Modern Quantitative Analysis Experiments for Non-Chemistry Majors

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PREFACE

Although there are many laboratory manuals available for courses in quantitative analysis, emphasis in these is placed on classical experiments or on techniques useful to students whose primary interest is chemistry. For several years at Louisiana State University in New Orleans, experiments have been introduced that were oriented to non-chemistry majors, which were modern, relevant and interesting to students in other fields, i. e., clinical chemistry, medical technology, biology, medicine, dentistry, pharmacy, veterinary science, etc. The experiments were carefully designed to be challenging and non "cook-book" in nature, and were intended to demonstrate the general importance and applicability of quantitative analysis to their fields of interest. A resurgence of interest and enthusiasm from the students performing these experiments, and a belief that these experiments would be of interest and benefit to students at other colleges and universities prompted the author to write this manual. All of the experiments are reliable and can be performed by sophomore, junior or senior level students with little difficulty.

This manual is intended to complement, rather than replace, available texts in quantitative analysis, and to provide experiments that demonstrate the principles learned in a course in modern quantitative analysis, such as that taught in a chemistry department or at a pharmacy or medical school. Each chapter is preceded by a short resume of the basic theory applicable to the experiments in the chapter. Each experiment is supplemented with a short, concise discussion of the principles upon which the experiment is based. This material helps to insure that the student gains sufficient understanding of the method and the object of the experiment, so that each experiment is a profitable experience.

A selected bibliography is provided at the end of each chapter as a source of additional information. Each experiment contains a discussion of the experiment, a brief, pertinent reference section, a list of all apparatus and reagents needed to perform the experiment, the procedure to be followed, an outline of the calculations to be performed, and a list of questions designed to test the

students' grasp of the experiment.

The manual is divided into 4 main sections:

Part I — Titrimetry, which consists of experiments in acid-base, redox and complexometric titrations.

Part II — Electrochemical Methods, which is subdivided into potentiometry, amperometry and coulometry.

Part III — Optical Methods, which is subdivided into molecular absorption, molecular emission and atomic absorption and emission spectroscopy.

Part IV — Separation Methods, which contains sections on gas chromatography, electrophoresis, ion exchange, liquid-solid, TLC and gel filtration.

This laboratory manual was designed for use in non-chemistry majors quantitative analysis courses, in both large and small universities. Experiments are provided covering a range of levels of achievement, and have been designed utilizing equipment normally available in most laboratories.

Almost all of the experiments can be performed in a single 3 to 4 hour laboratory period when properly planned and prepared in advance by a laboratory instructor. It is anticipated that most courses will have time for only about 15 of these experiments -- 30 have been provided so that sufficient latitude exists for selection of a set of experiments designed for the needs of the particular students in different disciplines. Although primarily intended for those in the bio-medical areas, the manual should prove useful for any course in modern chemical analysis.

Experiments in the classical areas of quantitative analysis, i.e., gravimetry, have been purposefully left out since there are very few modern labs that currently do analysis of this type today. Emphasis has been placed, rather, on new modern techniques, i.e., ion-selective electrodes, atomic absorption, electrophoresis, TLC, DEAE-ion exchange, fluorescence, etc. Furthermore, it was intended to provide relevant experiments for bio-medical students, i.e., chloride in blood by complexometric titration and by coulometry; glucose in blood spectrophotometrically and amperometrically; urea and cholesterol in blood spectrophotometrically; Mg^{++} in blood by fluorescence; separation and identification of pharmaceutical products by TLC, etc.

The author wishes to acknowledge the suggestions and advance of colleagues and students, especially those who have helped design experiments used in this manual: Dr. Larry Hargis, who co-authored the book on Modern Instrumental Analysis, some of the experiments from which are contained herein; Dr. Mary Good, who first sparked the interest of students at LSUNO

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in quantitative analysis with her manual, Separations and Analysis; Dr. S. S. Kuan, who designed some of the separations experiments, and Dr. T. Rohm, who designed the coulometry experiment, as well as those whose open literature publications suggested some of the experiments outlined herein. In addition, I would like to thank Mrs. Mercedes Weiser who typed the entire book for photo-offset printing.

George G. Guilbault

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TITRIMETRY

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Chapter 1

ACID-BASE TITRIMETRY

GENERAL

The determination of an acid by titration with a base or the assay of a base by reaction with acid is one of the oldest and most widely used volumetric methods. In these determinations a measured sample of the acid or base is dissolved or diluted in water and titrated with a "standard" acid or base. The standard solution is of known concentration, hence, the amount of sample can be calculated by determining the number of equivalents of titrant required for complete reaction:

Volume of titrant (liter) x normality of titrant = number of equivalents of acid or base (1)

or

Volume of acid x normality of acid = volume of base (liter) x normality of base (2)

The number of equivalents of the sample can be calculated from Eq. (1). The amount of sample in grams can easily be determined from Eq. (3).

Grams of sample = equivalents of sample x gram-equivalent weight of sample (3)

or

Grams of sample = liter x N x g-equiv. wt.

Before any given acid-base reaction can be used as the basis of a volumetric determination a number of requirements must be met:

1. The acid-base reaction involved in the determination must be rapid and stoichiometric, and go essentially to completion.

2. A method for determining the equivalent point (equal equivalents of acid and base) must be available. This might be the use of a chemical indicator or a physicochemical method such as potentiometry.

3. A standard solution must be available for use as a titrant.

The standard solution can be prepared by accurately weighing out an acid or base (a primary standard) and diluting it to a known volume. A primary standard material must be chemically pure, easily weighed (not hygroscopic, etc.), and must react completely with the material to be determined. Very often the standard solution desired cannot be prepared directly and must be standardized against a primary standard solution. A good example is a standard solution of NaOH. Solid NaOH is very hygroscopic and difficult to weigh accurately; thus standard solutions of NaOH must be prepared by standardization against a primary standard acid. A standard solution prepared in this fashion is referred to as a secondary standard.

Acid-base reactions that have small equilibrium constants, such as reactions between weak acids and weak bases, are not useful for volumetric determinations. Reactions between strong acids and weak bases or strong bases and weak acids are possible provided the concentrations are maintained at fairly high levels (i.e., 0.1 M) and the equilibrium constant for the weak acid or base is not too small ($> 10^{-7}$).

INDICATION OF EQUIVALENCE POINT

Suitable chemical indicators include the classic colorimetric compounds which exhibit different colors in acid and basic solution. These compounds are usually either weak acids or weak bases and ionize as follows:

$$HI \rightleftharpoons H^+ + I^-$$

or

$$IOH \rightleftharpoons I^+ + OH^-$$

where I represents all of the indicator compound except the acid or base form. If the nonionized compound has one color and the ion another, the compound can

be used as an acid-base indicator. The value of the ionization constant (K_i) will determine the pH at which the indicator color change will occur. For example, if the indicator is of the weak acid type:

$$K_i = \frac{[H^+][I^-]}{[HI]} \tag{4}$$

and

$$[H^+] = K_i \frac{[HI]}{[I^-]} \tag{5}$$

In basic solution the ionized I^- will be in excess and in acid solution the nonionized HI will predominate. Thus Eq. (5) can be rewritten:

$$[H^+] = K_i \frac{[\text{acid color}]}{[\text{basic color}]} \tag{6}$$

For the acid color to be distinct the ratio of $[HI]/[I^-]$ must be about 10 and for the basic color to predominate the ratio must be about 0.1; i.e., $[H^+]$ for the acid color will be approximately 10 K_i and for the basic color it will be about 0.1 K_i. For example, if $K_i = 1 \times 10^{-5}$, then the $[H^+]$ for the acid color would be 1×10^{-4} (pH = 4), and for the basic color it would be 1×10^{-6} (pH = 6). Thus the color change of the indicator will be at a pH = $pK_i \pm 1$, and an indicator should be chosen whose pK approximately equals the pH expected at the end point of the titration. Some common acid-base indicators and the pH over which they change color are presented in Table 1. In acid-base

TABLE 1
Acid-Base Indicators

Indicator	Acid form		Base form	
	Color	pH	Color	pH
Thymol blue	Red	1.2	Yellow	2.8
Bromphenol blue	Yellow	3.0	Purple	4.6
Methyl orange	Red	3.1	Yellow	4.4
Methyl red	Red	4.2	Yellow	6.2
Bromthymol blue	Yellow	6.0	Blue	7.6
Phenol red	Yellow	6.4	Red	8.0
Thymol blue	Yellow	8.0	Blue	9.6
Phenolphthalein	Colorless	8.0	Red	9.8

reactions where a rapid change in pH occurs near the equivalence point [Fig. 1(a), 2] any indicator in Table 1 could be used. However, for a weak acid titrated with strong base [curve 1, Fig. 1(a)] an indicator changing in the pH range 8-11 must be used, such as phenolphthalein. For the titration of a weak base, such as ammonia, with a strong acid, e. g., HCl, an indicator changing in the pH range 4-7 must be used, such as bromphenol blue [Curve 4, Fig. 1 (b)].

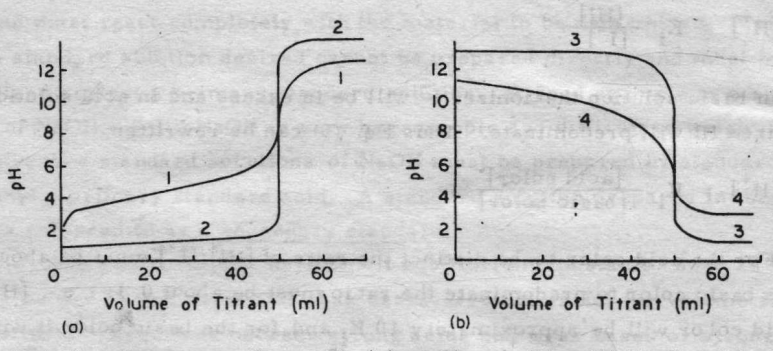

FIG. 1. Typical titration curves for acids (a) and bases (b). (1) Weak acid-strong base (i. e., acetic with NaOH); (2) strong acid-strong base (i. e., HCl with NaOH); (3) strong base-strong acid (i. e., NaOH with HCl); (4) weak base-strong acid (i. e., NH_3 with HCl).

Alternatively, it is possible to determine the equivalence point of an acid-base reaction by a potentiometric titration using a pH meter. With a pH meter one can read the pH after successive additions of titrant so that a complete titration curve (pH vs volume of titrant) can be constructed (Fig. 2). Proper analysis of this curve will indicate the equivalence point. In such a titration two electrodes, usually a standard calomel electrode and a reference glass electrode are used, which are plugged into the pH meter. The glass

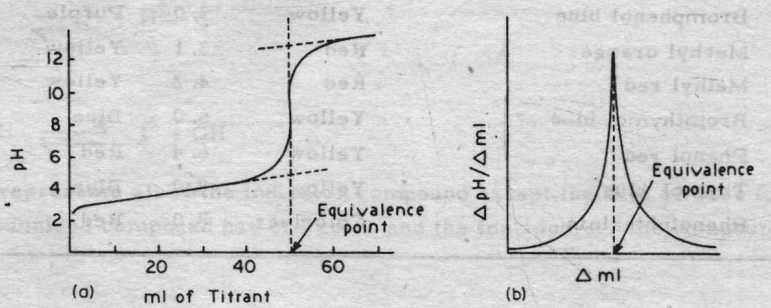

FIG. 2. Analysis of titration curve. (a) Graphical method; (b) first derivative method.

electrode-calomel electrode system behaves as an electrochemical cell; changes in the total potential occur as the $[H^+]$ is increased or decreased. A schematic of the total cell is as follows:

$$\underset{\text{Glass electrode}}{\text{Pt, Ag, AgCl} \mid H^+ (0.1\ \underline{M}) \mid\mid H^+ (x\ \underline{M}) \mid} \underset{\text{Calomel electrode}}{\text{KCl (satd), } Hg_2Cl_2\text{, Hg}}$$

The potential of the system is defined as

$$E = k + 0.0591\ pH \tag{7}$$

The potential of the cell system is displayed on a meter (usually in pH units) and the particular pH meter is standardized with a set of solutions of known pH.

The end point of the titration can be determined either graphically [Fig. 2(a)] where the equivalence point is defined as the midpoint of the rapidly changing portion of the curve, or by the first derivative method [Fig. 2(b)] as the point at which the curve reaches a maximum.

MEDIA FOR TITRATION

Acid-base titrations can be performed in either aqueous (i.e., H_2O) or nonaqueous solution. In this chapter two experiments are given. The first describes the aqueous titration of bicarbonate in blood; the second, the nonaqueous titration of an organic base. In both experiments, chemical indicators are used to determine the end point of the titration. The use of potentiometry to determine the end point of a titration is demonstrated in Experiment 6 of Chapter 4.

Suggested Readings

R. A. Day and A. L. Underwood, Quantitative Analysis, 2nd ed., Prentice-Hall, Englewood Cliffs, N. J., 1967, Ch. 4.

J. S. Fritz and G. H. Schenk, Quantitative Analytical Chemistry, Allyn and Bacon, Boston, Mass., 1969, Ch. 8, 9.

Experiment 1 DETERMINATION OF BICARBONATE IN BLOOD

PURPOSE

The titration, in aqueous solution, of bicarbonate ion in blood is demonstrated. Sodium hydroxide is used as titrant.

Suggested Reading

N. W. Tietz, Fundamentals of Clinical Chemistry, Saunders, Philadelphia, Pa., 1970, pp. 625-636.

THEORY

About 95% of all of the CO_2 in human blood exists as bicarbonate ion, HCO_3^-; the remainder exists as dissolved CO_2. The pH of blood is controlled very rigidly at 7.4 because of the CO_2-bicarbonate equilibrium in blood (Henderson-Hasselbach equation). Standard nomograms are available that relate the pH, CO_2, and HCO_3^- concentrations (thus an assay of two of these variables allow calculation of the third):

$$pH = pK + \log \frac{[HCO_3^-]}{[CO_2]}$$

The clinical laboratory uses the assay of HCO_3^- as a diagnostic aid. Bicarbonate is determined by adding an excess of 0.01 M HCl to volatilize the HCO_3^- as CO_2, swirling to allow the CO_2 to escape, and then back-titrating the excess HCl with 0.01 M NaOH.

APPARATUS

Analytical balance
Burets: 10-ml (1), 50-ml (1)
Pipets: 0.1-ml (1), 1.00-ml (1), 4-ml (1), 6-ml (1), 50-ml (2)
Volumetric flasks: 100-ml (1), 500-ml (1), 1-liter (2)
Erlenmeyer flasks: 25-ml (4), 250-ml (4)
Meker burner (1)
Gooch crucible (1)
Test tubes (2)
Bottle: 1-liter (1)
Florence flask: 1-liter (1)

REAGENTS AND SOLUTIONS

1% Saline solution — Prepare by dissolving about 10 g of NaCl in 1.0 l of CO_2-free water.

HCl, concentrated

NaOH, C. P. pellets

Phenol red indicator — Prepare by grinding 0.1 g of phenol red (phenolsulfonaphthalein) in a mortar with 5.7 ml of 0.05 M NaOH. Transfer to a 100-ml volumetric flask and dilute to the mark with CO_2-free water.

Phenolphthalein indicator — Dissolve 1.0 g of phenolphthalein powder in 90 ml of alcohol. Dilute to 100 ml with distilled water.

Antifoam A (Dow Corning Corporation)

Serum (obtain from a local hospital) — A 10-15 ml sample (20-30 ml of whole blood) should be adequate for triplicate determinations by a class of 30 students. The analysis should be performed on the day the blood is drawn. Fluoride should be added to prevent glycolysis, or breakdown of glucose, which can change the pH. The fluoride inhibits the glycolysis-causing enzyme and stabilizes the pH for about 2 hr. Touch the end of a stirring rod to antifoam A and rotate it in the pooled serum sample. This will prevent excess foaming when the sample is swirled.