CHAPTER 38

Selected Methods of Analysis

Chemistry is primarily an experimental science. This chapter presents a variety of laboratory experiments, from classical titrations and gravimetry to instrumental methods such as chromatography and spectroscopy. Detailed directions are given for each experiment.

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This chapter contains detailed directions for performing a variety of chemical analyses. The methods have been chosen to introduce you to analytical techniques that are widely used by chemists. For most of these analyses, the composition of the samples is known to the instructor. Thus, you will be able to judge how well you are mastering these techniques.

Your chances of success in the laboratory will greatly improve if you take time before you enter the laboratory to read carefully and understand each step in the method and to develop a plan for how and when you will perform each step.

The discussion in this section is aimed at helping you develop efficient work habits in the laboratory and also at providing you with some general information about an analytical chemistry laboratory. Before you start an analysis, you should understand the significance of each step in the procedure to avoid the pitfalls and potential sources of error that are inherent in all analytical methods. Information about these steps can usually be found in (1) preliminary discussion sections, (2) earlier chapters that are referred to in the discussion section, and (3) the "Notes" that follow many of the procedures. If, after reading these materials, you still do not understand the reason for doing one or more of the steps in the method, consult your instructor before you begin laboratory work.

The Accuracy of Measurements

In looking over an analytical procedure, you should decide which measurements must be made with maximum precision, and thus with maximum care, as opposed to those that can be carried out rapidly with little concern for precision. Generally, measurements that appear in the equation used to compute the results must be performed with maximum precision. The remaining measurements can and should be made less carefully to conserve time. The words *about* and *approximately* are frequently used to indicate that a measurement does not have to be done carefully. For example, you should not waste time and effort to measure a volume to ± 0.02 mL when an uncertainty of ± 0.5 mL or even ± 5 mL will have no discernible effect on the results.

In some procedures, a statement such as "weigh three 0.5-g samples to the nearest 0.1 mg" is encountered. In this instance, samples of perhaps 0.4 to 0.6 g are

acceptable, but their masses must be known to the nearest 0.1 mg. The number of significant figures in the specification of a volume or a mass is also a guide to the care that should be taken in making a measurement. For example, the statement "add 10.00 mL of a solution to the beaker" indicates that you should measure the volume carefully with a buret or a pipet, with the aim of limiting the uncertainty to perhaps ±0.02 mL. In contrast, if the directions read "add 10 mL," the measurement can be made with a graduated cylinder.

Time Utilization

You should study carefully the time requirements of the several unit operations involved in an analysis *before work is started.* This study will reveal operations that require considerable elapsed, or clock, time but little or no operator time. Examples of such operations include drying a sample in an oven, cooling a sample in a desiccator, or evaporating liquid on a hot plate. Efficient workers use such periods to perform other operations or perhaps to begin a new analysis. Some people find it worthwhile to prepare a written time schedule for each laboratory period to avoid dead time.

Time planning is also needed to identify places where an analysis can be interrupted for overnight or longer, as well as those operations that must be completed without a break.

Reagents

Directions for the preparation of reagents accompany many of the procedures. Before preparing such reagents, be sure to check to see if they are already prepared and available on a side shelf for general use.

If a reagent is known to be hazardous, you should plan *in advance of the laboratory period* the steps that you should take to minimize injury or damage. Furthermore, you must acquaint yourself with the rules that apply in your laboratory for the disposal of waste liquids and solids. These rules vary from one part of the country to another and even among laboratories in the same locale.

Water

Some laboratories use deionizers to purify water; others employ stills for this purpose. The terms "distilled water" and "deionized water" are used interchangeably in the directions that follow. Either type is satisfactory for the procedures in this chapter.

You should use tap water only for preliminary cleaning of glassware. The cleaned glassware is then rinsed with at least three small portions of distilled or deionized water.

38A AN INTRODUCTORY EXPERIMENT

The purpose of this experiment is to introduce several of the tools, techniques, and skills necessary for work in the analytical chemistry laboratory. The techniques are considered one at a time, as unit operations. It is important to learn proper techniques and to acquire individual skills before attempting additional laboratory experiments.

38A-1 Using the Analytical Balance

Discussion

In this experiment, you will obtain the mass of five new pennies—first by determining the mass of each penny individually. Then you will determine the mass of all five pennies at once, remove one penny at a time, and calculate the individual masses of the pennies by finding the difference. The pair of masses determined for

a particular penny by the two different methods should agree to within a few tenths of a milligram. From the data, you will determine the mean and median values, the standard deviation, and the relative standard deviation of the masses of the pennies.

You will then weigh an unknown aluminum cylinder and report the mass of this unknown.

PROCEDURE

1. After you have been instructed in the use of the balance and have become familiar with its use, obtain a set of pennies, an unknown aluminum cylinder, and a pair of tweezers from the instructor.
2. Do not handle the pennies or the cylinder with your fingers; always use the tweezers. If you are using a mechanical balance, be sure to have the balance in the "off" or "complete arrest" position whenever removing anything from or adding anything to the balance pan.
3. Before you begin to determine masses, zero your analytical balance carefully. Select five pennies at random from the vial containing the pennies, and weigh each penny on your balance. Enter the data in your laboratory notebook. Keep track of the identity of each penny by placing each one on a labeled piece of paper.
4. Check the zero setting on your balance. Place these same five pennies on the balance pan, determine their total mass, and record it.
5. Remove one of the pennies from the balance, obtain the mass of the remaining four, and record the mass.
6. Repeat this process, removing one penny at a time. Obtain the individual masses by subtraction. This process is known as weighing by difference, which is the way many mass determinations are done in the analytical laboratory.
7. Finally, check the zero on your balance, and find the mass of the unknown aluminum cylinder.

38A-2 Making Quantitative Transfers

Discussion

The following experiment is designed to provide experience in the correct use of the volumetric flask.

PROCEDURE

1. Weigh a 50-mL beaker on a triple-beam balance or an appropriate electronic top-loading balance.
2. Adjust the balance for an additional 0.4 g and add solid $KMnO_4$ to the beaker until the beam is again balanced. If you have an electronic balance with a tare function, depress the tare button to set the balance to zero. Then add $KMnO_4$ until the balance reads about 0.4 g. Note that chemicals should never be returned to a stock bottle, as this may contaminate the bottle.
3. Dissolve the potassium permanganate in the beaker using about 20 mL of distilled water. Stir gently to avoid loss. This is nearly a saturated solution, and some care is required to dissolve the crystals completely.
4. Quantitatively transfer the solution to a 100-mL volumetric flask fitted with a small funnel. To prevent solution from running down the outside of the beaker,

pour it down the stirring rod, and then touch the rod to the spout of the beaker to remove the last drop. Add more water to the beaker, stir, and repeat the procedure.

5. Repeat the procedure until no trace of the color of the permanganate remains in the beaker. Note the number of washings that is required to quantitatively transfer the permanganate from the beaker to the flask.

6. Rinse the last portion of solution from the stirring rod into the volumetric flask with a stream of water from the wash bottle. Rinse the funnel and remove it. Dilute the solution in the flask until the bottom of the meniscus is even with the graduation mark. Stopper, invert, and shake the flask. Return it to the upright position, and allow the air bubble to return all the way to the top of the neck.

7. Repeat until the solution is completely homogeneous; about 10 inversions and shakings are required. Save the solution for Part 38A-3.

38A-3 Delivering an Aliquot

Discussion

Whenever a buret or pipet is used to deliver a measured volume of solution, the liquid it contains before measurement should have the same composition as the solution to be dispensed. The following operations are designed to illustrate how to rinse and fill a pipet and how to deliver an aliquot of solution.

PROCEDURE

1. Fill a pipet with the solution of potassium permanganate and let it drain.

2. Draw a few milliliters of distilled water from a 50-mL beaker into the pipet, rinse all internal surfaces of the pipet, and discard the rinse solution. Do not fill the pipet completely; this is wasteful, time-consuming, and inefficient. Just draw in a small amount, tilt the pipet horizontally, and turn it to rinse the sides.

3. Determine the minimum number of such rinsings required to completely remove the permanganate color from the pipet. If your technique is efficient, three rinsings should be enough.

4. Again fill the pipet with permanganate solution, and proceed as before. This time determine the minimum volume of rinse water required to remove the color by collecting the rinsings in a graduated cylinder. Less than 5 mL are enough with efficient technique. In the rinsing operations, was the water in the 50-mL beaker contaminated with permanganate? If a pink color shows that it was, repeat the exercise with more care.

5. As a test of your technique, ask the laboratory instructor to observe and comment on the following operation: Rinse a 10-mL pipet several times with the solution of potassium permanganate you prepared.

6. Pipet 10 mL of the permanganate solution into a 250-mL volumetric flask.

7. Carefully dilute the solution to volume, trying to mix the contents as little as possible.

8. Mix the solution by repeatedly inverting and shaking the flask. Note the effort that is required to disperse the permanganate color uniformly throughout the solution.

9. Rinse the pipet with the solution in the volumetric flask. Pipet a 10-mL aliquot of the solution into a conical flask.

38A-4 Calibrating a Pipet

Discussion

The proper manual technique for calibrating an analytical transfer pipet is readily learned with practice, care, and attention to detail. With the possible exception of mass determinations, this experiment has the potential of being the most accurate and precise set of measurements that you will ever make.

PROCEDURE

1. Clean a 10-mL pipet. When a pipet, buret, or other piece of volumetric glassware is cleaned properly, no droplets of reagent remain on the internal surfaces when they are drained. This is very important for accurate and reproducible results. If reagent adheres to the inside of a pipet, you cannot deliver the nominal volume of the pipet. If you clean a pipet or any other glassware with alcoholic KOH, use the bottle of cleaning solution only inside the sink and rinse it off thoroughly before returning it to the shelf. Do not put the bottle of cleaning solution directly on a bench top; it may ruin the surface. The solution is very corrosive. If your fingers feel slippery after use, or if some part of your body develops an itch, wash the area thoroughly with water.

2. Obtain a pipetting bulb, a 50-mL Erlenmeyer flask with a dry stopper, a 400-mL beaker of distilled water equilibrated to room temperature, and a thermometer.

3. Determine the mass of the flask and stopper and record it to the nearest 0.1 mg. Do not touch the flask with your fingers after this weighing. Use tongs or a folded strip of waxed paper to manipulate the flask.

4. Measure and record the temperature of the water.

5. Pipet 10.00 mL of the distilled water into the flask using the technique described on page 41. Stopper the flask, determine the mass of the flask and the water that it contains, and record the mass.

6. In the same way, add a second pipet of water to the flask; remove the stopper just before the addition. Replace the stopper, and once again determine and record the mass of the flask and the water. Following each trial, determine the mass of water added to the flask by the pipet.

7. Repeat this process until you have determined four consecutive masses of water that agree within a range of 0.02 g. If the determinations of the mass of water delivered by the pipet do not agree within this range, your pipetting technique may be suspect. Consult your instructor for assistance in finding the source of the error, and then repeat the experiment until you are able to deliver four consecutive volumes of water with the precision cited.

8. Correct the mass for buoyancy as described on page 24, and calculate the volume of the pipet in milliliters.

9. Report the mean, the standard deviation, and the relative standard deviation of the volume of your pipet. Calculate and report the 95% confidence interval for the volume of your pipet.

38A-5 Reading Buret Sections

Discussion

The following exercise will give you practice in reading a buret and confirming the accuracy of your readings.

PROCEDURE

1. Obtain a set of five buret sections from your instructor.
2. Invert each section, and tap the section lightly to remove any solvent that might remain in the sealed tip.
3. Record the number and reading of each buret section on the form provided. Use a buret reading card to make the readings to the nearest 0.01 mL.
4. Check your readings against the known values provided by your instructor.

38A-6 Reading a Buret

Discussion

The following exercise demonstrates the proper way to use a buret.

PROCEDURE

1. Mount a buret in a buret stand, and fill the buret with distilled water.
2. Wait at least 30 seconds before taking the initial reading. Use a buret reading card to take readings. A buret reading card can be easily constructed by applying a piece of black electrical tape to a 3″ × 5″ card. Never adjust the volume of solution in a buret to exactly 0.00 mL. Attempting to do so will introduce bias into the measurement process and waste time.
3. Now let about 5 mL run into a 250-mL Erlenmeyer flask. Wait at least 30 seconds and take the "final reading." The amount of solution in the Erlenmeyer flask is equal to the difference between the final reading and the initial reading. Record the final reading in your laboratory notebook, and then ask your instructor to take the final reading. Compare the two readings. They should agree within 0.01 mL. Notice that the final digit in the buret reading is your estimate of the distance between two consecutive 0.1-mL marks on the buret.
4. Refill the buret, and take a new zero reading. Now add 30 drops to the Erlenmeyer flask, and take the final reading. Calculate the mean volume of one drop; repeat this using 40 drops, and again calculate the mean volume of a drop. Record these results and compare them.
5. Finally, practice adding half-drops to the flask. Calculate the mean volume of several half-drops, and compare your results with those that you obtained with full drops. When you perform titrations, you should attempt to determine end points to within half a drop to achieve good precision.

Charles D. Winters

Buret section constructed from a discarded buret. Broken burets are carefully cleaned and cut into pieces about 10 cm in length. The upper end of each section is carefully sealed by glassblowing, and the opposite end is drawn out to a tip. The tipped end is then cut so that there is approximately a 1-mm opening in the tipped end of the buret section. A hypodermic syringe fitted with a large-bore needle is then used to add distilled water to each section until it is about half full. The tipped end of each section is then sealed by glassblowing, and the sections are stored upside-down in a test tube rack or a wooden block with holes drilled to accommodate the sections. Each buret section should be permanently marked with a unique number.

38A-7 Sampling[1]

Discussion

In most analytical methods, only a small fraction of the entire population is analyzed. The results from the determination of an analyte in a laboratory sample are assumed to be similar to the concentration of the analyte in the whole population. Consequently, a laboratory sample taken from the entire batch must be representative of the population.

In this experiment, you will investigate how the sample size influences the uncertainty associated with the sampling step. Generally, the required sample size must

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[1]J. E. Vitt and R. C. Engstrom, *J. Chem. Educ.,* **1999**, *76,* 99, **DOI**: 10.1021/ed076p99.

increase as the sample heterogeneity increases, as the fraction of the analyte decreases, or as the desired uncertainty decreases. The model system used in this experiment consists of a collection of plastic beads that are identical in size, shape, and density but that are different in color. If p represents the fraction of the particles of the analyte (beads of the first color), then $1 - p$ is the fraction of the second type of particles (beads of the second color). If a sample of n particles is drawn from the population, then the number of particles of the analyte in the sample should be np. It can be shown that the standard deviation of the number of particles of analyte np obtained from a sample of the two-component mixture is $\sqrt{np(1 - p)}$. The relative standard deviation (σ_r) is then

$$\sigma_r = \frac{\sqrt{np(1 - p)}}{np} = \sqrt{\frac{1 - p}{np}}$$

This equation suggests that, as the number of particles sampled increases, the relative uncertainty decreases. Using a mixture of beads of two colors, you will determine the uncertainty of sampling as a function of sample size.

PROCEDURE

1. Stir the container of beads thoroughly, and withdraw a sample of beads using a small beaker. Make sure that the beaker is full to the top but not overflowing.
2. Empty the beads into a counting tray, and count the number of beads of each color.
3. Repeat Step 1 using a medium-size beaker and then the larger beaker. Record the total number of beads in your sample and the percentage of beads of a color indicated by your instructor. Each student in your class will collect and count three similar samples and enter the data on a class chart that will be provided by your instructor. After all data are entered, the chart will be copied and distributed to all students in your class.

CALCULATIONS

1. Using the compiled class data, calculate the mean percentage of beads of the specified color and the relative standard deviation of that percentage for each sample size.
2. Using the equation given previously, based on sampling theory, calculate the theoretical relative standard deviation using the values of p and the mean number of particles for each of the three sample sizes.
3. Compare your class data with the theoretical result. Does the relative standard deviation decrease as the sample size increases, as predicted by sampling theory?
4. Use the equation for the relative standard deviation to find the number of beads that would have to be sampled to achieve a relative standard deviation of 0.002.
5. Suggest two reasons why this theory might not be adequate to describe the sampling of many materials for chemical analysis.

38A-8 Determining Sampling Error by Flow Injection Analysis[2]

Discussion

The overall variance in analyzing a laboratory sample s_o^2 can be considered to be the sum of the method variance s_m^2 and the sampling variance s_s^2 (see Section 8B-2). We can further decompose the method variance into the sum of the variances due to sample preparation s_p^2 and the final measurement step s_f^2.

$$s_o^2 = s_s^2 + s_p^2 + s_f^2$$

We can estimate the final measurement variance s_f^2 by making replicate measurements on the same sample. The sample preparation variance s_p^2 can be estimated by propagation of the uncertainties in this step. If we then obtain the overall variance s_o^2 from replicate measurements on different samples, the sampling variance s_s^2 is readily obtained by subtraction.

The determination of phosphate by a colorimetric flow-injection procedure is used to obtain the needed data. The reaction is

$$H_3PO_4 + 12MoO_4^{2-} + 24H^+ \rightleftharpoons H_3PMo_{12}O_{40} + 12H_2O$$

The 12-molybdophosphoric acid $H_3PMo_{12}O_{40}$, usually abbreviated as 12-MPA, is then reduced to phosphomolybdenum blue, PMB, by a suitable reducing agent such as ascorbic acid.

$$12\text{-MPA} + \text{ascorbic acid} \rightarrow \text{PMB} + \text{dehydroascorbic acid}$$
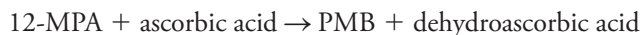
The absorbance of the PMB product is then measured at 650 nm in the flow injection colorimeter.

PREPARATION OF SOLUTIONS

1. *Nitric acid solution, 0.4 M.* Add 26 mL of concentrated HNO_3 to a 1-L flask and dilute to the mark with distilled water.
2. *Molybdate reagent, 0.005 M, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.* Dissolve 0.618 g ammonium heptamolybdate in 0.40 M HNO_3 in a 100-mL volumetric flask. Dilute to the mark with 0.40 M HNO_3.
3. *Ascorbic acid reagent, 0.7% in 1% glycerin.* Add 0.7 g of ascorbic acid and about 0.8 mL of glycerin to a 100-mL volumetric flask and dilute to the mark with distilled water (Note).
4. *Phosphate stock solution, 100 ppm phosphate.* Add 0.0143 g KH_2PO_4 to a 100-mL volumetric flask and dilute to the mark with distilled water.
5. *Phosphate working solutions, 10, 20, 30, 40, and 60 ppm phosphate.* Each student should prepare these solutions in 25-mL volumetric flasks.

Note
The glycerin is used as a surfactant in the flow injection analysis system.

[2]R. D. Guy, L. Ramaley, and P. D. Wentzell, *J. Chem. Educ.,* **1998**, *75,* 1028, **DOI**: 10.1021/ed075p1028.

PROCEDURE

Students should work in pairs during this experiment. If you are Student 1, pre-pare the unknown solid mixture (Note 1). Mix and grind the sample with a mortar and pestle for at least 10 minutes. After mixing and grinding, transfer the mixture to a clean sheet of white paper to form a pie-shaped pile. Using a spatula, divide the pie into six equal wedges. From each wedge, remove a portion that is nominally 0.10 g, and accurately determine its mass. Transfer each portion to separate 10-mL volumetric flasks, and dilute with distilled water. Return the remaining solid mixture back to the mortar and briefly mix. Transfer the mixture again to a sheet of white paper, and form a new pie-shaped pile. Again divide the pile into six wedges. Now remove a portion that is nominally 0.25 g, and accurately weigh it. Repeat for the other five wedges. Transfer these to separate 25-mL volumetric flasks, and di-lute to the mark with distilled water. Repeat the process for nominal masses of 0.50 g, diluting to 50 mL; 1.0 g, diluting to 100 mL; and 2.50 g, diluting to 250 mL. In the end, Student 1 should have five sets with six solutions in each set. Each set should have the same nominal concentration but different masses of the unknown mixture.

While Student 1 is preparing the samples, Student 2 should obtain the data for a calibration curve using the phosphate standards. If you are Student 2, use the flow injection analysis system, as shown in Figure 38-1. The product is detected after re-action at 650 nm with a flow-through detection cell. Inject each phosphate stan-dard three times, and measure the peak absorbance for each standard. Determine the mean values of the peak absorbance for each standard versus concentration. By this time, Student 1 should have the unknown samples prepared.

Now inject the unknown samples in triplicate. Each set should require 18 injec-tions. For the final solution in the last set, do 10 replicate injections to obtain a good estimate of the final measurement variance, s_f^2.

Data Analysis
Enter the calibration curve data taken by Student 2 into a spreadsheet and use linear least-squares analysis to obtain the calibration curve equation. Enter the data for the five sets of unknown samples, and use the least-squares equation to calculate the concentration of phosphate in each of the 30 samples. Express the concentration of phosphate as the mass percentage of KH_2PO_4 in the original mixture. Your spread-sheet should look similar to the spreadsheet shown in Figure 38-2. Generate a plot of percent KH_2PO_4 versus sample mass. Note the importance of sample size in the spread of the data.

Now decompose the variance into its various components and estimate the In-gamells' sampling constant K_s (see Section 8B-3). A spreadsheet similar to that
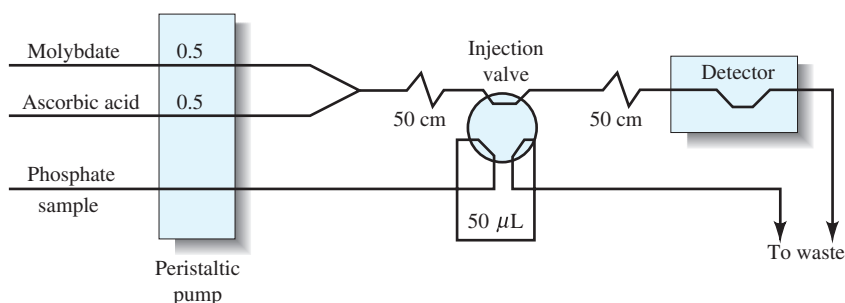

Figure 38-1 Flow injection analysis configuration for determining phosphate. Flow rates are in mL/min. Tygon tubing was 0.8-mm i.d.

	A	B	C	D	E	F
1	Nominal mass, g	Sample No	Actual mass, g	Solution volume, mL	Peak absorbance	Concn, %KH₂PO₄
2	0.10	1		10.00		
3		2		10.00		
4		3		10.00		
5		4		10.00		
6		5		10.00		
7		6		10.00		
8	0.25	1		25.00		
9		2		25.00		
10		3		25.00		
11		4		25.00		
12		5		25.00		
13		6		25.00		
14	0.50	1		50.00		
15		2		50.00		
16		3		50.00		
17		4		50.00		
18		5		50.00		
19		6		50.00		
20	1.00	1		100.0		
21		2		100.0		
22		3		100.0		
23		4		100.0		
24		5		100.0		
25		6		100.0		
26	2.50	1		250.0		
27		2		250.0		
28		3		250.0		
29		4		250.0		
30		5		250.0		
31		6		250.0		

Figure 38-2 Spreadsheet for data entry for unknown phosphate samples.

shown in Figure 38-3 can be constructed to carry out these calculations. The overall standard deviation s_o can be obtained by determining the standard deviation of all 30 results shown in Figure 38-2 (standard deviation of the last column). The standard deviation of the final measurement s_f can be determined from the 10 replicate measurements made on the last solution of the unknown mixture. Be certain to convert the peak absorbances to percent KH_2PO_4 before calculating the standard deviation.

The standard deviation in the results due to sample preparation can be calculated by propagating the measurement uncertainties in the sample preparation step. The only sources of uncertainty are the uncertainties in mass and volume. The following equation is appropriate for s_p:

$$s_p = \text{avg. \% } KH_2PO_4 \times \sqrt{\frac{2s_m^2}{(\overline{m})^2} + \frac{s_V^2}{(V)^2}}$$

where $\overline{m}$ is the average mass and V is the volume. There is a factor of 2 in front of the mass variance because two measurements are made to determine the mass: the tare

	A	B	C	D	E	F	G	H	I
1	Nominal mass, g	Average mass, g	Avg. %KH₂PO₄	s_o	s_f	s_p	s_s	%RSD₅	K_s
2	0.10								
3	0.25								
4	0.50								
5	1.00								
6	2.50								

Figure 38-3 Spreadsheet for decomposition of variances and calculation of the sampling constant.

TABLE 38-1

Standard Deviations in Mass and Volume			
Nominal Mass, g	**Solution Volume, mL**	**S_{mass}, g**	**S_{vol}, mL**
0.10	10	0.0001	0.02
0.25	25	0.0001	0.03
0.50	50	0.0001	0.05
1.00	100	0.001	0.08
2.50	250	0.001	0.12

and the mass measurement itself. The standard deviations in mass and volume can be taken, as shown in Table 38-1.

The final calculation of the sampling variance is done by subtracting the variances due to sample preparation and final measurement from the overall variance. Taking the square root gives the sampling standard deviation (Note 2). Finally, the sampling constant is obtained by multiplying the % relative standard deviation (RSD) squared and the average mass of the sample (see Equation 8-7).

Notes

1. Unknowns should contain 0.40 to 0.64 g of solid KH_2PO_4 added to about 80 g of solid NaCl.
2. The sampling standard deviation will usually be the largest component of the overall variance.

38B   GRAVIMETRIC METHODS OF ANALYSIS

General aspects, calculations, and typical applications of gravimetric analysis are discussed in Chapter 12.

38B-1 The Gravimetric Determination of Chloride in a Soluble Sample

Discussion

The chloride content of a soluble salt can be determined by precipitation as silver chloride.

$$Ag^+ + Cl^- \rightarrow AgCl(s)$$
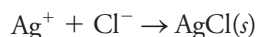
The precipitate is collected in a weighed filtering crucible and is washed. After the precipitate has been dried to a constant mass at 110°C, its mass is determined.

The solution containing the sample is kept slightly acidic during the precipitation to eliminate possible interference from anions of weak acids (such as CO_3^{2-}) that form sparingly soluble silver salts in a neutral environment. A moderate excess of silver ion is needed to diminish the solubility of silver chloride, but a large excess is avoided to minimize coprecipitation of silver nitrate.

Silver chloride forms first as a colloid and is subsequently coagulated with heat. Nitric acid and the small excess of silver nitrate promote coagulation by providing a moderately high electrolyte concentration. Nitric acid in the wash solution main-tains the electrolyte concentration and eliminates the possibility of peptization during the washing step; the acid subsequently decomposes to give volatile products when the precipitate is dried. See Section 12A-2 for additional information concerning the properties and treatment of colloidal precipitates.

In common with other silver halides, finely divided silver chloride undergoes photodecomposition:

$$2AgCl(s) \xrightarrow{h\nu} 2Ag(s) + Cl_2(g)$$
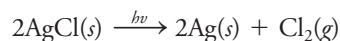
The elemental silver produced in this reaction is responsible for the violet color that develops in the precipitate. In principle, this reaction leads to low results for chloride ion. In practice, however, its effect is negligible provided that direct and prolonged exposure of the precipitate to sunlight is avoided.

If photodecomposition of silver chloride occurs before filtration, the additional reaction

$$3Cl_2(aq) + 3H_2O + 5Ag^+ \rightarrow 5AgCl(s) + ClO_3^- + 6H^+$$
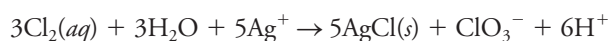
tends to cause high results.

In the usual procedure, some photodecomposition of silver chloride is inevitable. It is worthwhile to minimize exposure of the solid to intense sources of light as much as possible.

Because silver nitrate is expensive, any unused reagent should be collected in a storage container; similarly, precipitated silver chloride should be retained after the analysis is complete.[3]

PROCEDURE

Clean three medium-porosity sintered-glass or porcelain filtering crucibles by allowing about 5 mL of concentrated HNO_3 to stand in each for about 5 min. Use a vacuum (see Figure 2-16) to draw the acid through the crucible. Rinse each crucible with three portions of tap water, and then discontinue the vacuum. Next, add about 5 mL of 6 M NH_3 and wait for about 5 min before drawing it through the filter. Finally, rinse each crucible with six to eight portions of distilled or deionized water. Provide each crucible with an identifying mark. Dry the crucibles to constant mass by heating at 110°C while the other steps in the analysis are being carried out. The first drying should be for at least 1 hr; subsequent heating periods can be somewhat shorter (30 to 40 min). This process of heating and drying should be repeated until the mass becomes constant to within 0.2 to 0.3 mg.

Transfer the unknown to a weighing bottle and dry it at 110°C (see Figure 2-9) for 1 to 2 hr; allow the bottle and contents to cool to room temperature in a desiccator. Weigh (to the nearest 0.1 mg) individual samples by difference into 400-mL beakers (Note 1). Dissolve each sample in about 100 mL of distilled water to which 2 to 3 mL of 6 M HNO_3 have been added.

Slowly, and with good stirring, add 0.2 M $AgNO_3$ to each of the cold sample solutions until AgCl is observed to coagulate (Notes 2 and 3), and then introduce an additional 3 to 5 mL. Heat almost to boiling, and digest the solids for about 10 min. Add a few drops of $AgNO_3$ to confirm that precipitation is complete. If more precipitate forms, add about 3 mL of $AgNO_3$, digest, and again test for completeness of

> WARNING: Concentrated nitric acid is extremely corrosive. If you get any on your skin, wash immediately with copious amounts of water.

> Be sure to label your beakers and crucibles.

> To *digest* means to heat an unstirred precipitate in the **mother liquor**, that is, the solution from which it is formed.

[3]Silver can be removed from silver chloride and from surplus reagent by reduction with ascorbic acid; see J. W. Hill and L. Bellows, *J. Chem. Educ.,* **1986**, *63*(4), 357, **DOI**: 10.1021/ed063p357; for recovery (as $AgNO_3$) based on ion exchange, see also J. P. Rawat and S. Iqbal M. Kamoonpuri, *J. Chem. Educ.,* **1986**, *63*(4), 537, **DOI**: 10.1021/ed063p537. For a potential hazard in the recovery of silver nitrate, see D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Chem. Int.,* **1987**, *9*(1), 3.

precipitation. Pour any unused $AgNO_3$ into a waste container (*not* into the original reagent bottle). Cover each beaker, and store in a dark place for at least 2 hr (preferably until the next laboratory period).

Read the instructions for filtration in Section 2F. Decant the supernatant liquids through weighed filtering crucibles. Wash the precipitates several times (while they are still in the beaker) with a solution consisting of 2 to 5 mL of 6 M HNO_3 per liter of distilled water; decant these washings through the filters. Quantitatively transfer the AgCl from the beakers to the individual crucibles with fine streams of wash solution; use rubber policemen to dislodge any particles that adhere to the walls of the beakers. Continue washing until the filtrates are essentially free of Ag^+ ion (Note 4).

Dry the precipitate at 110°C for at least 1 hr. Store the crucibles in a desiccator while they cool. Determine the mass of the crucibles and their contents. Repeat the cycle of heating, cooling, and weighing until consecutive weighings agree to within 0.2 mg. Calculate the percentage of Cl^- in the sample.

When the analysis is complete, remove the precipitates by gently tapping the crucibles over a piece of glazed paper. Transfer the collected AgCl to a container for silver wastes. Remove the last traces of AgCl by filling the crucibles with 6 M NH_3 and allowing them to stand.

Notes

1. Consult with the instructor concerning an appropriate sample size.
2. Determine the approximate amount of $AgNO_3$ needed by calculating the volume that would be required if the unknown were pure NaCl.
3. Use a separate stirring rod for each sample and leave it in its beaker throughout the determination.
4. To test the washings for Ag^+, collect a small volume in a test tube and add a few drops of dilute HCl. Washing is judged complete when little or no turbidity develops.

38B-2 The Gravimetric Determination of Tin in Brass

Discussion

Brasses are important alloys. Copper is ordinarily the principal constituent, with lesser amounts of lead, zinc, tin, and possibly other elements as well. Treatment of a brass with nitric acid results in the formation of the sparingly soluble "metastannic acid" $H_2SnO_3 \cdot xH_2O$; all other constituents are dissolved. The solid is filtered, washed, and ignited to SnO_2.

The gravimetric determination of tin provides experience in the use of ashless filter paper and is frequently performed in conjunction with a more inclusive analysis of a brass sample.

PROCEDURE

Provide identifying marks on three porcelain crucibles and their covers. During waiting periods in the experiment, bring each set of crucibles and covers to constant mass by ignition at 900°C in a muffle furnace.

Do not dry the unknown. If so instructed, rinse it with acetone to remove any oil or grease. Weigh (to the nearest 0.1 mg) approximately 1-g samples of the unknown into 250-mL beakers. Cover the beakers with watch glasses. *Place the beakers in the hood,* and cautiously introduce a mixture containing about 15 mL of concentrated HNO_3 and 10 mL of H_2O. Digest the samples for at least 30 min;

add more HNO_3 if necessary. Rinse the watch glasses, then evaporate the solutions to about 5 mL, but not to dryness (Note 1).

Add about 5 mL of 3 M HNO_3, 25 mL of distilled water, and one quarter of a tablet of filter paper pulp to each sample; heat without boiling for about 45 min. Collect the precipitated $H_2SnO_3 \cdot xH_2O$ on fine-porosity ashless filter papers (see Section 2F-3 and Notes 2 and 3). Use many small volumes of hot 0.3 M HNO_3 to wash the last traces of copper from the precipitate. Test for completeness of washing with a drop of $NH_3(aq)$ on the top of the precipitate; wash further if the precipitate turns blue.

Remove the filter paper and its contents from the funnels, fold, and place in crucibles that (with their covers) have been brought to constant mass (see Figure 2-14). Ash the filter paper at as low a temperature as possible. There must be free access of air throughout the charring (see Section 2F-3 and Figure 2-15). Gradually increase the temperature until all the carbon has been removed. Then bring the covered crucibles and their contents to constant mass in a 900°C furnace (Note 4).

Calculate the percentage of tin in the unknown.

Notes

1. It is often time-consuming and difficult to redissolve the soluble components of the residue after a sample has been evaporated to dryness.
2. The filtration step can be quite time-consuming and once started cannot be interrupted.
3. If the unknown is to be analyzed electrolytically for its lead and copper content (see Section 38K-1), collect the filtrates in tall-form beakers. The final volume should be about 125 mL; evaporate to that volume if necessary. If the analysis is for tin only, the volume of washings is not important.
4. Partial reduction of SnO_2 may cause the ignited precipitate to appear gray. In this case, add a drop of nitric acid, cautiously evaporate, and ignite again.

38B-3 The Gravimetric Determination of Nickel in Steel

Discussion

The nickel in a steel sample can be precipitated from a slightly alkaline medium with an alcoholic solution of dimethylglyoxime (see Section 12C-3). Interference from iron(III) is eliminated by masking with tartaric acid. The product is freed of moisture by drying at 110°C.

> Iron(III) forms a highly stable complex with tartrate ion, which prevents it from precipitating as $Fe_2O_3 \cdot xH_2O$ in slightly alkaline solutions.

The bulky character of nickel dimethylglyoxime limits the mass of nickel that can be accommodated conveniently and thus the sample mass. Care must be taken to control the excess of alcoholic dimethylglyoxime used. If too much is added, the alcohol concentration becomes sufficient to dissolve appreciable amounts of the nickel dimethylglyoxime, which leads to low results. If the alcohol concentration becomes too low, however, some of the reagent may precipitate and cause a positive error.

PREPARATION OF SOLUTIONS

1. *Dimethylglyoxime, 1%* (*w/v*). Dissolve 10 g of dimethylglyoxime in 1 L of ethanol. (This solution is sufficient for about 50 precipitations.)
2. *Tartaric acid, 15%* (*w/v*). Dissolve 225 g of tartaric acid in sufficient water to give 1500 mL of solution. Filter before use if the solution is not clear. (This solution is sufficient for about 50 precipitations.)

PROCEDURE

Clean and mark three medium-porosity sintered-glass crucibles (Note 1); bring them to constant mass by drying at 110°C for at least 1 hr.

Weigh (to the nearest 0.1 mg) samples containing 30 to 35 mg of nickel into individual 400-mL beakers (Note 2). In the hood, dissolve each sample in about 50 mL of 6 M HCl with gentle warming. Carefully add approximately 15 mL of 6 M HNO_3, and boil gently to expel any oxides of nitrogen that may have been produced. Dilute to about 200 mL and heat to boiling. Introduce about 30 mL of 15% tartaric acid and sufficient concentrated $NH_3(aq)$ to produce a faint odor of NH_3 in the vapors over the solutions (Note 3); then add another 1 to 2 mL of $NH_3(aq)$. If the solutions are not clear at this stage, proceed as directed in Note 4. Make the solutions acidic with HCl (no odor of NH_3), heat to 60° to 80°C, and add about 20 mL of the 1% dimethylglyoxime solution. With good stirring, add 6 M NH_3 until a slight excess exists (faint odor of NH_3) plus an additional 1 to 2 mL. Digest the precipitates for 30 to 60 min, cool for at least 1 hr, and filter.

Wash the solids with water until the washings are free of Cl^- (Note 5). Bring the crucibles and their contents to constant mass at 110°C. Report the percentage of nickel in the sample. The dried precipitate has the composition $Ni(C_4H_7O_2N_2)_2$ (288.92 g/mol).

Notes

1. Medium-porosity porcelain filtering crucibles or Gooch crucibles with glass pads can be substituted for sintered-glass crucibles in this determination.
2. Use a separate stirring rod for each sample and leave it in the beaker throughout.
3. The presence or absence of excess NH_3 is readily established by odor; use a waving motion with your hand to waft the vapors toward your nose.
4. If $Fe_2O_3 \cdot xH_2O$ forms on addition of NH_3, acidify the solution with HCl, introduce additional tartaric acid, and neutralize again. Alternatively, remove the solid by filtration. Thorough washing with a hot NH_3/NH_4Cl solution is required; the washings are combined with the solution containing the bulk of the sample.
5. Test the washings for Cl^- by collecting a small portion in a test tube, acidifying with HNO_3, and adding a drop or two of 0.1 M $AgNO_3$. Washing is judged complete when little or no turbidity develops.

38C NEUTRALIZATION TITRATIONS

Discussion

Neutralization titrations are performed with standard solutions of strong acids or bases. While a single solution (of either acid or base) is sufficient for the titration of a given type of analyte, it is convenient to have standard solutions of both acid and base available in case back-titration is needed to locate the end point more exactly. The concentration of one solution is established by titration against a primary standard; the concentration of the other is then determined from the acid/base ratio (that is, the volume of acid needed to neutralize 1.000 mL of the base).

38C-1 The Effect of Atmospheric Carbon Dioxide on Neutralization Titrations

Water in equilibrium with the atmosphere is about 1×10^{-5} M in carbonic acid as a consequence of the equilibrium

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq)$$
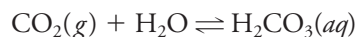
At this concentration level, the amount of 0.1 M base consumed by the carbonic acid in a typical titration is negligible. With more dilute reagents (<0.05 M), however, the water used as a solvent for the analyte and in the preparation of reagents must be freed of carbonic acid by boiling for a brief period.

Water that has been purified by distillation rather than by deionization is often supersaturated with carbon dioxide and may thus contain sufficient acid to affect the results of an analysis.[4] The instructions that follow are based on the assumption that the amount of carbon dioxide in the water supply can be neglected without causing serious error. For further discussion of the effects of carbon dioxide in neutralization titrations, see Section 16A-3.

38C-2 Preparation of Indicator Solutions for Neutralization Titrations

Discussion

The theory of acid/base indicators is discussed in Section 14A-2. An indicator exists for virtually any pH range between 1 and 13.[5] Directions follow for the preparation of indicator solutions suitable for most neutralization titrations.

PROCEDURE

Stock solutions ordinarily contain 0.5 to 1.0 g of indicator per liter. (One liter of indicator is sufficient for hundreds of titrations.)

1. *Bromocresol green.* Dissolve the sodium salt directly in distilled water.
2. *Phenolphthalein, thymolphthalein.* Dissolve the solid indicator in a solution consisting of 800 mL of ethanol and 200 mL of distilled or deionized water.

38C-3 Preparation of Dilute Hydrochloric Acid Solutions

Discussion

The preparation and standardization of acids are considered in Sections 16A-1 and 16A-2.

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[4]Water that is to be used for neutralization titrations can be tested by adding 5 drops of phenolphthalein to a 500-mL portion. Less than 0.2 to 0.3 mL of 0.1 M OH^- should suffice to produce the first faint pink color of the indicator. If a larger volume is needed, the water should be boiled and cooled before it is used to prepare standard solutions or to dissolve samples.

[5]See, for example, J. A. Dean, *Analytical Chemistry Handbook,* New York: McGraw-Hill, 1995, pp. 3.31–3.33.

PROCEDURE

For a 0.1 M solution, add about 8 mL of concentrated HCl to about 1 L of distilled water (Note). Mix thoroughly, and store in a glass-stoppered bottle.

Note

It is advisable to eliminate CO_2 from the water by means of preliminary boiling if very dilute solutions (<0.05 M) are being prepared.

38C-4 Preparation of Carbonate-Free Sodium Hydroxide

Discussion

See Sections 16A-3 and 16A-4 for information concerning the preparation and standardization of bases.

Standard solutions of base are reasonably stable as long as they are protected from contact with the atmosphere. Figure 38-4 shows an arrangement for preventing the uptake of atmospheric carbon dioxide during storage and when the reagent is dispensed. Air entering the vessel is passed over a solid absorbent for CO_2, such as soda lime or Ascarite II.[6] The contamination that occurs as the solution is transferred from this storage bottle to the buret is ordinarily negligible.

As an alternative to the storage system shown in Figure 38-4, a tightly capped low-density polyethylene bottle can usually provide sufficient short-term protection against the uptake of atmospheric carbon dioxide. Before capping, the flexible bottle is squeezed to minimize the interior air space. Care should also be taken to keep the bottle closed except during the brief periods when the contents are being transferred to a buret. Sodium hydroxide solutions will ultimately cause a polyethylene bottle to become brittle.
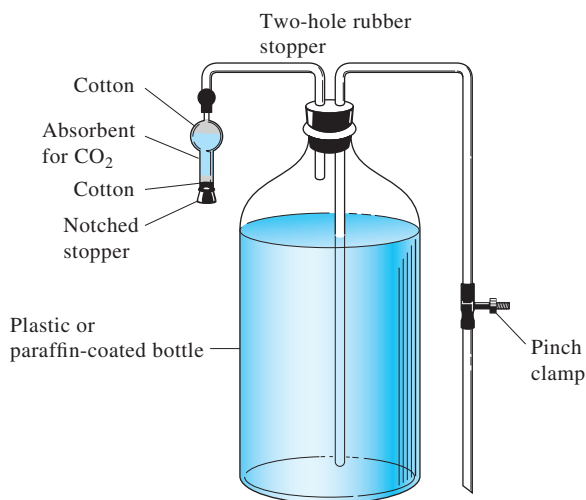

Figure 38-4 Arrangement for storage of standard base solutions.

[6]Thomas Scientific, Swedesboro, NJ. Ascarite II consists of sodium hydroxide deposited on a nonfibrous silicate structure.

The concentration of solutions of sodium hydroxide decreases slowly (0.1 to 0.3% per week) when the base is stored in glass bottles. The loss in strength is caused by the reaction of the base with the glass to form sodium silicates. For this reason, standard solutions of base should not be stored for extended periods (longer than 1 or 2 weeks) in glass containers. In addition, bases should never be kept in glass-stoppered containers because the reaction between the base and the stopper may cause the stopper to "freeze" after a brief period. Finally, to avoid the same type of freezing, burets with glass stopcocks should be promptly drained and thoroughly rinsed with water after use with standard base solutions. This problem is avoided with burets equipped with Teflon stopcocks.

> Solutions of bases should be stored in polyethylene bottles rather than glass because of the reaction between bases and glass. Such solutions should never be stored in glass-stoppered bottles; after standing for a period, removal of the stopper often becomes impossible.

PROCEDURE

If so directed by the instructor, prepare a bottle for protected storage (see Figure 38-4). Transfer 1 L of distilled water to the storage bottle (see the Note in Section 38C-3). Decant 4 to 5 mL of 50% NaOH into a small container (Note 2), add it to the water, and *mix thoroughly. Use extreme care in handling* 50% NaOH, which is highly corrosive. If the reagent comes into contact with skin, *immediately* flush the area with *copious* amounts of water.

Protect the solution from unnecessary contact with the atmosphere.

Notes

1. A solution of base that will be used up within 2 weeks can be stored in a tightly capped polyethylene bottle. After each removal of base, squeeze the bottle while tightening the cap to minimize the air space above the reagent. The bottle will become embrittled after extensive use as a container for bases.
2. Be certain that any solid Na_2CO_3 in the 50% NaOH has settled to the bottom of the container and that the decanted liquid is absolutely clear. If necessary, filter the base through a glass mat in a Gooch crucible; collect the clear filtrate in a test tube inserted into the filter flask.

38C-5 The Determination of the Acid/Base Ratio

Discussion

If both acid and base solutions have been prepared, it is useful to determine their volumetric combining ratio. Knowledge of this ratio and the concentration of one solution permits calculation of the molarity of the other.

PROCEDURE

Instructions for placing a buret into service are given in Sections 2G-4 and 2G-6; consult these instructions if necessary. Place a test tube or a small beaker over the top of the buret that holds the NaOH solution to minimize contact between the solution and the atmosphere.

Record the initial volumes of acid and base in the burets to the nearest 0.01 mL. *Do not attempt to adjust the initial reading to zero.* Deliver 35 to 40 mL of the acid into a 250-mL conical flask. Touch the tip of the buret to the inside wall of the flask, and rinse down with a little distilled water. Add two drops of phenolphthalein

(Note 1) and then sufficient base to render the solution a definite pink. Introduce acid dropwise to discharge the color, and again rinse down the walls of the flask. Carefully add base until the solution again acquires a faint pink hue that persists for at least 30 s (Notes 2 and 3). Record the final buret volumes (again, to the nearest 0.01 mL). Repeat the titration. Calculate the acid/base volume ratio. The ratios for duplicate titrations should agree to within 1 to 2 ppt. Perform additional titrations, if necessary, to achieve this order of precision.

Notes
1. The volume ratio can also be determined with an indicator that has an acidic transition range, such as bromocresol green. If the NaOH is contaminated with carbonate, the ratio obtained with this indicator will differ significantly from the value obtained with phenolphthalein. In general, the acid/base ratio should be evaluated with the indicator that is to be used in subsequent titrations.
2. Fractional drops can be formed on the buret tip, touched to the wall of the flask, and then rinsed down with a small amount of water from a squeeze bottle.
3. The phenolphthalein end point fades as CO_2 is absorbed from the atmosphere.

38C-6 Standardization of Hydrochloric Acid against Sodium Carbonate

Discussion

See Section 16A-2.

PROCEDURE

Dry a quantity of primary-standard Na_2CO_3 for about 2 hr at 110°C (see Figure 2-9), and cool in a desiccator. Weigh individual 0.20-g to 0.25-g samples (to the nearest 0.1 mg) into 250-mL conical flasks, and dissolve each in about 50 mL of distilled water. Introduce 3 drops of bromocresol green, and titrate with HCl until the solution just begins to change from blue to green. Boil the solution for 2 to 3 min, cool to room temperature (Note 1), and complete the titration (Note 2).

Determine an indicator correction by titrating approximately 100 mL of 0.05 M NaCl and 3 drops of indicator. Boil briefly, cool, and complete the titration. Subtract any volume needed for the blank from the titration volumes. Calculate the concentration of the HCl solution.

Notes
1. The indicator should change from green to blue as CO_2 is removed during heating. If no color change occurs, an excess of acid was added originally. This excess can be back-titrated with base, provided that the acid/base combining ratio is known; otherwise, the sample must be discarded.
2. It is permissible to back-titrate with base to establish the end point with greater certainty.

38C-7 Standardization of Sodium Hydroxide against Potassium Hydrogen Phthalate

Discussion

See Section 16A-4.

PROCEDURE

Dry a quantity of primary-standard potassium hydrogen phthalate (KHP) for about 2 hr at 110°C (see Figure 2-9), and cool in a desiccator. Weigh individual 0.7-g to 0.8-g samples (to the nearest 0.1 mg) into 250-mL conical flasks, and dissolve each in 50 to 75 mL of distilled water. Add 2 drops of phenolphthalein; titrate with base until the pink color of the indicator persists for 30 s (Note). Calculate the concentration of the NaOH solution.

Note
It is permissible to back-titrate with acid to establish the end point more precisely. Record the volume used in the back-titration. Use the acid/base ratio to calculate the net volume of base used in the standardization.

38C-8 The Determination of Potassium Hydrogen Phthalate in an Impure Sample

Discussion

The unknown is a mixture of KHP and a neutral salt. This analysis is conveniently performed concurrently with the standardization of the base.

PROCEDURE

Consult with the instructor concerning an appropriate sample size. Then follow the directions in Section 38C-7.

38C-9 Determining the Acid Content of Vinegars and Wines

Discussion

The total acid content of a vinegar or a wine is readily determined by titration with a standard base. It is customary to report the acid content of vinegar in terms of acetic acid, the principal acidic constituent, even though other acids are present. Similarly, the acid content of a wine is expressed as percent tartaric acid, even though there are other acids in the sample. Most vinegars contain about 5% acid (w/v) expressed as acetic acid; wines ordinarily contain somewhat less than 1% acid (w/v) expressed as tartaric acid.

PROCEDURE

1. *If the unknown is a vinegar* (Note 1), pipet 25.00 mL into a 250-mL volumetric flask and dilute to the mark with distilled water. Mix thoroughly, and pipet 50.00-mL aliquots into 250-mL conical flasks. Add about 50 mL of water and 2 drops of phenolphthalein (Note 2) to each, and titrate with standard 0.1 M NaOH to the first permanent ($\approx$30 s) pink color.

   Report the acidity of the vinegar as percent (w/v) CH_3COOH (60.053 g/mol).

2. *If the unknown is a wine,* pipet 50.00-mL aliquots into 250-mL conical flasks, add about 50 mL of distilled water and 2 drops of phenolphthalein to each (Note 2), and titrate to the first permanent (≈ 30 s) pink color.

Express the acidity of the sample as percent (w/v) tartaric acid, $C_2H_4O_2$ (COOH)$_2$ (150.09 g/mol) (Note 3).

Notes

1. The acidity of bottled vinegar tends to decrease on exposure to air. It is recommended that unknowns be stored in individual vials with snug covers.

2. The amount of indicator used should be increased as necessary to make the color change visible in colored samples.

3. Tartaric acid has two acidic hydrogens, both of which are titrated at a phenolphthalein end point.

38C-10 The Determination of Sodium Carbonate in an Impure Sample

Discussion

The titration of sodium carbonate is discussed in Section 16A-2 in connection with its use as a primary standard; the same considerations apply for the determination of carbonate in an unknown that has no interfering contaminants.

PROCEDURE

Dry the unknown at 110°C for 2 hr, and then cool in a desiccator. Consult with the instructor on an appropriate sample size. Then follow the instructions in Section 38C-6.

Report the percentage of Na_2CO_3 in the sample.

38C-11 The Determination of Amine Nitrogen by the Kjeldahl Method

Discussion

These directions are suitable for the Kjeldahl determination of protein in materials such as blood meal, wheat flour, pasta products, dry cereals, and pet foods. Simple modifications permit the analysis of unknowns containing highly oxidized forms of nitrogen in a broad range of materials.[7]

In the Kjeldahl method (see Section 16B-1), the organic sample is digested in hot concentrated sulfuric acid, which converts amine nitrogen in the sample to ammonium sulfate. After cooling, the sulfuric acid is neutralized by the addition of an excess of concentrated sodium hydroxide. The ammonia liberated by this treatment is then distilled into a measured excess of a standard solution of acid; the excess is determined by back-titration with standard base.

Figure 38-5 illustrates typical equipment for a Kjeldahl distillation. The long-necked container, which is used for both digestion and distillation, is called a Kjeldahl flask. In the apparatus in Figure 38-5a, the base is added slowly by partially

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[7]See *Official Methods of Analysis,* online ed., Washington, DC: Association of Official Analytical Chemists, http://www.eoma.aoac.org/.
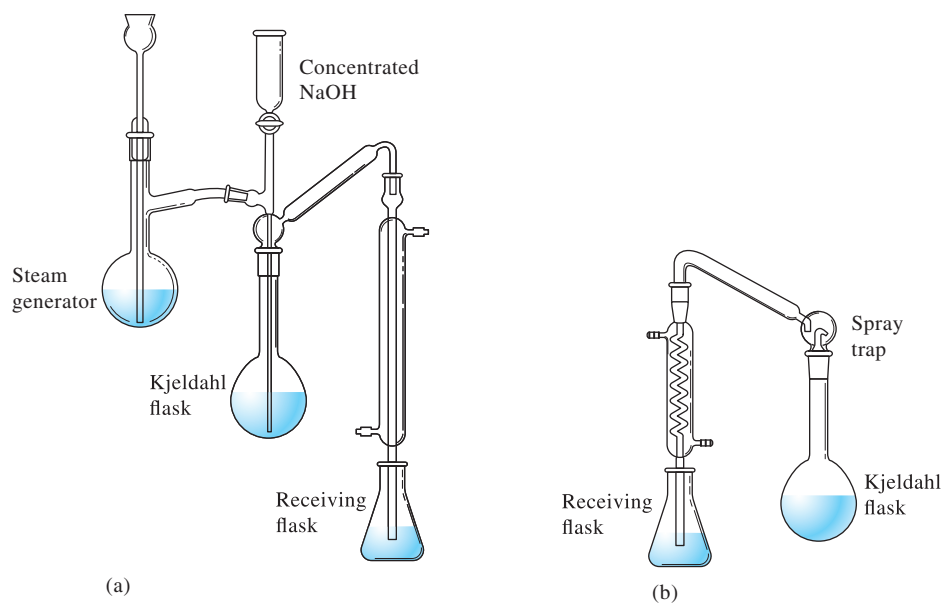
Figure 38-5   Kjeldahl distillation apparatus.

opening the stopcock from the NaOH storage vessel; the liberated ammonia is then carried to the receiving flask by steam distillation.

In an alternative method (see Figure 38-5b), a dense, concentrated sodium hydroxide solution is carefully poured down the side of the Kjeldahl flask to form a second, lower layer. The flask is then quickly connected to a spray trap and an ordinary condenser before loss of ammonia can occur. Only then are the two layers mixed by gentle swirling of the flask.

Quantitative collection of ammonia requires the tip of the condenser to extend into the liquid in the receiving flask throughout the distillation step. The tip must be removed before heating is discontinued, however. Otherwise, the liquid will be drawn back into the apparatus.

Two methods are commonly used to collect and determine the ammonia liberated from the sample. In one, the ammonia is distilled into a measured volume of standard acid. After the distillation is complete, the excess acid is back-titrated with standard base. An indicator with an acidic transition range is required because of the acidity of the ammonium ions present at equivalence. A convenient alternative, which requires only one standard solution, involves the collection of the ammonia in an unmeasured excess of boric acid, which retains the ammonia by the reaction

$$H_3BO_3 + NH_3 \rightarrow NH_4{}^+ + H_2BO_3{}^-$$
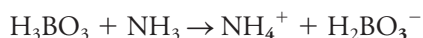
The dihydrogen borate ion produced is a reasonably strong base that can be titrated with a standard solution of hydrochloric acid.

$$H_2BO_3{}^- + H_3O^+ \rightarrow H_3BO_3 + H_2O$$
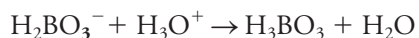
At the equivalence point, the solution contains boric acid and ammonium ions; an indicator with an acidic transition interval (such as bromocresol green) is again required.

PROCEDURE

Preparing Samples

Consult with the instructor on sample size. *If the unknown is powdered* (such as blood meal), weigh samples onto individual 9-cm filter papers (Note 1). Fold the paper around the sample and drop each into a Kjeldahl flask. (The paper keeps the samples from clinging to the neck of the flask.) *If the unknown is not powdered* (such as breakfast cereals or pasta), the samples can be weighed by difference directly into the Kjeldahl flasks.

Add 25 mL of concentrated H_2SO_4, 10 g of powdered K_2SO_4, and the catalyst (Note 2) to each flask.

Digestion

Clamp the flasks in a slanted position in a hood or vented digestion rack. Heat carefully to boiling. Discontinue heating briefly if foaming becomes excessive; never allow the foam to reach the neck of the flask. Once foaming ceases and the acid is boiling vigorously, the samples can be left unattended; prepare the distillation apparatus during this time. Continue digestion until the solution becomes colorless or faint yellow; 2 to 3 hr may be needed for some materials. If necessary, cautiously replace the acid lost by evaporation.

When digestion is complete, discontinue heating, and allow the flasks to cool to room temperature; swirl the flasks if the contents show signs of solidifying. Cautiously add 250 mL of water to each flask and again allow the solution to cool to room temperature.

Distillation of Ammonia

Arrange a distillation apparatus similar to that shown in Figure 38-5. Pipet 50.00 mL of standard 0.1 M HCl into the receiver flask (Note 3). Clamp the flask so that the tip of the adapter extends below the surface of the standard acid. Circulate water through the condenser jacket.

Hold the Kjeldahl flask at an angle and gently introduce about 60 mL of 50% (w/v) NaOH solution, taking care to minimize mixing with the solution in the flask. *The concentrated caustic solution is highly corrosive and should be handled with great care* (Note 4). Add several pieces of granulated zinc (Note 5) and a small piece of litmus paper. *Immediately* connect the Kjeldahl flask to the spray trap. Cautiously mix the contents by gentle swirling. The litmus paper should be blue after mixing is complete, indicating that the solution is basic.

Bring the solution to a boil, and distill at a steady rate until one half to one third of the original volume remains. Control the rate of heating to prevent the liquid in the receiver flask from being drawn back into the Kjeldahl flask. After distillation is judged complete, lower the receiver flask to bring the adapter well clear of the liquid. Discontinue heating, disconnect the apparatus, and rinse the inside of the condenser with small portions of distilled water, collecting the washings in the receiver flask. Add 2 drops of bromocresol green to the receiver flask, and titrate the residual HCl with standard 0.1 M NaOH to the color change of the indicator.

Report the percentage of nitrogen and the percentage of protein (Note 6) in the unknown.

Notes

1. If filter paper is used to hold the sample, carry a similar piece through the analysis as a blank. Acid-washed filter paper is frequently contaminated with measurable amounts of ammonium ion and should be avoided if possible.

2. Any of the following catalyze the digestion: a crystal of $CuSO_4$, 0.1 g of selenium, 0.2 g of $CuSeO_3$. The catalyst can be omitted, if desired.

3. A modification of this procedure uses about 50 mL of 4% boric acid solution instead of the standard HCl in the receiver flask. After distillation is complete, the ammonium borate produced is titrated with standard 0.1 M HCl, with 2 to 3 drops of bromocresol green as indicator.

4. If any sodium hydroxide solution comes into contact with your skin, wash the affected area *immediately* with copious amounts of water.

5. Granulated zinc (10 to 20 mesh) is added to minimize bumping during the distillation; it reacts slowly with the base to produce small bubbles of hydrogen that prevent superheating of the liquid.

6. The percentage of protein in the unknown is calculated by multiplying the % N by an appropriate factor: 5.70 for cereals, 6.25 for meats, and 6.38 for dairy products.

38D PRECIPITATION TITRATIONS

As noted in Section 17B-2, most precipitation titrations make use of a standard silver nitrate solution as titrant. Directions follow for the volumetric titration of chloride ion using an adsorption indicator.

38D-1 Preparing a Standard Silver Nitrate Solution

PROCEDURE

Use a top-loading balance to transfer the approximate mass of $AgNO_3$ to a weighing bottle (Note 1). Dry at 110°C for about 1 hr but not much longer (Note 2), and then cool to room temperature in a desiccator. Weigh the bottle and contents (to the nearest 0.1 mg). Transfer the bulk of the $AgNO_3$ to a volumetric flask using a powder funnel. Cap the weighing bottle, and reweigh it and any solid that remains. Rinse the powder funnel thoroughly. Dissolve the $AgNO_3$, dilute to the mark with water, and mix well (Note 3). Calculate the molar concentration of this solution.

Notes

1. Consult with the instructor concerning the volume and concentration of $AgNO_3$ to be prepared. The mass of $AgNO_3$ to be taken is as follows:

Silver Ion Concentration, M	Approximate Mass (g) of $AgNO_3$ Needed to Prepare		
	1000 mL	500 mL	250 mL
0.10	16.9	8.5	4.2
0.05	8.5	4.2	2.1
0.02	3.4	1.8	1.0

2. Prolonged heating causes partial decomposition of $AgNO_3$. Some discoloration may occur, even after only 1 hr at 110°C; the effect of this decomposition on the purity of the reagent is ordinarily imperceptible.

3. Silver nitrate solutions should be stored in a dark place when not in use.

38D-2 The Determination of Chloride by Titration with an Adsorption Indicator

Discussion

In this titration, the anionic adsorption indicator dichlorofluorescein is used to locate the end point. With the first excess of titrant, the indicator is incorporated into the counter-ion layer surrounding the silver chloride and imparts color to the solid (page 413). To obtain a satisfactory color change, it is desirable to maintain the particles of silver chloride in the colloidal state. Dextrin is added to the solution to stabilize the colloid and prevent its coagulation.

PREPARATION OF SOLUTIONS

Dichlorofluorescein indicator (sufficient for several hundred titrations). Dissolve 0.2 g of dichlorofluorescein in a solution prepared by mixing 75 mL of ethanol and 25 mL of water.

PROCEDURE

Dry the unknown at 110°C for about 1 hr; allow it to return to room temperature in a desiccator. Weigh individual samples (to the nearest 0.1 mg) into individual conical flasks, and dissolve them in appropriate volumes of distilled water (Note 1). To each, add about 0.1 g of dextrin and 5 drops of indicator. Titrate (Note 2) with $AgNO_3$ to the first permanent pink color of silver dichlorofluoresceinate. Report the percentage of Cl^- in the unknown.

Notes

1. Use 0.25-g samples for 0.1 M $AgNO_3$ and about half that amount for 0.05 M reagent. Dissolve the former in about 200 mL of distilled water and the latter in about 100 mL. If 0.02 M $AgNO_3$ is to be used, weigh a 0.4-g sample into a 500-mL volumetric flask, and take 50-mL aliquots for titration.
2. Colloidal AgCl is sensitive to photodecomposition, particularly in the presence of the indicator; attempts to perform the titration in direct sunlight will fail. If photodecomposition appears to be a problem, establish the approximate end point with a rough preliminary titration, and use this information to estimate the volumes of $AgNO_3$ needed for the other samples. For each subsequent sample, add the indicator and dextrin only after most of the $AgNO_3$ has been added, and then complete the titration without delay.

38D-3 The Determination of Chloride by a Weight Titration

Discussion

The Mohr method uses CrO_4^{2-} ion as an indicator in the titration of chloride ion with silver nitrate. The first excess of titrant results in the formation of a red silver chromate precipitate, which signals the end point.

Instead of a buret, a balance is employed in this procedure to determine the mass of silver nitrate solution needed to reach the end point. The concentration of the silver nitrate is most conveniently determined by standardization against primary-standard

sodium chloride, although direct preparation by mass is also feasible. The reagent concentration is expressed as weight (mass) molarity (mmol $AgNO_3$/g of solution). See Section 13D-1 for additional details.

PREPARATION OF SOLUTIONS

(a) *Silver nitrate, approximately 0.1 mmol/g of solution* (sufficient for about 10 titrations). Dissolve about 4.5 g of $AgNO_3$ in about 500 mL of distilled water. Standardize the solution against weighed quantities of reagent-grade NaCl as directed in Note 1 of the procedure. Express the concentration as weight (mass) molarity (mmol $AgNO_3$/g of solution). When not in use, store the solution in a dark place.

(b) *Potassium chromate, 5%* (sufficient for about 10 titrations). Dissolve about 1.0 g of K_2CrO_4 in about 20 mL of distilled water.

Note

Alternatively, standard $AgNO_3$ can be prepared directly by weight. To do so, follow the directions in Section 38D-1 for weighing out a known amount of primary-standard $AgNO_3$. Use a powder funnel to transfer the weighed $AgNO_3$ to a 500-mL polyethylene bottle that has been previously weighed to the nearest 10 mg. Add about 500 mL of water and weigh again. Calculate the weight molarity.

DIRECTIONS FOR PERFORMING A WEIGHT TITRATION

Prepare a reagent dispenser from a 60-mL polyethylene bottle with a screw cap equipped with a fine delivery tip. The tip can be prepared by constricting the opening of an ordinary medicine dropper in a flame. With a cork borer, make a hole in the cap that is slightly smaller than the outside diameter of the tip. Carefully force the tip through the hole; apply a bead of epoxy cement to seal the tip to the cap. Label the bottle.

Fill the reagent dispenser with a quantity of the standard titrant, and tighten the screw cap firmly. Weigh the bottle and its contents to the nearest milligram. Introduce a suitable indicator into the solution of the analyte. Grasp the dispenser so that its tip is below the lip of the flask and deliver several increments of the reagent by squeezing the bottle while rotating the flask with your other hand. When it is judged that only a few more drops of reagent are needed, ease the pressure on the bottle so that the flow stops; then touch the tip to the inside of the flask and further reduce the pressure on the dispenser so that the liquid in the tip is drawn back into the bottle as the tip is removed from the flask. Set the dispenser on a piece of clean, dry glazed paper and rinse down the inner walls of the flask with a stream of distilled or deionized water. Add reagent a drop at a time until the end point is reached (Note). Weigh the dispenser and record the data.

Note

Increments smaller than an ordinary drop can be added by forming a partial drop on the tip and then touching the tip to the wall. Rinse the walls with wash water to combine the partial drop with the bulk of solution.

PROCEDURE

Dry the unknown at 110°C for at least 1 hr (Note). Cool in a desiccator. Consult with your instructor for a suitable sample size. Weigh (to the nearest 0.1 mg) individual samples into 250-mL conical flasks, and dissolve in about 100 mL of distilled water. Add small quantities of $NaHCO_3$ until effervescence ceases. Introduce about 2 mL of K_2CrO_4 solution, and titrate to the first permanent appearance of red Ag_2CrO_4.

Determine an indicator blank by suspending a small amount of chloride-free $CaCO_3$ in 100 mL of distilled water containing 2 mL of K_2CrO_4.

Correct reagent masses for the blank. Report the percentage of Cl^- in the unknown.

Dispose of AgCl and reagents as directed by the instructor.

Note

The $AgNO_3$ is conveniently standardized concurrently with the analysis. Dry reagent-grade NaCl for about 1 h. Cool; then weigh (to the nearest 0.1 mg) 0.25-g portions into conical flasks and titrate as previously.

38E COMPLEX-FORMATION TITRATIONS WITH EDTA

See Section 17D for a discussion of the analytical uses of EDTA as a chelating reagent. Directions follow for direct titration of magnesium and determination of the hardness of natural water.

38E-1 Preparation of Solutions

PROCEDURE

A pH-10 buffer and an indicator solution are needed for these titrations.

1. *Buffer solution, pH 10* (sufficient for 80 to 100 titrations). Dilute 57 mL of concentrated NH_3 and 7 g of NH_4Cl in sufficient distilled water to give 100 mL of solution.
2. *Eriochrome Black T indicator* (sufficient for about 100 titrations). Dissolve 100 mg of the solid in a solution containing 15 mL of ethanolamine and 5 mL of absolute ethanol. This solution should be freshly prepared every 2 weeks; refrigeration slows its deterioration.

> Calmagite is a more stable, but more expensive alternative to Eriochrome Black T.

38E-2 Preparation of Standard 0.01 M EDTA Solution

Discussion

See Section 17D-1 for a description of the properties of reagent-grade $Na_2H_2Y \cdot 2H_2O$ and its use in the direct preparation of standard EDTA solutions.

PROCEDURE

Dry about 4 g of the purified dihydrate $Na_2H_2Y \cdot 2H_2O$ (Note 1) at 80°C to remove superficial moisture. Cool to room temperature in a desiccator. Weigh (to the

nearest milligram) about 3.8 g into a 1-L volumetric flask (Note 2). Use a powder funnel to ensure quantitative transfer; rinse the funnel well with water before removing it from the flask. Add 600 to 800 mL of water (Note 3) and swirl periodically. Dissolution may take 15 min or longer. When all the solid has dissolved, dilute to the mark with water and mix well (Note 4). In calculating the molarity of the solution, correct the mass of the salt for the 0.3% moisture it ordinarily retains after drying at 80°C.

Notes

1. Directions for the purification of the disodium salt are described by W. J. Blaedel and H. T. Knight, *Anal. Chem.,* **1954**, *26*(4), 741, **DOI**: 10.1021/ac60088a040.
2. The solution can be prepared from the anhydrous disodium salt, if desired. The mass taken should be about 3.6 g.
3. Water used in the preparation of standard EDTA solutions must be totally free of polyvalent cations. If any doubt exists concerning its quality, pass the water through a cation-exchange resin before use.
4. As an alternative, an EDTA solution that is approximately 0.01 M can be prepared and standardized by direct titration against a Mg^{2+} solution of known concentration (using the directions in Section 38E-3).

38E-3 The Determination of Magnesium by Direct Titration

Discussion

See Section 17D-7.

PROCEDURE

Submit a clean 500-mL volumetric flask to receive the unknown, dilute to the mark with water, and mix thoroughly. Transfer 50.00-mL aliquots to 250-mL conical flasks; add 1 to 2 mL of pH-10 buffer and 3 to 4 drops of Eriochrome Black T indicator to each. Titrate with 0.01 M EDTA until the color changes from red to pure blue (Notes 1 and 2).

Express the results as parts per million of Mg^{2+} in the sample.

Notes

1. The color change tends to be slow in the vicinity of the end point. Care must be taken to avoid overtitration.
2. Other alkaline earths, if present, are titrated along with the Mg^{2+}; removal of Ca^{2+} and Ba^{2+} can be accomplished with $(NH_4)_2CO_3$. Most polyvalent cations are also titrated. Precipitation as hydroxides or the use of a masking reagent may be needed to eliminate this source of interference.

38E-4 The Determination of Calcium by Displacement Titration

Discussion

A solution of the magnesium/EDTA complex is useful for the titration of cations that form more stable complexes than the magnesium complex but for which no indicator is available. Magnesium ions in the complex are displaced by a chemically

equivalent quantity of analyte cations. The remaining uncomplexed analyte and the liberated magnesium ions are then titrated with Eriochrome Black T as the indicator. Note that the concentration of the magnesium solution is not important; all that is necessary is that the molar ratio between Mg^{2+} and EDTA in the reagent be exactly unity.

PROCEDURE

Preparation of the Magnesium/EDTA Complex, **0.1 M (sufficient for 90 to 100 titrations)**

To 3.72 g of $Na_2H_2Y \cdot 2H_2O$ in 50 mL of distilled water, add an equivalent quantity (2.46 g) of $MgSO_4 \cdot 7H_2O$. Add a few drops of phenolphthalein, followed by sufficient 0.1 M NaOH to turn the solution faintly pink. Dilute to about 100 mL with water. The addition of a few drops of Eriochrome Black T to a portion of this solution buffered to pH 10 should cause a dull violet color to develop. Moreover, a single drop of 0.01 M Na_2H_2Y solution added to the violet solution should cause a color change to blue, and an equal quantity of 0.01 M Mg^{2+} should cause a change to red. The composition of the original solution should be adjusted with additional Mg^{2+} or H_2Y^{2-} until these criteria are met.

Titration

Weigh a sample of the unknown (to the nearest 0.1 mg) into a 500-mL beaker (Note 1). Cover with a watch glass, and carefully add 5 to 10 mL of 6 M HCl. After the sample has dissolved, remove CO_2 by adding about 50 mL of deionized water and boiling gently for a few minutes. Cool, add a drop or two of methyl red, and neutralize with 6 M NaOH until the red color is discharged. Quantitatively transfer the solution to a 500-mL volumetric flask, and dilute to the mark. Take 50.00-mL aliquots of the diluted solution for titration, treating each as follows: Add about 2 mL of pH-10 buffer, 1 mL of Mg/EDTA solution, and 3 to 4 drops of Eriochrome Black T or Calmagite indicator. Titrate (Note 2) with standard 0.01 M Na_2H_2Y to a color change from red to blue.

Report the number of milligrams of CaO in the sample.

Notes
1. The sample taken should contain 150 to 160 mg of Ca^{2+}.
2. Interferences with this titration are substantially the same as those encountered in the direct titration of Mg^{2+} and are eliminated in the same way.

38E-5 The Determination of Hardness in Water

Discussion

See Section 17D-9.

PROCEDURE

Acidify 100.0-mL aliquots of the sample with a few drops of HCl, and boil gently for a few minutes to eliminate CO_2. Cool, add 3 to 4 drops of methyl red, and neutralize with 0.1 M NaOH. Introduce 2 mL of pH-10 buffer and 3 to 4 drops of

Eriochrome Black T, and titrate with standard 0.01 M Na_2H_2Y to a color change from red to pure blue (Note).

Report the results in terms of milligrams of $CaCO_3$ per liter of water.

Note

The color change is sluggish if Mg^{2+} is absent. In this event, add 1 to 2 mL of 0.1 M MgY^{2-} before starting the titration. This reagent is prepared by adding 2.645 g of $MgSO_4 \cdot 7H_2O$ to 3.722 g of $Na_2H_2Y \cdot 2H_2O$ in 50 mL of distilled water. This solution is rendered faintly alkaline to phenolphthalein and is diluted to 100 mL. A small portion, mixed with pH-10 buffer and a few drops of Eriochrome Black T indicator, should have a dull violet color. A single drop of 0.01 M EDTA solution should cause a color change to blue, while an equal volume of 0.01 Mg^{2+} should cause a change to red. If necessary, adjust the composition with EDTA or with Mg^{2+} until these criteria are met.

38F   TITRATIONS WITH POTASSIUM PERMANGANATE

The properties and uses of potassium permanganate are described in Section 20C-1. Directions follow for the determination of iron in an ore and calcium in a limestone.

38F-1 Preparation of 0.02 M Potassium Permanganate

Discussion

See page 516 for a discussion of the precautions needed in the preparation and storage of permanganate solutions.

PROCEDURE

Dissolve about 3.2 g of $KMnO_4$ in 1 L of distilled water. Keep the solution at a gentle boil for about 1 hr. Cover and let stand overnight. Remove MnO_2 by filtration (Note 1) through a fine-porosity filtering crucible (Note 2) or through a Gooch crucible fitted with glass mats. Transfer the solution to a clean glass-stoppered bottle; store in the dark when not in use.

Notes
1. Heating and filtering can be omitted if the permanganate solution is standardized and used on the same day.
2. Remove the MnO_2 that collects on the fritted plate with 1 M H_2SO_4 containing a few milliliters of 3% H_2O_2, followed by a rinse with copious quantities of water.

38F-2 Standardization of Potassium Permanganate Solutions

Discussion

See Section 20C-1 for a discussion of primary standards for permanganate solutions. Directions follow for standardization with sodium oxalate.

PROCEDURE

Dry about 1.5 g of primary-standard $Na_2C_2O_4$ at 110°C for at least 1 hr. Cool in a desiccator; weigh (to the nearest 0.1 mg) individual 0.2-g to 0.3-g samples into 400-mL beakers. Dissolve each in about 250 mL of 1 M H_2SO_4. Heat each solution to 80°C to 90°C, and titrate with $KMnO_4$ while stirring with a thermometer. The pink color imparted by one addition should be permitted to disappear before any further titrant is introduced (Notes 1 and 2). Reheat if the temperature drops below 60°C. Take the first persistent ($\approx$ 30 s) pink color as the end point (Notes 3 and 4). Determine a blank by titrating an equal volume of the 1 M H_2SO_4.

   Correct the titration data for the blank, and calculate the concentration of the permanganate solution (Note 5).

Notes
1. Promptly wash any $KMnO_4$ that spatters on the walls of the beaker into the bulk of the liquid with a stream of water.
2. Finely divided MnO_2 will form along with Mn^{2+} if the $KMnO_4$ is added too rapidly, and it will cause the solution to acquire a faint brown discoloration. Precipitate formation is not a serious problem so long as sufficient oxalate remains to reduce the MnO_2 to Mn^{2+}; the titration is simply discontinued until the brown color disappears. The solution must be free of MnO_2 at the end point.
3. The surface of the permanganate solution rather than the bottom of the meniscus can be used to measure titrant volumes. Alternatively, backlighting with a flashlight or a match will permit reading of the meniscus in the conventional manner.
4. A permanganate solution should not be allowed to stand in a buret any longer than necessary because partial decomposition to MnO_2 may occur. Freshly formed MnO_2 can be removed from a glass surface with 1 M H_2SO_4 containing a small amount of 3% H_2O_2.
5. As noted on page 519, this procedure yields concentrations that are a few tenths of a percent low. For more accurate results, introduce from a buret sufficient permanganate to react with 90% to 95% of the oxalate (about 40 mL of 0.02 M $KMnO_4$ for a 0.3-g sample). Let the solution stand until the permanganate color disappears. Then warm to about 60°C and complete the titration, taking the first permanent pink ($\approx$ 30 s) as the end point. Determine a blank by titrating an equal volume of the 1 M H_2SO_4.

38F-3 The Determination of Calcium in a Limestone

Discussion

In common with a number of other cations, calcium is conveniently determined by precipitation with oxalate ion. The solid calcium oxalate is filtered, washed free of excess precipitating reagent, and dissolved in dilute acid. The oxalic acid liberated in this step is then titrated with standard permanganate or some other oxidizing reagent. This method is applicable to samples that contain magnesium and the alkali metals. Most other cations must be absent since they either precipitate or coprecipitate as oxalates and cause positive errors in the analysis.

Factors Affecting the Composition of Calcium Oxalate Precipitates   It is essential that the mole ratio between calcium and oxalate be exactly unity in the precipitate and thus in solution at the time of titration. A number of precautions are

needed to ensure this condition. For example, the calcium oxalate formed in a neutral or an ammoniacal solution is likely to be contaminated with calcium hydroxide or a basic calcium oxalate, either of which will cause low results. The formation of these compounds is prevented by adding the oxalate to an acidic solution of the sample and slowly forming the desired precipitate by the dropwise addition of ammonia. The coarsely crystalline calcium oxalate that is produced under these conditions is readily filtered. Losses resulting from the solubility of calcium oxalate are negligible above pH 4, provided that washing is limited to freeing the precipitate of excess oxalate.

Coprecipitation of sodium oxalate becomes a source of positive error in the determination of calcium whenever the concentration of sodium in the sample exceeds that of calcium. The error from this source can be eliminated by reprecipitation.

Magnesium, if present in high concentration, may also be a source of contamination. An excess of oxalate ion helps prevent this interference through the formation of soluble oxalate complexes of magnesium. Prompt filtration of the calcium oxalate can also help prevent interference because of the pronounced tendency of magnesium oxalate to form supersaturated solutions from which precipitate formation occurs only after an hour or more. These measures do not suffice for samples that contain more magnesium than calcium. In this case, **reprecipitation** of the calcium oxalate becomes necessary.

> **Reprecipitation** is a method of minimizing coprecipitation errors by dissolving the initial precipitate and then reforming the solid.

The Composition of Limestones

Limestones are composed principally of calcium carbonate; dolomitic limestones contain large amounts of magnesium carbonate as well. Calcium and magnesium silicates are also present in smaller amounts, along with the carbonates and silicates of iron, aluminum, manganese, titanium, sodium, and other metals.

Hydrochloric acid is an effective solvent for most limestones. Only silica, which does not interfere with the analysis, remains undissolved. Some limestones are more readily decomposed after they have been ignited; a few yield only to a carbonate fusion.

The method that follows is remarkably effective for determining calcium in most limestones. Iron and aluminum, in amounts equivalent to that of calcium, do not interfere. Small amounts of manganese and titanium can also be tolerated.

PROCEDURE

Sample Preparation

Dry the unknown for 1 to 2 hr at 110°C, and cool in a desiccator. If the material is readily decomposed in acid, weigh 0.25-g to 0.30-g samples (to the nearest 0.1 mg) into 250-mL beakers. Add 10 mL of water to each sample and cover with a watch glass. Add 10 mL of concentrated HCl dropwise, taking care to avoid losses due to spattering as the acid is introduced.

Precipitation of Calcium Oxalate

Add 5 drops of saturated bromine water to oxidize any iron in the samples and boil gently (*use the hood*) for 5 min to remove the excess Br_2. Dilute each sample solution to about 50 mL, heat to boiling, and add 100 mL of hot 6% (w/v) $(NH_4)_2C_2O_4$ solution. Add 3 to 4 drops of methyl red, and precipitate CaC_2O_4 by slowly adding 6 M NH_3. As the indicator starts to change color, add the NH_3 at a rate of one drop every 3 to 4 s. Continue until the solutions become the intermediate yellow-orange color of the indicator (pH 4.5 to 5.5). Allow the solutions to stand for no more than

30 min (Note) and filter; medium-porosity filtering crucibles or Gooch crucibles with glass mats are satisfactory. Wash the precipitates with several 10-mL portions of cold water. Rinse the outside of the crucibles to remove residual $(NH_4)_2C_2O_4$, and return them to the beakers in which the CaC_2O_4 was formed.

Titration

Add 100 mL of water and 50 mL of 3 M H_2SO_4 to each of the beakers containing the precipitated calcium oxalate and the crucible. Heat to 80°C to 90°C, and titrate with 0.02 M permanganate. The temperature should be greater than 60°C throughout the titration; reheat if necessary.

Report the percentage of CaO in the unknown.

Note

The period of standing can be longer if the unknown contains no Mg^{2+}.

38F-4 The Determination of Iron in an Ore

Discussion

The common ores of iron are hematite (Fe_2O_3), magnetite (Fe_3O_4), and limonite ($2Fe_2O_3 \cdot 3H_2O$). Steps in the analysis of these ores are (1) dissolution of the sample, (2) reduction of iron to the divalent state, and (3) titration of iron(II) with a standard oxidant.

The Decomposition of Iron Ores   Iron ores often decompose completely in hot concentrated hydrochloric acid. The rate of attack by this reagent is increased by the presence of a small amount of tin(II) chloride. The tendency of iron(II) and iron(III) to form chloro complexes accounts for the effectiveness of hydrochloric acid over nitric or sulfuric acid as a solvent for iron ores.

Many iron ores contain silicates that may not be entirely decomposed by treatment with hydrochloric acid. Incomplete decomposition is indicated by a dark residue that remains after prolonged treatment with the acid. A white residue of hydrated silica, which does not interfere in any way, is indicative of complete decomposition.

The Prereduction of Iron   Because part or all of the iron is in the trivalent state after decomposition of the sample, prereduction to iron(II) must precede titration with the oxidant. Any of the methods described in Section 20A-1 can be used. Perhaps the most satisfactory prereductant for iron is tin(II) chloride:

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$
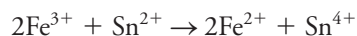
The only other common species reduced by this reagent are the high oxidation states of arsenic, copper, mercury, molybdenum, tungsten, and vanadium.

The excess reducing agent is eliminated by the addition of mercury(II) chloride:

$$Sn^{2+} + 2HgCl_2 \rightarrow Hg_2Cl_2(s) + Sn^{4+} + 2Cl^-$$

The slightly soluble mercury(I) chloride (Hg_2Cl_2) does not reduce permanganate, nor does the excess mercury(II) chloride ($HgCl_2$) reoxidize iron(II). Care must be taken, however, to prevent the occurrence of the alternative reaction

$$Sn^{2+} + HgCl_2 \rightarrow Hg(l) + Sn^{4+} + 2Cl^-$$

Elemental mercury reacts with permanganate and causes the results of the analysis to be high. The formation of mercury, which is favored by an appreciable excess of tin(II), is prevented by careful control of this excess and by the rapid addition of excess mercury(II) chloride. A proper reduction is indicated by the appearance of a small amount of a silky white precipitate after the addition of mercury(II). Formation of a gray precipitate at this juncture indicates the presence of metallic mercury; the total absence of a precipitate indicates that an insufficient amount of tin(II) chloride was used. In either event, the sample must be discarded.

The Titration of Iron(II)   The reaction of iron(II) with permanganate is smooth and rapid. The presence of iron(II) in the reaction mixture, however, induces the oxidation of chloride ion by permanganate, a reaction that does not ordinarily proceed rapidly enough to cause serious error. High results are obtained if this parasitic reaction is not controlled. Its effects can be eliminated through removal of the hydrochloric acid by evaporation with sulfuric acid or by introduction of *Zimmermann-Reinhardt reagent,* which contains manganese(II) in a fairly concentrated mixture of sulfuric and phosphoric acids.

The oxidation of chloride ion during a titration is believed to involve a direct reaction between this species and the manganese(III) ions that form as an intermediate in the reduction of permanganate ion by iron(II). The presence of manganese(II) in the Zimmermann-Reinhardt reagent is believed to inhibit the formation of chlorine by decreasing the potential of the manganese(III)/manganese(II) couple. Phosphate ion is believed to exert a similar effect by forming stable manganese(III) complexes. Moreover, phosphate ions react with iron(III) to form nearly colorless complexes so that the yellow color of the iron(II)/chloro complexes does not interfere with the end point.[8]

PREPARATION OF REAGENTS

The following solutions suffice for about 100 titrations.

1. *Tin(II) chloride, 0.25 M.* Dissolve 60 g of iron-free $SnCl_2 \cdot 2H_2O$ in 100 mL of concentrated HCl; warm if necessary. After the solid has dissolved, dilute to 1 L with distilled water and store in a well-stoppered bottle. Add a few pieces of mossy tin to help preserve the solution.
2. *Mercury(II) chloride, 5% (w/v).* Dissolve 50 g of $HgCl_2$ in 1 L of distilled water.
3. *Zimmermann-Reinhardt reagent.* Dissolve 300 g of $MnSO_4 \cdot 4H_2O$ in 1 L of water. Cautiously add 400 mL of concentrated H_2SO_4 and 400 mL of 85% H_3PO_4, and dilute to 3 L.

PROCEDURE

Sample Preparation
Dry the ore at 110°C for at least 3 hr, and then allow it to cool to room temperature in a desiccator. Consult with the instructor for a sample size that will require 25 to 40 mL of standard 0.02 M $KMnO_4$. Weigh samples into 500-mL conical flasks. To

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[8]The mechanism by which the Zimmermann-Reinhardt reagent acts has been the subject of much study. For a discussion of this work, see H. A. Laitinen, *Chemical Analysis,* New York: McGraw-Hill, 1960, pp. 369–72.

A Tuttle flask cover is a small inverted hat-shaped piece of glassware that fits inside the necks of flasks during boiling to prevent loss of solution. The device has a low center of gravity and is less likely to fall off the flask than a watch glass.

each, add 10 mL of concentrated HCl and about 3 mL of 0.25 M $SnCl_2$ (Note 1). Cover each flask with a small watch glass or Tuttle flask cover. Heat the flasks in a hood at just below boiling until the samples are decomposed and the undissolved solid, if any, is pure white (Note 2). Use another 1 to 2 mL of $SnCl_2$ to eliminate any yellow color that may develop as the solutions are heated. Heat a blank consisting of 10 mL of HCl and 3 mL of $SnCl_2$ for the same amount of time.

After the ore has been decomposed, remove the excess Sn(II) by the dropwise addition of 0.02 M $KMnO_4$ until the solutions become faintly yellow. Dilute to about 15 mL. Add sufficient $KMnO_4$ solution to impart a faint pink color to the blank, then decolorize with one drop of the $SnCl_2$ solution.

Take samples and blank individually through subsequent steps to minimize air oxidation of iron(II).

Reduction of Iron

Heat the sample solution nearly to boiling and make dropwise additions of 0.25 M $SnCl_2$ until the yellow color just disappears, then add two more drops (Note 3). Cool to room temperature, and rapidly add 10 mL of 5% $HgCl_2$ solution. A small amount of silky white Hg_2Cl_2 should precipitate (Note 4). The blank should be treated with the $HgCl_2$ solution.

Titration

Following addition of the $HgCl_2$, wait 2 to 3 min. Then add 25 mL of Zimmermann-Reinhardt reagent and 300 mL of water. Titrate *immediately* with standard 0.02 M $KMnO_4$ to the first faint pink that persists for 15 to 20 s. Do not add the $KMnO_4$ rapidly at any time. Correct the titrant volume for the blank.

Report the percentage of Fe_2O_3 in the sample.

Notes

1. The $SnCl_2$ hastens decomposition of the ore by reducing iron(III) oxides to iron(II). Insufficient $SnCl_2$ is indicated by the appearance of yellow iron(III)/chloride complexes.
2. If dark particles persist after the sample has been heated with acid for several hours, filter the solution through ashless paper, wash the residue with 5 to 10 mL of 6 M HCl, and retain the filtrate and washings. Ignite the paper and its contents in a small platinum crucible. Mix 0.5 to 0.7 g of Na_2CO_3 with the residue, and heat until a clear melt is obtained. Cool, add 5 mL of water, and then cautiously add a few milliliters of 6 M HCl. Warm the crucible until the melt has dissolved, and combine the contents with the original filtrate. Evaporate the solution to 15 mL and continue the analysis.
3. The solution may not become entirely colorless but instead may acquire a faint yellow-green hue. Further additions of $SnCl_2$ will not alter this color. If too much $SnCl_2$ is added, it can be removed by adding 0.02 M $KMnO_4$ and repeating the reduction.
4. The absence of precipitate indicates that insufficient $SnCl_2$ was used and that the reduction of iron(III) was incomplete. A gray residue indicates the presence of elemental mercury, which reacts with $KMnO_4$. The sample must be discarded in either event.
5. These directions can be used to standardize a permanganate solution against primary-standard-grade iron. Weigh (to the nearest 0.1 mg) 0.2-g lengths of electrolytic iron wire into 250-mL conical flasks and dissolve in about 10 mL of concentrated HCl. Dilute each sample to about 75 mL. Then take each individually through the reduction and titration steps.

38G TITRATIONS WITH IODINE

The oxidizing properties of iodine, the composition and stability of triiodide solutions, and the applications of this reagent in volumetric analysis are discussed in Section 20C-3. Starch is ordinarily employed as an indicator for iodometric titrations.

38G-1 Preparation of Reagents

PROCEDURE

(a) *Iodine approximately 0.05 M.* Weigh about 40 g of KI into a 100-mL beaker. Add 12.7 g of I_2 and 10 mL of water. Stir for several minutes (Note 1). Introduce an additional 20 mL of water, and stir again for several minutes. Carefully decant the bulk of the liquid into a storage bottle containing 1 L of distilled water. It is essential that any undissolved iodine remain in the beaker (Note 2).

(b) *Starch indicator* (sufficient for about 100 titrations). Rub 1 g of soluble starch and 15 mL of water into a paste. Dilute to about 500 mL with boiling water, and heat until the mixture is clear. Cool; store in a tightly stoppered bottle. For most titrations, 3 to 5 mL of the indicator are used.

The indicator is readily attacked by airborne organisms and should be freshly prepared every few days.

Notes

1. Iodine dissolves slowly in the KI solution. Thorough stirring is needed to hasten the process.
2. Any solid I_2 inadvertently transferred to the storage bottle will cause the concentration of the solution to increase gradually. Filtration through a sintered-glass crucible eliminates this potential source of difficulty.

38G-2 Standardization of Iodine Solutions

Discussion

Arsenic(III) oxide, long a favored primary standard for iodine solutions, is now seldom used because of the elaborate federal regulations governing the use of even small amounts of arsenic-containing compounds. Barium thiosulfate monohydrate and anhydrous sodium thiosulfate have been proposed as alternative standards.[9] Perhaps the most convenient method of determining the concentration of an iodine solution is the titration of aliquots with a sodium thiosulfate solution that has been standardized against pure potassium iodate. Instructions for this method follow.

PREPARATION OF REAGENTS

1. *Sodium thiosulfate, 0.1 M.* Follow the directions in Sections 38H-1 and 38H-2 for the preparation and standardization of this solution.
2. *Starch indicator.* See Section 38G-1(b).

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[9]W. M. McNevin and O. H. Kriege, *Anal. Chem.,* **1953**, *25*(5), 767, **DOI**: 10.1021/ac60077a023.

PROCEDURE

Transfer 25.00-mL aliquots of the iodine solution to 250-mL conical flasks, and dilute to about 50 mL. *Take each aliquot individually through subsequent steps.* Introduce approximately 1 mL of 3 M H_2SO_4, and titrate immediately with standard sodium thiosulfate until the solution becomes a faint straw yellow. Add about 5 mL of starch indicator and complete the titration, taking as the end point the change in color from blue to colorless (Note).
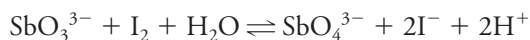
Note
The blue color of the starch/iodine complex may reappear after the titration has been completed because of the air oxidation of iodide ion.

38G-3 The Determination of Antimony in Stibnite

Discussion

The analysis of stibnite, a common antimony ore, is a typical application of iodometry and is based on the oxidation of Sb(III) to Sb(V):

$$SbO_3^{3-} + I_2 + H_2O \rightleftharpoons SbO_4^{3-} + 2I^- + 2H^+$$

The position of this equilibrium is strongly dependent on the hydrogen ion concentration. To force the reaction to the right, it is common practice to carry out the titration in the presence of an excess of sodium hydrogen carbonate, which consumes the hydrogen ions as they are produced.

Stibnite is an antimony sulfide ore containing silica and other contaminants. Provided that the material is free of iron and arsenic, the analysis of stibnite for its antimony content is straightforward. Samples are decomposed in hot concentrated hydrochloric acid to eliminate sulfide as gaseous hydrogen sulfide. Care is needed to prevent loss of volatile antimony(III) chloride during this step. The addition of potassium chloride helps by favoring formation of nonvolatile chloro complexes such as $SbCl_4^-$ and $SbCl_6^{3-}$.

Sparingly soluble basic antimony salts, such as SbOCl, often form when the excess hydrochloric acid is neutralized; these react incompletely with iodine and cause low results. The difficulty is overcome by adding tartaric acid, which forms a soluble complex ($SbOC_4H_4O_6^-$) from which antimony is rapidly oxidized by the reagent.

PROCEDURE

Dry the unknown at 110°C for 1 hr, and allow it to cool in a desiccator. Weigh individual samples (Note 1) into 500-mL conical flasks. Introduce about 0.3 g of KCl and 10 mL of concentrated HCl to each flask. Heat the mixtures (*use the hood*) to just below boiling until only white or slightly gray residues of SiO_2 remain.

Add 3 g of tartaric acid to each sample and heat for an additional 10 to 15 min. Then, with good swirling, add water (Note 2) from a pipet or buret until the volume is about 100 mL. If reddish Sb_2S_3 forms, discontinue dilution and heat further to eliminate H_2S; add more HCl if necessary.

Add 3 drops of phenolphthalein, and neutralize with 6 M NaOH to the first faint pink of the indicator. Discharge the color by the dropwise addition of 6 M HCl, and then add 1 mL in excess. Introduce 4 to 5 g of $NaHCO_3$, taking care to avoid losses of solution by spattering during the addition. Add 5 mL of starch indicator, rinse down the inside of the flask, and titrate with standard 0.05 M I_2 to the first blue color that persists for 30 s.

Report the percentage of Sb_2S_3 in the unknown.

Notes
1. Samples should contain 1.5 to 2 mmol of antimony; consult with the instructor for an appropriate sample size. Weighings to the nearest milligram are adequate for samples larger than 1 g.
2. The slow addition of water, with efficient stirring, is essential to prevent the formation of SbOCl.

38H TITRATIONS WITH SODIUM THIOSULFATE

Numerous methods are based on the reducing properties of iodide ion:

$$2I^- \rightarrow I_2 + 2e^-$$
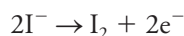
Iodine, the reaction product, is ordinarily titrated with a standard sodium thiosulfate solution, with starch serving as the indicator:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

A discussion of thiosulfate methods is found in Section 20B-2.

38H-1 Preparation of 0.1 M Sodium Thiosulfate

PROCEDURE

Boil about 1 L of distilled water for 10 to 15 min. Allow the water to cool to room temperature; then add about 25 g of $Na_2S_2O_3 \cdot 5H_2O$ and 0.1 g of Na_2CO_3. Stir until the solid has dissolved. Transfer the solution to a clean glass or plastic bottle, and store in a dark place.

38H-2 Standardization of Sodium Thiosulfate against Potassium Iodate

Discussion

Solutions of sodium thiosulfate are conveniently standardized by titration of the iodine produced when an unmeasured excess of potassium iodide is added to a known volume of an acidified standard potassium iodate solution. The reaction is

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Note that each mole of iodate results in the production of three moles of iodine. The procedure that follows is based on this reaction.

PREPARATION OF SOLUTIONS

1. *Potassium iodate, 0.0100 M.* Dry about 1.2 g of primary-standard KIO_3 at 110°C for at least 1 hr and cool in a desiccator. Weigh (to the nearest 0.1 mg) about 1.1 g into a 500-mL volumetric flask; use a powder funnel to ensure quantitative transfer of the solid. Rinse the funnel well, dissolve the KIO_3 in about 200 mL of distilled water, dilute to the mark, and mix thoroughly.
2. *Starch indicator.* See Section 38G-1(b).

PROCEDURE

Pipet 50.00-mL aliquots of standard iodate solution into 250-mL conical flasks. *Treat each sample individually from this point to minimize error resulting from the air oxidation of iodide ion.* Introduce 2 g of iodate-free KI, and swirl the flask to hasten solution. Add 2 mL of 6 M HCl, and immediately titrate with thiosulfate until the solution becomes pale yellow. Introduce 5 mL of starch indicator, and titrate with constant stirring to the disappearance of the blue color. Calculate the molarity of the iodine solution.

38H-3 Standardization of Sodium Thiosulfate against Copper

Discussion

Thiosulfate solutions can also be standardized against pure copper wire or foil. This procedure is advantageous when the solution is to be used for the determination of copper because any systematic error in the method tends to be canceled.

Copper(II) is reduced quantitatively to copper(I) by iodide ion:

$$2Cu^{2+} + 4I^- \rightarrow 2CuI(s) + I_2$$
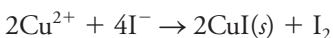
The importance of CuI formation in forcing this reaction to completion can be seen from the following standard electrode potentials:

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \qquad E^0 = 0.15 \text{ V}$$
$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^0 = 0.54 \text{ V}$$
$$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s) \qquad E^0 = 0.86 \text{ V}$$

The first two potentials suggest that iodide should have no tendency to reduce copper(II); the formation of CuI, however, favors the reduction. The solution must contain at least 4% excess iodide to force the reaction to completion. Moreover, the pH must be less than 4 to prevent the formation of basic copper species that react slowly and incompletely with iodide ion. The acidity of the solution cannot be greater than about 0.3 M, however, because of the tendency of iodide ion to undergo air oxidation, a process catalyzed by copper salts. Nitrogen oxides also catalyze the air oxidation of iodide ion. A common source of these oxides is the nitric acid ordinarily used to dissolve metallic copper and other copper-containing solids. Urea is used to scavenge nitrogen oxides from solutions:

$$(NH_2)_2CO + 2HNO_2 \rightarrow 2N_2(g) + CO_2(g) + 3H_2O$$
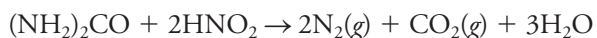
The titration of iodine by thiosulfate tends to yield slightly low results owing to the adsorption of small but measurable quantities of iodine on solid CuI. The adsorbed iodine is released only slowly, even when thiosulfate is in excess; transient and premature end points result. This difficulty is largely overcome by the addition of thiocyanate ion. The sparingly soluble copper(I) thiocyanate replaces part of the copper iodide at the surface of the solid:

$$CuI(s) + SCN^- \rightarrow CuSCN(s) + I^-$$
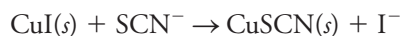
Accompanying this reaction is the release of the adsorbed iodine, which thus becomes available for titration. The addition of thiocyanate must be delayed until most of the iodine has been titrated to prevent interference from a slow reaction between the two species, possibly

$$2SCN^- + I_2 \rightarrow 2I^- + (SCN)_2$$
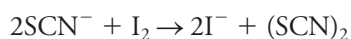
PREPARATION OF SOLUTIONS

1. *Urea, 5% (w/v).* Dissolve about 5 g of urea in sufficient water to give 100 mL of solution. Approximately 10 mL will be needed for each titration.
2. *Starch indicator.* See Section 38G-1(b).

PROCEDURE

Use scissors to cut copper wire or foil into 0.20-g to 0.25-g portions. Wipe the metal free of dust and grease with a filter paper; do not dry it by heating. The pieces of copper should be handled with paper strips, cotton gloves, or tweezers to prevent contamination by contact with the skin.

Use a weighed watch glass or weighing bottle to obtain the mass of individual copper samples (to the nearest 0.1 mg) by difference. Transfer each sample to a 250-mL conical flask. Add 5 mL of 6 M HNO_3, cover with a small watch glass, and warm gently (*use the hood*) until the metal has dissolved. Dilute with about 25 mL of distilled water, add 10 mL of 5% (w/v) urea, and boil briefly to eliminate nitrogen oxides. Rinse the watch glass, collecting the rinsings in the flask. Cool.

Add concentrated NH_3 dropwise and with thorough mixing to produce the intensely blue $Cu(NH_3)_4^{2+}$; the solution should smell faintly of ammonia (Note). Make dropwise additions of 3 M H_2SO_4 until the color of the complex just disappears, and then add 2.0 mL of 85% H_3PO_4. Cool to room temperature.

Treat each sample individually from this point on to minimize the air oxidation of iodide ion. Add 4.0 g of KI to the sample, and titrate immediately with $Na_2S_2O_3$ until the solution becomes pale yellow. Add 5 mL of starch indicator, and continue the titration until the blue color becomes faint. Add 2 g of KSCN; swirl vigorously for 30 s. Complete the titration, using the disappearance of the blue starch/I_2 color as the end point.

Calculate the molar concentration of the $Na_2S_2O_3$ solution.

Note

Do not sniff vapors directly from the flask; instead, waft them toward your nose with a waving motion of your hand.

38H-4 The Determination of Copper in Brass

Discussion

The standardization procedure described in Section 38H-3 is readily adapted to the determination of copper in brass, an alloy that also contains appreciable amounts of tin, lead, and zinc (and perhaps minor amounts of nickel and iron). The method is relatively simple and applicable to brasses with less than 2% iron. A weighed sample is treated with nitric acid, which causes the tin to precipitate as a hydrated oxide of uncertain composition. Evaporation with sulfuric acid to the appearance of sulfur trioxide eliminates the excess nitrate, redissolves the tin compound, and possibly causes the formation of lead sulfate. The pH is adjusted through the addition of ammonia, followed by acidification with a measured amount of phosphoric acid. An excess of potassium iodide is added, and the liberated iodine is titrated with standard thiosulfate. See Section 38H-3 for additional discussion.

PROCEDURE

If so directed, free the metal of oils by treatment with an organic solvent; briefly heat in an oven to drive off the solvent. Weigh (to the nearest 0.1 mg) 0.3-g samples into 250-mL conical flasks, and introduce 5 mL of 6 M HNO_3 into each; warm (*use the hood*) until solution is complete. Add 10 mL of concentrated H_2SO_4, and evaporate (*use the hood*) until copious white fumes of SO_3 are given off. Allow the mixture to cool. Cautiously add 30 mL of distilled water, boil for 1 to 2 min, and again cool.

Follow the instructions in the third and fourth paragraphs of the procedure in Section 38H-3.

Report the percentage of Cu in the sample.

38I   TITRATIONS WITH POTASSIUM BROMATE

Applications of standard bromate solutions to the determination of organic functional groups are described in Section 20C-4. Directions follow for the determination of ascorbic acid in vitamin C tablets.

38I-1 Preparation of Solutions

PROCEDURE

1. *Potassium bromate, 0.015 M.* Transfer about 1.5 g of reagent-grade potassium bromate to a weighing bottle, and dry at 110°C for at least 1 hr. Cool in a desiccator. Weigh approximately 1.3 g (to the nearest 0.1 mg) into a 500-mL volumetric flask; use a powder funnel to ensure quantitative transfer of the solid. Rinse the funnel well, and dissolve the $KBrO_3$ in about 200 mL of distilled water. Dilute to the mark, and mix thoroughly.

    Solid potassium bromate can cause a fire if it comes into contact with damp organic material (*such as paper towels in a waste container*). Consult with the instructor concerning the disposal of any excess.

2. *Sodium thiosulfate, 0.05 M.* Follow the directions in Section 38G-1; use about 12.5 g of $Na_2S_2O_3 \cdot 5H_2O$ per liter of solution.

3. *Starch indicator.* See Section 38G-1(b).

38I-2 Standardization of Sodium Thiosulfate against Potassium Bromate

Discussion

Iodine is generated by the reaction between a known volume of standard potassium bromate and an unmeasured excess of potassium iodide:

$$BrO_3^- + 6I^- + 6H^+ \rightarrow Br^- + 3I_2 + 3H_2O$$
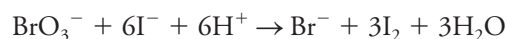
The iodine produced is titrated with the sodium thiosulfate solution.


PROCEDURE

Pipet 25.00-mL aliquots of the $KBrO_3$ solution into 250-mL conical flasks and rinse the interior walls with distilled water. Treat each sample individually beyond this point. Introduce 2 to 3 g of KI and about 5 mL of 3 M H_2SO_4. Immediately titrate with $Na_2S_2O_3$ until the solution is pale yellow. Add 5 mL of starch indicator, and titrate to the disappearance of the blue color.

Calculate the concentration of the thiosulfate solution.

38I-3 The Determination of Ascorbic Acid in Vitamin C Tablets by Titration with Potassium Bromate

Discussion

Ascorbic acid, $C_6H_8O_6$, is cleanly oxidized to dehydroascorbic acid by bromine:
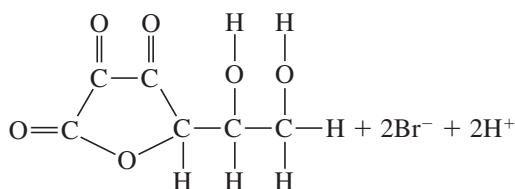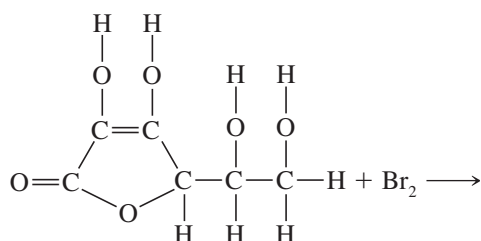
Ascorbic acid oxidation by bromine.

An unmeasured excess of potassium bromide is added to an acidified solution of the sample. The solution is titrated with standard potassium bromate to the first permanent appearance of excess bromine; this excess is then determined iodometrically with standard sodium thiosulfate. The entire titration must be performed without delay to prevent air oxidation of the ascorbic acid.

PROCEDURE

Weigh (to the nearest milligram) 3 to 5 vitamin C tablets (Note 1). Pulverize them thoroughly in a mortar, and transfer the powder to a dry weighing bottle. Weigh

individual 0.40-g to 0.50-g samples (to the nearest 0.1 mg) into dry 250-mL conical flasks. Treat each sample individually beyond this point. Dissolve the sample (Note 2) in 50 mL of 1.5 M H_2SO_4; then add about 5 g of KBr. Titrate immediately with standard $KBrO_3$ to the first faint yellow due to excess Br_2. Record the volume of $KBrO_3$ used. Add 3 g of KI and 5 mL of starch indicator; back-titrate (Note 3) with standard 0.05 M $Na_2S_2O_3$.

Calculate the average mass (in milligrams) of ascorbic acid (176.12 g/mol) in each tablet.

Notes
1. This method is not applicable to chewable vitamin C tablets.
2. The binder in many vitamin C tablets remains in suspension throughout the analysis. If the binder is starch, the characteristic color of the complex with iodine appears on addition of KI.
3. The volume of thiosulfate needed for the back-titration seldom exceeds a few milliliters.

38J   POTENTIOMETRIC METHODS

Potentiometric measurements provide a highly selective method for the quantitative determination of numerous cations and anions. A discussion of the principles and applications of potentiometric measurements is found in Chapter 21. Detailed instructions are given in this section on the use of potentiometric measurements to locate end points in volumetric titrations. In addition, a procedure for the direct potentiometric determination of fluoride ion in drinking water and in toothpaste is described.

38J-1   General Directions for Performing a Potentiometric Titration

The procedure that follows is applicable to the titrimetric methods described in this section. With the proper choice of indicator electrode, it can also be applied to most of the volumetric methods given in Sections 38B through 38H.

PROCEDURE

1. Dissolve the sample in 50 to 250 mL of water. Rinse a suitable pair of electrodes with deionized water, and immerse them in the sample solution. Provide magnetic (or mechanical) stirring. Position the buret so that reagent can be delivered without splashing.
2. Connect the electrodes to the meter, commence stirring, and record the initial buret volume and the initial potential (or pH).
3. Record the meter reading and buret volume after each addition of titrant. Introduce fairly large volumes (about 5 mL) at the beginning. Withhold a succeeding addition until the meter reading remains constant within 1 to 2 mV (or 0.05 pH unit) for at least 30 s (Note). Judge the volume of reagent to be added by estimating a value for $\Delta E/\Delta V$ after each addition. In the immediate vicinity of the equivalence point, introduce the reagent in 0.1-mL increments. Continue the

titration 2 to 3 mL beyond the equivalence point, increasing the volume increments as $\Delta E/\Delta V$ again becomes smaller.

Note
Stirring motors occasionally cause erratic meter readings; it may be advisable to turn off the motor while meter readings are being made.

38J-2 Potentiometric Titration of Chloride and Iodide in a Mixture

Discussion

Figure 17-4, page 411, is a theoretical argentometric titration curve for a mixture of iodide and chloride ions. Initial additions of silver nitrate result in formation of silver iodide exclusively because the solubility of that salt is only about 5×10^{-7} that of silver chloride. It can be shown that this solubility difference is great enough to delay formation of silver chloride until all but $7 \times 10^{-5}\%$ of the iodide has precipitated. Thus, short of the equivalence point, the curve is essentially indistinguishable from that for iodide alone (see Figure 17-4). Just beyond the iodide equivalence point, the silver ion concentration is determined by the concentration of chloride ion in the solution, and the titration curve becomes essentially identical to that for chloride ion by itself.

Curves resembling Figure 17-4 can be obtained experimentally by measuring the potential of a silver electrode immersed in the analyte solution. Hence, a chloride/iodide mixture can be analyzed for each of its components. This technique is not as applicable to the analysis of iodide/bromide or bromide/chloride mixtures, however, because the solubility differences between the silver salts are not great enough. Thus, the more soluble salt begins to form in significant amounts before precipitation of the less soluble salt is complete. The silver indicator electrode can be a commercial billet type or simply a polished wire. A calomel electrode can be used as reference, although diffusion of chloride ion from the salt bridge may cause the results of the titration to be measurably high. This source of error can be eliminated by placing the calomel electrode in a potassium nitrate solution that is in contact with the analyte solution by means of a KNO_3 salt bridge. Alternatively, the analyte solution can be made slightly acidic with several drops of nitric acid; a glass electrode can then serve as the reference electrode because the pH of the solution and thus its potential will remain essentially constant throughout the titration.

The titration of mixtures demonstrates how a potentiometric titration can have multiple end points. The potential of the silver electrode is proportional to pAg. Thus, a plot of E_{Ag} against titrant volume yields an experimental curve with the same shape as the theoretical curve shown in Figure 17-4. (The ordinate units will be different, of course.)

Experimental curves for the titration of I^-/Cl^- mixtures do not show the sharp discontinuity that occurs at the first equivalence point of the theoretical curve (see Figure 17-4). More important, the volume of silver nitrate needed to reach the I^- end point is generally somewhat greater than theoretical. This effect is the result of coprecipitation of the more soluble AgCl during formation of the less soluble AgI. An overconsumption of reagent thus occurs in the first part of the titration. The total volume closely approaches the correct amount.

Despite this coprecipitation error, the potentiometric method is useful for the analysis of halide mixtures. With approximately equal quantities of iodide and chloride, relative errors can be kept within 2% relative.

PREPARATION OF REAGENTS

1. *Silver nitrate, 0.05 M.* Follow the instructions in Section 38C-1.
2. *Potassium nitrate salt bridge.* Bend an 8-mm glass tube into a U-shape with arms that are long enough to extend nearly to the bottom of two 100-mL beakers. Heat 50 mL of water to boiling, and stir in 1.8 g of powdered agar; continue to heat and stir until a uniform suspension is formed. Dissolve 12 g of KNO_3 in the hot suspension. Allow the mixture to cool somewhat. Clamp the U-tube with the openings facing up, and use a medicine dropper to fill it with the warm agar suspension. Cool the tube under a cold-water tap to form the gel. When the bridge is not in use, immerse the ends in 2.5 M KNO_3.

PROCEDURE

Obtain the unknown in a clean 250-mL volumetric flask; dilute to the mark with water, and mix well.

Transfer 50.00 mL of the sample to a clean 100-mL beaker, and add a drop or two of concentrated HNO_3. Place about 25 mL of 2.5 M KNO_3 in a second 100-mL beaker, and make contact between the two solutions with the agar salt bridge. Immerse a silver electrode in the analyte solution and a calomel reference electrode in the second beaker. Titrate with $AgNO_3$ as described in Section 38J-1. Use small increments of titrant in the vicinity of the two end points.

Plot the data, and establish end points for the two analyte ions. Plot a theoretical titration curve, assuming the measured concentrations of the two constituents to be correct.

Report the mass in milligrams of I^- and Cl^- in the sample or as otherwise instructed.

38J-3 The Potentiometric Determination of Solute Species in a Carbonate Mixture

Discussion

A glass/calomel electrode system can be used to locate end points in neutralization titrations and to estimate dissociation constants. As a preliminary step to the titrations, the electrode system is standardized against a buffer of known pH.

The unknown is issued as an aqueous solution prepared from one or perhaps two adjacent members of the following series: $NaHCO_3$, Na_2CO_3, or NaOH (see Section 16B-2). The object is to determine which of these components were used to prepare the unknown as well as the weight percent of each solute.

Most unknowns require a titration with either standard acid or standard base. A few may require separate titrations, one with acid and one with base. The initial pH of the unknown provides guidance concerning the appropriate titrant(s); studying Figure 16-3 and Table 16-2 may be helpful in interpreting the data.

PREPARATION OF SOLUTIONS

Standardized 0.1 M HCl and/or 0.1 M NaOH. Follow the directions in Sections 38C-3 through 38C-7.

PROCEDURE

Obtain the unknown in a clean 250-mL volumetric flask. Dilute to the mark and mix well. Transfer a small amount of the diluted unknown to a beaker, and determine its pH. Titrate a 50.00-mL aliquot with standard acid or standard base (or perhaps both). Use the resulting titration curves to select indicator(s) suitable for end point detection, and perform duplicate titrations with these.

Identify the solute species in the unknown, and report the mass/volume percent of each. Calculate the approximate dissociation constant that can be obtained for any carbonate-containing species from the titration data. Estimate the ionic strength of the solution and correct the calculated constant to give an approximate thermodynamic dissociation constant.

38J-4 The Direct Potentiometric Determination of Fluoride Ion

Discussion

The solid-state fluoride electrode (see Section 21D-6) has found extensive use in the determination of fluoride in a variety of materials. Directions follow for the determination of this ion in drinking water and in toothpaste. A total ionic strength adjustment buffer (TISAB) is used to adjust all unknowns and standards to essentially the same ionic strength; when this reagent is used, the concentration of fluoride, rather than its activity, is measured. The pH of the buffer is about 5, a level at which F^- is the predominant fluorine-containing species. The buffer also contains cyclohexylaminedinitrilotetraacetic acid, which forms stable chelates with iron(III) and aluminum(III), thus freeing fluoride ion from its complexes with these cations.

Review Sections 21D and 21F before undertaking these experiments.

PREPARATION OF SOLUTIONS

1. *Total ionic strength adjustment buffer* (*TISAB*). This solution is marketed commercially under the trade name TISAB.[10] Sufficient buffer for 15 to 20 determinations can be prepared by mixing (with stirring) 57 mL of glacial acetic acid, 58 g of NaCl, 4 g of cyclohexylaminedinitrilotetraacetic acid, and 500 mL of distilled water in a 1-L beaker. Cool the contents in a water or ice bath, and carefully add 6 M NaOH to a pH of 5.0 to 5.5. Dilute to 1 L with water, and store in a plastic bottle.
2. *Standard fluoride solution, 100 ppm.* Dry a quantity of NaF at 110°C for 2 hr. Cool in a desiccator; then weigh (to the nearest milligram) 0.22 g into a 1-L volumetric flask. (*Caution! NaF is highly toxic. Immediately* wash any skin touched by this compound with copious quantities of water.) Dissolve in water, dilute to the mark, mix well, and store in a plastic bottle. Calculate the exact concentration of fluoride in parts per million.

    A standard F^- solution can be purchased from commercial sources.

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[10]Thermo Electron Corp., Beverly, MA.

PROCEDURE

The apparatus for this experiment consists of a solid-state fluoride electrode, a saturated calomel electrode, and a pH meter. A sleeve-type calomel electrode is needed for the toothpaste determination because the measurement is made on a suspension that tends to clog the liquid junction. The sleeve must be loosened momentarily to renew the interface after each series of measurements.

Determining Fluoride in Drinking Water
Transfer 50.00-mL portions of the water to 100-mL volumetric flasks, and dilute to the mark with TISAB solution.

Prepare a 5-ppm F^- solution by diluting 25.0 mL of the 100-ppm standard to 500 mL in a volumetric flask. Transfer 5.00-, 10.0-, 25.0-, and 50.0-mL aliquots of the 5-ppm solution to 100-mL volumetric flasks, add 50 mL of TISAB solution, and dilute to the mark. (These solutions correspond to 0.5, 1.0, 2.5, and 5.0 ppm F^-, respectively, in the 50-mL water sample, not in the 100-mL volumetric flask.)

After thorough rinsing and drying with paper tissue, immerse the electrodes in the 0.5-ppm standard. Stir mechanically for 3 min; then record the potential. Repeat with the remaining standards and samples.

Plot the measured potential against the log of the concentration of the standards. Use this plot to determine the concentration in parts per million of fluoride in the unknown.

Determining Fluoride in Toothpaste[11]
Weigh (to the nearest milligram) 0.2 g of toothpaste into a 250-mL beaker. Add 50 mL of TISAB solution, and boil for 2 min with good mixing. Cool and then transfer the suspension quantitatively to a 100-mL volumetric flask, dilute to the mark with distilled water, and mix well. Follow the directions for the analysis of drinking water, beginning with the second paragraph.

Report the concentration of F^- in the sample in parts per million.

38K ELECTROGRAVIMETRIC METHODS

A convenient example of an electrogravimetric method of analysis is the simultaneous determination of copper and lead in a sample of brass. Additional information concerning electrogravimetric methods is found in Section 22C.

38K-1 The Electrogravimetric Determination of Copper and Lead in Brass

Discussion
This procedure is based on the deposition of metallic copper on a cathode and of lead as PbO_2 on an anode. As a first step, the hydrous oxide of tin ($SnO_2 \cdot xH_2O$) that forms when the sample is treated with nitric acid must be removed by filtration. Lead dioxide is deposited quantitatively at the anode from a solution with a high nitrate ion concentration; copper is only partially deposited on the cathode under these conditions.

It is, therefore, necessary to eliminate the excess nitrate after deposition of the PbO_2 is complete. Removal is accomplished through the addition of urea:

$$6NO_3^- + 6H^+ + 5(NH_2)_2CO \rightarrow 8N_2(g) + 5CO_2(g) + 13H_2O$$
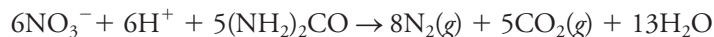
Copper then deposits quantitatively from the solution after the nitrate ion concentration has been decreased.

PROCEDURE

Preparation of Electrodes

Immerse the platinum electrodes in hot 6 M HNO_3 for about 5 min (Note 1). Wash them thoroughly with distilled water, rinse with several small portions of ethanol, and dry in an oven at 110°C for 2 to 3 min. Cool and weigh both anodes and cathodes to the nearest 0.1 mg.

Preparation of Samples

It is not necessary to dry the unknown. Weigh (to the nearest 0.1 mg) 1-g samples into 250-mL beakers. Cover the beakers with watch glasses. Cautiously add about 35 mL of 6 M HNO_3 (*use the hood*). Digest for at least 30 min; add more acid if necessary. Evaporate to about 5 mL but never to dryness (Note 2).

To each sample, add 5 mL of 3 M HNO_3, 25 mL of water, and one quarter of a tablet of filter paper pulp; digest without boiling for about 45 min. Filter off the $SnO_2 \cdot xH_2O$, using a fine-porosity filter paper (Note 3); collect the filtrates in tall-form electrolysis beakers. Use many small washes with hot 0.3 M HNO_3 to remove the last traces of copper; test for completeness with a few drops of $NH_3(aq)$. The final volume of filtrate and washings should be between 100 and 125 mL; either add water or evaporate to attain this volume.

Electrolysis

With the current switch off, attach the cathode to the negative terminal and the anode to the positive terminal of the electrolysis apparatus. Briefly turn on the stirring motor to be sure the electrodes do not touch. Cover the beakers with split watch glasses and commence the electrolysis. Maintain a current of 1.3 A for 35 min.

Rinse the cover glasses, and add 10 mL of 3 M H_2SO_4 followed by 5 g of urea to each beaker. Maintain a current of 2 A until the solutions are colorless. To test for completeness of the electrolysis, remove one drop of the solution with a medicine dropper, and mix it with a few drops of $NH_3(aq)$ in a small test tube. If the mixture turns blue, rinse the contents of the tube back into the electrolysis vessel, and continue the electrolysis for an additional 10 min. Repeat the test until no blue $Cu(NH_3)_4^{2+}$ is produced.

When electrolysis is complete, discontinue stirring but leave the current on. Rinse the electrodes thoroughly with water as they are removed from the solution. After rinsing is complete, turn off the electrolysis apparatus (Note 4), disconnect the electrodes, and dip them in acetone. Dry the cathodes for about 3 min and the anodes for about 15 min at 110°C. Allow the electrodes to cool in air, and then weigh them.

Report the percentages of lead (Note 5) and copper in the brass.

Notes

1. Alternatively, grease and organic materials can be removed by heating platinum electrodes to redness in a flame. Do not touch electrode surfaces with your fingers after cleaning because grease and oil cause nonadherent deposits that can flake off during washing and weighing.
2. Chloride ion must be totally excluded from this determination because it attacks the platinum anode during electrolysis. This reaction not only is destructive but also causes positive errors in the analysis by codepositing platinum with copper on the cathode.
3. If desired, the tin content can be determined gravimetrically by ignition of the $SnO_2 \cdot xH_2O$ to SnO_2.
4. It is important to maintain a potential between the electrodes until they have been removed from the solution and washed. Some copper may redissolve if this precaution is not observed.
5. Experience has shown that a small amount of moisture is retained by the PbO_2 and that better results are obtained if 0.8643 is used instead of 0.8662, the stoichiometric factor.

38L COULOMETRIC TITRATIONS

In a coulometric titration, the "reagent" is a constant direct current of exactly known magnitude. The time required for this current to oxidize or reduce the analyte quantitatively (directly or indirectly) is measured. See Section 22D-5 for a discussion of this electroanalytical method.

38L-1 The Coulometric Titration of Cyclohexene

Discussion[12]

Many olefins react sufficiently rapidly with bromine to permit their direct titration. The reaction is carried out in a largely nonaqueous environment with mercury(II) as a catalyst. A convenient way of performing this titration is to add excess bromide ion to a solution of the sample and to generate the bromine at an anode that is connected to a constant-current source. The electrode processes are

$$2Br^- \rightarrow 2Br_2 + 2e^- \qquad \text{anode}$$
$$2H^+ + 2e^- \rightarrow H_2(g) \qquad \text{cathode}$$
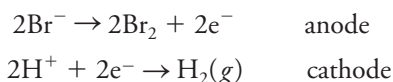
The hydrogen produced does not react with bromine rapidly enough to interfere. The bromine reacts with an olefin, such as cyclohexene, to give the addition product:
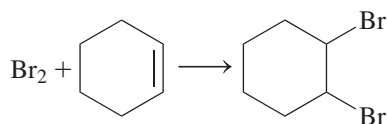
The amperometric method with twin-polarized electrodes (page 630) provides a convenient way to detect the end point in this titration. A potential difference of 0.2 to

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[12]This procedure was described by D. H. Evans, *J. Chem. Educ.,* **1968**, *45*, 88, **DOI**: 10.1021/ed045p88.

0.3 V is maintained between two small electrodes. This potential is not sufficient to cause the generation of hydrogen at the cathode. Thus, short of the end point, the cathode is polarized and no current is observed. At the end point, the first excess of bromine depolarizes the cathode and produces a current. The electrode reactions at the twin indicator electrodes are

$$2Br^- \rightarrow 2Br_2 + 2e^- \qquad \text{anode}$$
$$Br_2 + 2e^- \rightarrow 2Br^- \qquad \text{cathode}$$
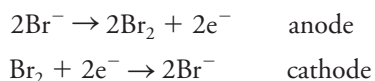
The current is proportional to the bromine concentration and is readily measured with a microammeter.

A convenient way to perform several analyses is to initially generate sufficient bromine in the solvent to give a readily measured current, say 20 µA. An aliquot of the sample is then introduced, after which the current immediately decreases and approaches zero. Generation of bromine is again commenced, and the time needed to regain a current of 20 µA is measured. A second aliquot of the sample is added to the same solution, and the process is repeated. Several samples can thus be analyzed without changing the solvent.

The procedure that follows is for the determination of cyclohexene in a methanol solution. Other olefins can be determined as well.

PREPARATION OF SOLVENT

Dissolve about 9 g of KBr and 0.5 g of mercury(II) acetate (Note 1) in a mixture consisting of 300 mL of glacial acetic acid, 130 mL of methanol, and 65 mL of water (sufficient for about 35 mmol of Br_2.) (***Caution!*** *Mercury compounds are highly toxic, and the solvent is a skin irritant. If inadvertent contact occurs, flood the affected area with copious quantities of water.)*

PROCEDURE

Obtain the unknown in a 100-mL volumetric flask; dilute to the mark with methanol, and mix well. The temperature of the methanol should be between 18°C and 20°C (Note 2).

Add sufficient acetic acid/methanol solvent to cover the indicator and generator electrodes in the electrolysis vessel. Apply about 0.2 V to the indicator electrodes. Activate the generator electrode system, and generate bromine until a current of about 20 µA is indicated on the microammeter. Stop the generation of bromine, record the indicator current to the nearest 0.1 µA, and set the timer to zero. Transfer 10.00 mL of the unknown to the solvent; the indicator current should decrease to almost zero. Resume bromine generation. Produce bromine in smaller and smaller increments by activating the generator for shorter and shorter periods as the indicator current rises and approaches the previously recorded value. Read and record the time needed to reach the original indicator current. Reset the timer to zero, introduce a second aliquot of sample (make the volume larger if the time needed for the first titration was too short, and conversely), and repeat the process. Titrate several aliquots.

Report the mass in milligrams of cyclohexene in the unknown.

Notes
1. Mercury(II) ions catalyze the addition of bromine to olefinic double bonds.
2. The coefficient of expansion for methanol is 0.11%/°C; thus, significant volumetric errors result if the temperature is not controlled.

38M   VOLTAMMETRY

Various aspects of polarographic and amperometric methods are considered in Chapter 23. Two examples that illustrate these methods using traditional polarography are described in this section. Enormous diversity exists in the instrumentation available for these determinations today. It will thus be necessary for you to consult the manufacturer's operating instructions concerning the details of operation for the particular instrument you will use.

38M-1 The Polarographic Determination of Copper and Zinc in Brass

Discussion

The percentage of copper and zinc in a sample of brass can be determined from polarographic measurements. The method is particularly useful for rapid, routine analyses; in return for speed, however, the accuracy is considerably lower than that obtained with volumetric or gravimetric methods.

The sample is dissolved in a minimum amount of nitric acid. It is not necessary to remove the $SnO_2 \cdot xH_2O$ produced. Addition of an ammonia/ammonium chloride buffer causes the precipitation of lead as a basic oxide. A polarogram of the supernatant liquid has two copper waves. The one at about -0.2 V (versus SCE) corresponds to the reduction of copper(II) to copper(I), and the one at about -0.5 V represents further reduction to the metal. The analysis is based on the total diffusion current of the two waves. The zinc concentration is determined from its wave at -1.3 V. For instruments that permit current offset, the copper waves are measured at the highest feasible sensitivity. These waves are then suppressed by the offset control of the instrument, and the zinc wave is obtained, again at the highest possible sensitivity setting.

PREPARATION OF SOLUTIONS

1. *Copper(II) solution, 2.5 × 10⁻²M.* Weigh (to the nearest milligram) 0.4 g of copper wire. Dissolve in 5 mL of concentrated HNO_3 (*use the hood*). Boil briefly to remove oxides of nitrogen; then cool, dilute with water, transfer quantitatively to a 250-mL volumetric flask, dilute to the mark with water, and mix thoroughly.
2. *Zinc(II) solution, 2.5 × 10⁻²M.* Dry reagent-grade ZnO for 1 hr at 110°C, cool in a desiccator, and weigh 0.5 g (to the nearest milligram) into a small beaker. Dissolve in a mixture of 25 mL of water and 5 mL of concentrated HNO_3. Transfer to a 250-mL volumetric flask, and dilute to the mark with water.
3. *Gelatin, 0.1%.* Add about 0.1 g of gelatin to 100 mL of boiling water.
4. *Ammonia/ammonium chloride buffer* (sufficient for about 15 polarograms). Mix 27 g of NH_4Cl and 35 mL of concentrated ammonia in sufficient distilled water to give about 500 mL. This solution is about 1 M in NH_3 and 1 M in NH_4^+.

PROCEDURE

Calibration

Use a buret to transfer 0.00-, 1.00-, 8.00-, and 15.00-mL portions of standard Cu(II) solution to 50-mL volumetric flasks. Add 5 mL of gelatin solution and 30 mL of buffer to each. Dilute to the mark, and mix well. Prepare an identical series of Zn(II) solutions.

Rinse the polarographic cell three times with small portions of a copper(II) solution, then fill the cell. Bubble nitrogen through the solution for 10 to 15 min to remove oxygen. Apply a potential of about -1.6 V, and adjust the sensitivity until the detector gives a response that is essentially fully scale. Obtain a polarogram, scanning from 0 to -1.5 V (versus SCE). Measure the limiting current at a potential just beyond the second wave. Obtain a diffusion current by subtracting the current for the blank (Note) at this same potential. Calculate i_d/c.

Sample Preparation

Weigh 0.10-g to 0.15-g (to the nearest 0.5 mg) samples of brass into 50-mL beakers, and dissolve in 2 mL of concentrated HNO_3 (*use the hood*). Boil briefly to eliminate oxides of nitrogen. Cool, add 10 mL of distilled water, and transfer each quantitatively to a 50-mL volumetric flask; dilute to the mark with water, and mix well.

Transfer 10.00 mL of the diluted sample to another 50.0-mL volumetric flask, add 5 mL of gelatin and 30 mL of buffer, dilute to the mark with water, and mix well.

Analysis

Follow the directions in the second paragraph. Evaluate the diffusion currents for copper and zinc.

Calculate the percentage of Cu and Zn in the brass sample.

Note

The polarogram for the blank (that is, 0 mL of standard) should be obtained at the sensitivity setting used for the standard with the lowest metal-ion concentration.

38M-2 The Amperometric Titration of Lead

Discussion

Amperometric titrations are discussed in Section 23C-4. In the procedure that follows, the lead concentration of an aqueous solution is determined by titration with a standard potassium dichromate solution. The reaction is

$$Cr_2O_7^{2-} + 2Pb^{2+} + H_2O \rightarrow 2PbCrO_4(s) + 2H^+$$

The titration can be performed with a dropping mercury electrode maintained at either 0 or -1.0 V (versus SCE). At 0 V, the current remains near zero short of the end point but rises rapidly immediately thereafter as a result of the reduction of dichromate, which is now in excess. At -1.0 V, both lead ion and dichromate ion are reduced. The current thus decreases in the region short of the end point (reflecting the decreases in the lead ion concentration as titrant is added), passes through a minimum at the end point, and rises as dichromate becomes available. The end

point at -1.0 V should be the easier of the two to locate exactly. Removal of oxygen is unnecessary, however, for the titration at 0 V.

PREPARATION OF SOLUTIONS

1. *Supporting electrolyte.* Dissolve 10 g of KNO_3 and 8.2 g of sodium acetate in about 500 mL of distilled water. Add glacial acetic acid to bring the pH to 4.2 (pH meter); about 20 mL of the acid will be required (sufficient for about 20 titrations).
2. *Gelatin, 0.1%.* Add 0.1 g of gelatin to 100 mL of boiling water.
3. *Potassium dichromate, 0.01 M.* Use a powder funnel to weigh about 0.75 g (to the nearest 0.5 mg) of primary-standard $K_2Cr_2O_7$ into a 250-mL volumetric flask. Dilute to the mark with distilled water, and mix well.
4. *Potassium nitrate salt bridge.* See Section 38J-2.

PROCEDURE

Obtain the unknown (Note) in a clean 100-mL volumetric flask; dilute to the mark with distilled water, and mix well. Perform the titration in a 100-mL beaker. Locate a saturated calomel electrode in a second 100-mL beaker, and provide contact between the solutions in the two containers with the KNO_3 salt bridge.

The corrected current is given by

$$(i_d)_{corr} = i_d\left(\frac{V + v}{V}\right)$$

where V is the original volume, v is the volume of reagent added, and i_d is the uncorrected current.

Transfer a 10.00-mL aliquot of the unknown to the titration beaker. Add 25 mL of the supporting electrolyte and 5 mL of gelatin. Insert a dropping mercury electrode into the sample solution. Connect both electrodes to the polarograph. Measure the current at an applied potential of 0 V. Add 0.01 M $K_2Cr_2O_7$ in 1-mL increments; record the current and volume after each addition. Continue the titration to about 5 mL beyond the end point. Correct the currents for volume change and plot the data. Evaluate the end-point volume.

Repeat the titrations at -1.0 V. For these titrations, you must bubble nitrogen through the solution for 10 to 15 min before the titration and after each addition of reagent. The flow of nitrogen must, of course, be interrupted during the current measurements. Again, correct the currents for volume change, plot the data, and determine the end-point volume.

Report the mass of Pb in the unknown in milligrams.

Note

A stock 0.0400 M solution can be prepared by dissolving 13.5 g of reagent-grade $Pb(NO_3)_2$ in 10 mL of 6 M HNO_3 and diluting to 1 L with water. Unknowns should contain 15 to 25 mL of this solution.

38N   METHODS BASED ON THE ABSORPTION OF RADIATION

Molecular absorption methods are discussed in Chapter 26. Directions follow for (1) the use of a calibration curve for the determination of iron in water, (2) the use of a standard-addition procedure for the determination of manganese in steel, and (3) a spectrophotometric determination of the pH of a buffer solution.

38N-1 The Cleaning and Handling of Cells

The accuracy of spectrophotometric measurements is critically dependent on the availability of good-quality matched cells. These should be calibrated against one another at regular intervals to detect differences resulting from scratches, etching, and wear. Equally important is the proper cleaning of the exterior sides (the windows) just before the cells are inserted into a photometer or spectrophotometer. The preferred method is to wipe the windows with a lens paper soaked in methanol; the methanol is then allowed to evaporate, leaving the windows free of contaminants. It has been shown that this method is far superior to the usual procedure of wiping the windows with a dry lens paper, which tends to leave a residue of lint and a film on the window.

38N-2 The Determination of Iron in a Natural Water

Discussion

The red-orange complex that forms between iron(II) and 1,10-phenanthroline (orthophenanthroline) is useful in determining iron in water supplies. The reagent is a weak base that reacts to form phenanthrolinium ion, $phenH^+$, in acidic media. Complex formation with iron is thus best described by the equation

$$Fe^{2+} + 3phenH^+ \rightleftharpoons Fe(phen)_3^{2+} + 3H^+$$
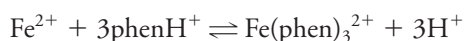
The structure of the complex is shown in Section 19E-1. The formation constant for this equilibrium is 2.5×10^6 at 25°C. Iron(II) is quantitatively complexed in the pH range between 3 and 9. A pH of about 3.5 is ordinarily recommended to prevent precipitation of iron salts, such as phosphates.

An excess of a reducing reagent, such as hydroxylamine or hydroquinone, is needed to maintain iron in the +2 oxidation state. The complex, once formed, is very stable.

This determination can be performed with a spectrophotometer set at 508 nm or with a photometer equipped with a green filter.

PREPARATION OF SOLUTIONS

1. *Standard iron solution, 0.01 mg/mL.* Weigh (to the nearest 0.2 mg) 0.0702 g of reagent-grade $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ into a 1-L volumetric flask. Dissolve in 50 mL of water that contains 1 to 2 mL of concentrated sulfuric acid; dilute to the mark and mix well.
2. *Hydroxylamine hydrochloride* (sufficient for 80 to 90 measurements). Dissolve 10 g of $H_2NOH \cdot HCl$ in about 100 mL of distilled water.
3. *Orthophenanthroline solution* (sufficient for 80 to 90 measurements). Dissolve 1.0 g of orthophenanthroline monohydrate in about 1 L of water. Warm slightly if necessary. Each milliliter is sufficient for no more than about 0.09 mg of Fe. Prepare no more reagent than needed; it darkens on standing and must then be discarded.
4. *Sodium acetate, 1.2 M* (sufficient for 80 to 90 measurements). Dissolve 166 g of $NaOAc \cdot 3H_2O$ in 1 L of distilled water.

PROCEDURE

Preparation of the Calibration Curve
Transfer 25.00 mL of the standard iron solution to a 100-mL volumetric flask and 25 mL of distilled water to a second 100-mL volumetric flask. Add 1 mL of hydroxylamine, 10 mL of sodium acetate, and 10 mL of orthophenanthroline to each flask. Allow the mixtures to stand for 5 min; dilute to the mark and mix well.

 Clean a pair of matched cells for the instrument. Rinse each cell with at least three portions of the solution it is to contain. Determine the absorbance of the standard with respect to the blank.

 Repeat this procedure with at least three other volumes of the standard iron solution; attempt to encompass an absorbance range between 0.1 and 1.0. Plot a calibration curve.

Determination of Iron
Transfer 10.00 mL of the unknown to a 100-mL volumetric flask; treat in exactly the same way as the standards, measuring the absorbance with respect to the blank. Alter the volume of unknown taken to obtain absorbance measurements for replicate samples that are within the range of the calibration curve.

 Report the concentration of iron in the unknown in parts per million.

38N-3 The Determination of Manganese in Steel

Discussion

Small quantities of manganese are readily determined photometrically by the oxidation of Mn(II) to the intensely colored permanganate ion. Potassium periodate is an effective oxidizing reagent for this purpose. The reaction is

$$5IO_4^- + 2Mn^{2+} + 3H_2O \rightarrow 5IO_3^- + 2MnO_4^- + 6H^+$$
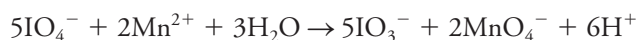
Permanganate solutions that contain an excess of periodate are quite stable.

 There are few interferences to the method. The presence of most colored ions can be compensated for with a blank. Cerium(III) and chromium(III) are exceptions; these yield oxidation products with periodate that absorb to some extent at the wavelength used for the measurement of permanganate.

 The method given here is applicable to steels that do not contain large amounts of chromium. The sample is dissolved in nitric acid. Any carbon in the steel is oxidized with peroxodisulfate. Iron(III) is eliminated as a source of interference by complexation with phosphoric acid. The standard-addition method (see Section 8D-3) is used to establish the relationship between absorbance and amount of manganese in the sample.

 A spectrophotometer set at 525 nm or a photometer with a green filter can be used for the absorbance measurements.

PREPARATION OF SOLUTIONS

Standard manganese(*II*) *solution* (sufficient for several hundred analyses). Weigh 0.1 g (to the nearest 0.1 mg) of manganese into a 50-mL beaker, and dissolve in about 10 mL of 6 M HNO_3 (*use the hood*). Boil gently to eliminate oxides of

nitrogen. Cool; then transfer the solution quantitatively to a 1-L volumetric flask. Dilute to the mark with water, and mix thoroughly. The manganese in 1 mL of the standard solution, after being converted to permanganate, causes a volume of 50 mL to increase in absorbance by about 0.09.

PROCEDURE

The unknown does not require drying. If there is evidence of oil, rinse the sample with acetone and dry briefly. Weigh (to the nearest 0.1 mg) duplicate samples (Note 1) into 150-mL beakers. Add about 50 mL of 6 M HNO_3 and boil gently (*use the hood*); heating for 5 to 10 min should suffice. Cautiously add about 1 g of ammonium peroxydisulfate, and boil gently for an additional 10 to 15 min. If the solution is pink or has a deposit of MnO_2, add 1 mL of NH_4HSO_3 (or 0.1 g of $NaHSO_3$) and heat for 5 min. Cool; transfer quantitatively (Note 2) to 250.0-mL volumetric flasks. Dilute to the mark with water, and mix well. Use a 20.00-mL pipet to transfer three aliquots of each sample to individual beakers. Treat as follows:

Aliquot	Volume of 85% H_3PO_4, mL	Volume of Standard Mn, mL	Mass of KIO_4, g
1	5	0.00	0.4
2	5	5.00 (Note 3)	0.4
3	5	0.00	0.0

Boil each solution gently for 5 min, cool, and transfer it quantitatively to a 50-mL volumetric flask. Mix well. Measure the absorbance of aliquots 1 and 2 using aliquot 3 as the blank (Note 4).

Report the percentage of manganese in the unknown.

Notes
1. The sample size depends on the manganese content of the unknown; consult with the instructor.
2. If there is evidence of turbidity, filter the solutions as they are transferred to the volumetric flasks.
3. The volume of the standard addition may be dictated by the absorbance of the sample. It is useful to obtain a rough estimate by generating permanganate in about 20 mL of sample, diluting to about 50 mL, and measuring the absorbance.
4. A single blank can be used for all measurements, provided that the samples weigh within 50 mg of one another.

38N-4 The Spectrophotometric Determination of pH

Discussion

The pH of an unknown buffer is determined by addition of an acid/base indicator and spectrophotometric measurement of the absorbance of the resulting solution. Because there is overlap between the spectra for the acid and base forms of the indicator, it is necessary to evaluate individual molar absorptivities for each form at two wavelengths. See page 733 for further discussion.

The relationship between the two forms of bromocresol green in an aqueous solution is described by the equilibrium

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$
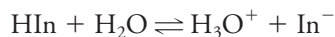
for which

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]} = 1.6 \times 10^{-5}$$

The spectrophotometric evaluation of $[In^-]$ and $[HIn]$ permits the calculation of $[H_3O^+]$ and thus pH.

PREPARATION OF SOLUTIONS

1. *Bromocresol green, 1.0×10^{-4} M* (sufficient for about five determinations). Dissolve 40.0 mg (to the nearest 0.1 mg) of the sodium salt of bromocresol green (720 g/mol) in water, and dilute to 500 mL in a volumetric flask.
2. *HCl, 0.5 M.* Dilute about 4 mL of concentrated HCl to approximately 100 mL with water.
3. *NaOH, 0.4 M.* Dilute about 7 mL of 6 M NaOH to about 100 mL with water.

PROCEDURE

Determination of Individual Absorption Spectra
Transfer 25.00-mL aliquots of the bromocresol green indicator solution to two 100-mL volumetric flasks. To one add 25 mL of 0.5 M HCl; to the other add 25 mL of 0.4 M NaOH. Dilute to the mark and mix well.

Obtain the absorption spectra for the acid and conjugate-base forms of the indicator between 400 and 600 nm, using water as a blank. Record absorbance values at 10-nm intervals routinely and at closer intervals as needed to define maxima and minima. Evaluate the molar absorptivities for HIn and In^- at wavelengths corresponding to their absorption maxima.

Determination of the pH of an Unknown Buffer
Transfer 25.00 mL of the stock bromocresol green indicator to a 100-mL volumetric flask. Add 50.0 mL of the unknown buffer, dilute to the mark, and mix well. Measure the absorbance of the diluted solution at the wavelengths for which absorptivity data were calculated.

Report the pH of the buffer.

38O   MOLECULAR FLUORESCENCE

The phenomenon of fluorescence and its analytical applications are discussed in Chapter 27. Directions follow for the determination of quinine in beverages, in which the quinine concentration is typically between 25 and 60 ppm.

38O-1 The Determination of Quinine in Beverages[13]

Discussion

Solutions of quinine fluoresce strongly when excited by radiation at 350 nm. The relative intensity of the fluorescence peak at 450 nm provides a sensitive method for the determination of quinine in beverages. Preliminary measurements are needed to define a concentration region in which fluorescence intensity is either linear or nearly so. The unknown is then diluted as necessary to produce readings within this range.

PREPARATION OF REAGENTS

1. *Sulfuric acid, 0.05 M.* Add about 17 mL of 6 M H_2SO_4 to 2 L of distilled water.
2. *Quinine sulfate standard, 1 ppm.* Weigh (to the nearest 0.5 mg) 0.100 g of quinine sulfate into a 1-L volumetric flask, and dilute to the mark with 0.05 M H_2SO_4 (sufficient for 60 to 70 analyses). Transfer 10.00 mL of this solution to another 1-L volumetric flask, and again dilute to the mark with 0.05 M H_2SO_4. This latter solution contains 1 ppm of quinine; it should be prepared daily and stored in the dark when not in use.

PROCEDURE

Determination of a Suitable Concentration Range

Set the fluorometer for a 350-nm excitation wavelength. To find a suitable working range, measure the relative fluorescence intensity of the 1-ppm standard at an emission wavelength of 450 nm (or with a suitable filter that transmits in this range). Use a graduated cylinder to dilute 10 mL of the 1-ppm solution with 10 mL of 0.05 M H_2SO_4; again measure the relative fluorescence. Repeat this dilution and measurement process until the relative intensity approaches that of a blank consisting of 0.05 M H_2SO_4. Make a plot of the data, and select a suitable range for the analysis (that is, a region within which the plot is linear).

Preparation of a Calibration Curve

Use volumetric glassware to prepare three or four standards that span the linear region; measure the fluorescence intensity for each. Plot the data.

Analysis

Obtain an unknown. Make suitable dilutions with 0.05 M H_2SO_4 to bring its fluorescence intensity within the calibration range.

Determine the concentration of quinine in the unknown in parts per million.

38P ATOMIC SPECTROSCOPY

Several methods of analysis based on atomic spectroscopy are discussed in Chapter 28. One such application is atomic absorption, which is demonstrated in the experiment that follows.

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[13]These directions were adapted from J. E. O'Reilly, *J. Chem. Educ.,* **1975**, *52*, 610, **DOI**: 10.1021/ed052p610.

38P-1 The Determination of Lead in Brass by Atomic Absorption Spectroscopy

Discussion

Brasses and other copper-based alloys contain from 0% to about 10% lead as well as tin and zinc. Atomic absorption spectroscopy permits the quantitative determination of these elements. The accuracy of this procedure is not as great as that obtainable with gravimetric or volumetric measurements, but the time needed to acquire the analytical information is considerably less.

A weighed sample is dissolved in a mixture of nitric and hydrochloric acids, the latter being needed to prevent the precipitation of tin as metastannic acid, $SnO_2 \cdot xH_2O$. After suitable dilution, the sample is aspirated into a flame, and the absorption of radiation from a hollow cathode lamp is measured.

PREPARATION OF SOLUTIONS

Standard lead solution, 100 mg/L. Dry a quantity of reagent-grade $Pb(NO_3)_2$ for about 1 hr at 110°C. Cool; weigh (to the nearest 0.1 mg) 0.17 g into a 1-L volumetric flask. Dissolve in a solution of 5 mL water and 1 to 3 mL of concentrated HNO_3. Dilute to the mark with distilled water, and mix well.

PROCEDURE

Weigh duplicate samples of the unknown (Note 1) into 150-mL beakers. Cover with watch glasses, and then dissolve (*use the hood*) in a mixture consisting of about 4 mL of concentrated HNO_3 and 4 mL of concentrated HCl (Note 2). Boil gently to remove oxides of nitrogen. Cool; transfer the solutions quantitatively to a 250-mL volumetric flask, dilute to the mark with water, and mix well.

Use a buret to deliver 0-, 5-, 10-, 15-, and 20-mL portions of the standard lead solution to individual 50-mL volumetric flasks. Add 4 mL of concentrated HNO_3 and 4 mL of concentrated HCl to each, and dilute to the mark with water.

Transfer 10.00-mL aliquots of each sample to 50-mL volumetric flasks, add 4 mL of concentrated HCl and 4 mL of concentrated HNO_3, and dilute to the mark with water.

Set the monochromator at 283.3 nm, and measure the absorbance for each standard and the sample at that wavelength. Take at least three—and preferably more—readings for each measurement.

Plot the calibration data. Report the percentage of lead in the brass.

Notes

1. The mass of sample depends on the lead content of the brass and on the sensitivity of the instrument used for the absorption measurements. A sample containing 6 to 10 mg of lead is reasonable. Consult with the instructor.
2. Brasses that contain a large percentage of tin require additional HCl to prevent the formation of metastannic acid. The diluted samples may develop some turbidity on prolonged standing; a slight turbidity has no effect on the determination of lead.

38P-2 The Determination of Sodium, Potassium, and Calcium in Mineral Waters by Atomic Emission Spectroscopy

Discussion

A convenient method for the determination of alkali metals and alkaline earth metals in water and in blood serum is based on the characteristic spectra these elements emit when they are aspirated into a natural gas/air flame. The accompanying directions are suitable for the determination of the three elements in water samples. **Radiation buffers** (page 799) are used to minimize the effect of each element on the emission intensity of the others.

A **radiation buffer** is a substance that is added in large excess to both samples and standards to swamp out the effect of matrix species and thus minimize interferences (see Section 8D-3).

PREPARATIONS OF SOLUTIONS

1. *Standard calcium solution, approximately 500 ppm.* Dry a quantity of $CaCO_3$ for about 1 hr at 110°C. Cool in a desiccator; weigh (to the nearest milligram) 1.25 g into a 600-mL beaker. Add about 200 mL of distilled water and about 10 mL of concentrated HCl; cover the beaker with a watch glass during the addition of the acid to avoid loss due to spattering. After reaction is complete, transfer the solution quantitatively to a 1-L volumetric flask, dilute to the mark, and mix well.

2. *Standard potassium solution, approximately 500 ppm.* Dry a quantity of KCl for about 1 hr at 110°C. Cool; weigh (to the nearest milligram) about 0.95 g into a 1-L volumetric flask. Dissolve in distilled water, and dilute to the mark.

3. *Standard sodium solution, approximately 500 ppm.* Proceed as in b, using 1.25 g (to the nearest milligram) of dried NaCl.

4. *Radiation buffer for the determination of calcium.* Prepare about 100 mL of a solution that has been saturated with NaCl, KCl, and $MgCl_2$, in that order.

5. *Radiation buffer for the determination of potassium.* Prepare about 100 mL of a solution that has been saturated with NaCl, $CaCl_2$, and $MgCl_2$, in that order.

6. *Radiation buffer for the determination of sodium.* Prepare about 100 mL of a solution that has been saturated with $CaCl_2$, KCl, and $MgCl_2$, in that order.

PROCEDURE

Preparation of Working Curves

Add 5.00 mL of the appropriate radiation buffer to each of a series of 100-mL volumetric flasks. Add volumes of standard that will produce solutions that range from 0 to 10 ppm in the cation to be determined. Dilute to the mark with water, and mix well.

Measure the emission intensity for each solution, taking at least three readings for each. Aspirate distilled water between each set of measurements. Correct the average values for background luminosity, and prepare a working curve from the data.

Repeat for the other two cations.

Analysis of a Water Sample

Prepare duplicate aliquots of the unknown as directed for preparation of working curves. If necessary, use a standard to calibrate the response of the instrument to the

working curve; then measure the emission intensity of the unknown. Correct the data for background. Determine the cation concentration in the unknown by comparison with the working curve.

38Q APPLICATION OF ION-EXCHANGE RESINS

38Q-1 The Separation of Cations

The application of ion-exchange resins to the separation of ionic species of opposite charge is discussed in Section 31D. Directions follow for the ion-exchange separation of nickel(II) from zinc(II) based on converting the zinc ions to negatively charged chloro complexes. After separation, each of the cations is determined by EDTA titration.

Discussion

The separation of the two cations is based on differences in their tendency to form anionic complexes. Stable chlorozincate(II) complexes (such as $ZnCl_3^-$ and $ZnCl_4^{2-}$) are formed in 2 M hydrochloric acid and retained on an anion-exchange resin. In contrast, nickel(II) is not complexed appreciably in this medium and passes rapidly through such a column. After separation is complete, elution with water effectively decomposes the chloro complexes and permits removal of the zinc.

    Both nickel and zinc are determined by titration with standard EDTA at pH 10. Eriochrome Black T is the indicator for the zinc titration. Bromopyrogallol Red or murexide is used for the nickel titration.

PREPARATION OF SOLUTIONS

1. *Standard EDTA.* See Section 38E-2.
2. *pH-10 buffer.* See Section 38E-1.
3. *Eriochrome Black T indicator.* See Section 38E-1.
4. *Bromopyrogallol Red indicator* (sufficient for 100 titrations). Dissolve 0.5 g of the solid indicator in 100 mL of 50% (v/v) ethanol.
5. *Murexide indicator.* The solid is approximately 0.2% indicator by mass in NaCl. Approximately 0.2 g is needed for each titration. The solid preparation is used because solutions of the indicator are quite unstable.

PREPARATION OF ION-EXCHANGE COLUMNS

A typical ion-exchange column is a cylinder 25 to 40 cm in length and 1 to 1.5 cm in diameter. A stopcock at the lower end permits adjustment of liquid flow through the column. A buret makes a convenient column. It is recommended that two columns be prepared to permit the simultaneous treatment of duplicate samples.

    Insert a plug of glass wool to retain the resin particles. Then introduce sufficient strong-base anion-exchange resin (Note) to give a 10- to 15-cm column. Wash the column with about 50 mL of 6 M NH_3, followed by 100 mL of water and 100 mL of 2 M HCl. At the end of this cycle, the flow should be stopped so that the liquid level remains about 1 cm above the resin column. *At no time should the liquid level be allowed to drop below the top of the resin.*

Note
Amberlite CG 400 or its equivalent can be used.

PROCEDURE

Obtain the unknown, which should contain 2 to 4 mmol of Ni^{2+} and Zn^{2+}, in a clean 100-mL volumetric flask. Add 16 mL of 12 M HCl, dilute to the mark with distilled water, and mix well. The resulting solution is approximately 2 M in acid. Transfer 10.00 mL of the diluted unknown onto the column. Place a 250-mL conical flask beneath the column, and slowly drain until the liquid level is barely above the resin. Rinse the interior of the column with several 2- to 3-mL portions of the 2 M HCl; lower the liquid level to just above the resin surface after each washing. Elute the nickel with about 50 mL of 2 M HCl at a flow rate of 2 to 3 mL/min.

Elute the Zn(II) by passing about 100 mL of water through the column, using the same flow rate; collect the liquid in a 500-mL conical flask.

Titration of Nickel
Evaporate the solution containing the nickel to dryness to eliminate excess HCl. Avoid overheating; the residual $NiCl_2$ must not be permitted to decompose to NiO. Dissolve the residue in 100 mL of distilled water, and add 10 to 20 mL of pH-10 buffer. Add 15 drops of Bromopyrogallol Red indicator or 0.2 g of murexide. Titrate to the color change (blue to purple for Bromopyrogallol Red, yellow to purple for murexide).

Calculate the number of milligrams of nickel in the unknown.

Titration of Zinc
Add 10 to 20 mL of pH-10 buffer and 1 to 2 drops of Eriochrome Black T to the eluate. Titrate with standard EDTA solution to a color change from red to blue.

Calculate the mass of zinc in the unknown in milligrams.

38Q-2 Determination of Magnesium by Ion-Exchange Chromatography

Discussion

Magnesium hydroxide in milk of magnesia tablets can be determined by dissolving the sample in a minimum of acid and diluting to a known volume. The excess acid is established by titrating several aliquots of the diluted sample with standard base. Other aliquots are passed through a cation-exchange column, where magnesium ion is retained and replaced in solution by a chemically equivalent quantity of hydrogen ion:

$$Mg^{2+} + 2H^+_{res} \rightleftharpoons Mg^{2+}_{res} + 2H^+$$
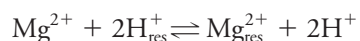
The acid in the eluate is then titrated; the difference between the volumes of base needed for the two series of titrations is proportional to the magnesium ion in the sample. Thus,

$$\text{net mmol } H^+ = 2 \times \text{mmol } Mg^{2+}$$

PROCEDURE

Step 1. Prepare approximately 1 L of 0.05 M NaOH. Standardize this solution against weighed portions of dried primary-standard potassium hydrogen phthalate (KHP); use about 0.4-g (to the nearest 0.1 mg) samples of KHP for each standardization.

Step 2. Record the number of tablets in your sample. Transfer the tablets to a clean 500-mL volumetric flask (Note 1). Dissolve them in a minimum volume of 3 M HCl (4 to 5 mL/tablet should be sufficient). Then dilute to the mark with distilled water.

Step 3. Titrate the free acid in several 15.00-mL aliquots of the dissolved sample; phenolphthalein is a satisfactory indicator.

Step 4. Condition the column with about 15 mL of 3 M HCl (Note 2), followed by three 15-mL portions of distilled water. *Never permit the liquid level to drop below the top of the column packing.*

Step 5. Charge each column with a 15.00-mL aliquot of the sample. Elute at a rate of about 2 to 3 mL/min. Wash the column with three 15-mL portions of water. Collect eluate and washings in a conical flask. Repeat this step with additional aliquots of the sample (Note 3).

Step 6. Titrate the eluted samples (and washings) with standard base. Correct the total volume for that needed to titrate the free acid, and calculate the mass of $Mg(OH)_2$ in milligrams in each tablet.

Notes

1. The sample will dissolve more quickly if the tablets are first ground in a mortar. If you choose this alternative, you will need to know (a) the total mass of your tablets and (b) the mass of ground sample that you transfer to the volumetric flask.

2. The volume of the sample aliquots and the volume of base used in the several titrations must be measured carefully (to the nearest 0.01 mL). *All other volumes can and should be approximations only.*

3. A 25-mL buret packed to a depth of about 15 cm with Dowex-50 cation-exchange resin makes a satisfactory column. Reconditioning after 4 or 5 elutions is recommended.

38R GAS-LIQUID CHROMATOGRAPHY

As noted in Chapter 32, gas-liquid chromatography permits the analyst to separate the components of complex mixtures. The accompanying directions are for the determination of ethanol in beverages.

38R-1 The Gas Chromatographic Determination of Ethanol in Beverages[14]

Discussion

Ethanol is conveniently determined in aqueous solutions by means of gas chromatography. The method is readily extended to measurement of the *proof* of alcoholic beverages. By definition, the proof of a beverage is two times its volume percent of ethanol at 60°F.

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[14]Adapted from J. J. Leary, *J. Chem. Educ.,* **1983**, *60,* 675, **DOI**: 10.1021/ed060p675.

The operating instructions pertain to a $^1/_4$-in. (o.d.) $\times$ 0.5-m Poropack column containing 80- to 100-mesh packing. A thermal conductivity detector is needed. (Flame ionization is not satisfactory because of its insensitivity to water.)

The determination is based on a calibration curve in which the ratio of the area under the ethanol peak to the area under the ethanol-plus-water peak is plotted as a function of the volume percent of ethanol:

$$\text{vol \% EtOH} = \frac{\text{vol EtOH}}{\text{vol soln}} \times 100\%$$

This relationship is not strictly linear. At least two reasons can be cited to account for the curvature. First, the thermal conductivity detector responds linearly to mass ratios rather than volume ratios. Second, at the high concentrations involved, the volumes of ethanol and water are not strictly additive, as would be required for linearity. That is,

$$\text{vol EtOH} + \text{vol H}_2\text{O} \neq \text{vol soln}$$

PREPARATION OF STANDARDS

Use a buret to measure 10.00, 20.00, 30.00, and 40.00 mL of absolute ethanol into separate 50-mL volumetric flasks (Note). Dilute to volume with distilled water, and mix well.

Note

The coefficient of thermal expansion for ethanol is approximately five times that for water. It is thus necessary to keep the temperature of the solutions used in this experiment constant to $\pm1°C$ during volume measurements.

PROCEDURE

The following operating conditions have yielded satisfactory chromatograms for this determination:

Column temperature	100°C
Detector temperature	130°C
Injection-port temperature	120°C
Bridge current	100 mA
Flow rate	60 mL/min

Inject a 1-μL sample of the 20% (v/v) standard, and record the chromatogram. Obtain additional chromatograms, adjusting the recorder speed until the water peak has a width of about 2 mm at half-height. Then vary the volume of sample injected and the attenuation until peaks with a height of at least 40 mm are produced. Obtain chromatograms for the remainder of the standards (including pure water and pure ethanol) in the same way. Measure the area under each peak, and plot $\text{area}_{\text{EtOH}}/(\text{area}_{\text{EtOH}} + \text{area}_{\text{H}_2\text{O}})$ as a function of the volume percentage of ethanol.

Obtain chromatograms for the unknown. Report the volume percentage of ethanol.

WEB WORKS

Material Safety Data Sheets (MSDSs) are an important resource for anyone using chemicals. These documents provide essential information on the properties and toxicity of chemicals that are used in the laboratory. Go to **www.cengage.com/chemistry/skoog/fac9**. From the Chapter Resources menu, choose Web Works. Locate the Chapter 38 section, and click on the link to a comprehensive listing of most of the Internet sites that present MSDSs. Go to one of the sites and look up the MSDS for oxalic acid. Browse through the entire MSDS, read the reactivity data, note its chemical properties, and find the first-aid treatment for ingestion of oxalic acid. Chemical manufacturers are required by law to furnish an MSDS for every chemical that they sell, and many of them can be found on the Internet. It is a good idea to examine the MSDS for any substance that you use in the laboratory.