

Chemical Analysis, A Look at the Past, Present, and Future

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Abstract: This paper has a fourfold purpose: 1) to explain what a chemical analysis is; 2) to look at some of the history and important personalities involved its development; 3) to give reasons for renewing the interest of today's chemistry community in chemical analysis; and 4) to encourage one or two colleges or universities in the USA to consider offering substantial, practical courses in chemical analysis, with sufficient hands-on laboratory training to prepare students who want to become chemical analysts. Even though instrumental analysis has taken over the major role in the analytical chemistry laboratory, important needs remain for chemical analysis, among which are establishing standards for instrumental calibration, determining gold and silver by fire assay, and determining elements at major levels. Additionally, in some cases, chemical analysis and instrumental analysis can be used in tandem, and looking for opportunities to do this needs to become an integral part of analytical chemistry methods development. Emphasized is the overwhelming importance of the watershed event of the Karlsruhe Congress of 1860 and the subsequent happenings surrounding it, because the outcome of that Congress changed the face of all of science up to that point, including chemical analysis. The importance of the application of physical chemistry to chemical analysis is discussed, and the value of using organic reagents and polymers is considered. It is hoped that this paper will speak not only to college and university analytical chemistry students but also to working analytical chemists, almost all of whom were educated after chemical analysis courses with substantial classroom and laboratory instruction had been discontinued from their college chemistry curricula.

1. What is a chemical analysis?

A chemical analysis is one that can be performed without an external calibration standard, and the result can be calculated using only atomic weights, definite chemical reactions, and experimentally determined weights. Only gravimetry (together with its special form of fire assay) and gravimetric titrimetry can be done in this manner.

We are far enough removed from the decade of WWII to see that it was a watershed period marking the end of the development and general use of chemical analysis and the beginning of the development and general use of instrumental analysis. Although the use of instrumental analysis had been growing slowly up until that time, most samples were analyzed chemically. However, since the end of WWII, instrumental analysis has assumed more and more importance because of the ever-present demands for increased sensitivity, speed, and cost reduction. After World War II, the existing under-utilized, as well as subsequently-developed instrumentation, was made practical by advances in electronics and computers. At present, we have instrumental sensitivities and speeds that would have been unimaginable even a few years ago, but new demands will keep pushing "fast" and "ultratrace" to new levels.

Because analytical chemists in the workforce today were educated after the beginning of the instrumental era in the late 1940s, it is useful to review the history of chemical analysis, because an awareness of the history of a discipline provides a perspective for evaluating current conditions and needs, and for anticipating and working toward future possibilities.

2. The development of gravimetry

Gravimetry is the determination of an element or species through the measurement of the weight of a well-characterized insoluble product of a definite chemical reaction involving that element or species. The history of the development of gravimetry amounts to tracing the early history of chemistry.

Chemistry is at least as old as recorded history, and fire assay, what today is considered a special form of gravimetry, goes back to ancient times. Based on what we can deduce from the evidence written in historical accounts, fire assay evolved in Asia Minor sometime between 3,000 BCE and 2,500 BCE, and recently-discovered gold and silver artifacts suggest that fire assay may go back even further.

Although an early description of fire assay appeared in Pliny the Elder's *Naturalis Historiae* (*The Natural History*) in 77 CE, what we consider modern fire assay began to appear in the 12th century, when "cupellation" was first mentioned in English literature, and in the 13th century, when "parting" was first mentioned in French literature. By the 15th century fire assay had spread throughout the rest of Europe, and by the 16th century it had been developed and refined almost to perfection. In 1556 George Bauer's book, *De Re Metallica* (*On the Nature of Metals*) was published posthumously under his pen name, Georgius Agricola, and in this book he described fire assay in essentially the same way that it is done today. His book remained the leading textbook for miners and metallurgists for nearly two centuries. Governments, geochemical exploration companies, mining companies, smelting companies, universities, and private analytical laboratories depend on fire assay for accurate results in determining precious metals. In many countries fire assay has been adopted by their court system as the preferred method for determining precious metals in legal disputes.

Today, *A Textbook of Fire Assaying* by Edward Everett Bugbee remains the standard book on fire assay. The revised third edition was published in 1940, and the entire book is posted online (1). The United States Geological Survey (USGS) Bulletin 1445 is another valuable resource on fire assaying (2).

For valid fire assay results, the small powdered laboratory ore sample of about 30 g used for the fire assay must be representative of its source, which might be a several-ton ore sample at a mine. This means that everything must be done to ensure that through the many subsampling steps from the several-ton mine ore sample, through the various milling and grinding processes, to the final thirty grams of ore for the fire assay, that each subsampling step produces a representative sample of the larger sample that preceded it.

A brief description of the steps in the fire assay of a gold and silver ore is as follows. (For the sake of simplifying the discussion, it will be assumed that other than gold and silver, any other precious metals are present only at trace levels.)

The fire assay begins by preparing a fluxing mixture for the subsequent fusing process. A flux is a dry mixture of substances that together allow for the chemical reactions to take place that break down the ore sample, leading to a molten lead button containing the gold and silver, together with a molten, less-dense slag which floats on top of the molten lead button. About thirty grams of ore sample are thoroughly blended with about thirty to forty grams of fluxing mixture in a bone ash fluxing crucible. This mixture is called a "charge."

The fluxing crucible with its charge is placed in a muffle furnace at about 1100°C, and as the crucible heats, several things happen simultaneously: the particles of lead oxide in the flux are reduced to lead, and at the same time, the minerals and other ingredients in the charge fuse into a viscous liquid with a density much lower than either lead oxide or lead, and so the particles of lead fall through the fused

liquid, taking up the freed gold and silver from the surrounding particles of ore. This results in a small liquid mass of lead at the bottom of the crucible, which contains all the gold and silver.

The fusion usually takes about forty-five minutes, after which the crucible is removed from the furnace, and the molten mixture is quickly poured into an iron mold shaped like an upside-down cone with the tip of the cone at the bottom of the mold. When the molten mixture is poured, the blob of molten lead pours out first, and sinks to the bottom of the iron mold, and the less-dense molten slag follows, and floats on top of the molten lead. The iron mold is allowed to cool and everything solidifies with the lead button containing the gold and silver on the bottom and the slag on the top. After cooling, the solid conically-shaped slag with the lead on the bottom falls out of the mold. The solid lead piece containing the gold and silver is easily separated from the solid slag with one's fingers or a gentle hammer blow. This piece of lead is commonly referred to as a "lead button," or more correctly, a "doré."

The next step is called "cupellation," which separates the silver and the gold from the lead in the doré. Cupellation is an oxidizing fusion done using a small bone ash dish, called a cupel, which has a gentle spherical depression in the top where the doré is placed. The cupel with the doré is placed in a furnace at about 800°C, where the lead is rapidly oxidized to lead oxide, most of which is absorbed by the porous cupel. (The small portion of vaporized lead oxide must be collected by an exhaust hood with a proper filter to trap the lead oxide vapor.) The cupel is removed from the furnace and allowed to cool. The remaining tiny gold and silver bead is weighed.

The final step is called "parting," which separates the silver from the gold in the tiny bead. The bead is usually pounded flat to increase its surface area, and then it is treated with hot, dilute nitric acid, which selectively dissolves the silver, leaving the solid gold behind. Thus the gold and silver are "parted," with gold remaining as a solid and silver dissolved in the dilute nitric acid. The tiny gold piece is weighed, and the weight of the silver is obtained by subtracting the weight of the gold from the weight of the gold and silver bead. See (3) for a very well-done, five-part video series on fire assay produced by the International Precious Metals Institute (IPMI).

What we recognize as experimental chemistry did not emerge until the end of the sixteenth century. Later, with the publication of his famous book *The Sceptical Chymist* (*The Skeptical Chemist*) in 1661, Robert Boyle began the long process of putting chemistry on a sound scientific basis. In this book Boyle dismissed Aristotle's four elements of fire, air, water, and earth, and Paracelsus' three principles of sulfur, mercury, and salt. Instead, Boyle advocated a comprehensive experimental approach before attempting any theoretical statements. (Note: All of the personalities introduced in this paper are gathered into an accompanying spreadsheet in the order they appear in this paper, together with their first name, last name, birth date, and death date.)

As the influence of Paracelsus waned, chemists' interest shifted from medicine to mineralogy and metallurgy. Unfortunately, for another century chemists were influenced by the phlogiston theory, which was first advocated in 1681 by Johann Jeremias Becher and popularized by Georg Ernst Stahl. According to this theory, when a metal burns or rusts, it gives off a substance called phlogiston. When phlogistonists observed that iron gains weight when it rusts, they postulated that in some cases phlogiston had negative weight! As 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, Henry Cavendish, Carl Wilhelm Scheele, Daniel Rutherford, and Joseph Priestley. Although Priestley was one of the last staunch defenders of the phlogiston theory, he initiated its downfall in 1774 when he isolated a gas by heating

mercuric oxide in a closed system. He gave the name “dephlogisticated air” to the oxygen 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 de Lavoisier dealt the death blow to the phlogiston theory by performing quantitative experiments with mercury and air in a closed system. Through those experiments, 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 weight, and his use of the balance, made him the forefather of the quantitative era of chemistry.

At about the same time, the Swedish chemist, Torbern Olof Bergman, outlined the first systematic schemes for both qualitative and quantitative analysis, as well as assembling a descriptive list of all of the available reagents known at that time. His gravimetric method for silica is clearly recognizable as a direct forerunner of the one we still use today. Strangely enough, Bergman remained a firm believer in the phlogiston theory all his life.

Although titrimetry was being used in France to some extent, at the turn of the 19th century, almost all chemical analyses were done by gravimetry. Bergman used gravimetric factors to calculate the amounts of iron, lead, copper, and silver present in the various precipitates from his gravimetric procedures, and others became interested in the analysis of minerals and industrial materials. It was found that under certain conditions fire assay tended to give low results for silver, and so Andreas Sigismund Marggraf worked out an alternative gravimetric determination of silver as silver chloride as a substitute for the fire assay of silver.

At the turn of the 19th century chemistry entered a period of confusion. Gravimetry had been developing in an empirical manner all through the 18th century because the laws of chemical composition were not yet understood. Many chemists believed that substances combine in definite proportions because they knew that a certain weight of silver always gave the same weight of silver chloride. Jeremias Benjamin Richter, 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 own preconceptions. However, his work was a beginning in the right direction because he had an intuitive sense of the law of definite composition. Such was not the case with the French chemist Claude-Louis Berthollet, who wrongly postulated that the composition of a compound of two elements varies between maximum and minimum in all proportions. The clouds of confusion began to dissipate when Joseph-Louis Proust opposed Berthollet's view and 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 products of intermediate compositions exist. With this observation he came close to discovering the law of multiple proportions.

In 1808, John Dalton published the first part of his book, *New System of Chemical Philosophy* in which he proposed that matter was composed of small discrete particles. Although this concept dated back to the Greeks of 400 BCE, Dalton's theory was much more far-reaching because it explained the law of conservation of mass as well as the laws of definite composition and multiple proportions. Dalton realized that compounds are formed by uniting atoms of different elements having different relative weights that can be expressed by numbers, and thus the composition of chemical compounds could be expressed quantitatively. He constructed a table of atomic weights, but owing to the poor data available to him at that time, he was unable to demonstrate the simple relationships that intuitively he knew must exist.

Also in 1808, Joseph-Louis Gay-Lussac published a paper on the combining volumes of gases. He consistently found the volume ratios in gaseous reactions were small whole numbers. This result seemed to contradict Dalton's atomic theory because if one volume of Cl and one volume of H gave two volumes of HCl, then the "atoms" of chlorine and hydrogen must divide, which was a logical impossibility if the atomic theory were true. Amedeo Avogadro reconciled the dilemma in 1811 by assuming that equal volumes of gases under the same conditions contain the same number of particles which he called "molecules." He reasoned that these gaseous molecule split into "half-molecules" when they react. In effect, he supposed that some 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 unable to appreciate Avogadro's remarkable and revolutionary insight. Today we know that Avogadro's reasoning was correct, but the chemists of his day either rejected or ignored his hypothesis. Efforts in 1814 by André-Marie Ampère and in 1826 by Jean-Baptiste-André Dumas to revive Avogadro's hypothesis went unnoticed. The world of chemistry was not ready for Avogadro, and sadly, it would take another half century of confusion over atomic weights before Stanislao Cannizzaro would successfully revive Avogadro's hypothesis.

During this period of confusion, practical analysts with little interest in theoretical matters were doing accurate gravimetric analysis of metals, minerals, and water. Richard Kirwan published an outstanding book listing all the references on water analysis since the time of Bergman. Martin Heinrich Klaproth was a major figure in developing and understanding of the composition of minerals and characterizing elements in those minerals. He discovered U and Zr, and was involved in the discovery or co-discovery of Ti, Sr, Ce, Cr, Te and Be. Nicolas-Louis Vauquelin was involved in the co-discovery of Be and Cr, and also many organic compounds including asparagine, which was the first amino acid to be isolated.

The dominant figure of this period was the Swedish chemist Jöns Jacob Berzelius. During an extraordinarily productive period between 1807 and 1818, he devised the system of chemical symbols and notations that we still use today, and he determined, or redetermined, the atomic weights of most of the elements known at the time. Unfortunately, Berzelius had devised his theory of electrochemical dualism which prevented him from accepting Avogadro's hypothesis. Based on his interpretation of his experimental results, his theory suggested that all compounds are salts of two opposite primary materials, one of an acidic nature and another of a basic nature. For example, he considered potassium sulfate (K_2SO_4) to be a salt produced by the reaction of a basic K_2O and an acidic SO_3 . According to Berzelius, all chemicals, whether natural or artificial, mineral or organic, could be distinguished and specified qualitatively by identifying their electrically opposing constituents, as either "acids" or "bases." Despite his incorrect theory of electrochemical dualism, his expertise as an analyst was nothing short of incredible, and the atomic weights published in his 1828 table approach today's values, if one discounts the fact that a few of the elements listed were twice their correct values. Working with the equipment of his day, much of which he improved himself, Berzelius produced an amazing quantity of accurate chemical analytical work.

Although Berzelius was one of the world's greatest analysts, it is doubtful that he ever viewed himself as such. In contrast, Karl Remigius Fresenius thought of himself as an analytical chemist from the beginning of his remarkable career. After serving as an apprentice pharmacist in Frankfurt for several years, he moved to Bonn, where he took courses at the university, and also worked in the private laboratory of his professor of pharmacy, Ludwig Clamor Marquart, who had established a private pharmaceutical institute in Bonn. Working mostly alone and without instruction, Fresenius taught himself and kept good notes. Marquart was so impressed with these notes that he suggested they be published. *Anleitung zur qualitativen chemischen Analyse*, published in 1841, was an immediate success and was to see sixteen editions under Fresenius's authorship. The seventeenth edition was translated by

Charles Ainsworth Mitchell in 1921 as *Introduction to Qualitative Chemical Analysis*. Fresenius went on to the University of Giessen as a lecturer, worked in Justus von Liebig's laboratory, and earned his Ph.D. in 1842, using the second German edition of his qualitative analysis book as his thesis.

In 1845, Fresenius was appointed to the chair of chemistry, physics, and technology at the Agricultural College at Wiesbaden. Because the college administrators repeatedly refused to supply funds for a chemistry laboratory, he obtained a subsidy from the Duchy of Nassau, bought a house, and remodeled it into a private analytical laboratory. He opened the doors in 1848 with five students and one assistant, Emil Erlenmeyer. Only thirty years old, Fresenius was already an experienced analytical chemist. Shortly after assuming his teaching duties at Wiesbaden, he published his second book, *Anleitung zur quantitativen chemischen Analyse*, which ran to six editions and was translated into English in two volumes as *Quantitative Chemical Analysis* by Alfred Isaac 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. In addition to providing instruction, the institute rapidly became known throughout government, industry, and academia as a first-class analytical laboratory. In 1862 Fresenius founded *Zeitschrift für analytische Chemie* (*Journal of Analytical Chemistry*), the first journal devoted entirely to analytical chemistry. His influence throughout Europe and the entire world was enormous.

3. The development of titrimetry

Titrimetry is the determination of an element or species through the measurement of the weight of a chemical necessary to exactly complete a definite chemical reaction in a solution, usually aqueous, containing that element or species. Up until recent decades, the weight of the chemical had usually been obtained indirectly by measuring the volume of a standard solution of that chemical, but for very accurate work the amount of standard solution needed can be measured by weighing it. Today, more-and-more, gravimetric-based titrimetry is coming into use. (Please look ahead to section 9 of this paper for a further discussion of gravimetric-based titrimetry.)

The need of industry for rapid methods for 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 eighteenth century. Endpoints were determined by the "clear point," or the cessation of effervescence, or the use of a few plant-extract indicators. François-Antoine-Henri Descroizilles is considered the "father of titrimetry," because of he devised a method for determining the hypochlorite strength of bleaching solution tanks used in the textile industry. He added a measured amount of dilute sulfuric acid containing an indigo indicator to a graduated cylinder, and then slowly added the hypochlorite solution, whose bleaching strength was known to be optimum, until the color changed from blue to pale green, and he recorded the volume used. Then he took and slowly added a hypochlorite solution whose strength was below par until the color changed and recorded that volume. From the difference between the volumes of the two titrations he was able to calculate the strength of the below par bleaching solution, and thereby calculate how much more sodium hypochlorite had to be added to the tank of bleaching solution to bring it to the proper strength. Later Descroizilles 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, and thus he invented the forerunner of the buret.

Gay-Lussac's contributions to the development of titrimetry and the widespread use of his methods helped establish titrimetry as a part of chemical analysis. He improved Descroizilles' method for potash and made several improvements in the hypochlorite method. Most notably, he introduced the use the redox indicator.

As an analyst, Gay-Lussac is most famous for the silver assay method named after him. The French government had been losing money because under certain conditions, fire assay gives low results for silver. In 1829 the French mint asked Gay-Lussac to devise a rapid and simple assay method for silver with a relative precision and accuracy of less than 0.05%. Gay-Lussac made a 100-mL pipet which delivered 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 exactly 1.0000 g of silver. Then he 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 settle to the bottom of the flask. Then 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 achieved a relative precision and accuracy better than the requested 0.05%. To this day no improvements on Gay-Lussac's silver assay method have been made except the use of a potentiometric endpoint for deeply colored solutions or alloys of silver containing tin.

From 1835 to about 1855, many different titrimetric methods were developed but they were not widely used. However, as a result of Gay-Lussac's work titrimetry became known outside of France, especially in Germany and England. Nevertheless, it was still not possible to establish a general system of titrimetry because the concentrations of standard solutions had no chemical basis, there were no unique atomic weights, and stoichiometry was not yet understood.

Houtou de Labillardière discovered the usefulness of iodine in titrimetry in 1825, and in 1853 Robert Wilhelm Bunsen published an excellent paper describing the determination of over twenty elements by iodimetry. In that same year, Karl Leonhard Heinrich Schwarz made a great advance by recommending the use of sodium thiosulfate for titrating iodine. Nevertheless, many well-known analysts of the period remained contemptuous of titrimetry. Berzelius never used it, and Fresenius recommended against using it for important analyses.

Karl Friedrich Mohr did much to overcome the difficulties of titrimetry. He had studied under the direction of Heinrich Rose and Leopold Gmelin, who was Bunsen's predecessor at Heidelberg. Mohr took over his father's pharmacy in 1830, and in his spare time he experimented with various titrimetric methods. His contributions to titrimetry were many. He introduced ferrous ammonium sulfate as a standard for oxidizing agents (Mohr's salt), the use of potassium chromate as an internal indicator for chloride determinations (Mohr method), the use of oxalic acid as a primary standard for alkalimetry, and the important technique of back-titration. As for laboratory equipment, he invented the cork borer, the Mohr pinchcock, the pinchcock buret, and calibrated pipets, as well as perfecting and popularizing the Liebig condenser. After his book *Lehrbuch der chemisch analytischen Titrimethode (Textbook of Titrimetric Methods of Analytical Chemistry)* was 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. However, two important methods developed late in the 19th century should be mentioned. In 1883 Johan Gustaf Christoffer Thorsager Kjeldahl developed his well known method for the determination of nitrogen. He 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 and then back-titrated with standard sodium hydroxide. The method has remained unchanged to this day, except for the use of various catalysts to aid in the digestion, and the utilization of Lajos Winkler's discovery that the distilled ammonia can be absorbed into a boric acid solution and titrated directly with standard acid. Winkler is best remembered for his method for the determination of dissolved oxygen in water, which he published

in 1888. It is still known as the "Winkler Method," and is used unchanged to this day, particularly in environmental laboratories involved in testing natural water samples for their dissolved oxygen level.

4. The Karlsruhe Congress of 1860

By the late 1850s, advances in chemical analysis had come about as far as they could without a consistent table of atomic weights. Not only did atomic weight tables vary among different countries but also sometimes among different laboratories within the same country. To resolve this problem, Friedrich August Kekulé, along with the help of Charles Adolphe Wurtz and Carl Weltzien, invited delegates to an international congress at Karlsruhe, Germany in 1860. About 140 of the world's leading chemists attended (4).

Stanislao Cannizzaro, a young professor at the University of Genoa had realized for some time the value of Avogadro's hypothesis in resolving the problems surrounding atomic weights. He addressed the Karlsruhe Congress with great passion and pedagogical skill, showing how Avogadro's hypothesis could be used to establish the molecular weight of a gas, and he pointed out that by comparing the vapor densities of a series of gaseous compounds of a particular element, the molecular weight and atomic weight of that element could be determined. Although Cannizzaro pleaded with his colleagues for the adoption of atomic weights based on Avogadro's hypothesis, he was unable to sway the Congress members in his favor.

The Karlsruhe Congress adjourned having reached no agreement on atomic weights, but it was in the process of adjourning that the key event of the congress occurred. As the delegates departed, Cannizzaro's colleague, Angelo Pavesi from the University of Pavia, Italy, passed out pamphlets of Cannizzaro's 1858 publication, *Sunto di un corso di Filosofia chimica (Sketch of a Course of Chemical Philosophy)*. This pamphlet set forth clearly what Cannizzaro had been teaching his students at the University of Genoa. Although Cannizzaro's pamphlet had gone largely unnoticed in the literature, it did not go unnoticed in the hands of two of the congress delegates. Julius Lothar Meyer read the pamphlet twice on his homeward journey, and he said everything became clear to him as if scales had fallen from his eyes. Another recipient of the pamphlet was Dmitrii Ivanovitch Mendelèev, who later said that even though no agreement was arrived at through the Karlsruhe Congress, the truth of the law of Avogadro, as advocated by Cannizzaro, soon convinced everyone. Without the insight that both Meyer and Mendelèev gained from Cannizzaro's pamphlet, it is doubtful that they independently would have gone on to work out the periodic table in 1869.

The events surrounding the Karlsruhe Congress and its immediate aftermath changed everything! *It was indeed a watershed event.* In looking back over the history of the developments in the understanding of chemistry, it is safe to say that one can view the history of chemistry as "before the Karlsruhe Congress," and "after the Karlsruhe Congress." The confusion over atomic weights almost completely disappeared within a few years after the Congress met. Through what they learned at the Congress, it became possible for both Meyer and Mendelèev to independently construct the first periodic tables. It gave Mendelèev the insight to correct the atomic weights of some of the elements and also to use the patterns he saw in his table to predict the properties of the elements he knew must exist but were yet to be discovered. Analysts were able to write down correct stoichiometric formulas for their precipitates. Both gravimetry and titrimetry were placed on solid empirical ground.

5. Physical chemistry applied to chemical analysis

Placing gravimetry and titrimetry on solid scientific ground had to await the development of physical chemistry in the last third of the 19th century. A great breakthrough was made by the Norwegian brothers-in-law Cato Maximilian Guldberg and Peter Waage when they formulated the law of mass

action between the years of 1864 and 1879. Then in 1884 Jacobus Henricus van't Hoff made an elegant derivation of the law of mass action based on chemical thermodynamics. His clear and inspiring treatment of chemical dynamics brought the entire subject of reaction kinetics and equilibria before the chemical world. Subsequently, certain anomalies that occurred when the laws of physical chemistry were applied to solutions of electrolytes were explained in 1887 when the revolutionary theory of electrolytic dissociation was published by Svante August Arrhenius.

It was Wilhelm Ostwald who recognized the importance of the work done by van't Hoff and Arrhenius. Through his books, research, and personal contacts, Ostwald was influential in spreading the ideas of the new physical chemistry. With van't Hoff's founding of the journal *Zeitschrift für physikalische Chemie* (*Journal of Physical Chemistry*) in 1887, he championed the cause of physical chemistry as a science in its own right. In essence, Ostwald "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*) and with that book he began putting chemical analysis on a sound scientific basis. In his preface he noted that although the techniques of chemical analysis stood at a very high level, its scientific treatment had been almost completely neglected. Ostwald's book made a significant start toward correcting this deficiency. He discussed precipitation in detail, including the increase in particle size of standing crystalline precipitates – a process that became known as "Ostwald ripening." The most important part of the book dealt with chemical separations. By combining the law of mass action and Arrhenius' theory of electrolytic dissociation, he introduced the concepts of dissociation constants and solubility product constants.

Although Ostwald's little book broke new ground and was soon recognized as a classic, it suffered from significant omissions. For example, the phase rule of Josiah Willard Gibbs was not mentioned. It might be that Ostwald was unaware of Gibbs' 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 Walther Nernst, who originated the well-known Nernst equation in 1887 while he was working in Ostwald's own laboratory! Nernst went on to explore many of the analytical applications of his equation, and he is rightly considered the father of modern electroanalytical chemistry.

6. The continued importance of gravimetry – Gravimetry comes to the United States – the story of William Francis Hillebrand

In the mid-nineteenth century almost all the new developments in chemistry were taking place in Europe, and during that time Germany was the place to go for graduate education in chemistry. (Graduate schools did not develop in the United States until the end of the nineteenth century.) Justus von Liebig, who established a teaching laboratory at the University of Giessen, generated remarkable enthusiasm and camaraderie among his students, and his laboratory became a model for other graduate programs and teaching laboratories throughout Germany.

William Francis Hillebrand was born in Honolulu, Hawaii in 1853, and his story is a good example of how chemical analysis, particularly gravimetry, was brought to the United States from Europe. His father, a German-born medical doctor, had established a practice in Hawaii because his doctor advised him that Hawaii's climate would help him to recover from a serious illness. Hillebrand's father went on to make a full recovery.

Hillebrand's father's intended to return to Germany with the entire family, and so Hillebrand was sent to Cornell in 1870 to prepare for study at a German university. The family moved to Bonn in the summer

of 1872, and it was time for Hillebrand to choose a career. He had no interest in medicine, and he felt he lacked the mental qualifications for law or engineering. Hillebrand's father suggested chemistry – an idea that 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 1872, studied under the guidance of Bunsen and Gustav Kirchhoff, and earned 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. Realizing that organic chemistry did not appeal to him, he decided to finish his studies with a course in metallurgy and assaying at the mining academy at Freiberg.

In the fall of 1878 Hillebrand moved to the United States and spent the following nine months in the New York City area looking for a good work situation, but he failed to find anything. In the spring of 1879 the newspapers were saying a good deal about the new organization of the United States Geological Survey (USGS) with Clarence King as its first director. In June of 1879 Hillebrand moved to Denver, CO, and it seemed everyone there was talking about Leadville, CO. So he made his way a hundred miles further west to Leadville, and within a few days he found work as the third partner of a small assaying firm. A few months after joining the firm, the other two partners retired, leaving Hillebrand to run the business alone.

Over the following year an occasional assay customer was Samuel Franklin Emmons, who was in charge of the Rocky Mountain Division of USGS. At that time the great miners' strike was going on, and the assay business had become very poor. One day Emmons came to Hillebrand's assay firm with some samples, and out of the blue, he asked Hillebrand if he would like to take a position as a chemist in Emmons' division of USGS. Hillebrand considered this to be the offer of a lifetime and he quickly accepted. From 1880 to 1885, Hillebrand remained at the USGS Denver laboratory, but in 1885 he was transferred to the USGS Washington laboratory, which had been established in 1883, under Chief Chemist Frank Wigglesworth Clarke.

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. ("Complete" means complete for that time, and that included the elements Al, Ba, C, Ca, Cl, Cr, F, Fe, K, Li, Mg, Mn, Na, P, S, Si, Sr, Ti, and also H₂O. If the total of all these elements, plus water, added up to between 99.8% to 100.2%, the analysis of the rock was considered "complete.") The real significance of Hillebrand's work lay in his perfecting a separation scheme for materials as complex as carbonate and silicate rocks. Even in the late nineteenth century, the problem wasn't so much the lack of a suitable method for the final determination of a particular element, as it was the lack of suitable separation methods preceding the final determination – a problem that continues to challenge chemical analytical chemists to this day. In 1897 Hillebrand wrote a 50-page introduction to USGS Bulletin 148 on the methods of analysis of silicate rocks, and it was quickly translated into German. In 1900 Hillebrand revised and enlarged the introduction and it was printed as an independent document, Bulletin 176. The next edition appeared in 1907 as Bulletin 305, which included carbonate rocks, and it also was translated into German. The series culminated in 1919 with the well-known Bulletin 700, a book of 285 pages.

Hillebrand was unquestionably one of the world's leading chemical analysts when he was called to be Chief Chemist at the National Bureau of Standards (NBS) in 1909. In his new position, administrative duties more and more limited his time at the bench, but his steady stream of papers and books continued. Of equal importance was Hillebrand's expanding the NBS Standard Samples Program from a few cast irons to more than 60 materials. [Today, the Standard Reference Materials Program at the National Institute of Standards and Technology (NIST, formerly NBS) has over 1,300 Standard Reference Materials (SRMs) available covering a broad range of materials that are certified for either chemical composition or physical property.]

Hillebrand had a talent for gathering around him capable people, and his success in bringing Gustave Ernst Fredrick Lundell from Cornell University to NBS in 1917 is a good example. In 1923 he and Lundell began co-authorship of *Applied Inorganic Analysis*. Hillebrand died in 1925 before the book was completed, but by 1929 Lundell had gone on to finish it. The book soon became known as the "analyst's bible." In 1953, James Irvin Hoffman and Harry Aaron Bright brought out an updated and expanded second edition of *Applied Inorganic Analysis*, and it is still referred to as the "analyst's bible." In 1938, Lundell, together with Hoffman, wrote a companion volume to *Applied Inorganic Analysis*, entitled, *Outlines of Methods of Chemical Analysis*. This book became another classic, and if *Applied Inorganic Analysis* is known as the "analyst's bible," *Outlines of Methods of Chemical Analysis* should be known as "the commentary to the analyst's bible. The book contains ninety illustrations, each showing what happens when a particular reagent is added to a solution containing all or most of the elements in the short form of the periodic table, except of course the noble gases. The method of presentation is very ingenious, and the overall content of the book is a masterpiece.

Lundell was appointed Chief Chemist at NBS – a position he held until 1968. Under his leadership the scope and renown of NBS's efforts in chemical analysis grew. Lundell had a talent for picking the right person for a particular assignment. He also had an almost uncanny ability of sensing whether work on a project that had hit a snag should be stopped or continued. Often when a project had hit an obstacle, 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* (5), which is one of the greatest papers ever written on analytical chemistry. Even though it was written in 1933, the continuing relevance of Lundell's relatively short paper is remarkable. Because of its deep insight into the fundamentals of analytical chemistry, it should be required reading for all analytical chemistry majors as well as today's practicing analytical chemists. Lundell points out that the main challenge facing an analytical chemist is not the final step of actually determining the element of interest, but rather the separations that are involved in isolating the element of interest from other elements which will interfere in its determination. The previously-mentioned book by Lundell, *Outlines of Methods of Chemical Analysis* treats in depth how to make the necessary separations. (In Section 12 of this paper newer separation methods will be discussed that were unavailable to Lundell because they had not been discovered yet.)

7. Physical chemistry applied to gravimetry – the story of Theodore William Richards as an example of how physical chemistry was applied to gravimetry

The application of physical chemistry to gravimetry is perhaps best illustrated by the quest for accurate atomic weights by chemical methods. This work went on throughout the 19th century and into the first third of the 20th century. Berzelius was the first to take up this task in any systematic way, and during the first three decades of the 19th century he devoted himself to the determination of eleven atomic weights. Even though his values do not agree that well with modern atomic weights, his 1828 table was a remarkable achievement when one considers the laboratory equipment that was available to him at that time, and more importantly, the general confusion among all chemists because they lacked an understanding of Avogadro's hypothesis and its implications for establishing the weight relationships among the elements.

The twelve atomic weights established in the years just after the Karlsruhe Congress by the Belgian chemist, Jean Servais Stas, were considered to be of such high quality that their accuracy went unquestioned for many decades.

The chemical determination of atomic weights made use of weight ratios obtained through careful gravimetric analyses. From the mid-19th century until 1961, atomic weights were based on (O) = 16 (exactly). The atomic weights 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 atomic weight of an element was 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 did not realize the seriousness of the errors caused by the adsorption of gases and retention of water in solids, the occlusion and coprecipitation encountered by precipitation from concentrated solutions, and the solubility-product losses of precipitates into the surrounding supernatant solution.

It remained for Theodore William Richards to bring the chemical determination of atomic weights to maturity. He accomplished this by bringing to the task not only the necessary insights he obtained from the latest developments in physical chemistry at that time, but also his extraordinary genius as an experimentalist. Born to artistic and scholarly parents, he was schooled at home by his mother until the age of fourteen because she was convinced that the school curricula were geared to the slowest students. Richards entered Haverford College in Pennsylvania in 1883 and earned a B.S. in science in 1885. He then enrolled at Harvard University and received a B.A. in 1886, and an M.A. and a Ph.D. in 1888, with his thesis topic being the determination of the atomic weight of oxygen relative to hydrogen. Josiah Parsons Cooke, a man he had known since childhood, was his doctoral advisor. On the merits of his doctoral dissertation, Richards won a fellowship in 1888, for a year of travel and study in Germany where he was exposed to the important new developments in physical chemistry.

On his return to Harvard in the fall of 1889, he was appointed chemistry assistant, and he continued to work in Cooke's laboratory where he determined the atomic weights of Cu, Ba, Sr, Zn, Mg, and Ca. It was in his work on the atomic weight of Sr that Richards developed two important pieces of equipment. One was the nephelometer which permitted him to detect the exact equivalence point in the precipitation of silver chloride or silver bromide. The other was a quartz apparatus which made it possible for him to fuse materials in a quartz boat under anhydrous conditions, and then seal the quartz boat into a quartz weighing tube. This apparatus allowed him to eliminate the adsorption of water and gases in his precipitates.

With Cooke's death in 1894, it became necessary to provide for continuing instruction in physical chemistry, and being selected for the position, Richards was sent by Harvard in 1895 on his second trip to Europe to spend a semester with Wilhelm Ostwald at Leipzig, and another with Walther Nernst at Göttingen. Upon his return, and armed with the latest developments of the then-new theory of solutions, Richards resumed his research, tackling the atomic weights of Ni, Co, Fe, and U, along with doing further work on Ca.

Although Richards had improved on Stas' techniques, he never doubted the accuracy of Stas' values. However up to that point, most of Richards' work had not specifically overlapped Stas' work, but when Richards did find discrepancies between his values and Stas's values, Richards faulted himself rather than his forerunner. During these years Richards was promoted relatively quickly through the Harvard academic ranks from chemistry assistant to instructor, to assistant professor, and finally to full professor in 1901. In 1903 he was made chairman of Harvard's chemistry department.

In 1904 Richards determined the atomic weight of sodium in a sample of sodium bromide which he knew to be extremely pure because of its very sharp transition temperature. He obtained an atomic weight for sodium in this material that was significantly lower than Stas' value, assuming Stas' values for silver and bromine were correct. Richards could not disregard this discrepancy because it indicated either an impurity in Richards' sodium bromide or a flaw in Stas' work. Failing to find impurities in his sodium bromide, Richards set out to redetermine the atomic weights of Na and Cl. He launched a very careful quantitative study to determine three ratios, AgCl:NaCl, Ag:NaCl, and Ag:AgCl. Richards found that each step of this work was critically dependent on both the purity of the substances and the application of physical-chemical principles to the gravimetry involved. For example, 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 substances, and so he worked with much smaller amounts. Stas had made precipitations from concentrated solutions which led to the significant coprecipitation effects of inclusion, occlusion, and adsorption. Instead, Richards precipitated from dilute solutions to minimize these coprecipitation effects. Stas had dried under atmospheric conditions which led to the occlusion of nitrogen, oxygen and water from the air. Richards used his quartz bottling apparatus to eliminate these occlusion effects of drying under atmospheric conditions.

Richards obtained significantly lower values for the atomic weights of Na and Cl, which eventually necessitated the recalculation of all atomic weights which were in any way related to Na, Cl, or Ag. 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.

By 1906 several discrepancies had come to light, suggesting that Stas' atomic weight of silver was too high. Since most of the atomic weights were related to oxygen through silver, this created confusion and uncertainty throughout the whole table of atomic weights. Realizing that the relationship between silver and oxygen had to be known without doubt, Richards, together with Hobart Hurd Willard, designed a series of elegant preparations and gravimetric assays to determine the ratios $\text{LiClO}_4\text{:LiCl}$ and LiCl:Ag . Combining these ratios gave the atomic weight of silver directly in terms of oxygen, and in addition provided a new value for the atomic weight of lithium. Richards obtained an atomic weight of silver 0.05% lower than Stas' value, and at the same time he got a value for lithium 2% lower than Stas' value. This was probably the most careful of all of Richards' remarkable work.

Reading the original paper on this work as well as many of Richards' other important papers is comparable to listening to Mozart's symphonies. At some point every analytical chemist should treat himself or herself to this singular delight (see the suggested reading list at the end of this paper for a few of Richards' most important papers). Richards was involved in the determination of the atomic weight of 25 of the elements, and together with two of his students, Gregory Paul Baxter of Harvard and Otto Hönigschmid of Munich, 55 elements were covered. In 1912 Richards was appointed Erving Professor of Chemistry and Director of the new Wolcott Gibbs Memorial Laboratory at Harvard. In 1914 Richards received the Nobel Prize in chemistry, the first American to be so honored.

8. The continued importance of titrimetry – the story of Izaak Maurits Kolthoff, as an example of how physical chemistry was applied to titrimetry

As was the case with gravimetry, titrimetry developed first in Europe and then came to the United States, chiefly through the efforts of Izaak Maurits Kolthoff, who began his studies in his home country of The Netherlands at the University of Utrecht in Holland in 1911. Kolthoff's lack of certain prerequisites demanded by the chemistry department was a blessing in disguise, because instead, he enrolled in the school of pharmacy which brought him under the tutelage of Nicolaas Schoorl. Schoorl had studied at the University of Amsterdam where van't Hoff, Cornelis Adriaan Lobry de Bruyn, and

Hendrik Bakhius-Roozeboom were teaching, and so Schoorl was aware of the recent advances in physical chemistry. (It was Roozeboom who had introduced the European scientific community to Gibbs' phase rule.) Schoorl 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 so he launched his own investigation. He had already acquired a used copy of Wilhelm Ostwald's 1894 classic, and he was further encouraged by the 1909 paper of the Danish physiological chemist Søren Peter Lauritzto Sørensen, who had introduced the concept of pH. Kolthoff was further inspired in 1913 by the work of Joel Henry Hildebrand, who used the hydrogen reference electrode in electrometric titrations. Kolthoff borrowed pH measuring equipment, but within a year he had devised his own potentiometric apparatus. In 1915 he published his first paper on the titration of phosphoric acid. Kolthoff quickly realized how important physical chemistry would be for the development of analytical chemistry, but in those early years, sometimes the going was rough. Not realizing the significance of his early work, some chemistry faculty members criticized him. (Kolthoff was openly made fun of by both students and faculty members and he was contemptuously nick-named the "pH-H'er," which when said in Dutch comes out pay-ha-ha'er.) Some went so far as to try to block Kolthoff from publishing and lecturing. Despite such obstacles, he forged ahead and in 1918 presented his Ph.D. thesis on the "Fundamentals of Iodimetry," a topic he returned to again and again in succeeding years. In 1914 the Danish physical chemist Niels Janniksen Bjerrum published a book showing how to calculate both the shape of neutralization curves and the titration errors in visual endpoint determinations. Bjerrum's 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 by Nathaniel Howell Furman of Princeton University during 1928 and 1929 as *Volumetric Analysis*. A three-volume revision of the work appeared between 1942 and 1957.

In 1924 Kolthoff conducted a lecture tour of Canada and the United States, where he met both Furman and Willard of the University of Michigan. Willard had pioneered the technique of precipitation from homogeneous solution, and also had investigated the analytical uses of perchloric acid. Furman had made outstanding contributions in potentiometry, electrodeposition, and polarography, and together with Willard worked on the analytical applications of ceric salts. In 1927 Kolthoff accepted a professorship at the University of Minnesota and continued his monumental achievements which touched almost every area of analytical chemistry. In addition to becoming good friends, Kolthoff, Furman, and Willard became known as "The Big Three" in graduate education in analytical chemistry in United States. Between the years of 1932 and 1960 the three of them together supervised 120 analytical chemistry Ph.D.s. Kolthoff also influenced many thousands of undergraduate students through his well-known *Textbook of Quantitative Inorganic Analysis*, coauthored with Ernest Birger Sandell in 1936. A fourth edition appeared in 1969 under the title *Quantitative Chemical Analysis*, with Sandell, Edward J. Meehan, and Stanley Bruckenstein as coauthors.

9. An appeal for continuing the change from volumetric-based titrimetry to gravimetric-based titrimetry

Over the last few decades, in the few remaining colleges and universities where chemical analysis is still taught, more-and-more there has been a shift from volumetric-based titrimetry to gravimetric-based titrimetry. The same thing has been happening in commercial, private, and government analytical laboratories. When titrimetry is done with a titrant prepared on a weight/weight basis (mg of reacting species/g of titrant solution), then titrimetry joins gravimetry in being completely weight based. The change to gravimetric-based titrimetry affords four advantages: 1) both the analytical laboratory

operations and the calculations become much easier and straightforward; 2) volume measurements are eliminated, and weighings are the only laboratory measurements needed; 3) the effects of possible laboratory temperature fluctuations are eliminated; and 4) relatively expensive calibrated burets can be replaced with inexpensive 100 mL dropper bottles for making the titrations, and relatively expensive calibrated volumetric flasks can be replaced with inexpensive 1-L plastic bottles for preparing and storing the standard titrant solutions. Additionally, only two relatively inexpensive electronic balances are required – one that weighs up to about 150 g with 2 decimal places for determining the initial and final weights of the plastic-dropper-bottle gravimetric buret, and one that weighs up to about 1,500 g with 1 decimal place for determining the weights needed for the preparation of the standard titrant.

10. Where instruments supplement chemical methods – Using chemical analysis and instrumental analysis in tandem

For some time chemical analysts had been combining chemical and instrumental methods of analysis in individual situations. However, two papers by Silve Kallmann of Ledoux & Co., Teaneck, NJ, that appeared in the mid-1980s advocated a conscious, systematic approach of using both chemical analysis and instrumental analysis in concert (9), (10). In many instances, older chemical analyses can be reconstructed and revitalized by using them together with instrumental determinations. In other instances, entirely new methods are possible – some of them very elegant. Kallmann made an important contribution by suggesting that chemical analysts should continually be on the lookout for such possibilities as a part of their 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 by coprecipitation and occlusion. Such an impure precipitate can be redissolved and the contaminants determined by instrumental analysis. The second 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 chemical method for silica can be simplified greatly by isolating the precipitated silica from a single dehydration, and then, instead of doing a second dehydration, and sometimes a third, the tiny remainder of silicon in the filtrate from the first dehydration can be determined instrumentally. Kallmann pointed 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 mentioned earlier, the small amount of Cd present in most Zn ores is eluted together with the Zn on the ion-exchange column. 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 then determine the small amount of Cd separately by an instrumental method. The use of an instrumental determination together with a chemical determination does not degrade the overall precision of the chemical part of the determination as 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 positive biases of coprecipitation and occlusion and the negative bias of the solubility-product effect.

11. Where chemical methods are irreplaceable

Although chemical analysis will never be used to the extent that it was in the past, it will continue to be essential where instrumental methods do not work. However, in a review article written several decades ago in a major journal, a colleague of mine was already sounding the alarm regarding the disappearance of the chemical analyst in the analytical laboratories of the United States. My colleague wrote, "The last

two years have shown a continued acceleration of the trend away from chemical analysis in favor of high-speed, low overhead instrumentation. With the exception of a few techniques based on fundamental approaches, these high-speed instruments are dependent upon comparative methodology that requires calibration and validation with traceable standard reference materials. The loss of experience and knowledge in the area of chemical analytical chemistry, upon which so many of the extant reference materials are based, remains a crisis of growing proportions. Nowhere is this trend greater than in the U.S. where the wet chemical laboratory is vanishing from the steel industry." (8) As an illustration of the need for chemical analysis in industry, consider my own experiences several decades ago in two industrial analytical chemistry laboratories. While working for a corporation engaged in advanced ceramic research and production, analytical chemists in our laboratory were asked to make elemental assays (except oxygen) for each of the elements in the following ceramic materials: SiC, TiC, WC, BN, AlN, Si₃N₄, TiN, Al₂O₃, SiO₂, TiO₂, and Y₂O₃. In some cases samples were submitted that were mixtures of two or more of these compounds. In order to be dissolved, many of these compounds and compound mixtures required the use of acid mixtures containing HF, particularly HNO₃-HF mixtures. That meant the ceramic sample, together with the proper HNO₃-HF mix, had to be placed in a sealed Teflon™ container, which was further sealed in Paar™ high-temperature, high-pressure stainless steel vessel, and heated to 250° C for several hours. In most cases the required relative precision and accuracy of the result was 0.5% or better.

While working for a major forging company, analytical chemists in our laboratory were asked to assay aluminum-based, titanium-based, and nickel-based alloys for Al, Co, Cr, Mo, Sn, V, and Zn in the 5% – 60% range, with a required relative precision and accuracy of 0.2% or better. All of the requests for both the ceramics and the metal alloys finally arrived at my laboratory bench because instrumental methods had either not worked at all, or had failed to provide the necessary precision and accuracy. Without exception, each of the above assays was of considerable economic importance to both the industries involved. In all the above cases, the use of chemical analysis did provide the required precision and accuracy of 0.2%

12. Organic reagents applied to chemical analysis

Chemical 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. [This is the all-important point that G.E.F. Lundell made in his well-known paper, *The Chemical Analysis of Things as They Are* (5).] But because this is almost never the case, interfering elements must be removed. The elaborate scheme perfected by Hillebrand for the analysis of silicate and carbonate rocks is an example of a general separation scheme built on the experience of generations of chemical analysts. Hillebrand's separation scheme was based almost entirely on precipitation separations using inorganic reagents. His separation scheme stands as one of the monumental achievements of chemical analytical chemistry.

Beginning in the last century various organic reagents were introduced which could be used as precipitants in gravimetric determinations. They were 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 masked or removed. Most of these reagents were chelating agents, such as dimethylglyoxime, which is used for the determination of Ni, and α -benzoin oxime, which is used for the determination of Mo. In addition to being used as precipitants, these and other organic reagents were extremely useful when coupled with immiscible solvent extraction. For example, 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, balance Ti. Addition of cupferron to an acid solution of the alloy produces the water-insoluble cupferrates of Ti, V, and Fe. Extraction with chloroform dissolves these cupferrates, leaving Al in the aqueous phase for determination by either titrimetry or gravimetry.

In the 1930s it was found that certain aminopolycarboxylic acids formed stable, soluble complexes with many metals, and in the 1940s Gerold Schwarzenbach began a theoretical examination of these complexes. This work led to the development of the titration of calcium and magnesium with EDTA, and the introduction of 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 the most significant development for chemical analysis resulting from the use of organic reagents. In the middle of the nineteenth century, ion-exchange had been observed in certain natural materials, 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 tannic acid. Later, two kinds of crosslinked polystyrene resins were synthesized – one with ionizable acidic functional groups which could exchange with cations, and the other with ionizable basic functional groups which could exchange with anions.

Great advances in the understanding and use of ion-exchange resins occurred during WWII as a result of the Manhattan Project. In 1942 George Edward Boyd and his group used ion-exchange resins to separate plutonium from uranium. Later Boyd and his associates used ion-exchange to separate fission elements for subsequent chemical determination. Meanwhile, Frank Harold Spedding and his group at Ames, IA, performed large-scale separations of naturally occurring rare-earth elements. Because of the secrecy surrounding the Manhattan Project, none of this work was made public until after the war. Since that time, many ion-exchange separation procedures have been developed, which has created 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. Nevertheless, when one considers their usefulness in many otherwise very difficult situations, ion-exchange separations are worth the investment of time. The column is a simple large-bore glass tube with a stopcock at the end and a fritted glass disk inside the bottom of the bore to retain the ion-exchange resin within the column. For work with HF, similar polyethylene columns are available. The column is loaded with a suitable ion-exchange resin, being very careful to add a water slurry of the resin to the column in such a way that there are no air pockets. The resin is washed several times with dilute acid, and it is ready for use.

One of many separation examples is that Mn, Fe, Co, Ni, Cu and Zn dissolved in strong hydrochloric acid. The strong hydrochloric acid solution of these six elements is loaded onto the ion exchange column, and after successive elutions with hydrochloric acid of different concentrations, each element can be eluted separately, without any cross-contamination from any of the other elements. (6). This ion-exchange system has greatly simplified the assay for Zn in Zn ore concentrates. After dissolving the Zn ore concentrate in acid and volatilizing As, Sb, and Sn as their bromides, the solution is loaded onto an anion-exchange column on which all remaining interfering elements (except Cd) can be separated by elution with 0.5 M HCl. Zn and Cd are eluted together with 0.005 M HCl, and the Zn is determined by EDTA titrimetry after the Cd is masked as its iodide complex. The usually small amount of Cd can then be determined by an instrumental method, and because it is only a tiny part of the whole, the less precise instrumental determination does not degrade the overall precision and accuracy of the result.

The immense power of ion exchange is further illustrated by the complete separation of the common rock-forming elements (except silicon and phosphorus) using a single cation-exchange column (7). After acid dissolution of the rock sample and volatilization of the SiF_4 , the solution is loaded on a cation-exchange column and, by using 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 those of traditional chemical separation methods.

13. Chemical analysis training in a world obsessed with innovation

We have seen that chemical analysis has had a long and distinguished history, however, over the last two centuries, there has been a curious reversal in the status of chemical analysis. During the first two thirds of the nineteenth century, chemical analysts had excellent technique even though their scientific understanding was limited. Then during the last third of the nineteenth century, and extending through the first four decades of the twentieth century, chemical analysts had both good technique and good scientific understanding. But then after the end of WWII and extending up to the present, advances in scientific understanding and instrumentation have made it so almost all elemental determinations are being done by instrumental analysts. Today's instrumental analysts have excellent scientific understanding but very little, if any, educational or practical experience in the techniques of chemical analysis. Consider this 1988 advertisement that appeared more than three decades ago in the catalog of a well-known standards organization: "For over two years we have been providing sanctuary for members of an endangered species. Now, after proper care and nurturing, we are ready to re-introduce our specimens of this vanishing breed, so that they can provide services for the public. This creature to which we refer is the Classical Analytical Chemist. He or she is the primary source of accurate analyses, and is, therefore, extremely valuable to our industry." (11)

The situation has not changed much since 1988. Chemical analysis is as much a craft as it is a science. The "science" part of it can be passed on through "book-learning," but the "craft" part of it, which incorporates the practical knowledge and skills accumulated over generations, has to be passed on through "hands-on" training, overseen by persons knowledgeable of the science and skilled in the craft. That said, there are only a few trained and experienced chemical analysts still alive, and so there are vanishingly few qualified people left to train future qualified chemical analysts. With regard to this, despite my searching online, I have been unable to find even one college or university in the United States that offers comprehensive classroom and laboratory instruction in chemical analysis. One solution to this problem would be to step outside of academia and set up a private school where chemical analysts could be trained.

Ironically, the circumstances today in many ways mirror the state of affairs that Fresenius faced in the mid-19th century. Realizing this, a similar path followed by Fresenius a century and a half ago could be followed today by doing almost exactly what Fresenius did – set up a private school for training chemical analytical chemists. First, Fresenius got funding in the form of a subsidy from the duke of the Duchy of Nassau, which today would be equivalent to obtaining a private or government grant. Next, he purchased a house, which he converted into a teaching laboratory. With the glut of private and commercial real estate for rent or for sale these days, a similar thing could be done. Then Fresenius hired Emil Erlenmeyer as his first assistant, and probably gathered his first thirty students through newspaper and word-of-mouth advertising. There may still be a few people around today who could serve as assistants for such a teaching laboratory, and with proper advertising on the internet, in newspapers, and by word-of-mouth, there are probably interested students out there.

Fire assayists will always be needed, but there are only two schools that offer comprehensive training in fire assay, and neither of them are in the USA. One is the Precious Metals Assay and Training Institute (PMATI), in Mumbai, India, which offers several comprehensive courses of various lengths in the theory and practice of fire assay, all in the English language. The other school is the British Columbia Institute of Technology (BCIT), Vancouver, BC, CA, which offers a course in fire assay and mineral identification. I have not been able to find any USA schools that offer training in either fire assay or substantial training in chemical analysis. Chemical analysts are also required for certifying the reference materials upon which almost all instrumental methods depend. Industry will continue to rely on chemical analysts to decide if raw materials meet specifications and if finished products can be released

for sale. I speculate that many hundreds, and perhaps as many as several thousand, well-trained chemical analysts will be needed in the future.

Both the science and the "state of mind" necessary to be a good chemical analyst would have to be firmly imparted to each student in such a school and teaching laboratory. They would have to practice until they mastered the techniques of common analytical operations, and they would have to learn the craft by analyzing materials used in industry and government. From such an institution could flow a small but steady stream of qualified chemical analysts to serve in our industrial, mining, governmental, and private laboratories. The graduates of this school would have both the mental and manual skills necessary to do chemical analysis. They would be able to work according to Kolthoff's maxim – "Theory Guides, Experiment Decides." Perhaps such a school exists in the USA that I don't know about. If not, now is the time to establish one.

14. Names and dates of the 88 scientists, chemists, and assayers cited in this paper

A ? indicates where a first or middle name, or a date could not be found. The order of the names appear in the order that they are mentioned in this paper. An online Excel spreadsheet of this list will be made available.

Robert Boyle (1627-1691)
Aristotle (384-322 B.C.)
Paracelsus (1493-1541)
Johann Joachim Becher (1635-1682)
Georg Ernst Stahl (1660-1734)
Joseph Black (1728-1799)
Henry Cavendish (1731-1810)
Carl Wilhelm Scheele (1742-1786)
Daniel Rutherford (1749-1819)
Joseph Priestley (1733-1804)
Antoine-Laurent de Lavoisier (1743-1794)
Torbern Olof Bergman (1735-1784)
Andreas Sigismund Marggraf (1709-1782)
Jeremias Benjamin Richter (1762-1807)
Claude-Louis Berthollet (1748-1822)
Joseph-Louis Proust (1754-1826)
John Dalton (1766-1844)
Joseph-Louis Gay-Lussac (1788-1850)
Amedeo Avogadro (1776-1856)
André-Marie Ampère (1775-1836)
Jean-Baptiste-André Dumas (1800-1884)
Stanislao Cannizzaro (1826-1910)
Richard Kirwan (1735-1812)
Martin Heinrich Klaproth (1743-1817)
Nicholas-Louis Vauquelin (1763-1829)
Jöns Jacob Berzelius (1779-1848)
Carl Remigius Fresenius (1818-1897)
Ludwig Clamor Marquart (1804-1881)
Charles Ainsworth Mitchell (1867-1948)
Emil Erlenmeyer (1825-1909)

Alfred Isaac Cohn (?-?)
 Pliny the Elder (23-79)
 Edward Everett Bugbee (1876-1949)
 Georgius Agricola (pen name of George Bauer) (1494-1555)
 François-Antoine-Henri Descroizilles (1751-1825)
 Houtou de Labillardière (1775-1834)
 Robert Wilhelm Bunsen (1811-1899)
 Karl Leonhard Heinrich Schwarz (1824-1890)
 Karl Friedrich Mohr (1806-1879)
 Heinrich Rose (1795 -1864)
 Leopold Gmelin (1788 -1853)
 Johan Gustav Christoffer Thorsager Kjeldahl (1849 -1900)
 Lajos Winkler (1863 -1939)
 Friedrich August Kekulé (1829 -1896)
 Charles Adolphe Wurtz (1817 -1884)
 Karl Weltzien (1813 -1870)
 Angelo Pavesi (? -?, but a 19th century chemist)
 Julius Lothar Meyer (1830 -1895)
 Dmitrii Ivanovitch Mendelèev (1834 -1907)
 Justus von Liebig (1803 -1873)
 William Francis Hillebrand (1853 -1925)
 Gustav Kirchhoff (1824 -1887)
 Rudolph Fittig (1835 -1910)
 Samuel Franklin Emmons (1841 -1911)
 Frank Wigglesworth Clarke (1847 -1931)
 Gustave Ernst Fredrick Lundell (1881 -1950)
 James Irvin Hoffman (1893 -1964)
 Harry Aaron Bright (1890 -1961)
 Cato Maximilian Guldberg (1836 -1902)
 Peter Waage (1833 -1900)
 Jacobus Henricus van't Hoff (1852 -1911)
 Svante August Arrhenius (1859 -1927)
 Wilhelm Ostwald (1853 -1932)
 Josiah Willard Gibbs (1839 -1903)
 Walther Nernst (1864 -1941)
 Izaak Maurits Kolthoff (1894 -1993)
 Nicolaas Schoorl (1872 -1942)
 Søren Peter Lauritz Sørensen (1868 -1939)
 Joel Henry Hildebrand (1881 -1983)
 Theodore William Richards (1868 -1928)
 Jean Servais Stas (1813 -1891)
 Josiah Parsons Cooke (1827 -1894)
 Hobart Hurd Willard (1881 -1974)
 Gregory Paul Baxter (1876 -1953)
 Otto Höning Schmid (1878 -1945)
 Cornelis Adriaan Lobry van Troostenburg de Bruyn (1857-1904)
 Hendrik Bakhius-Roozeboom (1854-1907)
 Niels Janniksen Bjerrum (1879-1958)
 Nathaniel Howell Furman (1892-1965)
 Ernest Birger Sandell (1906-1984)

Edward J. Meehan (1912-2000)
Stanley Bruckenstein (b. 1927)
Gerold Schwarzenbach (1904-1978)
B.(?) A.(?) Adams (?-?)
E.(?) L.(?) Holmes (?-?)
George Edward Boyd (1911-2004)
Frank Harold Spedding (1902-1984)
Silve Kallmann (1915-1989)

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Footnotes

(1) <https://babel.hathitrust.org/cgi/pt?id=wu.89083896068&seq=327&view=1up>

(2) <https://pubs.usgs.gov/bul/1445/report.pdf>

(3) <https://www.youtube.com/playlist?list=PLYEyevnAWPD5-6CvIRhrwLDXudX8JIFyC>

(4) <https://www.degruyter.com/document/doi/10.1515/ci.2010.32.6.10/html?lang=en>

(5) Lundell, G.E.F. *Ind Eng Chem Anal Ed* **1933**, 5, 221-225

(6) Kraus, K.A.; Moore, G.E. *J Am Chem Soc* **1953** 75 1460-62

(7) Strelow, F.W.E.; Liebenberg, C.J.; Victor, A.H. *Anal. Chem.* **1974** 46 1409-1414

(8) Dulski, T.R. *Anal. Chem.* **1991** 63 65R

(9) Kallmann, S. *Anal. Chem.* **1984**, 56, 1020A-1028A

(10) Kallmann, S. in *Chemical Analysis of Metals*, Coyle, Francis T., Ed., ASTM: Philadelphia, **1987** pp 128-133

(11) Brammer Standards Company, Inc. Catalog Supplement, 1988; p 3

Suggested Readings and References

- Belcher, R. *Analyst*, 1978, 103, 29-36.
- Byrne, F.P., Ed.; *Some Fundamentals of Analytical Chemistry*, ASTM: Philadelphia, 1974.
- Cannizzaro, S. *Sketch of a Course of Chemical Philosophy*; Livingstone: Edinburgh, (Alembic Club Reprint 952 #18), 1969.
- Cerruti, L. *Metrologia*, **1994**, 31 159-166.
- Chirnside, R.C. *Analyst*, **1961**, 85 314-324.
- deMilt, C. J. *Chem. Educ.*, **1951**, 28 421-425.
- Dulski, Thomas R. *The Measure of All Things*; BookLocker.com, Inc.: St. Petersburg, FL, 2018.
- Epstein, M.S.; Moody, J.R. *Spectrochim. Acta*, **1991** 46B 1571-1575.
- Fassett, J.D.; Paulsen, P.J. *Anal. Chem.* **1989** 61 643A-649A.
- Findlay, A. *A Hundred Years of Chemistry*; 3rd ed., revised by Williams, T. I., Duckworth: London, 1965.
- Furman, N.H., editor, *Standard Methods of Chemical Analysis, The Elements*, Vol I, 6th ed., Krieger: New York, 1975.
- Hamilton, L.F., Simpson, S.G. *Quantitative Chemical Analysis*; 11th ed., Macmillan Company, 1958 (the forerunner of this book was the well-known *Talbot's Quantitative Chemical Analysis*, first published in 1897 and ran many editions until 1946. L.F. Hamilton edited Talbot's book from the 41st to the 47th editions)
- Hamilton, L.F., Simpson, S.G.; Ellis, D.W. *Calculations of Analytical Chemistry*; 7th ed., McGraw Hill: New York, 1969.
- Hillebrand, W.F. *J. Ind. Eng. Chem.* 1917, 9, 170-177
- Hillebrand, W.F.; Lundell, G.E.F.; Bright, H.A.; Hoffman, J. I. *Applied Inorganic Analysis*, 2nd ed.; Wiley: New York, 1953.
- Ihde, A.J. *The Development of Modern Chemistry*; Harper & Row: New York, 1964.
- Kodama, K. *Methods of Quantitative Inorganic Analysis*; Interscience: New York, 1963.
- Kolthoff, I.M.; Stenger, V.A.; Belcher, R.; Matsuyama, G. *Volumetric Analysis*; Interscience: New York, 3 vols. 1942, 1947, 1957.
- Kolthoff, I.M.; Sandell, E.B.; Meehan, E.J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; Macmillan: New York, 1969.
- Kolthoff, I.M. *Anal. Chem.*, **1973**, 45, 24A-37A.
- Laitinen, H.A.; Ewing, G. W., ed's., *A History of Analytical Chemistry*, Div. of Analytical Chemistry of the American Chemical Society: Washington, DC, 1977.
- Laitinen, H.A. *J. Res. Nat. Bur. Stand.* 1988, 93, 175-185.
- Lundell, G.E.F. *Ind. Eng. Chem. Anal. Ed. The Chemical Analysis of Things as They Are*, **1933**, 5, 221-225.
- Lundell, G.E.F.; Hoffman, J.I.; Bright, H.A. *Chemical Analysis of Iron and Steel*; Wiley: New York, 1931. Lundell, G.E.F.; Hoffman, J.I. *Outlines of Methods of Chemical Analysis*; Wiley: New York, 1938.
- Meinke, W.W. *Anal. Chem.*, **1970** 42 26A-38A.
- Partington, J.R. *A History of Chemistry*; Macmillan: New York, 1961, 1962, 1964 (3 vols.).
- Richards, T.W.; Wells, R.C. *J. Am. Chem. Soc.*, **1904**, 31, 235-243.
- Richards, T.W.; Wells, R.C. *J. Am. Chem. Soc.*, **1905**, 27, 459-529.
- Richards, T.W.; Köthner, P.; Tiede, E. *J. Am. Chem. Soc.*, **1909**, 31, 6-20.
- Richards, T.W.; Willard, H.H. *J. Am. Chem. Soc.*, **1910**, 32, 4-49.
- Richards, T.W. *Determinations of Atomic Weights*, Publication 125, Carnegie Institution of Washington: Washington, D.C., 1910.
- Szabadváry, F. *History of Analytical Chemistry*, Pergamon Press: New York, 1966.
- Szabadváry, F.; Robinson, A. *The History of Analytical Chemistry*, in *Comprehensive Analytical Chemistry*, Vol. X, Svehla, G., editor, Elsevier: New York, 1980.

Treadwell, F.P.; Hall W.T. *Analytical Chemistry*, 9th ed., Wiley: New York, 1942; Vol 2.
Washington, H.S. *The Chemical Analysis of Rocks*, 4th ed., Wiley: New York, 1930.
Wilson, H.N. *Analyst*, **1960**, 85, 540-550.
Wilson, H.N. *An Approach to Chemical Analysis*; Pergamon: New York, 1966.