STANDARD METHODS OF CHEMICAL ANALYSIS

SIXTH EDITION

Volume Two—Industrial and Natural Products and Noninstrumental Methods

Part A

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IN COLLABORATION WITH MANY CONTRIBUTORS
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PREFACE

Changes in the methods of chemical analysis, both major modifications and precise refinements, have been manifold during the twenty-five years since publication of the Fifth Edition of STANDARD METHODS OF CHEMICAL ANALYSIS. As a result of the development of new analytical techniques, as well as an expanding interest in the variety of materials subject to examination, analysis and analysts have recognized—and continue to stress—the necessity for comprehending the essential importance of substances considered insignificant only a few decades ago.

The preparation of a Sixth Edition of STANDARD METHODS OF CHEMICAL ANALYSIS was inevitable if the work were to maintain its utilitarian function in the onrush of contemporary change. Volume II, consequently, has undergone considerable expansion in content, evidenced by its physical size—approximately twice that of the Fifth Edition. Despite the changes in treatment and content, the purpose of this volume remains identical to that expressed in the First Edition. As an explanation of the aim of the present volume, we quote from the original Preface:

"This book is a compilation of carefully selected methods of technical analysis that have proven of practical value to the professional chemist. The subjects have been presented with sufficient detail to enable one with an elementary knowledge of analytical processes to follow the directions; on the other hand, lengthy exposition, theoretical dissertation, and experimental data are purposely avoided, in order to include a large amount of information in a compact, accessible form. References to original papers are given when deemed advisable."

The organization of the Sixth Edition is similar to that of the Fifth, but an extensive new part, *Apparatus, General Operations, and Reagents,* has been added. This consists of sixteen chapters, of which the following thirteen are new: *Standard Laboratory Apparatus; Detection of the Cations and Anions; Mechanical Separation; Separation by Precipitation; Separation by Electrolysis; Solvent Extraction; Separations by Distillation and Evaporation; Chromatography; Ion Exchange Methods in Analysis; Final Gravimetric Treatment; Acid-Base Titrations in Nonaqueous Solvents; Statistical Interpretations;* and *Quantitative Organic Analysis.*

In Part II, *Special Techniques for Industrial Products and Other Special Substances,* ten new chapters have been added: *Air Pollutants; Amino Acid Analysis of Protein Hydrolyzates; Chemical Analysis in Clinical Medicine; Fertilizers; Gas Analysis—Vacuum Techniques; Pesticides; Plastics; Silicates: Glasses, Rocks, and Ferrous Slags; Soils;* and *Vitamins.*

Almost without exception, chapters that appeared in the Fifth Edition have been completely rewritten. Of the fifty chapters appearing in this edition, only four have the same authors as previously. In those instances where chapters appearing in the Fifth Edition have been prepared for the Sixth Edition by different authors, they have been rewritten and not merely revised.

The editor has received much useful assistance from many sources, and wishes to express his gratitude here as well as later in the text. Special mention should be made of Professor N. Howell Furman, editor of the Fifth Edition, and Volume I of the Sixth Edition. As advisory editor of Volume II, he prepared the outline used in organizing the text, gave valuable assistance in securing contributors for the many chapters, and made many helpful suggestions and criticisms.

The editor wishes to acknowledge also the valuable assistance given by Dean Virgil Hunt of the Indianapolis Regional Campus of Indiana University in making available the many facilities of his department to aid the completion of this book. Furthermore, a number of people have rendered invaluable aid in typing portions of the manuscript, attending to correspondence, proofreading, and preparing the Index. These are: Janet Boling, Patricia Van Noy, Oka Negley, Ruth Moody, and Judy Call.

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The task of assembling and coordinating the material for this book has been simplified immensely by the remarkable spirit of cooperation exhibited by the various collaborators in all phases of the undertaking. The editor wishes to thank all contributors for their efforts toward bringing this book to its final form, and for making available the specialized information that it contains to all who may have need of the methods of practical chemical analysis.

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Part I

APPARATUS, GENERAL OPERATIONS, AND REAGENTS

Chapter 1

STANDARD LABORATORY APPARATUS

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Quantitative analysis is the determination of the quantity of one or more of the constituents present in a given material. Regardless of the method used to determine this quantity, somewhere in the operation a set of precise analytical weights and an analytical balance must be used. Therefore, the accuracy of all work rests fundamentally on the weights and balance that are employed. H. S. Washington states ". . . if the balance and weights are not accurate, and are not carefully taken care of, the labor and time expended on an analysis will largely go for naught. The balance and weights should therefore be regarded with a feeling akin to reverence, and the balance case looked upon, so to speak, as a 'sanctum sanctorum'."

WEIGHTS, BALANCES, AND WEIGHING

The Weights.—As is well known, the international metric system is used in scientific work, and the standard of mass is the international prototype kilogram which is in the custody of the International Bureau of Weights and Measures in France. Two copies of this standard, designated as the United States prototype kilograms, are at the National Bureau of Standards, Washington, D. C. These weights are the ultimate base for all gravimetric analysis.

The analyst should exercise extreme care in selecting the weights he uses. The material of which analytical weights are made must be hard, nonmagnetic, resistant to oxidization and corrosion, and unaffected by humidity. The entire surface of each weight must be smooth and highly polished, and must remain so in use. The weights must always be handled with the special lifter which the manufacturer provides with each set of weights. These lifters are especially designed, and the tips that come in contact with the weights must be smooth and made of a material that minimizes the abrasion of the weights during use. Nonmagnetic stainless steel is suitable for weights of 1 g. and larger. Platinum or an alloy of 96.5% platinum and 3.5% rhodium is suitable for fractional gram weights of 10 mg. or larger. Highly polished tantalum is suitable for the fractional gram weights of less than 10 mg.

The accuracy of a set of weights should never be taken for granted. This is true for a new set, as well as for a set that has been used. There are extreme variations in the quality of weights, and nothing except a test of each individual weight will prove its accuracy and constancy. It would be ideal if every set of weights that is used in analytical work were tested by the National Bureau of Standards,[1] but this may not be practical. Therefore, every first class laboratory should have available a set of weights certified by the National Bureau of Standards as conforming to Class M weights. These weights then can be used to determine the accuracy of the normal "working" weights. For weights to conform to Class M or Class S, they must be adjusted within the limits of error prescribed in Table 1-1.

The mere fact that a set of calibrated weights is not available is no excuse for an analyst to use questionable weights. Inaccurate weights often go undiscovered, either through ignorance or through fear that the calibration methods are too difficult or too time-consuming to be practicable in an ordinary analytical laboratory. A quick check for gross inaccuracies can be made by a few simple weighings. Since most gravimetric analyses are reported as ratios or percentages, it is usually sufficient that the set of weights used be nearly consistent among themselves, that is, the 1-g. weight be exactly 10 times the weight of the 100 milligram weight and the 10-g. weight be exactly 10 times the weight of the 1-g. weight. The method of calibration that can be used is that of Richards[2] in which one weight, perhaps the 10-g., is assumed correct; that is, it weighs 10.0000 g. The values of all other weights can be expressed in terms of this 10-g. weight.

The Analytical Balance.—The value of gravimetric analysis rests fundamentally on the accuracy of the instrument employed to determine the weight of the sample to be analyzed as well as to determine the weights of the various component parts. The instrument used is the analytical balance, which is the oldest form of instrument in use in analytical chemistry. The analytical balance is used to compare the weight of the sample to be analyzed to the standard unit of weight (mass), and likewise to compare the weights of the various separated components to the same standard unit of weight.

The fundamental requirements for a reliable analytical balance are:

A. It must be accurate and precise. It should give the same results when the same object is weighed several times.

B. It must have sufficient sensitivity. It must respond to slight changes in weight. For most analyses it is sufficiently sensitive if one can easily determine 0.1 mg.

C. Above all, the balance must be stable and well constructed. The beam must return to its horizontal position after swinging. The beam must not bend under its normal working load. All knife-edges must be sharp, lie in the same plane, and be parallel to one another. The plates on which the knife-edges rest when weighing should be made of a hard material, usually agate, highly polished, and perfectly smooth and flat. The knife-edges should remain sharp and the plates flat, "not cupped," when the balance is properly used.

There are three general types of analytical balances available to the analyst. One type of analytical balance is essentially an equal-armed lever, supported at the center and free to swing in a vertical plane. Balance pans are suspended from

[1] Schedules of fees charged by the National Bureau of Standards for the testing of weights and balances, methods of weighing and testing, and regulations governing their testing may be obtained free of charge from the National Bureau of Standards, Washington 25, D. C.

[2] Richards, T. W., J. Am. Chem. Soc., 22, 144, 1900.

TABLE 1-1. PRECISION OF CORRECTIONS AND TOLERANCES FOR CLASS M, HIGH PRECISION WEIGHTS, AND CLASS S, LABORATORY WEIGHTS

Denomination	Class M		Class S	
	Tolerance	Precision of Correction	Tolerance	Precision of Correction
100 g.	0.5 mg.	0.1 mg.	0.5 mg.	0.5 mg.
50	.3	.1	.3	0.1
20	.2	.01	.2	.1
10	.15	.01	.15	.05
5	.15	.01	.15	.05
2	.10	.01	.10	.05
1	.10	.01	.10	.05
500 mg.	.05	.001	.05	.01
200	.05	.001	.05	.01
100	.05	.001	.05	.01
50	.03	.001	.03	.01
20	.03	.001	.03	.01
10	.02	.001	.02	.01
5	.02	.001	.02	.01
2	.01	.001	.01	.01
1	.01	.001	.01	.01
0.5	.01	.001	.01	.01
0.2	.01	.001	.01	.01
0.1	.01	.001	.01	.01

each end of the beam or lever. The object to be weighed and the weights used are placed on these pans. Analytical balance of this type may differ in various constructional details, but all have the same fundamental features. The final weight is obtained by one of the methods of swings. A second type of analytical balance is constructed exactly like the previous type except that some kind of damper, usually of a magnetic type, is attached to one or both ends of the beam. The purpose of the damper is to eliminate the swinging of the balance. In fact, the oscillations are so completely damped that, if there is a small difference in the weights on the pans and the balance is released, the pointer will swing to one side and come to rest at the end of its swing. The scale is graduated in milligrams; thus, the point of rest indicates directly the weight of the object. Naturally, the exact point of rest must be determined either with a microscope, or the two images, pointer and scale, are magnified and projected on some type of viewing screen.

A third type of analytical balance may or may not be an equal-arm balance. In either case, it is a so-called damped balance. This type of balance may be called a one-pan balance. That is to say, attached to the beam on one side of the fulcrum is a counterpoise of sufficient weight to balance exactly the pan and