

# FROM ASSAYING TO ANALYTICAL CHEMISTRY; HOW AN ART BECAME A SCIENCE\*

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It is well known that some methods of analytical chemistry are very ancient. This is true above all for methods serving to detect counterfeits. Oldest of all are obviously techniques to check the genuineness of gold and coins, that is, assaying. The chemical or rather metallurgical method of cupellation was known already in the Antiquity, and one of the most ancient laws of physics was discovered by Archimedes when he checked the gold content of a crown. An organization for gold and coin control existed already in Babylon. From the Middle Ages, detailed standard specifications describing how to carry out the tests have survived. It was termed "Ars probandi", and the term "art" was retained to the end of the 18th century: art of assaying, Probierekunst in German. I first found the expression "chemical analysis" as subtitle in Robert Boyle's works, e.g.: The chymical analysis of seed pearls. However, the expression was rarely used even in the following century. Torbern Bergman who was the first to compile analytical methods only used it in the titles of two of his books: *De analysi aquarum* and *De analysi ferri*, in the second half of the 18th century. The word "analysis" spread first in investigations of water, presumably to differentiate them from ore analyses which at that time were mainly carried out using metallurgical methods. The title of Kirwan's book in 1799 was *Essay on the Analysis of Mineral Waters*. It appears that Lampsadius' textbook issued in Freiberg in 1801 was the first to carry the title *Handbuch der chemischen Analyse* in a universal sense. Only from this time on did assaying turn into analysis in the literature. However, this did not involve a change in contents, only in the term. Analysis continued to imply prescription-like descriptions of methods approved in practice. The methods had actually been developed in the 18th century, not owing to industrial or quality control requirements as one should be inclined to think, but out of scientific reasons. Man wanted to get acquainted with Nature, he was curious to find out what mineral waters contained, what were the components of ores and rocks, and for these purposes he invented qualitative detection and quantitative gravimetric methods.

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With the exception of gold alloys, there was still no need for chemical analysis to control the quality of man-made products. Although Pliny already mentioned the first analytical reagent, gall-nut extract to detect the purity of copper sulphate, this was not followed by other reagents for a long time. Requirements of quality control were satisfied for centuries by the organs of sense.

The quality of agricultural products was determined by taste and odour, that of industrial products (textiles, leather goods, metalware etc.) by touch, experience and use. The textile manufacturing industry which developed in the 18th century was the first to use chemicals whose quality could not satisfactorily be determined in this manner, although their utilization without quality control was risky. The concentrations of acids, alkalis and later hypochlorite solutions applied for bleaching fabrics were not indifferent: if they were too high, they destroyed the fabric. To determine the concentrations of these chemicals, titrimetric methods were invented from the end of the 18th century on, the first methods by Hume, Lewis and others in England. However, for the time being these methods were empirical indicating methods, not absolute determinations. Therefore the scientists investigating minerals and water at universities did not, for a long time, consider titrimetry as a scientific method, since they already used balances for weighing. Formerly the absolutely unfounded statement that chemistry became a quantitative science through Lavoisier, since it was he who introduced balances into chemistry, could be read all over the world in the introductions to books on chemistry. This misstatement is now slowly disappearing. We know that chemical use of the balance dates back to hundreds of years. The assayers already assiduously used balances. To be sure, they first transformed the substance to be determined, mainly metals, into the pure state by means of elaborate operations, and subsequently weighed it. Marggraf, in the middle of the 18th century, was the first to come to the conclusion that a given amount of silver would always yield identical amounts of silver chloride. If this proportion is once established, it is sufficient to weigh silver chloride only, and calculate silver using the rule of three. Let me cite Marggraf's words: "The silver must be precipitated from nitric acid — silver solution with rock salt solution. This must be added until the solution is no longer turbid. The solution must be allowed to stand overnight . . . After this the precipitate must be washed and dried. From 2 oz silver 2 oz, 5 drachms and 4 grains of precipitate is obtained. The increase of weight originates from the acid of rock salt, consequently one oz of this precipitate contains 6 drachms and a few grains of pure silver."

Bergman in his "De praecipitatis metallicis" (appeared in 1779) discusses in what chemicals various metals can be dissolved, with what chemicals they can be precipitated from the solution and presents a table indicating how many parts of the precipitate correspond to 100 parts of the metal.

The picture shows one page of this table. "Alk. minerale aerato" means carbonate, "alk. minerale phlogisticato" means hexacyanoferrate. The numerical values of the data are, of course, very erroneous, particularly in the last group. However, the proportions for silver chloride and lead sulphate, for instance, are surprisingly accurate.

From the above and similar practical analytical observations, some sort of intuition began to form that compounds are not composed at random, but obey certain ratios by weight. It was, however, extremely difficult to formulate this intuition. One can actually sense the agonies in contemporary books to find the words for the conjecture.

The man who deserves the main credit for creating stoichiometry is Jeremiah Benjamin Richter (1762–1807) who had a short unhappy life and never attained a professorship. It was he who invented the word itself. In

392 *De Præcipitatis Metallicis.*

100 part.	<i>Plumbi</i>	alk. min aërato	deder.	132
-	-	-	caustico	116
-	-	-	virriolato	143
-	-	-	phlogistic.	-
-	<i>Cupri</i>	-	aërato	194
-	-	-	caustico	158
-	-	-	phlogistic.	530
-	<i>Ferri</i>	-	aërato	225
-	-	-	caustico	170
-	-	-	phlogistic.	590
-	<i>Stanni</i>	-	aërato	131
-	-	-	caustico	130
-	-	-	phlogistic.	250
-	<i>Vismuti</i>	-	aërato	130
-	-	-	caustico	125
-	-	-	phlogistic.	180
-	-	aqua pura	-	113
-	<i>Niccoli</i>	-	aërato	135
-	-	-	caustico	128
-	-	-	phlogistic.	250
-	<i>Arsenici</i>	-	aërato	-
-	-	-	caustico	-
-	-	-	phlogistic.	180
-	<i>Cobalti</i>	-	aërato	160
-	-	-	caustico	140
-	-	-	phlogistic.	142
-	<i>Zinci</i>	-	aërato	193
-	-	-	caustico	161
-	-	-	phlogistic.	495
-	<i>Antimoni</i>	-	aërato	140
-	-	-	caustico	138
-	-	-	phlogistic.	138

Fig. 1. "Stoichiometric" table from Bergmans "De præcipitatis metallicis" (1779)

the introduction to his brilliant book (which, at that time, attracted no attention whatsoever) entitled in German "Anfangsgründe der Stöchiometrie oder Meßkunst chemischer Elemente", that is, Principles of Stoichiometry or Art of Measuring Chemical Elements one can read the following: "Because the mathematical part of chemistry . . . discusses the volume proportions of indivisible substances, I could not find a shorter and more appropriate name for it than the word Stoichiometry, from the Greek stocheion which means something like indivisible, and metreion which means the search for proportions."

Richter was an officer in the Prussian army, but was dismissed for disciplinary reasons. He then matriculated at the Königsberg University, where at that time Immanuel Kant held a professorship. This was, in fact, the moment when Kant declared that any science is a science to the extent it uses mathematics. Obviously, Kant did not simply make this enunciation, but looked around and saw what happened at the time in sciences.

The past 70 years had been the glorious period of mathematics. Innumerable new methods of higher mathematics had been developed, including differential and integral calculus finding rapid and successful application in physics, mechanics and astronomy. In these sciences, phenomena were being described more and more in the language of mathematics.

With this declaration, Kant implanted an inferiority complex into chemists, for lack of sufficient mathematics in their science. In fact, this complex keeps on up to the present. Since phenomena in chemistry can never be described by such elegant equations as in physics, we always have to toil for our equations, we have to fight them out. Our equations — including those of analytical chemistry — are never as beautifully simple as those of the physicists, but are full of individual factors, higher and fractional exponents, and are usually valid only for idealized cases never encountered in practice. To be sure, present-time papers on analytical chemistry frequently make the same mistake as Richter did: at all costs they construct mathematics to the given phenomenon, and even more than required by the case.

Richter, having listened to his professor's declaration, decided to place chemistry on mathematical foundations. This is already reflected in the title of his Ph. D. thesis: "De usu matheseos in chemia."

His starting point, a flash of genius, was the recognition that the reaction of neutral salts always yields neutral salts. Hence, if the composition of the initial salts is known, the composition of the reaction products will follow from it.

Later, Berzelius was one of the few who read Richter's book. The above thesis he termed law of neutrality had a great effect on him, and he appreciated it in his book. However, Berzelius read a great deal for his book, so that when he began to write it, he could not quite remember who wrote what. He attribut-

ed the law of neutrality by mistake to Wenzel, a contemporary of Richter, who also wrote a book at about the same time. Berzelius's book was read by many, so that Wenzel was praised for 150 years by the historians of chemistry for this law. I was much surprised when I read Richter's book and found the mentioned statement in it, while Wenzel's book quoted by Berzelius did not contain anything even faintly similar. It may be of interest that it was I who cut the pages, in 1958, of the copy of Richter's book in the library of the Budapest University. This is to show how little interest this book, appeared in 1792, has evoked.

However, Richter himself was also to blame for this, because he wanted to find more mathematics in chemistry than was right and proper.

He correctly recognized that by determining the composition of salts, values were obtained that he termed mass numbers (corresponding in effect to our equivalent weights), allowing to calculate proportions by weight of chemical reactions. By means of these values, he even formulated reaction equations in a singular manner, but based on correct principles, to express quantitative relationships of chemical reactions. As shown in the figure: the mass numbers constituting the initial salts yield the proportions by weight of the reaction products. For this purpose he experimentally determined the "acid and basic mass numbers" of a great number of salts.

First of all, however, he considered it necessary to acquaint his readers with mathematics. Apparently he did not hold a high opinion of the mathematical knowledge of chemists, since he started right at the beginning, namely: "If a number is added to another number, then the mark + must be placed between them . . . For example  $19 + 424$  means that we add 19 to 424, that is 443 . . .". Subsequently, however, he got through fairly rapidly to quadratic equations. In the next chapters of Vol. 1, he expounds so-called pure stoichiometry. This part contains infinite mathematical deductions over hundreds of pages on hypothetical relationships between density, mass number, affinity etc. I tried hard, but simply could not understand what Richter wanted to achieve with all this. Presumably his contemporaries felt the same way, and put the book aside. However, the valuable notions discussed above follow only in Vol. 2 and 3, dealing with so-called Applied Stoichiometry.

The equivalent weights given by Richter are very incorrect, even as compared to the level of analytical knowledge of the period. If one calculates back from analytical results of his contemporaries, for instance those of Wenzel mentioned earlier, very much better values than Richter's are obtained.

In my opinion, Richter changed his own results arbitrarily, with the intention of establishing a higher relationship. It is not rare that scientists have a cherished concept and wish to confirm it at all costs experimentally. If results do not agree with the concept, they help a bit with the data. Richter expected that his mass numbers will form arithmetic and geometric progres-

sions. He actually obtained what he expected, but to achieve this, experimental data had to be changed. So he presumably changed them, and this is the reason why his equivalent weights are so inaccurate.

None the less, his activity laid down the fundamentals of stoichiometric calculation, of the exact determination of equivalent weights. There was quite a lot of trouble with this word for a long time. Although Cavendish already used the word *equivalent* in 1767, e.g. as follows “as much fixed alkali as was equivalent to 46 grains of calcareous earth”, the term “equivalent

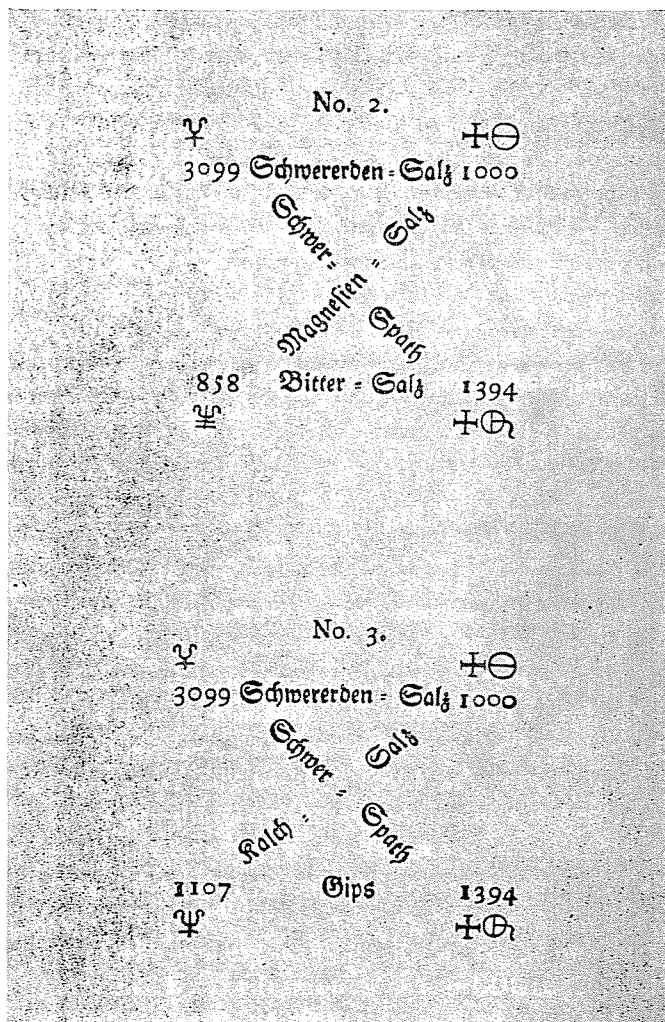


Fig. 2. Quantitative reaction equations from Richters “Anfangsgründe der Stöchiometrie oder Meßkunst chemischer Element” (1792)

weights" in the sense of Richter's concept, as values characterizing individual elements or groups of elements was first used by Wollaston in 1814. Wollaston, similarly to Berzelius, knew Richter's book, at least he had it in his library. Daltons' atomic weights, in contrast, were not derived from analytical practice, but based on theoretical considerations. The two sets of numbers were virtually in opposition for a long time. One of them was considered superfluous, or else the two were considered independent of one another, as seen from Wollaston's paper: "When we estimate the real weights of equivalents, Mr. Dalton conceives that we are estimating the aggregate weights of a given number of atoms, and consequently the proportion which the ultimate single atoms bear to each other . . . I have not been desirous of warping my numbers according to an atomic theory, but have endeavoured to make practical experience my sole guide." The two notions have only been connected when Frankland introduced the valence notion, mainly through Cannizaro's activities (1860).

Meanwhile, more and more titrimetric methods were developed, methods still in use like argentometry, permanganometry, iodometry, chromatometry etc. But the concentrations of the standard solutions were arbitrary, they served solely for a single type of titration, and consumption directly indicated the amount of the substance to be determined, usually expressed in some empirical degree units. Many such degree units existed at that time, water hardness degrees still reminding of those days. In 1843 Andrew Ure, had the brilliant idea to suggest standard solutions which contain atomic weight amounts dissolved in unit volume of the solvent, and can therefore universally be applied. By atomic weight he meant equivalent weight, since in those times terms were frequently confused. The idea was good, but came too early. Although equivalent weights were already fairly unequivocal, volume units were all the less so, least of all in Britain. The metric system was officially accepted and adopted by the majority of the world's countries only in 1876, but analysts — particularly in the Continent — changed to its use already earlier. In 1855, Mohr in Germany again came up with Ure's suggestion as his own idea: "In the titrimetric analysis the various strengths of the standard solution caused a great problem. While the work of the chemists was decreased by titrimetry, the number of bottles in their laboratory increased. Every discoverer of a new method prescribed the use of an entirely arbitrary standard solution. To avoid this, I have introduced a system which forms a unit with the calculation. This system is based on one litre of the solution containing the small atomic weights or one tenth of this expressed in grams of the substance dissolved."

"Small atomic weights" again mean equivalent weights. And since Mohr suggested grams and litres instead of grains and grainmeasures, his proposal was accepted by analysts all over the world.

Thus, calculation was made possible in analytical chemistry, but the

mode of calculation created with so much work only required the good old rule of three, nothing more, no higher mathematics, no higher equations. It conveyed nothing about the causes of analytical phenomena. The precipitate separated, the indicator changed over, but no ideas as to why, how, for what reason could be found in the books on analysis of the period.

No doubt, the situation was not better in other fields of chemistry. General chemistry broke up into special branches which became more and more separated. It appears as if rapidly developing organic chemistry in the second half of the past century would have no relation whatsoever to inorganic chemistry making little headway.

The branches of chemistry had no common grammar. This grammar was born with physical chemistry. Physical chemistry really used higher mathematics. This science developed slowly, from scattered observations partly in the domain of physics with thermodynamics, partly with reaction kinetics developing from the ancient concept of affinity, and partly from the completely novel field of electrochemistry. The latter gave rise to measuring, since electromotive force and conductivity changes could be recorded, and recorded facts allowed to make conclusions.

Wilhelmy, a German pharmacist was the first to describe, in 1850, a chemical reaction by a differential equation. He characterized acid inversion of cane sugar by the  $dz/dt$  equation which later became the general equation of the rate of reaction. Later Ostwald was very proud of this achievement, since — as he said — this was the first time that a chemical process could be expressed in the language of mathematics, thereby raising chemistry as a science to the level of physics. However, for a rather long time to come, the number of chemists who ventured into this field was low. Their majority preferred to make nice new organic syntheses, since biggest chances — and biggest money — could be found in this domain. Waage, professor of chemistry at the Oslo University also developed the law of mass action with the aid of his brother-in-law, the mathematician Guldberg, in 1867. Among their English precursors Harcourt and Esson publishing commonly, the latter was also a mathematician.

Josiah Willard Gibbs who transplanted thermodynamics into chemistry had also studied mathematics. Many others could be cited who stated and derived physicochemical basic laws, but were not chemists.

In 1880, many physicochemical laws existed already, but physical chemistry did not exist. This was probably due to the fact that those who were active in this field were no chemists, they only saw a part of chemistry, but not chemistry as a whole, and hence they could not recognize the application fields of the laws and thereby the relationships. Also, they were unable to deliver their subject in an appropriate expressive form intelligible to chemists. The great synthesis was created practically by one man of genius, the



Baltic German Wilhelm Ostwald. He discovered that the observations and findings of the physicists Kelvin, Clausius, Helmholtz and Gibbs in thermodynamics, those of Wilhelmy, Guldberg and Waage in reaction kinetics, those of Faraday, Hittorf and Kohlrausch in electrochemistry, those of van't Hoff, Arrhenius and many others in the field of solutions could be integrated into a comprehensive entirety allowing to explain most phenomena in chemistry. Ostwald was a brilliant writer and lecturer, an all-round man who was no profound specialist in any detail, but an excellent interpreter of the whole. And since he was not particularly familiar with higher mathematics, he could express everything in a clear and vivid manner intelligible to chemists. In Ostwald's time it appeared that the phenomena of chemistry could be interpreted without any contradiction. In addition, his splendid style was suitable to slide over problems appearing minute. He was an excellent teacher. A great number of future celebrated scientists, further developers of his work studied and worked at his Leipzig University department. To the luck of the new branch of science, Ostwald was a brilliant organizer too. He built the foundations for it with books, lectures and a new journal. I love to read Ostwald. His three-volume, very entertaining biography, for instance, is an important source of science history over a range of fifty years, the work of a man who strongly believed in what he did, so much so that he dared to write ironically about it. He had a subtle sense of irony and self-irony. He was involved in many debates, though not so much the chemist, but the later philosopher Ostwald. Though sharply fighting at first against all nature philosophies, he finally arrived at building up a nature philosophy himself: energetism. He was so much fascinated by the superb deductions of thermodynamics that he conceived energy to be some sort of a mystical protoproperty, so that the laws of energy — according to Ostwald — are suitable to explain social, cultural and even emotional phenomena. The titles of his books on philosophy are very characteristic: *Energetical Imperatives*, *Energetic Fundamentals of Cultural History*. His celebrated happiness equation is

$$G = k(E + W) (E - W)$$

where  $G$  is the amount of happiness sense,  $E$  is the sum of energies directed by the will,  $W$  is the energy used up for experiences opposing the will, i.e. the sum of the energies used for overcoming obstacles, while  $k$  is a factor for energetical-physical transitions which is dependent on the individual. Thus, the "happiness equation" is similar to many other scientific equations, insofar as it contains a factor that cannot be determined.

Ostwald fought with the obsession of an apostle for his philosophy termed "energetism". He even gave up his university department to consecrate

all his "energies" to the propagation of his philosophy, but he achieved little success. Lenin discarded his doctrine as being idealistic, while idealistic philosophers branded him as a materialist.

On the other hand, physical chemistry spread with great success, so much so that Ostwald could afford to joke about it. He was once asked what his new branch of science, physical chemistry really was. He replied: Physicists perform highly accurate measurements with very poor materials. Chemists measure inaccurately with high-purity materials. Physical chemistry reaches its conclusions by adopting poor materials from physics and inaccurate measurement from chemistry.

After having introduced his physico-chemical concept into general chemistry, he turned to the phenomena of analytical chemistry. By applying the law of mass action to Arrhenius's theory of acid-base dissociation, he established the concept of dissociation constants of acids and bases which he successfully applied in various fields: he calculated the ion product of water, and based on all these concepts he set up his indicator theory. On these fundamentals he was able to interpret acid-base processes, neutralization, hydrolysis, the behaviour of multivalent acids. To interpret gravimetric analysis, he again started from equilibrium laws, introducing the concept of the solubility product, which allowed to explain all phenomena in this field. Later, all this could analogously be applied to the formation process of co-ordination compounds.

Ostwald disclosed all these achievements together in a book comprising only 187 pages that appeared in 1894 under the title "Die wissenschaftlichen Grundlagen der analytischen Chemie", that is, *The Scientific Fundamentals of Analytical Chemistry*. Let me cite from the foreword: "analytical chemistry .. plays a very important role among the applications of scientific chemistry . . . It is a measure of its importance that it has been used since the earliest times and has thus collected almost all the scientific observations of quantitative chemistry. It is deplorable, however, that while the technique of analytical chemistry stands on a very high level, its scientific treatment is almost completely neglected . . . We have now, however, reached the stage where the phenomena of analytical chemistry can be examined in a scientific manner."

In the first part of the book, discussing analytical operations, he expounds the new definitions and concepts. Let me quote for instance from the chapter *Precipitation*:

"The object of the analyst is to develop such circumstances in the solution so that the solubility of the precipitate is decreased as much as possible . . . This can be reached by low temperature or by the addition of solvents which decrease the solubility. The solubility of a precipitate which is an electrolyte can be considerably decreased by the addition of a soluble electrolyte which has a common ion with the precipitate.

In the saturated aqueous solution of an electrolyte a complicated equilibrium is set up. The solid substance is in equilibrium with the undissociated substance in the solution, and this in turn is in equilibrium with the dissociated parts, i.e. with the ions. The first equilibrium is governed by the relative concentrations, mentioned previously, and as the concentration of the solid substance is constant, then the concentration of the undissociated part in the solution must also be fairly constant. In the second equilibrium for the most common case, i.e. dissociation to give monovalent ions, then if the concentrations of the ions are  $a$  and  $b$ , while that of the undissociated part is  $c$ , then:

$$ab = kc.$$

As  $c$  is constant at a given temperature, both the product  $kc$  and  $ab$  are constant. Therefore between the solid substance and the solution above it an equilibrium exists so that the product of the concentrations of the two ions has a definite value. This product can be referred to as the solubility product . . . In certain cases where the solubility product of a solid substance in solution is exceeded, super-saturation results. In cases where the solubility product is not reached, the solution will dissolve part of the solid material. This is very briefly the basis of the theory of precipitation . . .

The aim of the analyst is always to achieve the precipitation of a given ion. Barium sulphate is precipitated either for the determination of  $\text{SO}_4$  ions, when an exactly equivalent amount of barium salt is added, an amount of the  $\text{SO}_4$  ions remains in solution, this amount being equal to the  $\text{Ba}^{2+}$  ions formed from the solubility product equilibrium. If further amounts of barium salt are added, then one factor in the solubility product equation will increase, resulting in a decrease in the  $\text{SO}_4$  concentration, so that more barium sulphate will be precipitated. A further addition of barium salt will cause a similar effect; the concentration of  $\text{SO}_4$  ions, however, will never decrease to zero as the concentration of  $\text{Ba}^{2+}$  ions can never reach infinity.

Thus the well-known rule that in a precipitation the precipitant must be present in excess is easily explained. The greater the solubility of the precipitate, the greater is the excess of precipitant required."

In the second part of the book Ostwald deals with the reactions of individual ions and the methods for their determination. This is how the authors of earlier books on analytical chemistry also proceeded. They, however, just described how the determination should be carried out, while Ostwald explains for what reason this or that should be done.

Let me quote a few examples:

"Among the salts of monovalent copper only the halogen compounds are known . . . the iodide is sufficiently insoluble to be used for the determination of copper. If to the copper(II) salt potassium iodide is added, then cuprous

iodide and iodine are liberated:



The reaction does not proceed to completion as reverse reactions may also take place. To shift the position of equilibrium to the right it is necessary for one of the reaction products to be removed. Therefore the addition of sulphurous acid to the solution removes the iodine as it is liberated. This decrease in the concentration of the substances on the right hand side of the equation causes the reaction to go to completion . . .”

“A solution of mercury nitrate gives a precipitate with urea, but a solution of mercury chloride gives no precipitation. In mercury nitrate solution hydrolysis results in sufficient mercury(II) ions being present to exceed the solubility product of the urea complex, whereas in mercury chloride solution the number of mercury ions is very small and no precipitation occurs. Therefore, if mercury nitrate is added to a solution containing chloride ions and urea, no precipitation will occur until sufficient mercury nitrate has been added to combine with all the chloride ions. The first excess above this amount results in the precipitation of the urea complex.”

“The very slight solubility (of barium sulphate) is responsible for the formation of a very finely divided, strongly absorbent solid. This feature results in considerable errors in quantitative determinations. This error can be avoided by the formation of a coarse precipitate, i.e. by precipitating from hot acid solution . . .”

To be sure, the descriptive part is so lax that it is not likely to have given sufficient information to carry out any of the determinations in the laboratory. Obviously, however, this was not Ostwald’s aim, as indicated by the title of the book.

An invention made almost at the same time, in 1893, in Ostwald’s institute, yielded experimental proof for a number of Ostwald’s concepts. I am referring to the hydrogen electrode invented by Max Le Blanc. With its aid, another of Ostwald’s coworkers, his later successor Wilhelm Böttger performed the first potentiometric acid-base titration in 1897. This was theoretically based on the theorem formulated in 1889 by young Nernst, also in Ostwald’s institute, on the electromotive force of galvanic cells, which he soon extended to characterize potential differences arising between solutions having different concentrations. Thereby potentiometric titrations became feasible. In this rare case, theory actually preceded practice. The Nernst equation came first, and was subsequently followed by titration. Nernst expounded his theory only for solutions containing hydrogen ions. A further Ostwald pupil, Peters applied the Nernst equation to oxidation-reduction systems in the form as it is known up to the present. It gave rise to the definition of the

standard oxidation–reduction potential, allowing to extend the acid–base theories to the total oxidation–reduction range. Crotogino, in 1900, performed the first potentiometric oxidation–reduction titration, using a platinum electrode. To my regret, I was unable to find any data concerning the lives of either Peters or Crotogino.

From the differences in indicator change-over, the attention of Szily and Friedenthal was attracted to the significance of hydrogen ion concentration. In 1903 to 1905 they developed colorimetric methods for its determination, and invented synthetic buffer solutions. Salm, a German scientist, was the first, in 1907, to theoretically calculate the equivalence points of acid–base titrations using dissociation constants. Hildebrand, in the U.S.A., studied the theory of titration curves in 1913. Noyes, also an American, set up the well-known equations for the equivalence points of acids and bases of various strengths. Finally, Bjerrum, in Denmark, bringing to perfection and synthesizing the work of his predecessors, published the first scientific book on titrimetry entitled “Die Theorie der alkalimetrischen und acidimetrischen Titraktionen”, that is, *The Theory of Alkalimetric and Acidimetric Titrations*, in 1915. Proceeding in an analogous manner it was not difficult to develop the theory of oxidation–reduction, precipitation and complex titrations. In this context the names of Michaelis, Clark and Kolthoff should be mentioned.

Ostwald’s physical chemistry brilliantly succeeded in explaining classical and electroanalytical phenomena, but could not deal with optical methods.

However, colorimetry already existed in the first half of the 19th century, and emission and absorption spectral analysis proved successful for analytical purposes since 1860, the former mainly as qualitative method, the latter as quantitative method too.

Ostwald did not believe in the atom. In his opinion, the hypothesis of the atom was a remainder of some ancient mythical nature philosophy, and quite unnecessary.

In fact, the atom was just a hypothesis for thousands of years. To Ostwald’s bad luck, it first made its real appearance in the form of radioactivity, when Ostwald went to war against it. The battle ended in a draw. Ostwald had to admit the existence of elementary particles, the atom, however, turned out not to be a final particle, but a structure of smaller particles. Structure of matter, which up till then was lacking, now became a fundamental chapter in physical chemistry, suitable to explain the phenomena of optical analysis, and developing into ever more refined forms, as progress is achieved in the cognition of the fine structure of matter, this progress relying, above all, on investigations of similar phenomena. I believe this path is infinite. The theory of optical analysis is no applied physical chemistry any more, it is structure of matter itself.

It goes without saying that in this field again, physicists were the pioneers.

However, analytical chemists always briskly followed in their track. This agility always was typical for analytical chemistry. Whenever anything turned up and discussions were still going on what it really was, it was already utilized for determinations, for analytical studies. Let me just mention X-ray fluorescence, neutron activation, ESR, NMR, and lately Mössbauer methods. Chromatography was successfully used for separations when its theory was still practically non-existent.

The great historic merit of analytical chemistry consists in its shockingly audacious irresponsibility with which it grasps and utilizes for measurement such novel phenomena that still have no scientific background. I think that this is why it appears justified even at the present time to call analytical chemistry an art as it formerly was called. In fact, art is characterized by intuition, and intuition is what our predecessors have always resorted to, and to which we also resort.

### Summary

For a long time the qualitative assaying of industrial and agricultural products was sufficiently performed only by the organs of sense and practical experience, although for some special cases, e.g. gold, qualitative and quantitative analytical methods were available even in the old epochs. The word "chemical analysis" was found firstly by Robert Boyle, but it became commonly used only in the 19th century. Till that time this kind of knowledge was called "ars probandi" (art of assaying). In the 17-18th century the qualitative and gravimetric methods were developed in order to become acquainted first of all with the minerals, ores and mineral waters. At the end of the 18th century the titrimetric methods gained importance in the textile industry, where they served the purpose of qualitative testing of textile ingredients. In titrimetry absolute values were not calculated but only arbitrary empirical values were determined. For long the gravimetric method has consisted of the metal measurement of the component to be determined, although Marggraf referred to the fact that the quantity of silver can be calculated from the silver chloride. Bergman summarized in a table that how many measurable part of precipitate can be formed 100 parts of each individual metal. The pioneer of stoichiometric calculation and even of the word "stoichiometry" was Jeremiah Benjamin Richter about 1790. He determined analytical equivalent weights, but quite inaccurately. However, the word equivalent weight was used firstly by Wollaston, who in 1814—1816 published the first book including logarithmic analytical calculations and issued the first slide-rule. The titrimetric standard solutions containing the equivalent weights were suggested by Andrew Ure for general usage (1839), but they became wide-spread only after introduction and extension of the meter system, chiefly owing to Friedrich Mohr's activity (1856).

In the last century analytical chemistry was entirely a descriptive science, producing only formulas, while nothing was known of the reasons of phenomena.

The observations performed in the field of electrochemistry, affinity and examination of solutions were gathered by Wilhelm Ostwald who by this established a new independent branch of science, the physical chemistry, which became a common "grammar" of the different fields of chemistry. With this discipline he was the first to give a theoretical explanation to several phenomena in analytical chemistry, e.i. precipitate forming, indicator change, end-point titrations. He introduced the concepts of solubility product and dissociation constant. His fundamental book entitled "Die wissenschaftlichen Grundlagen der analytischen Chemie" was published in 1894. Only one year later it was issued in several other languages, such like English and Hungarian, too. The discovery of the hydrogen electrode and the potentiometric titration greatly contributed to the further development of the theory of titrations. At the beginning of our century Szily, Friedenthal, Soerensen, Salm, Noyes and Bjerrum have out-

standing merits in the more detailed elaboration of the theory of acid-base titrations, while the redox titrations are mainly owed to Peters, Clark, Michaelis and Kolthoff.

Although the analytical methods of absorption and emission optics have already been used since the middle of the last century, however, their theoretical explanation was given only after having got acquainted with the atomic structure.

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