

ADVANCED QUANTITATIVE ANALYSIS

A Companion Volume to
ELEMENTARY QUANTITATIVE ANALYSIS

by HOBART H. WILLARD and N. HOWELL FURMAN

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PREFACE

The graduate training of chemists should involve advanced work in each of the fundamental fields of chemistry: inorganic, physical, organic, and analytical. This advanced analytical chemistry should be divided about equally between chemical methods of analysis and physico-chemical or instrumental methods of analysis.

This book has been written as a text for that part of the work dealing with chemical methods of analysis and the emphasis has been placed upon chemistry. The book is largely devoid of physico-chemical theory but it is rich in the factual inorganic chemistry useful to the practicing chemist and essential to the development of chemical intuition in the embryonic chemist. The authors feel that nowhere else can so thorough a knowledge of inorganic chemistry be acquired as by an extensive study of the analytical chemistry of the elements.

This text has been designed as a companion volume to Willard and Furman, *Elementary Quantitative Analysis*. As such, the treatment of certain subjects has been deliberately made supplementary in nature rather than complete. This may occasionally cause the reader some inconvenience but a considerable saving in the size and cost of the book has been effected by eliminating extensive duplication of the material found in the elementary book; and this may be remembered in a few cases where it may be necessary to consult the beginning book for background material. Page references are given to the third edition of Willard and Furman; these will assist in correlating the information of the two texts.

The first third of the book is devoted to a discussion of the general methods of chemical analysis; the topics are taken up in the order in which they are met in the course of an analysis, the problems of sampling, the methods of decomposing and dissolving materials, the methods of concentrating small amounts of materials, the various methods of separating the elements, and so on through to the methods of reporting the results. The second third of the text is devoted to the analysis of iron ore, steel, and silicate rock, and has sections devoted to the analytical chemistry of each of the elements encountered. Directions for laboratory work accompany

this portion of the book. The last third of the book is a discussion of the analytical chemistry of each of the elements not studied earlier; the common and most of the rarer elements are treated. The order in which the elements are discussed is that of the periodic table, and sufficient information is given to supply the student with the basic information needed for solving the problems involved in the analysis of complex inorganic mixtures. A large number of references to the original literature have been included with sufficient information to make possible a decision as to the adaptability of a specific method to a particular case. The methods included are the result of a rather critical examination of a large number which have been proposed.

A discussion of the methods of determining the atomic weights of the elements has been included. The fundamental nature of this subject demands that the student be at least familiar with the principal aspects of the problem, and a knowledge of the care and refinement of technic requisite to attaining atomic weight precision and accuracy cannot fail to have a wholesome effect on the attitude of the student toward the results of his own laboratory work.

Although directed primarily toward the teaching of quantitative analysis at the graduate level, the book may also find use by the more advanced undergraduate students, particularly perhaps by those interested in metallurgical analysis.

The observing reader will not fail to note that the majority of the literature references given are to the *Analytical Edition of Industrial and Engineering Chemistry*. This is neither accident nor narrow nationalism. Analytical Chemistry in America has expanded and matured, and in its fifteen years, the *Analytical Edition* has kept pace, faithfully sifted and recorded the results, and accepted the responsibilities of the dominant journal in the field. At the same time there has emerged in this country a professionally conscious group of analytical chemists and teachers of analytical chemistry, its nucleus being the Division of Analytical and Micro Chemistry of the American Chemical Society. To a certain extent the references cited in this text mirror the progress of this group and it is sincerely hoped that this progress will continue unabated and the science and profession of analytical chemistry be further strengthened and developed.

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CHAPTER I

NOTES TO STUDENTS

ATTITUDE AND APPROACH TO LABORATORY WORK

So we have two classes of workers in the analytical field, the determinators and the analysts. The determinators, who are by far the more numerous, may in turn be divided into two general classes: first, the common determinators who follow a method explicitly, without knowledge or concern as to the reactions involved; and second, the educated determinators who can handle systems containing one or perhaps two variables, or who, like determinators of pH, are chiefly interested in group effects and make no effort to go beyond this. The first are the laborers. They need not be chemists, and they require constant supervision. The second are the white-collar workers who exhibit the usual extremes of workers in this classification. The determinator's salvation lies in the development of truly selective methods of analysis, and his final resting place will be a heaven in which he has a shelf containing 92 reagents, one for each element, where No. 13 is the infallible specific for aluminum, No. 26 the sure shot for iron, No. 39 the unfailing relief for yttrium and so on to uranium.

As for the analyst, he is a comparatively rare bird and is often referred to as a disappearing species, like the old family practitioner who does the best he can, guided by theory and experience, of which the most comforting is experience. It must be admitted that one of the reasons for the gradual disappearance of the analyst is the anomaly that, in spite of the fact that he works entirely with material things, his reward is chiefly spiritual. Who ever heard of a consulting analyst, or of an analyst who patented a new method of analysis or incorporated a company to promote its use? Other reasons for the scarcity of the analysts are perhaps the peculiar characteristics, some inherent and some acquired, that he must possess. He must have the inquisitive habit of a detective, for oftentimes the composition of the material under test is absolutely unknown. He must be an expert manufacturer of pure chemicals, for on this ability the success of his gravimetric determinations depends. He must be an efficient dispenser of liquids of which he knows the exact effect. And, above all, he must serve a long apprenticeship, and keep in constant practice.—LUNDELL.¹

¹ From "The Chemical Analysis of Things as They Are," *Ind. Eng. Chem., Anal. Ed.*, **5**, 221 (1933); recommended reading for all who would be chemists.

It is of the greatest importance that before beginning work the analyst should have a thorough understanding of the entire method of the analysis projected and should know the chemistry involved, the sources of error, the presence or absence of interfering materials, and the reasons for the order pursued and the mechanical details adopted. A worker who blindly follows a written procedure may develop skill in manipulation but will never become a chemist. The methods of analysis used in the courses for which this text is designed are typical ones which illustrate general principles and techniques. These may be applied to other cases than the ones studied, but this requires a complete knowledge of the reactions and principles involved. Therefore, in the recitation work, special emphasis will be laid upon the theory, general principles, chemical reactions, applications, and errors of the various methods, and little attention will be paid to manipulative details. Skill in manipulation is judged by the accuracy of the analyses, but a knowledge of the subject, which is of more importance, is judged by the ability to apply it to new problems and to familiar substances under new conditions and to detect errors and to devise possible improvements in old processes.

The greatest problem of laboratory work is the efficient use of the time available. Laboratory work should be planned ahead and arrangements made for carrying on simultaneously as many operations as possible. When long evaporations are required, the time should be filled in with other work; and long, preliminary operations should be started early enough so that they will be finished by the time they are wanted. Idle moments can be filled in with minor jobs such as cleaning glassware, marking and igniting crucibles, and so on. With proper planning there will be no waste of time and the effort of looking ahead will be amply rewarded.

The Use of the Literature. Acquiring a familiarity with the chemical literature is of fundamental importance in the training of a chemist. In schools where a special course in the use of the chemical library is given, this may be more or less compulsory; in other places it is largely a matter of individual effort. Next to actually having the knowledge itself, a knowledge of where to find information is most important. The details of the multitudinous methods which may be drawn upon are beyond the memory of any one chemist, and frequent reference to the literature is not only a remunerative method of avoiding mistakes but also a stimulating source of new ideas.

The methods of analyzing most commercially important materials have been largely standardized by the various societies such as The American Society for Testing Materials, The American Public Health Association, The Association of Official Agricultural Chemists, The United States Pharmacopoeial Convention, and others. The publications of these societies contain detailed directions for the analysis of many materials and together with the standard reference books of various subfields constitute the first literature to be consulted. An extensive bibliography of the chief texts in the various fields of analysis is given in Willard and Furman, 3rd Ed., pp. 480-492.

In the case of minerals, and to a lesser extent, alloys, it is not likely that there will be found in the literature a method of analysis of a particular subject, but the relevant material will probably be found under the elements composing the substance. Many of the best analytical separations are to be found only in the various chemical journals, and have not yet found their way into any of the books on the subject. In a science where so many new discoveries are constantly being published, no book can be fully up to date. A few hours spent in the library searching the journals is frequently a means of saving many hours in the laboratory rediscovering something already known and reported.

A definite and systematic plan for covering the literature on the analytical chemistry of a particular substance is given in the text by Soule.² Much excellent advice on the subject of the analytical literature will be found in this place, as well as an extensive bibliography of analytical books, compilations, and journals, together with comments on their general utility.

OUTLINE OF LABORATORY WORK

The laboratory work presented in this text has been chosen to illustrate a variety of methods with respect to the chemistry and the general procedure involved. A number of the determinations are those commonly made in commercial and industrial practice and they are on the whole more difficult than those carried out in the elementary courses. In fact some of the determinations are among the most difficult of all the analyst is called upon to make. The

² Soule, *Library Guide for the Chemist*, The McGraw-Hill Book Company, Inc., New York, 1938, pp. 168-183.

materials analyzed and the order in which the analyses are undertaken are, first, the analysis of iron ore or steel for the minor constituents, next the analysis of an alloy steel for the alloying metals, then the determination of sodium and potassium in an insoluble silicate, and finally the qualitative and quantitative analysis of some unknown substance.

For convenience the material dealing with iron ore and steel has been treated together, this being possible because many of the determinations made are common to both materials and have many similarities in the chemistry and procedure. The determinations made on iron ore or steel are: loss on ignition, total iron, aluminum, titanium, manganese, carbon, silica, phosphorus, and sulfur. Suggestions as to the general consideration of these analyses, the procedures to be followed, and the method of reporting the results are given on pp. 131 and 133.

The alloy steel is analyzed for chromium, vanadium, tungsten, and molybdenum. The material dealing with these metals follows the section devoted to iron ore and plain carbon steel. Nickel, copper, and cobalt, which could also rightfully be termed alloying metals, are dealt with in a later section of the book, but the discussion of the analytical chemistry of these metals includes the methods and procedures for their determination in steel.

The chapter dealing with the determination of sodium and potassium and the decomposition of insoluble silicates for their determination follows that on alloy steel. It is recommended that in the determination of sodium the sample be decomposed by the hydrofluoric acid-sulfuric acid or the hydrofluoric acid-perchloric acid method, and the sodium be determined directly by the triple acetate method; and that for the determination of potassium, the sample be decomposed by the hydrofluoric acid-fluosilicic acid distillation method, and the potassium determined by the perchlorate method.

The final problem is the qualitative and quantitative analysis of some unknown material such as a mineral, alloy, or commercial product. A careful qualitative analysis is made, bearing in mind the data which should be secured concerning the approximate composition. When the constituents are known, the name, nature and uses of the material should be found if possible. After the required information has been obtained, a report is submitted to the instructor, who will indicate any errors. Next a scheme is worked out for the complete quantitative analysis of the substance. The

principles discussed on pp. 39 and 404 should be considered carefully. Knowledge already gained and the information which can be found in the literature should be employed fully, and imagination and ingenuity should be exercised in devising new methods for difficult or new problems. The instructor will give advice when necessary. The proposed scheme of analysis is then submitted in written form to the instructor who will indicate any objections or possible improvements. Until the method of analysis has been approved, the analysis should not be started, otherwise time may be wasted on a method that will not serve the purpose. As the analysis proceeds, it may be found desirable to make further changes in the original plan, and if any improvement is seen, it should at once be discussed with the instructor. At the end, a detailed description of the method actually used is handed in for permanent record, together with any comments or suggestions, and the results of the analysis reported in the proper manner.

THE KEEPING OF RECORDS

As for estimating the accuracy of his work, it can be said that the determinator is usually an optimist in thought and expression, while the analyst is a confirmed pessimist. The determinator reports silica in glass as 71.61, if not 71.611. The analyst, who knows that he is doing nicely to insure results in the first decimal place, reports 71.6 and thus is honest with himself and deceives no one as to his powers.—LUNDELL.

The prime importance of a notebook is to preserve the record. Naturally, then, the principal concern is that the record be legible and intelligible at some later date when the record is cold and all memory of the event has been long lost. Preferably the notebook should be a bound book with fixed pages and of sufficient value that it will not be lightly discarded. The record should be kept in ink as this is most durable. The relevant data should all be entered, including the date, the source, character, and number or other designation of the sample, all weights and readings taken during the analysis, a brief mention of the method of analysis used, any numerical factors introduced, the results with any explanatory comment, and finally the signature of the analyst. The arrangement is entirely an individual matter, but should be intelligible to another without undue effort in the deciphering of shorthand symbols or sloppy penmanship. Among the emphatic *don'ts* of record keeping

is the very pernicious habit of jotting down significant data on loose scraps of paper. Equally bad is a numerical entry without explanation.

The problem of significant figures, methods of computation, the rejection of data, and related topics were discussed in Willard and Furman, 3rd Ed., pp. 63-71. A more extensive treatment of these subjects will be found in other places.³ The method of computation employed is a matter of convenience and speed for the individual. The rejection of data should be justified by some definite reason or observed fault in the process leading to the data. Data otherwise apparently satisfactory but in disagreement with other data on the same measurement should be rejected only on a probability basis when it can be shown that the departure from the mean is far greater than the average deviation, and this can not be done with less than four values. The selection of data is a matter of experience, critical evaluation, and honesty. The mathematical rules governing significant figures are more definite, and precision should not be confused with accuracy. But even in this, in chemical work, much is left to personal judgement and to good taste.

THE USE AND CARE OF PLATINUM WARE

Platinum is attacked by many substances, particularly at a high temperature. Free chlorine and bromine attack it easily, boiling, concentrated sulfuric acid slowly, and the following materials attack it so readily that they should never be heated in platinum vessels:

The hydroxides, nitrates, and cyanides of the alkali metals and barium;

All sulfides or mixtures containing sulfur and a carbonate or hydroxide;

Phosphorus, arsenic, and their alloys;

All metals, since they form alloys with platinum, and all compounds easily reducible by the carbon of the filter paper or by the flame gases, such as lead oxide, silver chloride, lead sulfate, or stannic oxide.

Phosphates are without action on platinum unless reduced to phosphides; because this may occur, owing to the action of the car-

³ Yoe and Crumpler, *Chemical Computations and Errors*, John Wiley & Sons, Inc., New York, 1940.

bon of the filter paper or to the flame gases, it is safer to ignite all phosphates, including pyrophosphates, in porcelain.

At high temperatures, platinum allows the gases of the flame to diffuse through it quite readily and this may cause the reduction of some substances not otherwise easily reduced. If the crucible is open, diffusion into the air is so rapid that this effect is much less noticeable, but in a covered crucible heated by a gas flame there is a strong reducing atmosphere in the crucible. Ferric oxide heated in this way is partly reduced to the metal; even in the presence of fused sodium carbonate some reduction seems to occur. The iron then alloys with the platinum, and no matter how thoroughly the latter is cleaned, it will tarnish on ignition, due to the formation of a film of ferric oxide. If this is removed and the crucible again heated, the same thing occurs. This contamination is so common that it is difficult to find a crucible entirely free from iron. It is advisable, therefore, to use a porcelain crucible for the ignition of iron compounds, or if platinum is used, to be sure that the crucible is placed in a slanting position with free access to air. Another illustration of this permeability of platinum is the reduction of sodium sulfate. This salt may be fused in an open crucible without change, but in a covered crucible it is partly reduced to sodium sulfide, as shown by treating it with dilute acid.

A platinum crucible should never be heated so that the inner cone of the flame touches it. This causes the formation of a carbide of platinum and makes the crucible very brittle. Whenever possible, the Meker burner should be used, since there is then no inner cone and the flame is uniform.

When the surface of platinum becomes gray or crystalline, it should be polished with sea sand or powdered pumice. If sand does not readily remove all stains, fusion with potassium or sodium bisulfate or sometimes borax, boiling with hydrochloric acid or with nitric acid (but never with a mixture of the two) will usually be effective. If this is not satisfactory, heating with a mixture of equal parts of concentrated hydrofluoric acid and hydrochloric acid or fusion with potassium acid fluoride will sometimes assist. Iron stains are readily removed by heating the covered crucible with a gram of ammonium chloride at the full heat of a burner.

Crucibles must always be kept polished, and must not be bent or injured in any way. If they become deformed, they should be reshaped on a form of the same style. Never try to rub out a dent

with a glass rod, or by any similar process, since it will only make matters worse. Take it to the instructor.

New platinum crucibles are often covered with a film of iron, which should be removed by boiling in hydrochloric acid for an hour or two before the crucible is heated. Otherwise the iron alloys with the platinum and can not afterwards be completely removed.

THE USE OF PERCHLORIC ACID

The very properties of perchloric acid which make it so extremely useful in the analytical laboratory are those which make its improper use hazardous. Hot, concentrated perchloric acid is a powerful oxidizing agent and a powerful dehydrating agent; cold and dilute, it has neither oxidizing nor dehydrating properties and has only the characteristics of a strong acid.⁴ When hot and concentrated, it is also a powerful solvent for such materials as stainless steel and ferro-alloys. This solvent power is often enhanced by mixing it with phosphoric acid or sulfuric acid.

It follows then, that perchloric acid is dangerous only when hot and concentrated and in the presence of some easily oxidizable material such as organic matter. Perchloric acid can be used to destroy organic matter, but nitric acid must always be added first while the perchloric acid is still dilute. Notable exceptions to this rule are coal and coke; here a contact catalyst such as chromic acid is used to speed the oxidation. The nitric acid oxidizes the easily oxidizable material which would act violently with concentrated perchloric acid, and the remaining more difficultly oxidizable material is then finally destroyed by the concentrated perchloric acid. Such procedures are widely used in the analysis of rubber, leather, coal, and similar materials for their inorganic constituents. A progression of colors, in the oxidation of organic material, changing from a light yellow, to a straw, to light brown, to dark brown, generally precedes a perchlorate explosion. If such a color change

⁴ A thorough discussion of the preparation, properties, and uses of perchloric acid will be found in the following booklets by G. Frederick Smith, published by The G. Frederick Smith Chemical Company of Columbus, Ohio: *Perchloric Acid*, 4th Ed., 1940; *Mixed Perchloric, Sulfuric and Phosphoric Acids and Their Applications in Analysis*, 1935; *Dehydration Studies Using Anhydrous Magnesium Perchlorate*, 1934; *Further Applications in the Use of Perchloric Acid in Analysis*, 1942.

is observed, dilute the solution immediately or leave the vicinity hurriedly.

Concentrated perchloric acid is marketed as 60 or 72 per cent acid and is a perfectly stable chemical which can be kept for any length of time. Anhydrous perchloric acid or acid of greater concentration than 85 per cent explodes ultimately on standing and should never be made in appreciable quantities or stored for any period of time. A monohydrate of perchloric acid, corresponding to 84.79 per cent perchloric acid, is perfectly stable and, having the properties of a salt, is thought to be oxonium perchlorate, OH_3ClO_4 . Commercial concentrated perchloric acid, on boiling at normal pressure, concentrates to a constant boiling mixture of 72.4 per cent perchloric acid and 27.6 per cent water, boiling at 203° . Boiling perchloric acid solutions of this concentration or lower concentrations is a perfectly safe operation.

Care should be exercised in places where quantities of perchloric acid are being boiled that the perchloric acid vapors are not allowed to accumulate as condensate, particularly on wood or dusty hoods or flues. Such hoods are best made of tile or transite and should be flushed out occasionally.

The filtration of a solution containing dilute perchloric acid on filter paper is perfectly permissible, but washing should be exceptionally thorough to remove all perchloric acid if the filter is to be ignited. Otherwise a violent deflagration or even an explosion may occur during the drying. An additional final washing with dilute ammonia, if permissible, eliminates this tendency.

Certain salts of perchloric acid, principally those of magnesium and barium, are excellent drying agents, the former rivalling phosphorus pentoxide in effectiveness. These are very stable compounds and highly satisfactory for practically all drying problems. They should not be used in the presence of a strong acid and organic matter, such as cotton, rubber stoppers, or organic liquids. Several serious explosions have resulted from drying with magnesium perchlorate organic liquids which had previously been in contact with sulfuric acid and had been poorly washed.

The perchlorates of all of the heavy metals are soluble in water, and surprisingly, some metal perchlorates are soluble in organic solvents. Advantage of this is taken in the separation of sodium and potassium. Solutions of perchlorates in organic solvents in the presence of acids are dangerous, however, and should never be heated or

trituated. Ethyl perchlorate and other perchlorate esters are violent explosives. An alcoholic solution of perchloric acid should never be heated unless considerable water is present and on no account should be evaporated.

When properly used, perchloric acid and its salts are without hazard, and hundreds of applications of them are being so continuously developed as to make perchloric acid almost as indispensable as nitric, sulfuric, and hydrochloric acids. In many cases perchloric acid has effected great savings in time and expense; it has simplified and improved the accuracy of many analytical procedures; and in many cases its application can be made to accomplish things which can be done by no other method. However, before using perchloric acid or its salts in a new application, consider the facts of the foregoing discussion.