

A HISTORY OF ANALYTICAL CHEMISTRY

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NOTICE

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PREFACE

In 1975 the American Chemical Society launched a project to prepare a history of the Society and of the various branches of chemistry, to be published in its centennial year, 1976. The executive committee of the Division of Analytical Chemistry decided that in addition to providing information for the ACS volume "A Century of Chemistry," it would undertake a centennial history project of its own.

There is no shortage of historical treatments of chemistry, but the analytical aspects are at best buried within more general treatments and at worst are omitted entirely. In the fourth volume of Partington's monumental "History of Chemistry," covering the 19th and 20th centuries, no section is explicitly devoted to analytical chemistry. Only five entries to analysis appear in the index, the longest being to a five-page account of organic analysis.

The outstanding historical work in the analytical field is the "History of Analytical Chemistry," by Ferenc Szabadváry (Pergamon Press, 1966). This excellent work is largely devoted to classical methods, with only one chapter of 15 pages on "Electrometric Analysis" and another of 12 pages on "Other Methods of Analysis" in a book of 401 pages.

Modern analytical chemistry is so diverse in its activities and in its origins that very few, if any, can profess to be expert in all of its current branches, let alone its historical background. It was therefore decided to call upon a wide variety of sources to assemble the first draft material and to use a two-step editorial process to integrate it into the final version.

Four major sections were identified to deal with the chemical, spectrochemical, electrochemical, and

separations aspects of analysis. A fifth section, on instrumentation, was later prepared, incorporating portions of these, supplemented by additional material. Each section was handled by a topical editor, and the final integration was achieved by the two co-editors. Individual contributors are acknowledged by topic rather than by distinct pages because in the process of eliminating gaps and overlaps the editors were obliged to omit and to rearrange many sections of the original contributions. The original papers, which contain many bibliographical references omitted from the final text, have been placed in microfilm storage and are available for purchase at a modest cost through the American Chemical Society.

For brevity we have chosen to de-emphasize those aspects of early work that have been repeatedly covered in general histories of chemistry. The topical editors were instructed to stress the American scene but to follow early developments to their origins, wherever they may have occurred. In the subject areas the treatment varies considerably, not only because of inherent differences in the historical development but also because some contributors chose to adhere more closely than others to the American viewpoint.

One of the difficulties inherent in historical research, at least as undertaken by amateurs with limited time and budget, is exemplified by the following comment. This was written by Professor R. A. Osteryoung of Colorado State University, who served as topical editor for electroanalytical chemistry, but its implications extend to all areas:

It will not be possible to be complete or completely accurate; information has been sought from those with the most knowledge in a given area, and from some original sources, but it has proved impossible to check everything. An example of the problem--albeit a personal one--may put things in perspective. Even as a non-historian attempting to put together material that would represent historical developments, it was realized that original records would help. For instance, in trying to trace the development of methods and schools, a genealogy appeared to be a reasonable approach. I wrote to Princeton University asking if they could supply a list of students who had received their Ph.D.s with the late Professor N. Howell Furman. A reply was received which stated, "Attached please find a list of Dr. Furman's Ph.D. students. We checked his publication list for names and then checked them out in the

Princeton University Alumni Directory (1974). I think this will be quite accurate." A number of distinguished names were included on that list, but one name, that of Professor C. N. Reilley of the University of North Carolina, did not appear, and yet I was certain that he had received his degree with Professor Furman. The list also noted that Professor L. B. Rogers, now at the University of Georgia but formerly at Purdue and MIT, had received his Ph.D. with Furman in 1942. This did not surprise me. However, a letter from Rogers did. It contained the following material: "When I visited Purdue last Monday for a final oral exam for one of my students, Harry Pardue commented about the fact that I had worked for Furman at Princeton. In case you happen to believe that also, I can set the record straight by stating that I worked for Earl R. Caley, who later went to Ohio State University." This incident is included simply to indicate the problem involved in an explicit view of who did what and where and when.

Professor Osteryoung chose to present the material of the electrochemistry chapter in the form of extensive quotations from the many contributors, tied together with his own comments. The spectrochemistry chapter, assembled by Professor J. D. Winefordner of the University of Florida, consists of a series of presentations from his contributors, some of which have been integrated for the sake of logical presentation without undue duplication. A similar format was adopted by Professor Bruno Jaselskis of Loyola University (Chicago) for the chapter on non-instrumental methods and by Dr. Donald Macnaughtan of Mobay Chemical Corp. for separations. The material on instrumentation was prepared by the editors.

The individuals invited to contribute were selected by the topical editors from contemporary practitioners in the various specialties. Some writers reflected a strongly European flavor, whereas others adopted a purely American viewpoint. To complicate matters, the development of a particular field did not follow a single path, even if a specific origin could be identified. Especially during times of war, normal channels of scientific communication were interrupted, and important developments followed parallel paths in different countries.

Rather than attempting to fill all of the gaps that could be recognized, the editors have chosen to compromise, in the interests of economy of length and of effort, permitting some omissions of foreign discoveries

and some differences in approach in the various sections. We hope that we may stimulate historians at home and abroad to explore this complex subject more fully.

Finally, it is hoped that this volume will not only provide historical perspective to students and practitioners of analytical chemistry but will also dramatize the wide scope of the modern day science of chemical characterization and measurement.

CONTRIBUTORS

Ralph N. Adams	Solid-electrode voltammetry
Herbert K. Alber	Microanalysis
Roger G. Bates	Potentiometry
L. S. Birks	X-ray analysis
David F. Boltz*	Molecular spectroscopy
Edward G. Brame, Jr.	Nuclear quadrupole resonance
Clark E. Bricker	Electroanalytical chemistry
Stanley Bruckenstein	Ring-disk electrode
Maurice M. Bursey	Mass spectroscopy
Earle R. Caley	Gravimetric analysis
Donald G. Davis	Chronopotentiometry
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Bruce R. Kowalski	Pattern recognition techniques
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Alfred O. C. Nier	Mass spectroscopy
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IZAAK MAURITS KOLTHOFF, 1894-

Educated in the Netherlands, Kolthoff has been associated with the University of Minnesota since 1927. His contributions in general and electroanalytical chemistry have been monumental.

FOREWORD

Status of Analytical Chemistry at the End of the 19th Century. In the last quarter of the 19th century the practice of quantitative chemical analysis was composed mainly of gravimetric and titrimetric methods and to a minor extent of colorimetry and gasometry. The Swede, Torbern Bergman (1735-1784), is generally considered the founder of qualitative and quantitative inorganic analysis. Volumetric analysis was also practiced in the 18th century and became a very popular method in the 19th century. The history of gas analysis dates back to the 18th-century scientists, including Priestley, Cavendish, Lavoisier, Scheele, and others, and in the 19th century (since 1838) particularly to Bunsen. The names of Liebig and Berzelius, and others in the 19th century will remain connected with the development of organic elementary analysis. The Dumas method (1831) for nitrogen analysis, as well as the Kjeldahl method (1883), are still finding practical application. Although microscopy and qualitative microanalysis were practiced in the 19th century, it was not until the beginning of this century that Fritz Pregl published his methods of micro-elementary analysis (1912) and Emich popularized quantitative microanalysis in general. In this country, Benedetti-Pichler, a student of the Austrian "microschool," has been one of the pioneers of microanalysis. Optical methods of analysis have been practiced for more than two centuries. Microscopy was introduced in the 18th century by Leeuwenhoek, a Dutchman, who characterized crystal habit in addition to observing many other objects. The polarizing microscope entered the field early in the 19th century. Flame reactions for detection of various ions were generally used in the 18th century, but it was not

until the 19th century that emission and absorption spectra of colored flames were investigated (Talbot, 1834; and others). It is well known that Kirchhoff and Bunsen are to be credited for introducing qualitative and quantitative spectroscopy for analytical purposes. Colorimetry has been practiced for a few centuries in a primitive way by comparing colors visually. The laws of extinction as a function of the length of the path (Bouguer, 1729; Lambert, 1760) and of concentration (Beer, Bernard, 1845) found application mainly in visual colorimetry. At the end of the last century visual spectrophotometers were available, but they were used mainly for theoretical work. They were too laborious to use in routine analysis. Electroanalytical chemistry was born at the very beginning of the last century when Cruikshank (1800) deposited several metals on a cathode and some halogens on the anode. Electrogravimetry was introduced for quantitative determinations by the American, Wolcott Gibbs (1864), more than 100 years ago and was particularly popularized by the German, Classen (1912), and the American, Edgar Fahs Smith. The latter greatly popularized this method of gravimetric analysis by his papers and his book, "Electrochemical Analysis," the first edition of which appeared in 1894. In the Preface to the second edition he states, "Thousands of analyses are now made annually by these methods. . . ." The father of modern electroanalytical chemistry is the German, Walther Nernst (1864-1941), who is still honored as one of the great chemists and physicists of this century.

In concluding this sketchy overview of the status of analytical chemistry about 100 years ago, it may be mentioned that a great number of separation methods were practiced at that time. Of course, filtration, sedimentation, centrifugation, distillation, and extraction are time-honored methods. Rudimentary principles of more modern methods of separation were known. For example, the use of paper chromatography is found in the literature of the dye industry of the early 1800s. Capillary analysis was described in several papers by the Austrian, Goppelsroeder. His studies are closely related to modern adsorption chromatography. Columnar chromatography was discovered in 1897 by the American, J. T. Day, who applied it to fractionating petroleum by adsorption on columns of fuller's earth. Ion exchange chromatography has been utilized in soil studies since the middle of the last century. A very detailed description of the development of classical methods of analysis is found in the outstanding book by F. Szabadváry, "History of Analytical Chemistry." The names of the Americans, G. E. F. Lundell and E. B. Sandell

(among others also not mentioned by Szabadváry), should be included; in the first half of this century they perfected classical gravimetry and the quantitative analysis of complex materials.

Development of Analytical Chemistry as a Scientific Discipline. The impact of analytical chemistry on the development of chemistry in general and physical chemistry in particular was well recognized by the German, Wilhelm Ostwald, in his classical book (1894) on the scientific fundamentals of analytical chemistry. It is generally recognized that Ostwald is the man who, in addition to his own original scientific contributions, has propagated in his books and papers the new discipline of physical chemistry. He is also the first chemist who recognized the great importance of the young branch of theoretical (physical) chemistry in analytical chemistry, and he may well be considered the pioneer of scientific analytical chemistry. In his book he emphasized the importance of classical analytical contributions to the development of theoretical chemistry but regrets that analytical chemists at the end of the 19th century did not take advantage of the application of fundamentals of the young field of physical chemistry. In the Preface of his book he writes:

Analytical chemistry, or the art of recognizing different substances and determining their constituents, takes a prominent position among the applications of the science, since the questions it enables one to answer arise wherever chemical processes are employed for scientific or technical purposes. Its supreme importance has caused it to be assiduously cultivated from a very early period in the history of chemistry, and its records comprise a large part of the quantitative work which is spread over the whole domain of the science.

It is generally recognized that science is essentially the study of *quantitative relationships* and that the interpretation of the factual information demands more *quantitative* measurements. Many famous chemists from the early days have enriched chemistry with laws and other contributions which are fundamental to quantitative analysis. Boyle, Priestley, Lavoisier, Scheele, Dalton, Davy, Gay-Lussac, and Berzelius, with others, are the builders of modern chemistry and are equally the co-builders of classical analytical chemistry, together with "*bona fide*" analytical chemists like the Swede, T. Bergman. Physical chemists,

physiological chemists, and biochemists at the end of the last and the beginning of the present century must be credited with the development of analytical chemistry as a scientific discipline. These scientists recognized the great importance to analytical chemistry provided by the very young discipline of physical chemistry. It is only fitting here to mention first the American, Josiah Willard Gibbs, who exactly 100 years ago in publications in the obscure *Journal of the Connecticut Academy* originated the principles of the phase rule as well as the concept of the chemical potential. The contributions of the Dutchman, Jacobus Henricus van't Hoff, who, among others, originated the osmotic law and accounted quantitatively for the effect of temperature on reaction rates and chemical equilibria, and who simultaneously with the Frenchman, Le Bel, 100 years ago published the theory of the asymmetric carbon atom (analytically applied in polarimetry), are fundamental to analytical chemistry. The same is true of the classical theory of electrolytic dissociation which originated with the Swedish genius, Svante Arrhenius.

The contributions of these three giants, together with those of Walther Nernst, have had a great impact on the development of analytical chemistry, especially of solution analysis. Although the contributions by Nernst and his school are treated in more detail in a later chapter; it should be mentioned here that it was in 1889 that Nernst published the very fundamental Nernst equation and, as mentioned earlier, can thus be considered the father of modern electroanalysis. In those days electroanalysis was confined to electrogravimetry. In the 1890s potentiometry and potentiometric titrations (precipitations, Behrend, 1893; redox, Crotochino, 1900; acid-base with the hydrogen electrode, Böttger, 1899; amperometric titrations, Salomon, 1897, Nernst and Merriam, 1905) all originated in Nernst's laboratory.

Applications of these fundamental studies to chemical analysis were made early this century by physical chemists, physiological chemists and biochemists. No exhaustive treatment can be given here. Singled out are a few basic contributions. First we refer to a very fundamental paper by the American, A. A. Noyes, in 1910 entitled "Quantitative Application of the Theory of Indicators to Volumetric Analysis." It is the forerunner of the 1914 monograph by the Danish physical chemist, Niels Bjerrum, who presented an exhaustive and still up-to-date treatment of acid-base titrations in water as solvent. Of classical value is the very fundamental paper published both in

French and German by the Danish physiological chemist, S. P. L. Sørensen (1909), who introduced the concept of pH and a set of buffer solutions covering the pH range 1 to 12. Also, of fundamental analytical importance are the two monographs by the German biochemist, L. Michaelis (1914 and 1916), and the book by the American biochemist, William Mansfield Clark (1920), which has remained a standard work ever since. Clark not only originated a set of buffer solutions which are still used the world over but also the sulfonephthaleins and many oxidation-reduction indicators of low reduction potential. Michaelis is still often referred to for his pioneer work on semiquinones. Greatly inspired by these fundamental analytical contributions, a Dutch (later American) analytical chemist started his work on acid-base indicators and electrometric titrations.*

In the early days of this century a generation of analytical chemists grew up who became impressed with the application of physical and general chemistry to the improvement of classical methods of analysis and techniques and to the development of new ones. To understand sources of error in gravimetric analysis and their (partial) elimination, studies were made of rates of formation of precipitates, the growth of crystalline precipitates, the effects of adsorption and occlusion of impurities, of adsorption of foreign materials, and of aging of precipitates. The method of homogeneous precipitation, originated by the American analytical chemist, H. H. Willard, was not an empirical discovery, but its development was based on an understanding of the effect of supersaturation on the rate of formation and growth of crystalline precipitates. At the end of the first quarter of this century and soon thereafter, quantitative analysis was no longer taught solely as a laboratory course, but the importance of the theory underlying these methods and techniques was emphasized for an understanding and future development of quantitative analysis.

In conclusion, the time-honored definition, "Qualitative (chemical) analysis deals with the detection and identification of the constituents of a sample, quantitative chemical analysis with the determination of their amounts," is essentially still valid today. What has changed are the explosive development of instrumentation, the addition of many physical and chemical techniques which are applied to modern qualitative and quantitative analysis, together with the

*Editor's note: This is Professor Kolthoff's modest reference to his own monumental contributions.

increasing demands made by other scientific disciplines and by society, in the fields of medical, environmental, and conservation chemistry, among others. The development of modern methods and techniques, leading to a fusion of chemical and physical analysis, is the subject of this text.

I. M. Kolthoff

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series of new catalytic titrations; Pardue and co-workers have used catalytic reactions for simultaneous multicomponent determinations; Hercules at Georgia has adapted chemiluminescent reactions for trace determinations of some metal ions; and Winefordner and co-workers at Florida have taken advantage of phosphorescent decay rates for one- and two-component determinations of drugs and other organics. Some of the characteristics of kinetic measurements have triggered other types of studies as well. For example, Crouch and Pardue have reevaluated photometric errors as they apply to kinetic analyses; Kuwana at Ohio State and Pardue have devised mechanical and electronic (vidicon) approaches to rapid scanning spectroscopy and have applied the instruments to fundamental kinetic studies of reaction mechanisms as well as multicomponent analyses; and several authors have described routine applications of stopped-flow spectrophotometry.

Pardue fully expects the latter chemical and instrumental concepts to play more dominant roles in kinetic analyses in the future. Indeed, because of the many developments alluded to in this brief historical account which have improved the operational characteristics and reliability of kinetic methods, it is expected that kinetic methods will soon be viewed as a viable complement to the more common equilibrium methods, and that kinetic methods will play a more dominant role in the total discipline of analytical chemistry. As indicated above, clinical chemists have already adapted these methods extensively, and other groups are expected to follow suit in the near future.