A Brief History of Inorganic Classical Analysis

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Abstract: The history of inorganic classical analysis is traced including biographical sketches of some of the important personalities in the development of gravimetry and titrimetry in Europe and the United States. The significance of the events surrounding the Karlsruhe Congress of 1860 is discussed, and the importance of the application of physical chemistry to the development of classical analysis is examined. The use of organic reagents in classical analysis is surveyed especially their use in chemical separations. The important advantages of the use of instrumental analysis and classical analysis in tandem is explored.

Introduction

Among the analytical methods used to determine chemical composition, there are two special methods based on reaction chemistry. These are gravimetry and titrimetry, and taken together they are called classical analysis. They are special because they lead directly to independent values of chemical quantities expressed in SI units. Gravimetry and titrimetry can be performed in such a way that their operation is completely understood, and all significant sources of error in the measurement process can be evaluated and expressed in SI units together with a complete uncertainty budget. Such chemical measurements are metrologically valid and stand alone. They have no need to be compared with a reference material of the quantity being measured and therefore are referred to by some as definitive or primary methods. Classical methods can be used to determine elements present at major levels (1 % to 100 %). See reference [1] for a detailed look at the terms, equations, errors, and uncertainties associated with classical analysis. For elements present at minor or trace levels (<1 % all the way down to one atom) instrumental methods are used. See reference [2] for a brief sketch of the history of instrumental analysis.

Gravimetry to the 1850s

Gravimetry is the determination of an element or species through the measurement of the mass of a well-characterized insoluble product of a definite chemical reaction involving that element or species. The insoluble product may be a gas evolved from solution, or it may be a non-volatile solid residue from a low temperature volatilization or high-temperature ignition. However, in most cases, the insoluble product is a precipitate formed in an aqueous solution. Tracing the history of gravimetry amounts to tracing the early history of chemistry. Chemistry is at least as old as recorded history, but what we recognize as experimental chemistry did not emerge until the end of l6th century. Later with the publication of his famous book *The Sceptical Chymist* in 1661, Robert Boyle (1627-1691) began the long process of putting chemistry on a sound scientific footing. In this book he firmly dismissed Aristotle's (384-322 B.C.) four elements of fire, air, water, and earth, and Paracelsus's (1493-1541) three principles of mercury, sulfur and salt. Instead, he advocated a comprehensive experimental approach before attempting any theoretical statements. As the influence of Paracelsus waned, chemistry's interest shifted from medicine to mineralogy and metallurgy. However, the minds of chemists were to be dominated for another century by the phlogiston theory, first advocated in 1681 by Johann Becher (1639-1682) and popularized by Georg Ernest Stahl (1659-1734). The theory claimed that when a metal burns or rusts it gives off a "substance" called phlogiston. When it was observed that iron gained mass when it rusted, the phlogistonists simply postulated that phlogiston had negative mass. Damaging as this theory was to the progress of chemistry, it did provide a general concept, the testing of which led to a study of chemical analysis and simple chemical reactions.

Among those making such studies were the gas chemists Joseph Black (1728-1799), Henry Cavendish (1731-1810), Carl Scheele (1742-1786), Daniel Rutherford (1749-1819), and Joseph Priestley (1733-1804). Although Priestley was one of the last staunch defenders of the phlogiston theory, he initiated its downfall with his discovery in 1774 of a gas which he isolated by heating mercuric oxide in a closed system. He gave the name "dephlogisticated air" to the oxygen which he collected. A few years earlier, Rutherford and Cavendish had independently discovered nitrogen which Rutherford called "phlogisticated air." Aware of Rutherford's and Priestley's work, Antoine Laurent Lavoisier (1743-1794) dealt the death blow to the phlogiston theory by performing quantitative experiments with mercury and air in a closed system. He correctly explained combustion, and demonstrated that air was a mixture of nitrogen and oxygen. His genius, his instinctive recognition of the law of conservation of mass, and his use of the balance, made him the forefather of the quantitative era in chemistry.

At about the same time, the Swedish chemist, Torbern Bergman (1735-1784), was setting down the first systematic scheme of qualitative and quantitative analysis. He described all of the available reagents known at the time, and he outlined a scheme of qualitative and quantitative analysis. His gravimetric method for silica is clearly recognizable as a direct forerunner of the one we use today. Strangely enough, Bergman remained a firm believer in the phlogiston theory all his life.

Although the use of titrimetry had already begun in France, almost all analyses at the turn of the 19th century were being done by gravimetry. For example, Sigismund Andreas Marggraf (1709-1782) had worked out the determination of silver as silver chloride as a substitute for fire assay which, under certain conditions, tended to give low results for silver. (Fire assay is the ancient art of isolating precious metals from an ore. The method is based on a high-temperature liquid-liquid extraction in which the ore is fused with a mixture of lead oxide, a flux, and a reducing agent. Molten lead is formed throughout as the mixture is heated and the precious metals pass into the lead. Upon cooling, a lead "button" forms at the bottom of the mass from which the precious metals can be separated.) Bergman was already using gravimetric factors to calculate the amounts of iron, lead, copper, and silver present in the various precipitates from his gravimetric procedures. Great interest was developing in the analysis of minerals and industrial materials.

At the turn of the 19th century chemistry entered a period of great confusion. Gravimetry had been developing all through the 18th century in an empirical manner because the laws of chemical composition were not understood. Many chemists believed that substances combined in definite proportions. For example, they knew that a certain mass of silver always gave the same mass of silver chloride. Jeremias Benjamin Richter (1762-1807), a mining engineer in Silesia, also believed that there was an equivalence inherent in chemical reactions. He tried to work out the mathematical relationships and coined the word "stoichiometry" for the proportions existing among various substances. Unfortunately, he was led down blind paths because he tried to force his data to fit his preconceptions. His work was a beginning in the right direction, however, because he had an intuitive sense of the law of definite composition. Such was not the case with the famous French chemist Claude Louis Berthollet (1748-1822), who wrongly postulated that the composition of a compound of two elements might vary between maximum and minimum in all proportions. Joseph Louis Proust (1755-1826) opposed Berthollet's view. Proust was a good analyst who presented experimental evidence that metals form oxides and sulfides of definite composition. He also recognized that if a metal forms two oxides, each has a definite composition, and no product of an intermediate composition exists. In this observation, of course, he came close to discovering the law of multiple proportions.

In 1808, John Dalton (1766-1844) published the first part of the first volume of *New System of Chemical Philosophy*. In this book, he proposed the idea that matter was composed of small discrete particles. Although this concept dated back to the Greeks of 400 B.C., Dalton's theory was much more far-reaching. From his atomic theory came a correct explanation of the law of conservation of mass and the laws of definite composition and multiple proportions. Dalton realized that compounds are formed by uniting atoms of different elements having different relative masses that can be expressed by numbers, and thus the composition of chemical compounds could be expressed quantitatively. He constructed a table of relative atomic masses, but owing to his poor data, he was unable to demonstrate the simple relationships that intuitively he knew must exist.

In 1808, Joseph Louis Gay-Lussac (1788-1850) published a paper on the combining volumes of gases. He consistently found the volume ratios in gaseous reactions to be small whole numbers. This gave rise to a seeming contradiction with Dalton's atomic theory since, if one volume of chlorine and one volume of hydrogen gave two volumes of HCl, then the "atoms" of chlorine and hydrogen must divide--a logical impossibility if the atomic theory were true. Amedeo Avogadro (1776-1856) published a paper in 1811 that reconciled the dilemma by starting with the assumption that equal volumes of gases under the same conditions contained the same number of particles which he called "molecules." He reasoned that these gaseous "molecules" split into "half-molecules" when they react. In effect, he supposed that elemental gases contained more than one atom, but he never used the term "atom." Dalton refused to accept Gay-Lussac's law, and so he was also unable to appreciate Avogadro's remarkable and revolutionary insight. We

know today that Avogadro's reasoning was correct, but the chemists of his day either rejected or simply ignored his hypothesis. Efforts in 1814 by Andre Marie Ampère (1775-1836) and in 1826 by Jean Baptiste Dumas (1800-1884) to revive Avogadro's hypothesis went unnoticed. The world of chemistry was not ready for Avogadro. Sadly, it would take a half century of confusion over the matter of relative atomic masses before Stanislao Cannizzaro (1826-1910) would successfully revive Avogadro's hypothesis.

During this period of confusion, practical analysts with little interest in theoretical matters were doing very accurate gravimetric analyses on metals, minerals, and water. Among these were Richard Kirwan (1735-1812), who published an outstanding book listing all the references on water analysis since the time of Bergman; Martin Heinrich Klaproth (1743-1817), who discovered many elements in his analyses of minerals; and Louis Nicolas Vauquelin (1763-1829), who was widely known for his pure reagent chemicals. However, the overwhelmingly dominant figure of this period was Jöns Jakob Berzelius (1779-1848). During an extraordinarily productive decade between 1807 and 1818, he devised the system of chemical symbols and notations we use today, and he determined the relative atomic mass of most of the elements known at the time. Unfortunately, during this period he devised his dualistic theory which prevented him from accepting Avogadro's hypothesis. Nevertheless, his expertise as an analyst was nothing short of incredible when consideration is given to the chemical knowledge and the analytical equipment of his time. Although Berzelius was one of the world's greatest analysts, it is doubtful that he ever viewed himself as such.

In contrast, Karl Remegius Fresenius (1818-1897) thought of himself as an analyst from the beginning of his remarkable career. Having worked for several years as an apprentice pharmacist in Frankfurt after completing high school, he went to Bonn where he took courses at the University and worked in the private laboratory of his teacher, the professor of pharmacy, Dr. Carl Marguart. Working mostly alone and without instruction, he taught himself and kept good notes. Marguart was so impressed with Fresenius's notes that he suggested they be published. *Anleitung zur qualitativen chemischen Analyse*, published in 1841, was an immediate success and was to see 16 editions under his authorship. The 17th edition, overseen by his son, was translated as *Introduction to Qualitative Chemical Analysis* by C. A. Mitchell in 1921. Fresenius went to the University of Giessen as a lecturer, worked in Justus Liebig's (1803-1873) laboratory, and earned his Ph.D. in 1842, using his new book, already in its second edition, as his thesis.

He was hired in 1845 as professor of chemistry, physics, and technology at the Agricultural College at Wiesbaden. The college administrators repeatedly refused to supply funds for a chemistry laboratory, so he leaned on his prosperous attorney-father for some money, bought a house, remodeled it into a private analytical laboratory, and opened the doors in 1848 with five students and one assistant, the young Emil Erlenmeyer (1826-1909). Only 30 years old at the time, Fresenius was already an experienced analyst. Shortly after assuming his teaching duties at Wiesbaden, he published his second book, *Anleitung zur quantitativen chemischen Analyse*, which ran to six editions. It was translated into English in two volumes as *Quantitative Chemical Analysis* by A. I. Cohn in 1904.

Fresenius's small house-laboratory would grow to become the world-renowned Fresenius Institute. By 1855 his laboratory had sixty students, all of whom were eligible to receive University credit for the time they spent there. Aside from teaching, the Institute rapidly gained a wide reputation throughout government, industry, and academia as an analytical laboratory. In 1862 Fresenius founded *Zeitschrift für analytische Chemie*, the first journal entirely devoted to analytical chemistry. His influence throughout Europe and the entire world was enormous.

Titrimetry to the 1850s

Titrimetry is the determination of an element or species through the measurement of the mass of a chemical necessary to exactly complete a definite chemical reaction in a solution containing that element or species. The mass of the chemical is usually obtained indirectly by measuring the volume of a standard solution of that chemical, but for very accurate work a mass titration should be used. There are titrimetric methods based on acid-base reactions, precipitation reactions, complexation reactions, and oxidation-reduction reactions. Endpoints generally are determined by observing a color change in an indicator. Endpoints also are commonly determined by observations of potential differences at electrodes, or of changes in conductivity.

Industry's need for rapid methods of determining acids, alkalis, carbonates, and hypochlorites provided the driving force for the development of titrimetry. Its early development was confined almost solely to France where it was practiced crudely in the 18th century. Endpoints were determined by the "clear point", the cessation of effervescence, or the use of a few plant-extract indicators. François Antoine Henri Descroizilles (1751-1825) devised a method for determining the hypochlorite strength of bleaching solution used in the textile industry. He added a measured amount of dilute sulfuric acid containing an indigo indicator to a graduated cylinder, slowly added the hypochlorite solution whose strength was being tested until the color changed from blue to pale green. He read the

volume from graduations on the side of the cylinder, and compared that volume to the volume necessary for a solution which had already proved to be suitable for textile whitening. Descroizilles later devised a method for determining the alkaline strength of potash. He used a graduated buret filled with dilute sulfuric acid and controlled the flow by covering a small hole in the top with his finger.

Gay-Lussac made great contributions to the development of titrimetry and the widespread use of his methods helped establish titrimetry as a part of classical analysis. He improved Descroizilles's method for potash and made several improvements in the hypochlorite method, the most significant of which was the introduction of the first redox indicator. As an analyst, he is most famous for the silver assay method named after him. The French government realized that they were losing money because of errors in the fire assay of silver, and in 1829, they asked him to devise a rapid and simple assay method with a relative error of less than 0.05 %. He made a 100 mL pipet which would deliver repeatedly to very high precision, and he prepared a standard chloride solution which he adjusted so that the delivery of his pipet was equivalent to 1.0000 g of silver. He then dissolved a bullion sample expected to contain just over 1 g of silver and added one pipet full of the standard solution. After vigorous agitation, the AgCl precipitate was allowed to flocculate and settled to the bottom of the flask. Using a 1/10 dilution of the standard chloride solution, he continued the titration in 1 mL increments, until no more turbidity was produced in the supernate. Using this procedure he was able to achieve a relative accuracy and precision better than the requested 0.05 %. To this day no improvements on this assay method have been made except the use of a potentiometric endpoint for deeply colored solutions or alloys of silver containing tin.

During the twenty-year period from about 1835 to 1855, there was a rapid development in many different titrimetric methods, but the general field of influence was not widespread. As a result of Gay-Lussac's work, titrimetry became more widely known outside France, especially in Germany and England. However, it was not yet possible to establish a general system of titrimetry since the concentrations of standard solutions had no chemical basis because of the lack of unique relative atomic masses and the lack of an understanding of stoichiometry. After Houton de la Billardière (1775-1834) discovered the usefulness of iodine in titrimetry in 1826, Robert Wilhelm Bunsen (1811-1899) published an excellent paper in 1853 which described the determination of over 20 elements by iodimetry. In that same year, Karl Leonhard Heinrich Schwarz (1824-1890) made a great advance in iodimetry by recommending the use of sodium thiosulfate for titrating iodine. Nevertheless, many famous analysts of the period remained contemptuous of titrimetry. Berzelius never used it, and Fresenius recommended against its use for important analyses.

Karl Friedrich Mohr (1806-1879) did much to overcome the difficulties of titrimetry. He had studied under Heinrich Rose (1795-1864) and Bunsen's predecessor at Heidelberg, Leopold Gmelin (1788-1853). Mohr took over his father's pharmacy shop in 1830, and in his spare time pursued his interest in experimenting with various titrimetric methods. Because he remained outside academia, he was never regarded as a scientist in Germany, but his contributions to titrimetry were many. He introduced the use of potassium chromate as an internal indicator for chloride determination (Mohr method), oxalic acid as a primary standard for alkalimetry, ferrous ammonium sulfate (Mohr's salt) as a standard for oxidizing agents, and the idea of back-titration. As for laboratory equipment, he invented the cork borer, the Liebig condenser, the Mohr pinch-cock, the pinch-cock buret, and calibrated pipets. After the appearance of his book *Lehrbuch der chemisch-analytischen Titrirmethode* (published in two parts in 1855 and 1856), titrimetric analysis became widely known all over Europe.

The publication of Mohr's books marked the end of the early history of titrimetry, although mention should be made of Johan Gustaf C. T. Kjeldahl (1849-1900) who developed his well known method for the determination of nitrogen in 1883. Kjeldahl discovered that sulfuric acid could be used to digest organic materials, converting free ammonia and "organically bound" nitrogen to ammonium sulfate. After adding excess strong caustic, he distilled the liberated ammonia into a known excess of standard sulfuric acid. He determined the excess sulfuric acid by adding a solution of potassium iodate and potassium iodide, which released an iodine equivalent for each acid equivalent. The iodine was determined by titration with sodium thiosulfate and starch indicator. The method has remained unchanged to this day, except for the use of various catalysts to aid in the digestion, and the discovery by Lauos Winkler (1863-1939) that the distilled ammonia can be absorbed into a boric acid solution and titrated directly with standard acid. Winkler contributed over 200 original papers on gravimetry and titrimetry, and he is probably best remembered for his titrimetric method for the determination of dissolved oxygen in water which he published in 1888.

The Karlsruhe Congress of 1860

By the late 1850s, advances in classical analysis had come about as far as they could without a consistent table of relative atomic masses. In addition to varying among countries, relative atomic mass tables within a country sometimes varied from laboratory to laboratory. In an attempt to resolve this problem, Friedrich August Kekulé (1829-1896), with the help of Charles Adolphe Wurtz

(1817-1884) and Carl Weltzien (1813-1870), invited delegates to an international congress at Karlsruhe, Germany in 1860. About 140 of the world's leading chemists attended with the goal of resolving the confusion over relative atomic masses. Among those in attendance was Stanislao Cannizzaro, a young professor at the University of Genoa. For some time he had realized the value of Avogadro's hypothesis in resolving the problems surrounding relative atomic masses, and he addressed the congress with great passion and pedagogical skill. He showed how Avogadro's hypothesis could be used to establish the relative molecular mass of a gas, and that by comparing the vapor densities of a series of gaseous compounds of a particular element, the molecular mass and relative atomic mass of that element could be established. Although Cannizzaro pleaded for the adoption of relative atomic masses based on Avogadro's hypothesis, he was unable to sway the members of the congress in his favor.

The Karlsruhe Congress adjourned having reached no agreement on relative atomic masses, but it was in adjourning that the key event of the congress occurred. As the delegates departed, Cannizzaro's colleague, Angelo Pavesi from the University of Pavia, passed out reprints of Cannizzaro's 1858 publication, *Sunto di un corso di Filosofia chimica (Sketch of a Course of Chemical Philosophy)*. This paper set forth clearly what Cannizzaro had been teaching his students at Genoa. Although his paper had gone largely unnoticed in the literature, it did not go unnoticed in the hands of the delegates. One of the recipients of the pamphlet was Julius Lothar Meyer (1830-1895) who read it twice on his homeward journey. He tells how everything became clear as if scales fell from his eyes. Another recipient of the pamphlet was Dmitrii Ivanovitch Mendelèev (1834-1907) who later said that even though no agreement was arrived at through the congress, the truth of the law of Avogadro, as advocated by Cannizzaro, soon afterward convinced everyone. Without the insight that both Meyer and Mendelèev gained from Cannizzaro's paper, it is doubtful that they independently would have gone on to work out the periodic table in 1869. It is hard to overestimate the impact of the events surrounding the Karlsruhe Congress. The confusion over relative atomic masses almost completely disappeared in just a few years. Analysts now were able to write down correct stoichiometric formulas for their precipitates, thus placing gravimetry on solid ground. However, both gravimetry and titrimetry would have to await the development of physical chemistry at the end of the 19th century in order to be placed on a firm scientific foundation.

Gravimetry Comes to the United States

In the mid-19th century almost all the new developments in chemistry were taking place in Europe. Graduate schools only began to develop in the United States toward the end of the 19th century. From about the middle of the 19th century, Germany was the place to go for graduate education in chemistry, and this was due in no small measure to the enthusiasm and inspiration of Justus Liebig who established a teaching laboratory at the University of Giessen. Because of the remarkable enthusiasm and camaraderie which he created among his students, his laboratory became a model for other graduate programs and teaching laboratories that spread to many other German universities.

William Francis Hillebrand (1853-1925) was born in Honolulu seven years before the Karlsruhe Congress, and his story is perhaps the best example of how classical analysis, particularly gravimetry, was brought to the United States from Europe. His father was born in Germany where he had been educated and trained as a medical doctor. He had established a practice in Hawaii because he had sought its climate in order to recover from a serious illness. Since it had always been his father's intent to have the entire family return to Germany, Hillebrand was sent to Cornell in 1870 in preparation for study at a German university.

The entire Hillebrand family moved to Bonn in the summer of 1872, and the time had arrived for Hillebrand to choose a career. He had no interest in medicine, and he felt he lacked the mental qualifications for law or engineering. His father suggested chemistry. This idea had not occurred to Hillebrand, but remembering with pleasure his study of the basics of chemistry back in Honolulu, he decided to give chemistry a try. He entered the University of Heidelberg in the fall of 1872, and studied under Bunsen and Gustav Kirchhoff (1824-1887), taking his Ph.D. in 1875. He stayed on at Heidelberg for another year of research, and then went to Strassburg for three semesters with Rudolph Fittig (1835-1910). Realizing that organic chemistry did not appeal to him, he decided to finish his studies at the mining academy at Freiberg in order to supplement his experience in mineral analysis under Bunsen. He had made up his mind to become an analytical chemist.

He returned to the U. S. in 1878, and failing to find immediate work in the East, followed some leads and made his way to Leadville, Colorado in 1879, where he became the third partner in a small assaying firm. An occasional customer was Samuel F. Emmons (1841-1911) who was in charge of the Rocky Mountain Division of the newly-formed United States Geological Survey (USGS). Emmons offered Hillebrand a job as a chemist with USGS. Hillebrand considered Emmons's offer the opportunity of a lifetime, and he quickly accepted. He remained in the Denver laboratory of USGS until 1885 when he was transferred to its Washington laboratory to work under the chief chemist, Frank W. Clarke (1847-1931).

Hillebrand's careful work set a new standard of excellence in the analysis of rocks and ores. During his 29 years at USGS, he made over 400 complete analyses of silicate rocks. The real significance of his work lay in the perfecting of a separation scheme for materials as complex as carbonate and silicate rocks. Even in the late 19th century, the problem wasn't so much the lack of a suitable method for the final determination of an element, as it was the lack of suitable separation methods preceding the final determination. This problem persists to the present day. In 1897 he wrote a 50-page introduction to USGS Bulletin No. 148 on the methods of analysis of silicate rocks. This was quickly translated into German. In 1900 this was rewritten and enlarged and printed as an independent document, Bulletin No. 176. The next edition which appeared in 1907 as Bulletin No. 305, included carbonate rocks, and this also quickly appeared in German. The series culminated in 1919 with the well-known Bulletin No. 700, a book of 285 pages. Hillebrand was unquestionably one of the world's leading analysts when he was called to be Chief Chemist at the National Bureau of Standards (NBS) in 1908. Administrative duties in his new position more and more limited his time at the bench, but the steady stream of books and papers continued. He greatly contributed to the increase of the standard samples program at NBS, expanding it from a few cast irons to over 60 materials. [Today, the Standard Reference Materials Program at the National Institute of Standards and Technology (NIST, formerly NBS) has over 1300 Standard Reference Materials available, covering a broad range of materials that are certified for chemical composition and/or physical property.] Hillebrand had a talent for gathering around him capable people, and his success in bringing Gustaf E. F. Lundell (1881-1950) from Cornell in 1917 is a good example. In 1923 he and Lundell began coauthorship of *Applied Inorganic Analysis*. Hillebrand died in 1925 before the work was completed, but by 1929 Lundell had gone on to finish the book which became known as the "analyst's bible." Together with Harry A. Bright (1890-1961) and James I. Hoffman (1893-1964), a second edition appeared in 1953. Also with Hoffman, Lundell wrote a companion volume, *Outlines of Methods of Chemical Analysis*, which went on to become another classic. Lundell was appointed Chief Chemist at NBS in 1937, and under his leadership, the scope and renown of its efforts in chemical analysis grew. He had a talent for picking the right person for a particular assignment, and he had an uncanny ability to sense whether work on a project that had hit a snag should be stopped or continued. Often his timely encouragement resulted in the solution of a seemingly hopeless problem. In 1933 Lundell published his well-known paper "The Chemical Analysis of Things as They Are" [3]. The continuing relevance of his insights is remarkable, and even though it was written in 1933, it should be required reading for all analytical chemists.

The Beginnings of Physical Chemistry

Physical chemistry did not emerge until the last third of the 19th century. A great breakthrough was made when the Norwegian brothers-in-law Cato M. Guldberg (1836-1902) and Peter Waage (1833-1900) worked out the law of mass action over the years 1864 to 1879. In 1884 Jacobus Henricus van't Hoff (1852-1911) made an elegant derivation of the law of mass action on thermodynamic grounds. His clear and inspiring treatment of chemical dynamics brought the entire subject of reaction kinetics and equilibria before the chemical world. Certain anomalies which arose when the laws of physical chemistry were applied to solutions of electrolytes were explained in 1887 when Svante August Arrhenius (1859-1922) published his revolutionary theory of electrolytic dissociation.

It was Wilhelm Ostwald (1853-1932) who recognized the importance of van't Hoff's and Arrhenius's work for chemical analysis. Through his books, his own research, and his wide personal contacts, Ostwald was influential in spreading the ideas of the new physical chemistry. With van't Hoff he founded Zeitschrift für physikalische Chemie 1887, and he championed the cause of physical chemistry as a science in its own right. In this way he "organized" physical chemistry at the end of the 19th century.

In 1894 Ostwald published *Die wissenschaftlichen Grundlagen der analytischen Chemie, (The Scientific Foundations of Analytical Chemistry)* which began the process of placing classical analysis on a scientific basis. In the preface, he noted that while the technique of chemical analysis stood at a very high level, its scientific treatment was almost completely neglected. Ostwald's book made a significant start at correcting this deficiency. He began by treating various separations and by discussing precipitation in detail including an explanation of the increase in particle size of standing crystalline precipitates. This process became known as "Ostwald ripening." The most important part of the book followed with a discussion of solution chemistry, where he derived the idea of the solubility product constant by combining the law of mass action and Arrhenius's theory of electrolytic dissociation. He also interpreted the properties of multi-protic acids, and acid-base indicators.

Although Ostwald's little book broke new ground and was soon recognized as a classic, it had significant omissions. For example, the phase rule of Josiah Willard Gibbs (1839-1903) was not mentioned. Perhaps Ostwald was simply unaware of Gibbs's work because it had been published in a rather obscure journal. However, it is difficult to understand why Ostwald made no mention of the work of Walter Nernst (1864-1941) who originated the famous Nernst equation while he was working in Ostwald's own laboratory in 1889.

Nernst went on to explore many of the analytical applications of his equation, and he is rightly considered the father of modern electroanalytical chemistry.

Physical Chemistry Applied to Gravimetry

The application of physical chemistry to gravimetry is best illustrated by the quest for accurate relative atomic masses by chemical methods. This work went on throughout the 19th century and the early years of the 20th century. Berzelius was the first to take up this task on any systematic scale, and he determined the relative atomic masses for most of the then-known elements. Even though his values do not agree well with modern relative atomic masses, his 1828 table was a remarkable achievement when one considers the laboratory equipment that was available to him, and more importantly, the general confusion among all chemists that resulted from their lack of understanding of Avogadro's hypothesis as well as its implications for establishing the mass relationships among the elements.

The twelve relative atomic masses established in the years just after the Karlsruhe Congress by the Belgian chemist, Jean Servias Stas (1813-1891), were considered to be of such high quality that their accuracy went unquestioned for several decades. The chemical determination of relative atomic masses made use of mass ratios obtained through careful gravimetric analyses. From the mid-19th century until 1961, relative atomic masses were referred to $A_r(O) = 16$ (exactly) by chemists. The relative atomic masses of most of the elements were related to oxygen through silver. Stas determined the ratio of silver to oxygen through chlorates, bromates, and iodates. For example the ratio $3O:KCl$ was established by the decomposition of purified $KClO_3$ to KCl, and the ratio $KCl:Ag$ was obtained through the precipitation of $AgCl$ using purified Ag which had been dissolved in HNO_3. The relative atomic mass of an element was then determined by carefully preparing its pure chloride or bromide and then precipitating that chloride or bromide with silver. Although Stas was a careful analyst who far outdistanced his predecessors, significant errors crept into his work. Because he did his work thirty years before the principles of physical chemistry were generally understood, he was unable to realize the seriousness of errors caused by such things as the adsorption of gases and retention of water in solids, occlusion and coprecipitation encountered by precipitation from concentrated solution, and solubility product losses of precipitates into the supernatant solution.

It remained for Theodore William Richards (1868-1928) to bring the chemical determination of relative atomic mass to maturity. He accomplished this by bringing to the task not only his extraordinary genius as an experimentalist but also the necessary insights from, what was for Richards, the latest developments of physical chemistry. Born to artistic and scholarly parents, he was schooled at home by his mother until the age of fourteen, at which time he entered Haverford College as a sophomore, graduating at the head of his class in 1885. During that summer he studied Greek with his mother and entered Harvard as the youngest member of the Senior class where he worked under Josiah Parsons Cooke (1827-1894). He graduated summa cum laude the following year and remained at Harvard in Cooke's laboratory, revising the relative atomic masses of hydrogen and copper. He earned his Ph.D. in 1888, and on the merits of his doctoral dissertation, he won a fellowship for a year of travel and study in Europe where he was exposed to the important new developments in physical chemistry.

Upon returning to Harvard in the fall of 1889, he was quickly promoted through the faculty ranks to assistant professor by 1894. During these years he determined the relative atomic masses of Cu, Ba, Sr, Zn, Mg, and Ca. It was in his work on the relative atomic mass of Sr that he developed two important pieces of equipment: a weighing tube, which made it possible for him to fuse materials in a quartz boat under controlled atmospheres and then place them in weighing bottles under anhydrous conditions; and the nephelometer, which permitted him to detect the exact equivalence point in the precipitation of silver chloride or silver bromide.

With Cooke's death in 1894, it became necessary to provide for continuing instruction in physical chemistry, and Richards, being selected for the position, was sent in 1895 by Harvard on his second trip to Europe to spend a semester with Ostwald at Leipzig and another with Nernst at Göttingen. Upon his return, and armed with the latest developments of the then-new theory of solutions, he resumed his research, tackling the relative atomic masses of Ni, Co, Fe, U and doing further work on Ca. Although Richards had improved on Stas's techniques, he had never doubted the accuracy of Stas's values. Indeed, most of Richards's work up to that point had not specifically overlapped with Stas's work. When discrepancies were noticed, Richards faulted his own work rather than that of his forerunner.

In 1904, however, Richards determined the relative atomic mass of sodium in a sample of sodium bromide which he knew to be very pure because of its sharp transition temperature. He obtained a relative atomic mass for sodium in this material that was significantly lower than Stas's value, assuming Stas's values for silver and bromine were correct. This discrepancy could not be disregarded,

because it indicated either an impurity in Richards's sodium bromide or a flaw in Stas's work. Failing to find impurities in his sodium bromide, Richards set out to redetermine the relative atomic masses of Na and Cl. He launched a very careful quantitative study to determine three ratios, AgCl:NaCl, Ag:NaCl, and Ag:AgCl. He found that each step of this work was critically dependent on both the purity of the materials and the application of physical chemical principles to the gravimetry involved. Stas had worked with large quantities in order to reduce weighing errors, but Richards saw that such an approach led to difficulties in the purification of materials. Stas had made precipitations from concentrated solutions which led to adsorption of soluble salts. Stas's drying under atmospheric conditions led to occlusion of oxygen and water. Richards worked with smaller quantities and insisted on applying rigorous standards for the purification of all materials. He precipitated from dilute solution to minimize occlusion and coprecipitation effects. His bottling apparatus and nephelometer were essential tools. He obtained significantly lower values for the relative atomic masses of Na and Cl, which eventually necessitated the recalculation of all relative atomic masses which were in any way related to Na, Cl, or Ag.

By 1906 several discrepancies had come to light, suggesting that Stas's relative atomic mass of silver was distinctly too high. Since most of the relative atomic masses were related to oxygen through silver, this created confusion and uncertainty throughout the whole table of relative atomic masses. Realizing that the relation between silver and oxygen had to be known without doubt, Richards, together with Hobart Hurd Willard (1881-1974), designed a series of elegant preparations and gravimetric assays to determine the ratios $LiClO_4$:LiCl and LiCl:Ag. Combining these ratios gave the relative atomic mass of silver directly in terms of oxygen, in addition to providing a new value for the relative atomic mass of Li. Richards obtained a relative atomic mass of silver 0.05 % lower than Stas's value, and at the same time got a value for Li, which turned out to be 2 % lower than Stas's value. This was probably the most careful of all of Richards's work, and remarkably his value for silver, after correction to A_r (^{12}C) = 12 exact, differs from today's mass-spectrometrically determined value by only 1 part in 10^5.

Reading the original paper on this work as well as many of Richard's other important papers is something like listening to Mozart's symphonies. At some point every analytical chemist should treat himself or herself to this singular delight (see the reading list for a few of Richards's most important papers). Richards was involved in the determination of the relative atomic mass of 25 of the elements, and together with two of his students, Gregory Paul Baxter (1876-1953) of Harvard, and Otto Honigschmidt (1878-1945) of Munich, 55 elements were covered. He received the 1914 Nobel Prize in chemistry, the first American to be so honored.

Physical Chemistry Applied to Titrimetry

The work of Izak Maurits Kolthoff (1894-1994) provides perhaps the best example of how physical chemistry can be applied to titrimetry. Kolthoff attended the University of Utrecht in 1911. His lack of certain prerequisites needed to study in the chemistry department was a blessing in disguise, because it brought him under the tutelage of Nicolaas Schoorl (1872-1942), who was teaching in the University's school of pharmacy. Schoorl had studied at the University of Amsterdam where van't Hoff, C.A. Lobry de Bruyn (1857-1904), and Hendrik Bakhius-Roozeboom (1854-1907) were teaching. (It was Roozeboom who had introduced the European scientific community to Gibbs's phase rule.) Schoorl was aware of all the recent advances in physical chemistry which he stressed in his teaching. He immediately recognized Kolthoff's talent and encouraged him to carry out independent research. Kolthoff had trouble understanding the proper selection of indicators for acid-base titrations, and he launched his own study into the matter. He had already acquired a used copy of Wilhelm Ostwald's 1894 classic, *Die wissenschaftlichen Grundlagen der analytischen Chemie (The Scientific Foundations of Analytical Chemistry)*. This important book began the process which put classical analysis on a scientific basis. Kolthoff was further encouraged by the 1909 paper of the Danish physiological chemist S.P.L. Sørensen (1868-1939), who introduced the concept of pH. He was inspired in 1913 by the work of Joel Hildebrand (1881-1983) who used the hydrogen reference electrode in electrometric titrations. Kolthoff borrowed pH measuring equipment from another professor, but within a year he had devised his own potentiometric apparatus in Schoorl's laboratory. He published his first paper in 1915 on the titration of phosphoric acid.

Kolthoff quickly realized how important physical chemistry would be for the development of analytical chemistry, but in those beginning years, the going was sometimes rough. Not realizing the significance of his early work, faculty members in the chemistry department sometimes criticized him. One member of the chemistry faculty went so far as to try to block him from publishing and lecturing. Kolthoff was disparagingly known by some as the "pH-er", which when pronounced in Dutch came out as "pay-h<u>a</u>er with <u>a</u> as in 'haha'". A colleague publicly criticized him and warned lecture students not to read any of the junk that Kolthoff published. When Kolthoff confronted the colleague and asked him to retract the statements, he was criticized for showing disrespect. Before his 1924 United States lecture tour, this same colleague warned Kolthoff that the Dutch had an excellent name in the United States, and that he (Kolthoff) could easily spoil it. Despite the criticism, Kolthoff forged ahead and in 1918 presented his Ph.D. thesis on the

"Fundamentals of Iodimetry", a topic he returned to again and again over the years. In 1914 the Danish physical chemist Niels J. Bjerrum (1879-1958) had published a book showing how to calculate both the shape of neutralization curves and the titration errors in visual end-point determinations. This work inspired Kolthoff to begin the development of a theoretical interpretation of all the methods of titrimetry. This work resulted in his well-known two-volume work, first published in German in 1926 and then translated as *Volumetric Analysis* by N. Howell Furman (1892-1965) in 1928 and 1929. A three-volume revision of the work appeared between the years 1942 and 1957. In 1927, Kolthoff accepted a professorship at the University of Minnesota where he remained for the rest of his remarkably long and productive career.

Titrimetry Comes to the United States

In 1924 Kolthoff made a lecture tour of Canada and the United States, where he met both Furman and Willard. After earning his Ph.D. under Richards at Harvard, Willard went to the University of Michigan where he pioneered the technique of precipitation from homogeneous solution and the analytical use of perchloric acid. At Princeton Furman at made outstanding contributions in potentiometry, electrodeposition, and polarography, and together with Willard he worked on the analytical applications of ceric salts.

In addition to becoming good friends, these men became "The Big Three" in graduate education in analytical chemistry in this country. In 1927 Kolthoff accepted a professorship at the University of Minnesota and continued his monumental achievements which touched almost every area of analytical chemistry. Between the years of 1932 and 1960 these three men supervised 120 Ph.D.s in analytical chemistry. Their educational progeny are into the third and fourth generations and number in the thousands. Kolthoff also has influenced many thousands of undergraduate students through his well-known *Textbook of Quantitative Inorganic Analysis* coauthored with Ernest B. Sandell (1906-1984) in 1936. A fourth edition under the title *Quantitative Chemical Analysis*, appeared in 1969, with Sandell, Edward J. Meehan (b. 1912), and Stanley Bruckenstein (b. 1927) as coauthors, and now that it is out of print, it is particularly treasured by those who own a copy.

Organic Reagents Applied to Classical Analysis

It is well known that classical analysis does not suffer from a lack of good analytical methods for the final gravimetric or titrimetric determination of an element provided that it occurs alone. But since this is never the case, separations must be made to remove interfering elements. The elaborate scheme perfected by Hillebrand for the analysis of rocks is an example of a general separation scheme built on the experience of generations of analysts. Based almost entirely on precipitation separations using inorganic reagents, it stands as one of the monumental achievements of classical analytical chemistry.

Beginning in the last century and extending up to the 1940s, various organic reagents were introduced which could be used as precipitants in gravimetric determinations. They turned out to be extremely useful because they were selective for a very few elements, and could be used to determine one of those elements when the others were absent or had been removed. Most of these organic reagents are chelation agents, and good examples are dimethylglyoxime, which is used for the gravimetric determination of Ni, and alpha-benzoin oxime, which is used for the gravimetric determination of Mo.

In addition to being used as precipitants in final determinations, these and other organic reagents proved to be extremely useful in separation techniques when coupled with immiscible solvent extraction. An example is cupferron which forms several insoluble cupferrates in strongly acidic aqueous solutions which can be easily and quickly extracted with chloroform in a separatory funnel. This procedure can be used for the separation of Al in a widely-used titanium alloy with the nominal composition of 6 % Al, 4 % V, 0.2 % Fe. Addition of cupferron to an acid solution of the alloy produces the insoluble cupferrates of Ti, V, and Fe. Extraction with chloroform leaves Al in the aqueous phase ready for determination by either titrimetry or gravimetry.

In the 1930s it was found that certain amino-polycarboxylic acids formed stable, soluble complexes with many metals, and in the 1940s, Gerold Schwarzenbach (1904-1978) began a theoretical examination of these complexes. These studies led him to the development of the titration of calcium and magnesium with EDTA and to the introduction of the first metallochromic indicators. Schwarzenbach's work made an extraordinary contribution to titrimetry and thousands of papers have appeared on EDTA-related methods.

Ion-exchange resins are perhaps the most significant development to classical analysis resulting from the use of organic reagents.

Ion exchange had been observed in certain natural materials in the 19th century, but these materials were unstable in acidic and alkaline solutions. In 1934, two British chemists, B. A. Adams and E. L. Holmes, discovered the cation-exchange properties of a synthetic organic polymer made from formaldehyde and phenolsulphonic acid. Later, cross-linked polystyrene resins with ionizable acidic or basic functional groups were synthesized which could exchange with cations or anions.

Great advances in the understanding and use of ion-exchange resins occurred during WW II in connection with the Manhattan Project. In 1942, George E. Boyd (b. 1911) and his group used ion-exchange resins to separate plutonium from uranium and other fission products. Later Boyd and his associates used ion exchange to separate the elements produced in fission prior to chemical analysis. Meanwhile, Frank H. Spedding (1902-1984) and his group at Ames, Iowa, made large-scale separations of naturally occurring rare-earth elements. Because of the necessary secrecy surrounding the Manhattan Project, none of this work was announced until after the war. Since that time, many ion-exchange separation procedures have been developed creating an extensive literature on the subject.

The equipment for ion-exchange is relatively simple, but unlike immiscible solvent extraction, ion-exchange separations are time-consuming. When one considers their usefulness, however, they are worth the investment of time. For example, using an anion exchange column, Mn, Fe, Co, Ni, Cu, and Zn in strong HCl can be separated completely from each other by successive elutions with hydrochloric acid of different concentrations [4]. This ion-exchange system has greatly simplified the separations necessary for the analysis of materials containing these elements. The immense power of ion exchange is further illustrated by the complete separation of the common rock-forming elements (except Si and P) using a single cation-exchange column [5]. After suitable acid dissolution of the rock sample and volatilization of SiF_4, the solution is placed on a cation-exchange column, and, by a series of eluants, V, Na, K, Ti, Zr, Fe, Mn, Mg, Ca, and Al are eluted in order. Although the procedure is slow, taking two 8-hour days, the separations are complete and the recoveries compare well with the traditional classical separation methods.

Classical and Instrumental Analysis in Tandem

T. W. Richards's use of the nephelometer is one of the early examples of how an instrumental method was used in tandem with a classical method for the evaluation of a bias or systematic error. Since that time analysts have been combining classical and instrumental methods of analysis in individual situations. However, two papers by Silve Kallmann (1915-1989) that appeared in the mid-1980s advocated a conscious, systematic approach to using both classical analysis and instrumental analysis in concert [6], [7]. In many instances, older classical analyses can be reconstructed and revitalized by using them together with instrumental determinations. In other instances, entirely new methods, some of them very elegant, are possible. Kallmann made an important contribution by suggesting that the classical analyst continually consider such possibilities as a part of the overall analytical approach to methods development.

There are at least two opportunities for combining instrumental determinations with gravimetry. The first is in checking the purity of precipitates. Despite the fact that every effort is made to choose optimum conditions for precipitation, many precipitates are significantly contaminated because of coprecipitation and occlusion. Such an impure precipitate can be redissolved and the contaminant(s) determined by instrumental analysis. The second area is in checking the filtrate from a gravimetric determination for solubility-product effects. No gravimetric precipitate is completely insoluble, but the filtrate can be examined by instrumental analysis for the small amount of the precipitate that remains in solution. For example, the classical method for silica can be simplified greatly by isolating the precipitated silica from a single dehydration, and then determining the remainder in the filtrate by spectrophotometry or atomic absorption spectroscopy. Kallmann points out other examples of how a method that may have been rejected because of a slightly soluble precipitate can now be reconstructed.

There are also opportunities for combining instrumental determinations with titrimetry. In the Zn assay of a Zn ore concentrate cited earlier, the small amount of Cd present in almost all Zn ores is eluted together with the Zn. The Cd can be separated from the Zn, but that requires either using a second ion-exchange column or masking the Cd through its iodide complex. The easiest way to deal with this problem is to titrate the Zn and Cd together, and determine the Cd separately by atomic absorption spectroscopy.

The use of an instrumental determination together with a classical determination does not degrade the overall precision so long as the instrumental method is used to determine only a very small part of the total. In addition, the accuracy of gravimetric determinations is increased by reducing the biases of coprecipitation and solubility-product effects. In some cases precision of gravimetric determinations is also improved. This occurs when, in a set of replicate gravimetric determinations, different amounts of the element being assayed remain in the individual filtrates and/or different amounts of coprecipitated materials are present in the individual

precipitates [8].

Conclusion

We have seen that classical analysis has had a long and distinguished history. The crude classical analyses of the past have been improved as better values for atomic masses became available, as the principles of physical chemistry were applied, as organic reagents were introduced, and as instrumental techniques became available for the evaluation of the systematic errors inherent in both gravimetry and titrimetry. Existing isotope dilution mass spectrometry and new high-performance inductively coupled plasma optical emission spectrometry, both of which are mass-ratio based, rival or even exceed classical analysis in precision, accuracy, and speed. Nevertheless, gravimetry and titrimetry will endure as accurate, directly SI-traceable, primary methods, provided that their systematic errors are properly evaluated using the best instrumental techniques available.

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