (2)$$

Now we carry out a χ^2 test (pronounced “ki squared”) to see if the observed distribution (the bars in Figure 1) agrees with the Gaussian curve. The statistic χ^2 is given by

$$\chi^2 = \sum \frac{(y_{\text{obs}} - y_{\text{calc}})^2}{y_{\text{calc}}} \quad (3)$$

where y_{obs} is the height of a bar on the chart, y_{calc} is the ordinate of the Gaussian curve (Equation 2), and the sum extends over all bars in the graph. The calculations for the data in Figure 1 are shown in Table 1.

At the bottom of Table 1 we see that χ^2 for all 21 bars is 43.231. In Table 2 we find a critical value of 31.4 for 20 degrees of freedom (degrees of freedom = one less than number of categories). Because χ^2 from Equation 2 exceeds the critical value, we conclude that *the distribution is not Gaussian*.

It would be reasonable to omit the smallest bars at the edge of the graph from the calculation of χ^2 because these bars contain the fewest observations but make large contributions to χ^2 . Suppose that we reject bars lying >3 standard deviations from the mean. This removes the two bars at the right side of Figure 1 which give the last two entries in Table 1. Omitting these two points gives $\chi^2 = 30.277$, which is still greater than the critical value of 28.9 for 18 degrees of freedom in Table 2. Our conclusion is that at the 95% confidence level the observed distribution in Figure 1 is not quite Gaussian. It is possible that exceptionally light coins are nicked and exceptionally heavy coins are dirty or corroded. You would need to inspect these coins to verify this hypothesis.

Table 1. Calculation of χ^2 for Figure 1

Mass (g)	Observed number of coins	Calculated ordinate of Gaussian curve	$y_{\text{obs}} - y_{\text{calc}}$	$\frac{(y_{\text{obs}} - y_{\text{calc}})^2}{y_{\text{calc}}}$
(x)	(y_{obs})	(y_{calc})		
2.415	3	1.060	1.940	3.550
2.425	4	2.566	1.434	0.801
2.435	1	5.611	-4.611	3.789
2.445	12	11.083	0.917	0.076
2.455	18	19.776	-1.776	0.159
2.465	29	31.875	-2.875	0.259
2.475	31	46.409	-15.409	5.116
2.485	69	61.039	7.961	1.038
2.495	75	72.519	2.481	0.085
2.505	95	77.829	17.171	3.788
2.515	83	75.453	7.547	0.755
2.525	65	66.077	-1.077	0.176
2.535	48	52.272	-4.272	0.349
2.545	26	37.354	-11.354	3.451
2.555	24	24.112	-0.112	0.001
2.565	9	14.060	-5.060	1.821
2.575	10	7.406	2.594	0.909
2.585	3	3.524	-0.524	0.078
2.595	4	1.515	2.485	4.076
2.605	3	0.588	2.412	9.894
2.615	1	0.206	0.794	3.060

χ^2 (all 21 points) = **43.231**

χ^2 (19 points — omitting bottom two points) = **30.277**

Table 2. Critical values of χ^2 that will be exceeded in 5% of experiments*

Degrees of freedom	Critical value	Degrees of freedom	Critical value	Degrees of freedom	Critical value
1	3.84	11	19.7	21	32.7
2	5.99	12	21.0	22	33.9
3	7.81	13	22.4	23	35.2
4	9.49	14	23.7	24	36.4
5	11.1	15	25.0	25	37.7
6	12.6	16	26.3	26	38.9
7	14.1	17	27.6	27	40.1
8	15.5	18	28.9	28	41.3
9	16.9	19	30.1	29	42.6
10	18.3	20	31.4	30	43.8

**Example:* The value of χ^2 from 15 observations is 17.2. This value is less than 23.7 listed for 14 (= 15-1) degrees of freedom. Because χ^2 does not exceed the critical value, the observed distribution is consistent with the theoretical distribution.

Reporting Your Results

Gathering data:

1. Attach a table of masses, with one column sorted by mass for each year.
2. Divide 1982 into two columns, one for light (zinc) and one for heavy (brass) pennies.
3. One year should be divided into one column from Denver and one from Philadelphia.

Discrepant data:

1. List the mean (\bar{x}) and standard deviation (s) for each column.
2. Discard data that lie outside of $\bar{x} \pm 4s$ and recompute \bar{x} and s .

Confidence intervals and t test:

1. For the year ≥ 1982 with highest average mass:

$$95\% \text{ confidence interval } (= \bar{x} \pm ts/\sqrt{n}) = \underline{\hspace{2cm}}$$

For the year ≥ 1982 with lowest average mass:

$$95\% \text{ confidence interval } = \underline{\hspace{2cm}}$$

Comparison of means with t -test:

$$t_{\text{calculated}} = \underline{\hspace{2cm}}$$

$$t_{\text{table}} = \underline{\hspace{2cm}}$$

Is the difference significant? $\underline{\hspace{2cm}}$

2. For the year ≤ 1982 with highest average mass:
 95% confidence interval = _____
 For the year ≤ 1982 with lowest average mass:
 95% confidence interval = _____
 Comparison of means with t test:
 $t_{\text{calculated}} =$ _____
 $t_{\text{table}} =$ _____
 Is the difference significant? _____
3. For Philadelphia versus Denver coins in one year:
 Philadelphia 95% confidence interval = _____
 Denver 95% confidence interval = _____
 Comparison of means with t test:
 $t_{\text{calculated}} =$ _____
 $t_{\text{table}} =$ _____
 Is the difference significant? _____

Gaussian distribution of masses:

Prepare a graph analogous to Figure 1 with labels showing the $\pm 3s$ limits.

Least-squares Analysis:

Prepare a graph analogous to Figure 2 and find the least-squares slope and intercept and their standard deviations.

$m \pm s_m =$ _____

$t_{95\% \text{ confidence}} =$ _____ $t_{99\% \text{ confidence}} =$ _____

95% confidence: $m \pm ts_m =$ _____.

Does interval include zero? _____

99% confidence: $m \pm ts_m =$ _____.

Does interval include 0? _____

Is there a systematic increase or decrease of penny mass with year? _____

χ^2 test:

Write Equation 2 for the smooth Gaussian curve that fits your bar graph.

Construct a table analogous to Table 1 to compute χ^2 for the complete data set.

Computed value of $\chi^2 =$ _____ Degrees of freedom = _____

Critical value of $\chi^2 =$ _____

Do the data follow a Gaussian distribution? _____

Now omit bars on the graph that are greater than 3 standard deviations away from the mean and calculate a new value of χ^2 with the reduced data set.

Computed value of $\chi^2 =$ _____ Degrees of freedom = _____

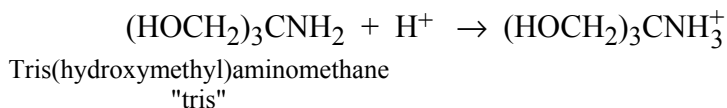
Critical value of $\chi^2 =$ _____

Does the reduced data set follow a Gaussian distribution? _____

1. T. H. Richardson, *J. Chem. Ed.* **1991**, 68, 310. In a related experiment, students measure the mass of copper in the penny as a function of the year of minting: R. J. Stolzberg, *J. Chem. Ed.* **1998**, 75, 1453.

5. Statistical Evaluation of Acid-Base Indicators

This experiment introduces you to the use of indicators and to the statistical concepts of mean, standard deviation, Q test, and t test.¹ You will compare the accuracy of different indicators in locating the end point in the titration of the base "tris" with hydrochloric acid:



REAGENTS

~0.1 M HCl: Each student needs ~500 mL of unstandardized solution, all from a single batch that will be analyzed by the whole class.

Tris: Solid, primary standard powder should be available (~4 g/student).

Indicators: Bromothymol blue (BB), methyl red (MR), bromocresol green (BG), methyl orange (MO), and erythrosine (E) should be available in dropper bottles. See Table 12-4 in the textbook for their preparation.

Color changes to use for the titration of tris with HCl are

BB: blue (pH 7.6) → yellow (pH 6.0) (end point is disappearance of green)

MR: yellow (pH 6.0) → red (pH 4.8) (end point is disappearance of orange)

BG: blue (pH 5.4) → yellow (pH 3.8) (end point is green)

MO: yellow (pH 4.4) → red (pH 3.1) (end point is first appearance of orange)

E: red (pH 3.6) → orange (pH 2.2) (end point is first appearance of orange)

PROCEDURE

Each student should carry out the following procedure with *one* of the indicators. Different students should be assigned different indicators so that at least four students evaluate each of the indicators.

1. Calculate the molecular mass of tris and the mass required to react with 35 mL of 0.10 M HCl. Weigh this much tris into a 125-mL flask.
2. It is good practice to rinse a buret with a new solution to wash away traces of previous reagents. Wash your 50-mL buret with three 10-mL portions of 0.1 M HCl and discard the washings. Tilt and rotate the buret so that the liquid washes the walls, and drain the liquid through the stopcock. Then fill the buret with 0.1 M HCl to near the 0-mL mark, allow a minute for the liquid to settle, and record the reading to the nearest 0.01 mL.

1. D. T. Harvey, *J. Chem. Ed.* **1991**, *68*, 329.

3. The first titration will be rapid, to allow you to find the approximate end point of the titration. Add ~20 mL of HCl from the buret to the flask and swirl to dissolve the tris. Add 2–4 drops of indicator and titrate with ~1-mL aliquots of HCl to find the end point.
4. From the first titration, calculate how much tris is required to cause each succeeding titration to require 35–40 mL of HCl. Weigh this much tris into a clean flask. Refill your buret to near 0 mL and record the reading. Repeat the titration in Step 3, but use 1 drop at a time near the end point. When you are very near the end point, use less than a drop at a time. To do this, carefully suspend a fraction of a drop from the buret tip and touch it to the inside wall of the flask. Carefully tilt the flask so that the bulk solution overtakes the droplet and then swirl the flask to mix the solution. Record the total volume of HCl required to reach the end point to the nearest 0.01 mL. Calculate the true mass of tris with the buoyancy equation 2-1 in the textbook (density of tris = 1.327 g/mL). Calculate the molality of HCl.
5. Repeat the titration to obtain at least six accurate measurements of the HCl molarity.
6. Use the Q test in Section 4-6 in the textbook) to decide whether any results should be discarded. Report your retained values, their mean, their standard deviation, and the relative standard deviation (s/\bar{x}).

DATA ANALYSIS

Pool the data from your class to fill in Table 1, which shows two possible results. The quantity s_x is the standard deviation of all results reported by many students. The pooled standard deviation, s_p , is derived from the standard deviations reported by each student. If two students see the end point differently, each result might be very reproducible, but their reported molarities will be different. Together, they will generate a large value of s_x (because their results are so different), but a small value of s_p (because each one was reproducible).

Select the pair of indicators giving average HCl molarities that are farthest apart. Use the t test (Equation 4-8 in the textbook) to decide whether the average molarities are significantly different from each other at the 95% confidence level. When you calculate the pooled standard deviation for Equation 4-8, the values of s_1 and s_2 in Equation 4-9 in the textbook are the values of s_x (not s_p) in Table 1. A condition for using Equations 4-8 and 4-9 is that the standard deviations for the two sets of measurements should not be “significantly different” from each other. Use the F test in Section 4-4 in the textbook to decide whether or not the standard deviations are significantly different. If they are significantly different, use Equations 4-8a and 4-9a for the t test.

Select the pair of indicators giving the second most different molarities and use the t test again to see whether or not this second pair of results is significantly different.

Table 1. Pooled data

Indicator	Number of measurements	Number of students	Mean HCl molarity (M) ^a		Relative standard deviation (%)	
	(<i>n</i>)	(<i>S</i>)	(\bar{x})	s_x (M) ^b	$100 s_x / \bar{x}$	s_p (M) ^c
BB	28	5	0.095 65	0.002 25	2.35	0.001 09
MR						
BG	29	4	0.086 41	0.001 13	1.31	0.000 99
MO						
E						

a. Computed from all values that were not discarded with the *Q* test.

b. s_x = standard deviation of all *n* measurements (degrees of freedom = *n* – 1)

c. s_p = pooled standard deviation for *S* students (degrees of freedom = *n* – *S*). Computed with the equation

$$s_p = \sqrt{\frac{s_1^2(n_1-1) + s_2^2(n_2-1) + s_3^2(n_3-1) + \dots}{n-S}}$$

where there is one term in the numerator for each student using that indicator.

REPORTING YOUR RESULTS

Your Individual Data

Trial	Mass of tris from balance (g)	True mass corrected for buoyancy (g)	HCl volume (mL)	Calculated HCl molarity (M)
1				
2				
3				
4				
5				
6				

On the basis of the *Q* test, should any molarity be discarded? If so, which one? _____

Mean value of retained results: _____

Standard deviation: _____

Relative standard deviation (%): _____

Pooled Class Data

1. Attach your copy of Table 1 with all entries filled in.
2. Compare the two most different molarities in Table 1. (Show your *F* and *t* tests and state your conclusion.)
3. Compare the two second most different molarities in Table 1.

6. Preparing Standard Acid and Base

Procedures for preparing standard 0.1 M HCl and standard 0.1 M NaOH are described at the end of Chapter 12 of the textbook. Unknown samples of sodium carbonate or potassium hydrogen phthalate (available from Thorn Smith¹) can be analyzed by the procedures described in this section.

1. Thorn Smith Inc., 7755 Narrow Gauge Road, Beulah, MI 49617. Phone: 231-882-4672;
e-mail: www.thornsmithlabs.com.

7. Using a pH Electrode for an Acid-Base Titration

In this experiment you will use a pH electrode to follow the course of an acid-base titration. You will observe how pH changes slowly during most of the reaction and rapidly near the equivalence point. You will compute the first and second derivatives of the titration curve to locate the end point. From the mass of unknown acid or base and the moles of titrant, you can calculate the molecular mass of the unknown. Section 12-5 of the textbook provides background for this experiment.

REAGENTS

Standard 0.1 M NaOH and standard 0.1 M HCl: From Experiment 6.

Bromocresol green and phenolphthalein indicators: See Table 12-4 in the textbook.

pH calibration buffers: pH 7 and pH 4. Use commercial standards.

Unknowns: Unknowns should be stored in a desiccator by your instructor.

Suggested acid unknowns: potassium hydrogen phthalate (Table 12-5, FM 204.23), 2-(*N*-morpholino)ethanesulfonic acid (MES, Table 10-2, FM 195.24), imidazole hydrochloride (Table 10-2, FM 104.54, hygroscopic), potassium hydrogen iodate (Table 12-5, FM 389.91).

Suggested base unknowns: tris (Table 12-5, FM 121.14), imidazole (FM 68.08), disodium hydrogen phosphate (Na_2HPO_4 , FM 141.96), sodium glycinate (may be found in chemical catalogs as glycine, sodium salt hydrate, $\text{H}_2\text{NCH}_2\text{CO}_2\text{Na}\cdot x\text{H}_2\text{O}$, FM 97.05 + $x(18.015)$). For sodium glycinate, one objective of the titration is to find the number of waters of hydration from the molecular mass.

PROCEDURE

1. Your instructor will recommend a mass of unknown (5-8 mmol) for you to weigh accurately and dissolve in distilled water in a 250-mL volumetric flask. Dilute to the mark and mix well.
2. Following instructions for your particular pH meter, calibrate a meter and glass electrode, using buffers with pH values near 7 and 4. Rinse the electrodes well with distilled water and blot them dry with a tissue before immersing in any new solution.
3. The first titration is intended to be rough, so that you will know the approximate end point in the next titration. For the rough titration, pipet 25.0 mL of unknown into a 125-mL flask. If you are titrating an unknown acid, add 3 drops of phenolphthalein indicator and titrate with standard 0.1 M NaOH to the pink end point, using a 50-mL buret. If you are titrating an unknown base, add 3 drops of bromocresol green indicator and titrate with standard 0.1 M HCl to the green end point. Add 0.5 mL of

titrant at a time so that you can estimate the equivalence volume to within 0.5 mL. Near the end point, the indicator temporarily changes color as titrant is added. If you recognize this, you can slow down the rate of addition and estimate the end point to within a few drops.

4. Now comes the careful titration. Pipet 100.0 mL of unknown solution into a 250-mL beaker containing a magnetic stirring bar. Position the electrode(s) in the liquid so that the stirring bar will not strike the electrode. If a combination electrode is used, the small hole near the bottom on the side must be immersed in the solution. This hole is the salt bridge to the reference electrode. Allow the electrode to equilibrate for 1 min with stirring and record the pH.
5. Add 1 drop of indicator and begin the titration. The equivalence volume will be four times greater than it was in Step 3. Add ~1.5-mL aliquots of titrant and record the exact volume, the pH, and the color 30 s after each addition. When you are within 2 mL of the equivalence point, add titrant in 2-drop increments. When you are within 1 mL, add titrant in 1-drop increments. Continue with 1-drop increments until you are 0.5 mL past the equivalence point. The equivalence point has the most rapid change in pH. Add five more 1.5-mL aliquots of titrant and record the pH after each.

DATA ANALYSIS

1. Construct a graph of pH versus titrant volume. Mark on your graph where the indicator color change(s) was (were) observed.
2. Following the example in Table 12-3 and Figure 12-6 of the textbook, compute the first derivative (the slope, $\Delta\text{pH}/\Delta V$) for each data point within ± 1 mL of the equivalence volume. From your graph, estimate the equivalence volume as accurately as you can, as shown in Figure 1.

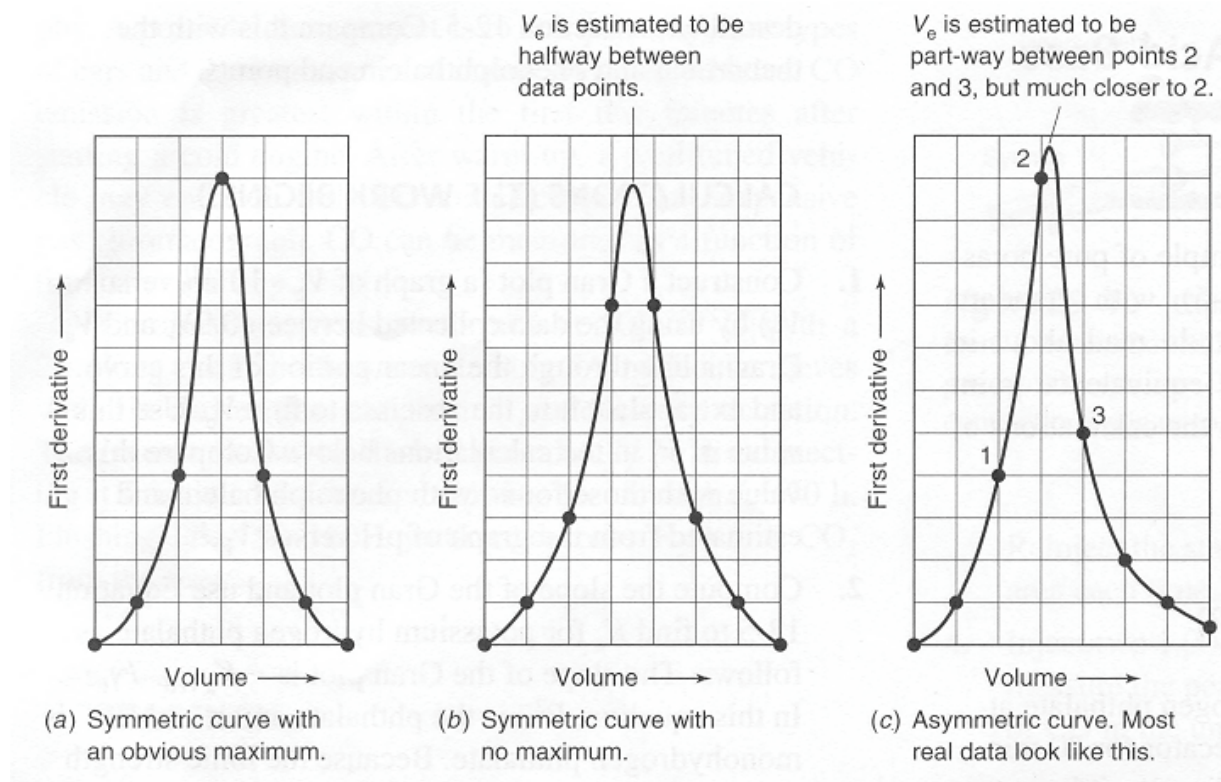
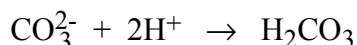
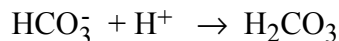


Figure 1. Examples of locating the maximum position of the first derivative of a titration curve.

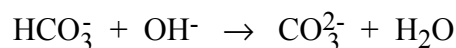
3. Following the example in Table 12-3, compute the second derivative (the slope of the slope, $\Delta(\text{slope})/\Delta V$). Prepare a graph like Figure 12-7 and locate the equivalence volume as accurately as you can.
4. Go back to your graph from Step 1 and mark where the indicator color changes were observed. Compare the indicator end point to the end point estimated from the first and second derivatives.
5. From the equivalence volume and the mass of unknown, calculate the molecular mass of the unknown.

8. Analysis of a Mixture of Carbonate and Bicarbonate

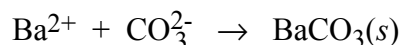
This procedure involves two titrations. First, total alkalinity ($= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$) is measured by titrating the mixture with standard HCl to a bromocresol green end point:



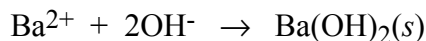
A separate aliquot of unknown is treated with excess standard NaOH to convert HCO_3^- to CO_3^{2-} :



Then all the carbonate is precipitated with BaCl_2 :



The excess NaOH is immediately titrated with standard HCl to determine how much HCO_3^- was present. A blank titration is required for the Ba^{2+} addition because Ba^{2+} precipitates some of the NaOH:



From the total alkalinity and bicarbonate concentration, you can calculate the original carbonate concentration.

REAGENTS

Standard 0.1 M NaOH and standard 0.1 M HCl: From Experiment 6.

CO₂-free water: Boil 500 mL of distilled water to expel CO₂ and pour the water into a 500-mL plastic bottle. Screw the cap on tightly and allow the water to cool to room temperature. Keep tightly capped when not in use.

10 wt % aqueous BaCl₂: 35 mL/student.

Bromocresol green and phenolphthalein indicators: See Table 12-4 in the textbook.

Unknowns: Solid unknowns (2.5 g/student) can be prepared from reagent-grade sodium carbonate or potassium carbonate and bicarbonate. Unknowns should be stored in a desiccator but should not be heated. Heating at 50°–100°C converts NaHCO₃ to Na₂CO₃.

PROCEDURE

1. Accurately weigh 2.0–2.5 g of unknown into a 250-mL volumetric flask by weighing the sample in a capped weighing bottle, delivering some to a funnel in the volumetric flask, and reweighing the bottle. Continue this process until the desired mass of reagent has been transferred to the funnel. Rinse the funnel repeatedly with small portions of CO₂-free water to dissolve the sample. Remove the funnel, dilute to the mark, and mix well.
2. *Total alkalinity:* Pipet a 25.00-mL aliquot of unknown solution into a 250-mL flask and titrate with standard 0.1 M HCl, using bromocresol green indicator as in Experiment 6 for standardizing HCl. Repeat this procedure with two more 25.00-mL aliquots.
3. *Bicarbonate content:* Pipet 25.00 mL of unknown and 50.00 mL of standard 0.1 M NaOH into a 250-mL flask. Swirl and add 10 mL of 10 wt % BaCl₂, using a graduated cylinder. Swirl again to precipitate BaCO₃, add 2 drops of phenolphthalein indicator, and immediately titrate with standard 0.1 M HCl. Repeat this procedure with two more 25.00-mL samples of unknown.
4. *Blank titration:* Titrate with standard 0.1 M HCl a mixture of 25 mL of water, 10 mL of 10 wt % BaCl₂, and 50.00 mL of standard 0.1 M NaOH. Repeat this procedure twice more. The difference in moles of HCl needed in steps 4 and 3 equals the moles of bicarbonate in the mixture.
5. From the results of step 2, calculate the total alkalinity and its standard deviation. From the results of steps 3 and 4, calculate the bicarbonate concentration and its standard deviation. Using the standard deviations as estimates of uncertainty, calculate the concentration (and uncertainty) of carbonate in the sample. Express the composition of the solid unknown in a form such as 63.4 (±0.5) wt % K₂CO₃ and 36.6 (±0.2) wt % NaHCO₃.

9. Analysis of an Acid-Base Titration Curve: The Gran Plot

In this experiment, you will titrate a sample of pure potassium hydrogen phthalate (Table 12-5) with standard NaOH. The Gran plot (which you should read about in Section 12-5) will be used to find the equivalence point and K_a . Activity coefficients are used in the calculations of this experiment.

PROCEDURE (AN EASY MATTER)

1. Dry about 1.5 g of potassium hydrogen phthalate at 105° C for 1 h and cool it in a desiccator for 20 min. Accurately weigh out ~1.5 g and dissolve it in water in a 250-mL volumetric flask. Dilute to the mark and mix well.
2. Following the instructions for your particular pH meter, calibrate a meter and glass electrode using buffers with pH values near 7 and 4. Rinse the electrode well with distilled water and blot it dry with a tissue before immersing in a solution.
3. Pipet 100.0 mL of phthalate solution into a 250-mL beaker containing a magnetic stirring bar. Position the electrode in the liquid so that the stirring bar will not strike the electrode. The small hole near the bottom on the side of the combination pH electrode must be immersed in the solution. This hole is the reference electrode salt bridge. Allow the electrode to equilibrate for 1 min (with stirring) and record the pH.
4. Add 1 drop of phenolphthalein indicator (Table 12-4) and titrate the solution with standard ~0.1 M NaOH. Until you are within 4 mL of the theoretical equivalence point, add base in ~1.5-mL aliquots, recording the volume and pH 30 s after each addition. Thereafter, use 0.4-mL aliquots until you are within 1 mL of the equivalence point. After that, add base 1 drop at a time until you have passed the pink end point by a few tenths of a milliliter. (Record the volume at which the pink color is observed.) Then add five more 1-mL aliquots.
5. Construct a graph of pH versus V_b (volume of added base). Locate the equivalence volume (V_e) as the point of maximum slope or zero second derivative, as described in Section 12-5. Compare this with the theoretical and phenolphthalein end points.

CALCULATIONS (THE WORK BEGINS!)

1. Construct a Gran plot (a graph of $V_b 10^{-\text{pH}}$ versus V_b) by using the data collected between $0.9V_e$ and V_e . Draw a line through the linear portion of this curve and extrapolate it to the abscissa to find V_e . Use this value of V_e in the calculations below. Compare this value with those found with phenolphthalein and estimated from the graph of pH versus V_b .
2. Compute the slope of the Gran plot and use Equation 12-5 to find K_a for potassium hydrogen phthalate as follows: The slope of the Gran plot is $-K_a \gamma_{\text{HP}^-} / \gamma_{\text{P}^{2-}}$. In this equation, P^{2-} is the phthalate anion and HP^- is monohydrogen phthalate. Because the ionic strength changes slightly as the titration proceeds, so also do the activity coefficients. Calculate the

ionic strength at $0.95V_e$, and use this "average" ionic strength to find the activity coefficients.

EXAMPLE Calculating Activity Coefficients

Find γ_{HP^-} and $\gamma_{\text{P}^{2-}}$ at $0.95V_e$ in the titration of 100.0 mL of 0.0200 M potassium hydrogen phthalate with 0.100 M NaOH.

Solution The equivalence point is 20.0 mL, so $0.95V_e = 19.0$ mL. The concentrations of H^+ and OH^- are negligible compared with those of K^+ , Na^+ , HP^- , and P^{2-} , whose concentrations are

$$[\text{K}^+] = \left(\frac{100}{119}\right)(0.0200) = 0.0168 \text{ M}$$

$$[\text{Na}^+] = \left(\frac{100}{119}\right)(0.100) = 0.0160 \text{ M}$$

$$[\text{HP}^-] = (0.050)\left(\frac{100}{119}\right)(0.0200) = 0.00084 \text{ M}$$

$$[\text{P}^{2-}] = (0.95)\left(\frac{100}{119}\right)(0.0200) = 0.0160 \text{ M}$$

The ionic strength is

$$\begin{aligned}\mu &= \frac{1}{2} \sum c_i z_i^2 \\ &= \frac{1}{2} [(0.0168) \cdot 1^2 + (0.0160) \cdot 1^2 + (0.00084) \cdot 1^2 + (0.0160) \cdot 2^2] = 0.0488 \text{ M}\end{aligned}$$

To estimate $\gamma_{\text{P}^{2-}}$ and γ_{HP^-} at $\mu = 0.0488 \text{ M}$, interpolate in Table 8-1. In this table, we find that the hydrated radius of P^{2-} —phthalate, $\text{C}_6\text{H}_4(\text{CO}_2^-)_2$ —is 600 pm. The size of HP^- is not listed, but we will suppose that it is also 600 pm. An ion with charge ± 2 and a size of 600 pm has $\gamma = 0.485$ at $\mu = 0.05 \text{ M}$ and $\gamma = 0.675$ at $\mu = 0.01 \text{ M}$. Interpolating between these values, we estimate $\gamma_{\text{P}^{2-}} = 0.49$ when $\mu = 0.0488 \text{ M}$. Similarly, we estimate $\gamma_{\text{HP}^-} = 0.84$ at this same ionic strength.

-
3. From the measured slope of the Gran plot and the values of γ_{HP^-} and $\gamma_{\text{P}^{2-}}$, calculate $\text{p}K_a$. Then choose an experimental point near $\frac{1}{3}V_e$ and one near $\frac{2}{3}V_e$. Use Equation 10-18 to find $\text{p}K_a$ with each point. (You will have to calculate $[\text{P}^{2-}]$, $[\text{HP}^-]$, $\gamma_{\text{P}^{2-}}$, and γ_{HP^-} at each point.) Compare the average value of $\text{p}K_a$ from your experiment with $\text{p}K_2$ for phthalic acid listed in Appendix G.

10. Kjeldahl Nitrogen Analysis

The Kjeldahl nitrogen analysis is widely used to measure the nitrogen content of pure organic compounds and complex substances such as milk, cereal, and flour. Digestion in boiling H_2SO_4 with a catalyst converts organic nitrogen into NH_4^+ . The solution is then made basic, and the liberated NH_3 is distilled into a known amount of HCl (Reactions 7-3 to 7-5 in the textbook). Unreacted HCl is titrated with NaOH to determine how much HCl was consumed by NH_3 . Because the solution to be titrated contains both HCl and NH_4^+ , we choose an indicator that permits titration of HCl without beginning to titrate NH_4^+ . Bromocresol green, with a transition range of pH 3.8 to 5.4, fulfills this purpose.

The Kjeldahl digestion captures amine ($-\text{NR}_2$) or amide ($-\text{C}[\text{=O}]\text{NR}_2$) nitrogens (where R can be H or an organic group), but not oxidized nitrogen such as nitro ($-\text{NO}_2$) or azo ($-\text{N}=\text{N}-$) groups, which must be reduced first to amines or amides.

REAGENTS

Standard NaOH and standard HCl: From Experiment 6.

Bromocresol green and phenolphthalein indicators: See Table 12-4 in the textbook.

Potassium sulfate: 10 g/student.

Selenium-coated boiling chips: Hengar selenium-coated granules are convenient. Alternative catalysts are 0.1 g of Se , 0.2 g of CuSeO_3 , or a crystal of CuSO_4 .

Concentrated (98 wt %) H_2SO_4 : 25 mL/student

Unknowns: Unknowns are pure acetanilide, N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES buffer, Table 10-2 in the textbook), tris(hydroxymethyl)aminomethane (tris buffer, Table 10-2), or the *p*-toluenesulfonic acid salts of ammonia, glycine, or nicotinic acid. Each student needs enough unknown to produce 2-3 mmol of NH_3 .

DIGESTION

1. Dry your unknown at 105°C for 45 min and accurately weigh an amount that will produce 2-3 mmol of NH_3 . Place the sample in a *dry* 500-mL Kjeldahl flask (Figure 7-2 in the textbook), so that as little as possible sticks to the walls. Add 10 g of K_2SO_4 (to raise the boiling temperature) and three selenium-coated boiling chips. Pour in 25 mL of 98 wt % H_2SO_4 , washing down any solid from the walls. (**CAUTION:** Concentrated H_2SO_4 eats people. If you get any on your skin, flood it immediately with water, followed by soap and water.)
2. In a fume hood, clamp the flask at a 30° angle away from you. Heat gently with a burner until foaming ceases and the solution becomes homogeneous. Continue boiling gently for an additional 30 min.

3. Cool the flask for 30 min *in the air*, and then in an ice bath for 15 min. Slowly, and with constant stirring, add 50 mL of ice-cold, distilled water. Dissolve any solids that crystallize. Transfer the liquid to the 500-mL 3-neck distillation flask in Figure 1. Wash the Kjeldahl flask five times with 10-mL portions of distilled water, and pour the washings into the distillation flask.

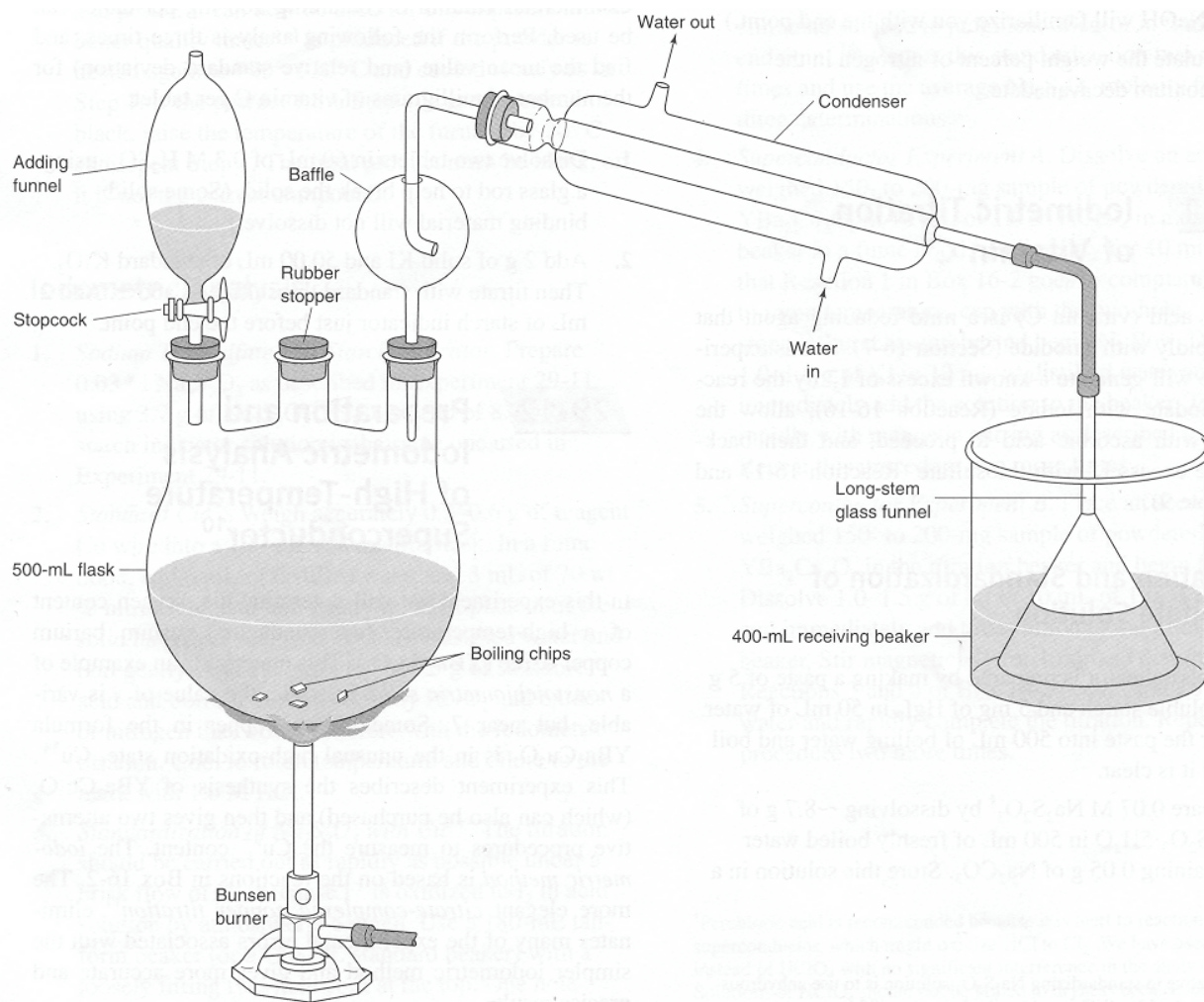


Figure 1. Apparatus for Kjeldahl Distillation.

DISTILLATION

1. Set up the apparatus in Figure 1 and tighten the connections well. Pipet 50.00 mL of standard 0.1 M HCl into the receiving beaker and clamp the funnel in place below the liquid level.

2. Add 5-10 drops of phenolphthalein indicator to the three-neck flask shown in Figure 23-3 and secure the stoppers. Pour 60 mL of 50 wt % NaOH into the adding funnel and drip this into the distillation flask over a period of 1 min until the indicator turns pink. (CAUTION: 50 wt % NaOH eats people. Flood any spills on your skin with water.) Do not let the last 1 mL through the stopcock, so that gas cannot escape from the flask. Close the stopcock and heat the flask gently until two-thirds of the liquid has distilled.
3. Remove the funnel from the receiving beaker *before* removing the burner from the flask (to avoid sucking distillate back into the condenser). Rinse the funnel well with distilled water and catch the rinses in the beaker. Add 6 drops of bromocresol green indicator solution to the beaker and carefully titrate to the blue end point with standard 0.1 M NaOH. You are looking for the first appearance of light blue color. (Practice titrations with HCl and NaOH beforehand to familiarize yourself with the end point.)
4. Calculate the wt % of nitrogen in the unknown.

11. EDTA Titration of Ca^{2+} and Mg^{2+} in Natural Waters

The most common multivalent metal ions in natural waters are Ca^{2+} and Mg^{2+} . In this experiment, we will find the total concentration of metal ions that can react with EDTA, and we will assume that this equals the concentration of Ca^{2+} and Mg^{2+} . In a second experiment, Ca^{2+} is analyzed separately after precipitating $\text{Mg}(\text{OH})_2$ with strong base.

REAGENTS

Buffer (pH 10): Add 142 mL of 28 wt % aqueous NH_3 to 17.5 g of NH_4Cl and dilute to 250 mL with water.

Eriochrome black T indicator: Dissolve 0.2 g of the solid indicator in 15 mL of triethanolamine plus 5 mL of absolute ethanol.

50 wt % NaOH: Dissolve 100 g of NaOH in 100 g of H_2O in a 250-mL plastic bottle. Store tightly capped. When you remove solution with a pipet, try not to disturb the solid Na_2CO_3 precipitate.

PROCEDURE

1. Dry $\text{Na}_2\text{H}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ (FM 372.24) at 80°C for 1 h and cool in the desiccator. Accurately weigh out ~ 0.6 g and dissolve it with heating in 400 mL of water in a 500-mL volumetric flask. Cool to room temperature, dilute to the mark, and mix well.
2. Pipet a sample of unknown into a 250-mL flask. A 1.000-mL sample of seawater or a 50.00-mL sample of tap water is usually reasonable. If you use 1.000 mL of seawater, add 50 mL of distilled water. To each sample, add 3 mL of pH 10 buffer and 6 drops of Eriochrome black T indicator. Titrate with EDTA from a 50-mL buret and note when the color changes from wine red to blue. Practice finding the end point several times by adding a little tap water and titrating with more EDTA. Save a solution at the end point to use as a color comparison for other titrations.
3. Repeat the titration with three samples to find an accurate value of the total $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentration. Perform a blank titration with 50 mL of distilled water and subtract the value of the blank from each result.
4. For the determination Ca^{2+} , pipet four samples of unknown into clean flasks (adding 50 mL of distilled water if you use 1.000 mL of seawater). Add 30 drops of 50 wt % NaOH to each solution and swirl for 2 min to precipitate $\text{Mg}(\text{OH})_2$ (which may not be visible). Add ~ 0.1 g of solid hydroxynaphthol blue to each flask. (This indicator is used because it remains blue at higher pH than does Eriochrome black T.) Titrate one sample rapidly to find the end point; practice finding it several times, if necessary.

5. Titrate the other three samples carefully. After reaching the blue end point, allow each sample to sit for 5 min with occasional swirling so that any $\text{Ca}(\text{OH})_2$ precipitate may redissolve. Then titrate back to the blue end point. (Repeat this procedure if the blue color turns to red upon standing.) Perform a blank titration with 50 mL of distilled water.
6. Calculate the total concentration of Ca^{2+} and Mg^{2+} , as well as the individual concentrations of each ion. Calculate the relative standard deviation of replicate titrations.

12. Synthesis and Analysis of Ammonium Decavanadate¹

The species in a solution of V^{5+} depend on both pH and concentration (Figure 1).

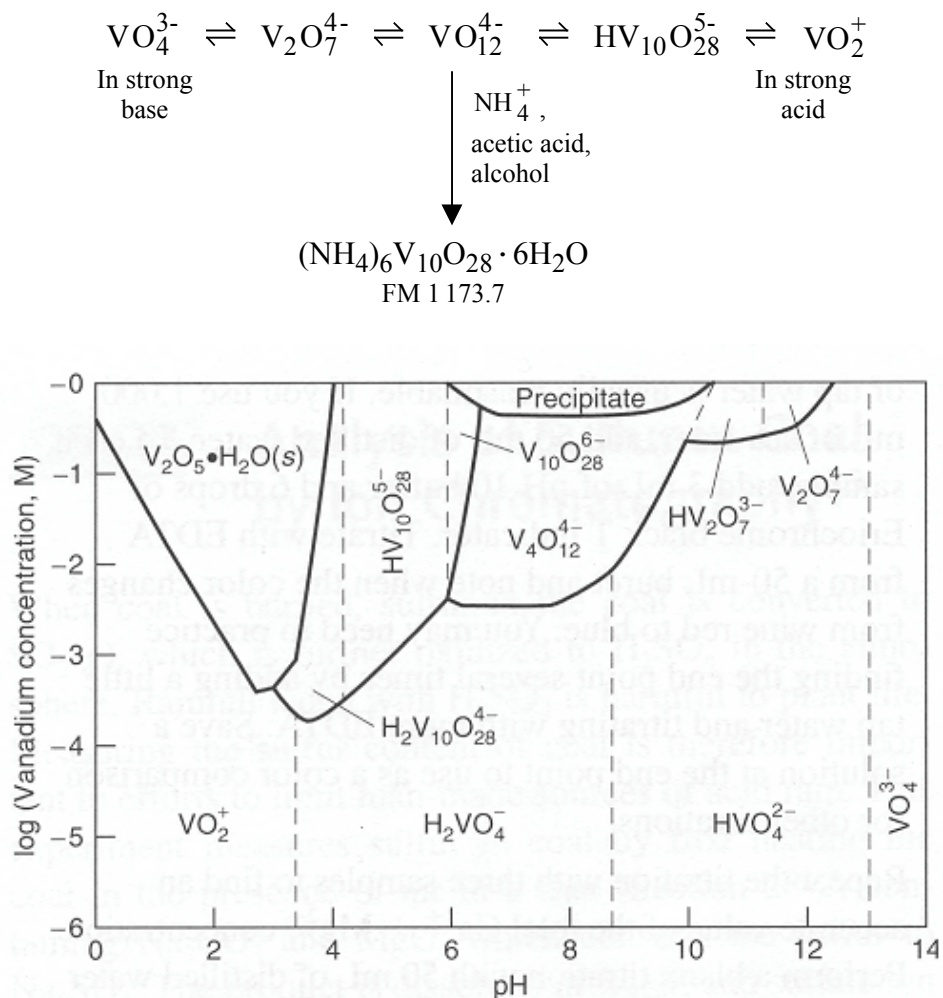


Figure 1. Phase diagram for aqueous vanadium(V) as a function of total vanadium concentration and pH. [From J. W. Larson, *J. Chem. Eng. Data* **1995**, *40*, 1276.]

The decavanadate ion ($\text{V}_{10}\text{O}_{28}^{6-}$), which we will isolate in this experiment as the ammonium salt, consists of 10 VO_6 octahedra sharing edges with one another (Figure 2).

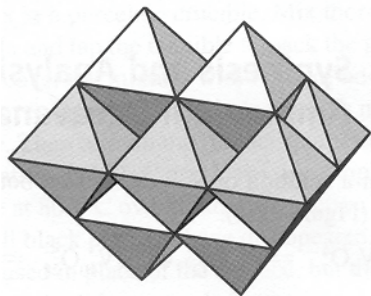
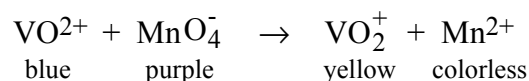
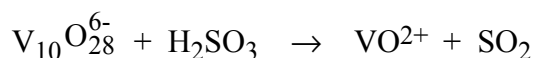


Figure 2. Structure of $\text{V}_{10}\text{O}_{28}^{6-}$ anion, consisting of VO_6 octahedra sharing edges with one another. There is a vanadium atom at the center of each octahedron.

After preparing this salt, we will determine the vanadium content by a redox titration and NH_4^+ by the Kjeldahl method. In the redox titration, V^{5+} will first be reduced to V^{4+} with sulfurous acid and then titrated with standard permanganate (Color Plate 9 in the textbook).



REAGENTS

Ammonium metavanadate (NH_4VO_3): 3 g/student.

50 vol % aqueous acetic acid: 4 mL/student.

95 % ethanol: 200 mL/student.

KMnO₄: 1.6 g/student or prepare 0.02 M KMnO_4 (~300 mL/student) for use by the class.

Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$): 1 g/student.

0.9 M H₂SO₄: (1 L/student) Slowly add 50 mL of concentrated (96–98 wt %) H_2SO_4 to 900 mL of H_2O and dilute to ~1 L.

1.5 M H₂SO₄: (100 mL/student) Slowly add 83 mL of concentrated (96–98 wt %) H_2SO_4 to 900 mL of H_2O and dilute to ~1 L.

Sodium bisulfite (NaHSO_3): 2 g/student.

Standard 0.1 M HCl: (75 mL/student) From Experiment 6.

Standard 0.1 M NaOH: (75 mL/student) From Experiment 6.

Phenolphthalein indicator: See Table 12-4 in the textbook.

Bromocreson green indicator: See Table 12-4 in the textbook.

50 wt % NaOH: 60 mL/student. Mix 100 g NaOH with 100 mL H_2O and dissolve.

SYNTHESIS

1. Heat 3.0 g of ammonium metavanadate (NH_4VO_3) in 100 mL of water with constant stirring (but not boiling) until most or all of the solid has dissolved. Filter the solution and add 4 mL of 50 vol % aqueous acetic acid with stirring.

2. Add 150 mL of 95% ethanol with stirring and then cool the solution in a refrigerator or ice bath.
3. After maintaining a temperature of 0°–10° C for 15 min, filter the orange product with suction and wash with two 15-mL portions of ice-cold 95% ethanol.
4. Dry the product in the air (protected from dust) for 2 days. Typical yield is 2.0–2.5 g.

ANALYSIS OF VANADIUM WITH KMnO_4

Preparation and Standardization of KMnO_4 ² (See Section 16-4 in the textbook)

1. Prepare a 0.02 M permanganate solution by dissolving 1.6 g of KMnO_4 in 500 mL of distilled water. Boil gently for 1 h, cover, and allow the solution to cool overnight. Filter through a clean, fine sintered-glass funnel, discarding the first 20 mL of filtrate. Store the solution in a clean glass amber bottle. Do not let the solution touch the cap.
2. Dry sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) at 105° C for 1 h, cool in a desiccator, and weigh three ~0.25-g samples into 500-mL flasks or 400-mL beakers. To each, add 250 mL of 0.9 M H_2SO_4 that has been recently boiled and cooled to room temperature. Stir with a thermometer to dissolve the sample, and add 90-95% of the theoretical amount of KMnO_4 solution needed for the titration. (This can be calculated from the mass of KMnO_4 used to prepare the permanganate solution. The chemical reaction is given by Equation 7-1 in the textbook.)
3. Leave the solution at room temperature until it is colorless. Then heat it to 55°–60° C and complete the titration by adding KMnO_4 until the first pale pink color persists. Proceed slowly near the end, allowing 30 s for each drop to lose its color. As a blank, titrate 250 mL of 0.9 M H_2SO_4 to the same pale pink color.

Vanadium Analysis

1. Accurately weigh two 0.3-g samples of ammonium decavanadate into 250-mL flasks and dissolve each in 40 mL of 1.5 M H_2SO_4 (with warming, if necessary).
2. In a fume hood, add 50 mL of water and 1 g of NaHSO_3 to each and dissolve with swirling. After 5 min, boil the solution gently for 15 min to remove SO_2 .
3. Titrate the warm solution with standard 0.02 M KMnO_4 from a 50-mL buret. The end point is taken when the yellow color of VO_2^+ takes on a dark shade (from excess MnO_4^-) that persists for 15 s.

ANALYSIS OF AMMONIUM ION BY KJELDAHL DISTILLATION

1. Set up the apparatus in Figure 1 of Experiment 10 and press the stoppers to make airtight connections. Pipet 50.00 mL of standard 0.1 M HCl into the receiving beaker and clamp the funnel in place below the liquid level.
2. Transfer 0.6 g of accurately weighed ammonium decavanadate to the three-neck flask and add 200 mL of water. Add 5–10 drops of phenolphthalein indicator (Table 12-4 in the textbook) and secure the stoppers. Pour 60 mL of 50 wt % NaOH into the adding funnel and drip this into the distillation flask over a period of 1 min until the indicator turns pink. (*Caution:* 50 wt % NaOH eats people. Flood any spills on your skin with water.) Do not let the last 1 mL through the stopcock, so that gas cannot escape from the flask. Close the stopcock and heat the flask gently until two-thirds of the liquid has distilled.
3. Remove the funnel from the receiving beaker *before* removing the burner from the flask (to avoid sucking distillate back into the condenser). Rinse the funnel well with distilled water and catch the rinses in the beaker. Add 6 drops of bromocresol green indicator solution (Table 12-4) to the beaker and carefully titrate to the blue end point with standard 0.1 M NaOH. You are looking for the first appearance of light blue color. (Several practice titrations with HCl and NaOH will familiarize you with the end point.)
4. Calculate the weight percent of nitrogen in the ammonium decavanadate.

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1. G. G. Long, R. L. Stanfield, and F. C. Hentz, Jr., *J. Chem. Ed.* **1979**, *56*, 195.
 2. R. M. Fowler and H. A. Bright, *J. Res. National Bureau of Standards* **1935**, *15*, 493.

13. Iodimetric Titration of Vitamin C⁹

Ascorbic acid (vitamin C) is a mild reducing agent that reacts rapidly with triiodide (See Section 16-7 in the textbook). In this experiment, we will generate a known excess of I⁻ by the reaction of iodate with iodide (Reaction 16-18), allow the reaction with ascorbic acid to proceed, and then back titrate the excess I⁻ with thiosulfate (Reaction 16-19 and Color Plate 11).

Preparation and Standardization of Thiosulfate Solution

1. Prepare starch indicator by making a paste of 5 g of soluble starch and 5 mg of HgI₂ in 50 mL of water. Pour the paste into 500 mL of boiling water and boil until it is clear.
2. Prepare 0.07 M Na₂S₂O₃²⁻ by dissolving ~8.7 g of Na₂S₂O₃·5H₂O in 500 mL of freshly boiled water containing 0.05 g of Na₂CO₃. Store this solution in a tightly capped amber bottle. Prepare ~0.01 M KIO₃ by accurately weighing ~1g of solid reagent and dissolving it in a 500-mL volumetric flask.
3. Standardize the thiosulfate solution as follows: Pipet 50.00 mL of KIO₃ solution into a flask. Add 2 g of solid KI and 10 mL of 0.5 M H₂SO₄. Immediately titrate with thiosulfate until the solution has lost almost all its color (pale yellow). Then add 2 mL of starch indicator and complete the titration. Repeat the titration with two additional 50.00-mL volumes of KIO₃ solution.

Analysis of Vitamin C

Commercial vitamin C containing 100 mg per tablet can be used. Perform the following analysis three times, and find the mean value (and relative standard deviation) for the number of milligrams of vitamin C per tablet.

1. Dissolve two tablets in 60 mL of 0.3 M H₂SO₄, using a glass rod to help break the solid. (Some solid binding material will not dissolve.)
2. Add 2 g of solid KI and 50.00 mL of standard KIO₃. Then titrate with standard thiosulfate as above. Add 2 mL of starch indicator just before the end point.

1. D. N. Bailey, *J. Chem. Ed.* **1974**, *51*, 488.

2. An alternative to standardizing Na₂S₂O₃ solution is to prepare anhydrous primary standard Na₂S₂O₃ by refluxing 21 g of Na₂S₂O₃·5H₂O with 100 mL of methanol for 20 min. Then filter the anhydrous salt, wash with 20 mL of methanol, and dry at 70°C for 30 min. [A. A. Woolf, *Anal. Chem.* **1982**, *54*, 2134.]

14. Preparation and Iodometric Analysis of a High-Temperature Superconductor¹

In this experiment you will determine the oxygen content of yttrium barium copper oxide ($\text{YBa}_2\text{Cu}_3\text{O}_x$). This material is an example of a *nonstoichiometric solid*, in which the value of x is variable, but near 7. Some of the copper in the formula $\text{YBa}_2\text{Cu}_3\text{O}_7$ is in the unusual high-oxidation state, Cu^{3+} . This experiment describes the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$, (which can also be purchased) and then gives two alternative procedures to measure the Cu^{3+} content. The *iodometric method* is based on the reactions in Box 16-2 in the textbook. The more elegant *citrate-complexed copper titration*² eliminates many experimental errors associated with the simpler iodometric method and gives more accurate and precise results.

Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_x$

1. Place in a mortar 0.750 g of Y_2O_3 , 2.622 g of BaCO_3 , and 1.581 g of CuO (atomic ratio Y:Ba:Cu = 1:2:3). Grind the mixture well with a pestle for 20 min and transfer the powder to a porcelain crucible or boat. Heat in the air in a furnace at $920^\circ\text{--}930^\circ\text{C}$ for 12 h or longer. Turn off the furnace and allow the sample to cool slowly *in the furnace*. This slow cooling step is critical for achieving an oxygen content in the range $x = 6.5\text{--}7$ in the formula $\text{YBa}_2\text{Cu}_3\text{O}_x$. The crucible may be removed when the temperature is below 100°C .
2. Dislodge the black solid mass gently from the crucible and grind it to a fine powder with a mortar and pestle. It can now be used for this experiment, but better quality material is produced if the powder is heated again to $920^\circ\text{--}930^\circ\text{C}$ and cooled slowly as in Step 1. If the powder from Step 1 is green instead of black, raise the temperature of the furnace by 20°C and repeat Step 1. The final product must be black, or it is not the correct compound.

Iodometric Analysis

1. *Sodium Thiosulfate and Starch Indicator*. Prepare 0.03 M $\text{Na}_2\text{S}_2\text{O}_3$ as described in Experiment 13, using 3.7 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ instead of 8.7 g. The starch indicator solution is the same one used in Experiment 13.
2. *Standard Cu^{2+}* . Weigh accurately 0.5–0.6 g of reagent Cu wire into a 100-mL volumetric flask. In a fume hood, add 6 mL of distilled water and 3 mL of 70 wt % nitric acid, and boil gently on a hot plate until the solid has dissolved. Add 10 mL of distilled water and boil gently. Add 1.0 g of urea or 0.5 g of sulfamic acid and boil for 1 min to destroy HNO_2 and oxides of nitrogen that would interfere with the iodometric titration. Cool to room temperature and dilute to the mark with 1.0 M HCl.
3. *Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ With Cu^{2+}* . The titration should be carried out as rapidly as possible under a brisk flow of N_2 , because I^- is oxidized to I_2 in acid solution by atmospheric oxygen. Use a 180-mL tall-form beaker (or a 150-mL standard beaker) with a loosely fitting two-hole cork at the top. One hole serves as the inert gas inlet and the other

is for the buret. Pipet 10.00 mL of standard Cu^{2+} into the beaker and flush with N_2 . Remove the cork just long enough to pour in 10 mL of distilled water containing 1.0–1.5 g of KI (freshly dissolved) and begin magnetic stirring. In addition to the dark color of iodine in the solution, suspended solid CuI will be present. Titrate with $\text{Na}_2\text{S}_2\text{O}_3$ solution from a 50-mL buret, adding 2 drops of starch solution just before the last trace of I_2 color disappears. If starch is added too soon, there can be irreversible attachment of I_2 to the starch and the end point is harder to detect. You may want to practice this titration several times to learn to distinguish the colors of I_2 and I_2/starch from the color of suspended $\text{CuI}(s)$. (Alternatively, Pt and calomel electrodes can be used instead of starch to eliminate subjective judgment of color in finding the end point.³) Repeat this standardization two more times and use the average $\text{Na}_2\text{S}_2\text{O}_3$ molarity from the three determinations.

4. *Superconductor Experiment A.* Dissolve an accurately weighed 150- to 200-mg sample of powdered $\text{YBa}_2\text{Cu}_3\text{O}_x$ in 10 mL of 1.0 M HClO_4 in a titration beaker in a fume hood. (Perchloric acid is recommended because it is inert to reaction with superconductor, which might oxidize HCl to Cl_2 . We have used HCl instead of HClO_4 with no significant interference in the analysis. Solutions of HClO_4 should not be boiled to dryness because of their explosion hazard.) Boil gently for 10 min, so that Reaction 1 in Box 16-2 goes to completion. Cool to room temperature, cap with the two-hole-stopper–buret assembly, and begin N_2 flow. Dissolve 1.0–1.5 g of KI in 10 mL of distilled water and immediately add the solution to the beaker. Titrate rapidly with magnetic stirring as described in Step 3. Repeat this procedure two more times.
5. *Superconductor Experiment B.* Place an accurately weighed 150- to 200-mg sample of powdered $\text{YBa}_2\text{Cu}_3\text{O}_x$ in the titration beaker and begin N_2 flow. Dissolve 1.0–1.5 g of KI in 10 mL of 1.0 M HClO_4 and immediately add the solution to the titration beaker. Stir magnetically for 1 min, so that the Reactions 3 and 4 of Box 16-2 occur. Add 10 mL of water and rapidly complete the titration. Repeat this procedure two more times.

CALCULATIONS

1. Suppose that mass, m_A , is analyzed in Experiment A and the volume, V_A , of standard thiosulfate is required for titration. Let the corresponding quantities in Experiment B be m_B and V_B . Let the average oxidation state of Cu in the superconductor be $2 + p$. Show that p is given by

$$p = \frac{V_B/m_B - V_A/m_A}{V_A/m_A} \quad (1)$$

and x in the formula $\text{YBa}_2\text{Cu}_3\text{O}_x$, is related to p as follows:

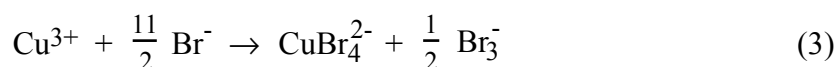
$$x = \frac{7}{2} + \frac{3}{2} (2 + p) \quad (2)$$

For example, if the superconductor contains one Cu^{3+} and two Cu^{2+} , the average oxidation state of copper is $7/3$ and the value of p is $1/3$. Setting $p = 1/3$ in Equation 2 gives $x = 7$. Equation 1 does not depend on the metal stoichiometry being exactly Y:Ba:Cu 1:2:3, but Equation 2 does require this exact stoichiometry.

2. Use the average results of Experiments A and B to calculate the values of p and x in Equations 1 and 2.
3. Suppose that the uncertainty in mass of superconductor analyzed is 1 in the last decimal place. Calculate the standard deviations for Steps 3, 4, and 5 of the iodometric analysis. Using these standard deviations as uncertainties in volume, calculate the uncertainties in the values of p and x in Equations 1 and 2.

Citrate-Complexed Copper Titration²

This procedure directly measures Cu^{3+} . The sample is first dissolved in a closed container with 4.4 M HBr, in which Cu^{3+} oxidizes Br^- to Br_3^- :



The solution is transferred to a vessel containing excess I^- , excess citrate, and enough NH_3 to neutralize most of the acid. Cu^{2+} is complexed by citrate and is not further reduced to $\text{CuI}(s)$. (This eliminates the problem in the iodometric titration of performing a titration in the presence of colored solid.) The Br_3^- from Reaction 3 oxidizes I^- to I_3^- :



and the I_3^- is titrated with thiosulfate.

Our experience with the iodometric procedure is that the precision in oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_x$, is ± 0.04 in the value of x . The uncertainty is reduced to ± 0.01 by the citrate-complexed copper procedure.

PROCEDURE

1. Prepare and standardize sodium thiosulfate solution as described in Steps 1–3 of the iodometric analysis in the previous section.
2. Place an accurately weighed 20- to 50-mg sample of superconductor in a 4-mL screw-cap vial with a Teflon cap liner and add 2.00 mL of ice-cold 4.4 M HBr by pipet. (The HBr is prepared by diluting 50 mL of 48 wt % HBr to 100 mL.) Cap tightly and gently agitate the vial for 15 min as it warms to room temperature. (We use a motor to rotate the sample slowly for 15 min.)

- Cool the solution back to 0° C and carefully transfer it to the titration beaker (used in the thiosulfate standardization) containing an ice-cold, freshly prepared solution made from 0.7 g of KI, 20 mL of water, 5 mL of 1.0 M trisodium citrate, and approximately 0.5 mL of 28 wt % NH₃. The exact amount of NH₃ should be enough to neutralize all but 1 mmol of acid present in the sample. When calculating the acid content, remember that each mole of YBa₂Cu₃O_x consumes 2x moles of HBr. (You can estimate that x is close to 7.) Wash the vial with three 1-mL aliquots of 2 M HBr to complete the quantitative transfer to the beaker.
- Add 0.1 mL of 1 wt % starch solution and titrate with 0.1 M standard Na₂S₂O₃ under a brisk flow of N₂, using a 250-mL Hamilton syringe to deliver titrant. The end point is marked by a change from dark blue (I₂-starch) to the light blue-green of the Cu²⁺-citrate complex.
- Run a blank reaction with CuSO₄ in place of superconductor. The moles of Cu in the blank should be the same as the moles of Cu in the superconductor. In a typical experiment, 30 mg of YBa₂Cu₃O_{6.88} required approximately 350 μL of Na₂S₂O₃ and the blank required 10 μL of Na₂S₂O₃. If time permits, run two more blanks. Subtract the average blank from the titrant in Step 4.
- Repeat the analysis with two more samples of superconductor.

CALCULATIONS

- From the thiosulfate required to titrate I₃⁻ released in Reaction 4, find the average moles of Cu³⁺ per gram of superconductor (1 mol S₂O₃²⁻ = 1 mol Cu³⁺) and the standard deviation for your three samples.
- Defining R as (mol Cu³⁺)/(g superconductor), show that z in the formula YBa₂Cu₃O_{7-x} is

$$z = \frac{1 - 666.20R}{2 - 15.999R} \quad (5)$$

where 666.20 is the formula mass of YBa₂Cu₃O₇ and 15.999 4 is the atomic mass of O.

- Using your average value of R and using its standard deviation as an estimate of uncertainty, calculate the average value of z and its uncertainty. Find the average value of x and its uncertainty in the formula YBa₂Cu₃O_x. If you are really daring, you should use Equation C-1 in Appendix C of the textbook for propagation of uncertainty in Equation 5.

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- D. C. Harris, M. E. Hills, and T. A. Hewston, *J. Chem. Ed.* **1987**, *64*, 847. Alternative syntheses of YBa₂Cu₃O_x are described by C. D. Cogdell, D. G. Wayment, D. J. Casadonte, Jr., and K. A. Kubat-Martin, *J. Chem. Ed.* **1995**, *72*, 840 and P. I. Djurovich and R. J. Watts, *J. Chem. Ed.* **1993**, *70*, 497.
 - E. H. Appelman, L. R. Morss, A. M. Kini, U. Geiser, A. Umezawa, G. W. Crabtree, and K. D. Carlson, *Inorg. Chem.* **1987**, *26*, 3237.
 - P. Phinyocheep and I. M. Tang, *J. Chem. Ed.* **1994**, *71*, A115.

15. Potentiometric Halide Titration with Ag^+

Mixtures of halides can be titrated with AgNO_3 solution as described in Section 7-5 in the textbook. In this experiment, you will use the apparatus in Figure 7-9 of the textbook to monitor the activity of Ag^+ as the titration proceeds. The theory of the potentiometric measurement is described in Section 15-2 of the textbook.

Each student is given a vial containing 0.22–0.44 g of KCl plus 0.50–1.00 g of KI (both weighed accurately). The object is to determine the quantity of each salt in the mixture. A 0.4 M bisulfate buffer (pH 2) should be available in the lab. It is prepared by titrating 1 M H_2SO_4 with 1 M NaOH to a pH near 2.0.

PROCEDURE

1. Pour your unknown carefully into a 50- or 100-mL beaker. Dissolve the solid in ~20 mL of water and pour it into a 100-mL volumetric flask. Rinse the sample vial and beaker many times with small portions of H_2O and transfer the washings to the flask. Dilute to the mark and mix well.
2. Dry 1.2 g of AgNO_3 at 105°C for 1 h and cool in a dessicator for 30 min with minimal exposure to light. Some discoloration is normal (and tolerable in this experiment) but should be minimized. Accurately weigh 1.2 g and dissolve it in a 100-mL volumetric flask.
3. Set up the apparatus in Figure 7-9 of the textbook. The silver electrode is simply a 3-cm length of silver wire connected to copper wire. (Fancier electrodes can be prepared by housing the connection in a glass tube sealed with epoxy at the lower end. Only the silver should protrude from the epoxy.) The copper wire is fitted with a jack that goes to the reference socket of a pH meter. The reference electrode for this titration is a glass pH electrode connected to its usual socket on the meter. If a combination pH electrode is employed, the reference jack of the combination electrode is not used. The silver electrode should be taped to the inside of the 100-mL beaker so that the Ag/Cu junction remains dry for the entire titration. The stirring bar should not hit either electrode.
4. Pipet 25.00 mL of unknown into the beaker, add 3 mL of bisulfate buffer, and begin magnetic stirring. Record the initial level of AgNO_3 in a 50-mL buret and add ~1 mL of titrant to the beaker. Turn the pH meter to the millivolt scale and record the volume and voltage. It is convenient (but is not essential) to set the initial reading to +800 mV by adjusting the meter.
5. Titrate the solution with ~1-mL aliquots until 50 mL of titrant have been added or until you can see two clear potentiometric end points. You need not allow more than 15–30 s for each point. Record the volume and voltage at each point. Make a graph of millivolts versus milliliters to find the approximate positions (± 1 mL) of the two end points.
6. Turn the pH meter to standby, remove the beaker, rinse the electrodes well with water, and blot them dry with a tissue. (Silver halide adhering to the glass electrode can be removed by soaking in concentrated sodium thiosulfate solution. This thorough cleaning is not

necessary between Steps 6 and 7 in this experiment. The silver halides in the titration beaker can be saved and converted back to pure AgNO_3 by using the procedure of E. Thall, *J. Chem. Ed.* **1981**, 58, 561.) Clean the beaker and set up the titration apparatus again. The beaker need not be dry.

7. Now perform an accurate titration, using 1-drop aliquots near the end points (and 1-mL aliquots elsewhere). You need not allow more than 30 s per point for equilibration.
8. Prepare a graph of millivolts versus milliliters and locate the end points as in Figure 7-8 of the textbook. The I^- end point is taken as the intersection of the two dashed lines in the inset of Figure 7-8. The Cl^- end point is the inflection point at the second break. Calculate milligrams of KI and milligrams of KCl in your solid unknown.

Analyzing Cl^- in Streams, Lakes, or Salt Water

A variation of the preceding procedure could make a class project in environmental analysis. For example, you could study changes in streams as a function of the season or recent rainfall. You could study stratification (layering) of water in lakes. The measurement responds to all ions that precipitate with Ag^+ , of which Cl^- is, by far, the dominant ion in natural waters.

You can use the electrodes in Figure 7-9, or you can construct the rugged combination electrode shown in Figure 1.¹ The indicator electrode in Figure 1 is a bare silver wire in contact with analyte solution. The inner (reference) chamber of the combination electrode contains a copper wire dipped into CuSO_4 solution. The inner electrode maintains a constant potential because the concentration of Cu^{2+} in the solution is constant. The solution makes electrical contact at the septum, where a piece of thread leaves enough space for solution to slowly drain from the electrode into the external sample solution.

PROCEDURE

1. Collect water from streams or lakes or from the ocean. To minimize bacterial growth, plastic jugs should be filled to the top and tightly sealed. Refrigeration is recommended.
2. Prepare 4 mM AgNO_3 solution with an accurately known concentration, as in Step 2 at the beginning of this experiment. One student can prepare enough reagent for five people by using 0.68 g of AgNO_3 in a 1-L volumetric flask.
3. Measure with a graduated cylinder 100 mL of a natural water sample and pour it into a 250-mL beaker. Position the combination electrode from Figure 1 or the pair of electrodes from Figure 7-9 of the textbook in the beaker so that a stirring bar will not hit the electrode.
4. Carry out a rough titration by adding 1.5-mL increments of titrant to the unknown and reading the voltage after 30 s to the nearest millivolt. Prepare a graph of voltage versus volume of titrant to locate the end point, which will not be as abrupt as those in Figure 7-8 of the textbook. If necessary, adjust the volume of unknown in future steps so that the end point comes at 20–40 mL. If you need less unknown, make up the difference with distilled water.

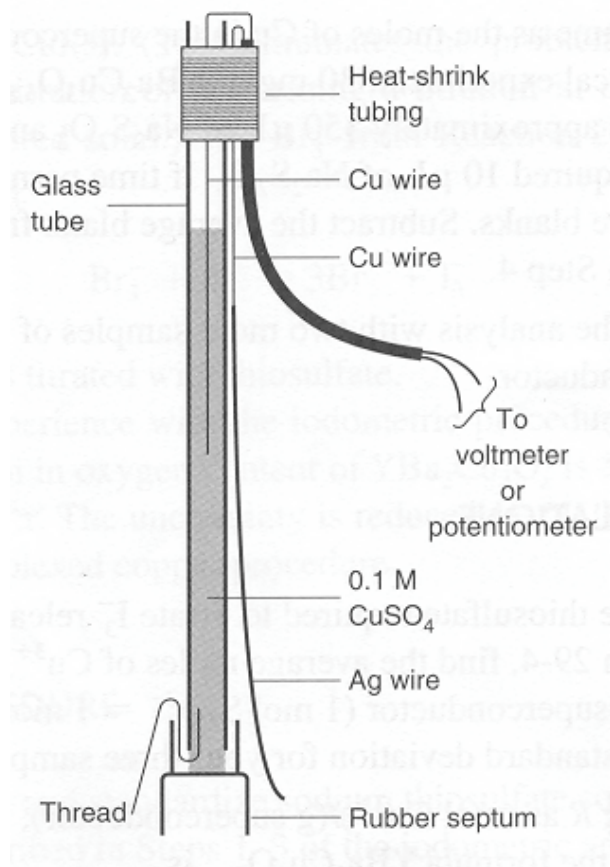


Figure 7. Combination electrode constructed from 8-mm-outer-diameter glass tubing. Strip the insulation off the ends of a two-wire copper cable. One bare Cu wire extends into the glass tube. A silver wire soldered to the other Cu wire is left outside the glass tube. The assembly is held together at the top with heat-shrink tubing. When ready for use, insert a cotton thread into the bottom of the tube and fit a 14/20 serum cap moistened with 0.1 M CuSO_4 over the end so that part of the thread is inside and part is outside. After adding 0.1 M CuSO_4 to the inside of the tube, the electrode is ready for use.

5. Carry out a more careful titration with fresh unknown. Add three-quarters of the titrant volume required to reach the equivalence point all at once. Then add ~ 0.4 -mL increments (8 drops from a 50-mL buret) of titrant until you are 5 mL past the equivalence point. Allow 30 s (or longer, if necessary) for the voltage to stabilize after each addition. The end point is the steepest part of the curve, which can be estimated by the method shown in Figure 1 of Experiment 7.
6. Calculate the molarity and parts per million ($\mu\text{g/mL}$) of Cl^- in the unknown. Use data from several studies with the same sample to find the mean and standard deviation of ppm Cl^- .

1. G. Lisensky and K. Reynolds, *J. Chem. Ed.* **1991**, 68, 334; R. Ramette, *Chemical Equilibrium* (Reading, MA: Addison-Wesley, 1981), p. 649.

16. Electrogravimetric Analysis of Copper

Most copper-containing compounds can be electrolyzed in acidic solution, with quantitative deposition of Cu at the cathode. Sections 17-1 to 17-2 of the textbook discuss this technique.

Students may analyze a preparation of their own (such as copper acetylsalicylate¹) or be given unknowns prepared from CuSO₄·5H₂O or metallic Cu. In the latter case, dissolve the metal in 8 M HNO₃, boil to remove HNO₂, neutralize with ammonia, and barely acidify the solution with dilute H₂SO₄ (Using litmus paper to test for acidity). Samples must be free of chloride and nitrous acid.² Copper oxide unknowns (soluble in acid) are available from Thorn Smith.³

The apparatus shown in Figure 17-5 of the textbook uses any 6–12 V direct-current power supply. A tall-form 150-mL beaker is the reaction vessel.

PROCEDURE

1. Handle the Pt gauze cathode with a tissue, touching only the thick stem, not the wire gauze. Immerse the electrode in hot 8 M HNO₃ to remove previous deposits, rinse with water and alcohol, dry at 105°C for 5 min, cool for 5 min, and weigh accurately. If the electrode contains any grease, it can be heated to red heat over a burner after the treatment above.⁴
2. The sample should contain 0.2–0.3 g of Cu in 100 mL. Add 3 mL of 98 wt % H₂SO₄ and 2 mL of freshly boiled 8 M HNO₃. Position the cathode so that the top 5 mm are above the liquid level after magnetic stirring is begun. Adjust the current to 2 A, which should require 3–4 V. When the blue color of Cu(II) has disappeared, add some distilled water so that new Pt surface is exposed to the solution. If no further deposition of Cu occurs on the fresh surface in 15 min at a current of 0.5 A, the electrolysis is complete. If deposition is observed, continue electrolysis and test the reaction for completeness again.
3. *Without* turning off the power, lower the beaker while washing the electrode with a squirt bottle. Then the current can be turned off. (If current is disconnected before removing the cathode from the liquid and rinsing off the acid, some Cu could redissolve.) Wash the cathode gently with water and alcohol, dry at 105° C for 3 min, cool in a desiccator for 5 min, and weigh.

1. E. Dudek, *J. Chem. Ed.* **1977**, *54*, 329.

2. J. F. Owen, C. S. Patterson, and G. S. Rice, *Anal. Chem.* **1983**, *55*, 990, describe simple procedures for the removal of chloride from Cu, Ni, and Co samples prior to electrogravimetric analysis.

3. Thorn Smith Inc., 7755 Narrow Gauge Road, Beulah, MI 49617. Phone: 231-882-4672; e-mail: www.thornsmithlabs.com.

4. Some metals, such as Zn, Ga, and Bi, form alloys with Pt and should not be deposited directly on the Pt surface. The electrode should be coated first with Cu, dried, and then used. Alternatively, Ag can be used in place of Pt for depositing these metals. Platinum anodes are attacked by Cl₂ formed by electrolysis of Cl⁻ solutions. To prevent chlorine attack, 1–3 g of a hydrazinium salt (per 100 mL of solution) can be used as an anodic depolarizer, because hydrazine is more readily oxidized than Cl⁻: N₂H₄ → N₂ + 4H⁺ + 4e⁻.