

EARLY EMINENT ENGLISH CONTRIBUTIONS TO THE DEVELOPMENT OF ANALYTICAL CHEMISTRY FROM BOYLE TO URE*

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Let me present a short survey of all that was accomplished by British chemists in analytical chemistry from the Middle Ages up to 100 years ago when the Society for Analytical Chemistry was established. It is, however, a very difficult task, because Great Britain is one of the four countries that have contributed most of all to progress in analytical chemistry. Thus the limit of my survey will therefore be restricted to achievements of world-wide importance.

You often meet views saying that this or that personage is the founder of a certain branch of science. Thus, ROBERT BOYLE is frequently referred to as the founder of analytical chemistry. Indeed, the first British man named in my book entitled *History of Analytical Chemistry* [1] is ROBERT BOYLE. His merits in our science are tremendous. And yet, every scientist continues where his foregoers had stopped. In my book, for instance, I wrote that ROBERT BOYLE was the first (in 1685) to use indicators, and to characterize acids and bases by their colour. He wrote: "Acids change the colour of a number of plant extracts, they replace the colour of the same plant fluids changed by alkalis, extracts which have previously been changed with alkalis and they lose their corrosive properties by unification with alkalis." Since then, I found out that indicators had been used already before Boyle. Luckily, these earlier data are also British. EDWARD JORDAN (1569–1632), in his book entitled *Discourse of Natural Bathes and Mineral Waters* (1631), wrote the following: "Whereby those mineral substances are stricken down from their concrete juices which held them, by addition of some opposite substance. And this is of two sorts: either salts, as tartar, soap, ashes, kelps, vrine etc. Or sour juices as vinegar, oil of vitriol etc. In which I have observed that the salts are proper to blue colours and the other to red; for example, take a piece of scarlet cloth, and wet it in oil of tartar and it presently becomes blue: dip it again in oil of vitriol and it becomes red again." ROBERT WITTY, in his book

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written in 1660, mentions the colour changes of syrup of violets, spirit of harts horn and brasil wood extract. Presumably, other British books on studies of water written at that time contain similar data. Thus, British analysts made use of indicators for detecting certain compounds already before Boyle. However, it remains Boyle's merit that, based on these observations, he defined the concepts acid and base. This is an impressive example for what has been said before: in science, everybody attains new recognitions by utilizing the work of his foregoers.

Anyhow, even if Boyle is not the father of analytical chemistry, he certainly is its godfather. I first met the expression "chymical analysis", in the sense that we know it today, in the works of Boyle. It was Boyle who first made use of hydrogen sulphide. In his book entitled *Memoirs of a Natural History of Mineral Waters*, he described the preparation of "volatile sulphureous spirit". He melted flowers of sulphur and potash and distilled the mixture with an aqueous solution of ammonium chloride. I repeated his experiment. As was to be expected, hydrogen sulphide was formed. Boyle used hydrogen sulphide to detect lead and tin in water. He stated that the former yielded a black precipitate, and the latter a yellowish one. It is interesting to note that after Boyle, the use of hydrogen sulphide fell into oblivion, so that this reagent was rediscovered only at the end of the 18th century by the Frenchman ROUELLE. Later Boyle spent a great deal of work attempting to find a reagent to test poisonous arsenic. With hydrogen sulphide, he obtained no precipitate, because he had diluted his stock solution with alkaline mineral water. He found sublimate to be a good reagent for arsenic.

Boyle made an attempt to measure the limit of detection of several reactions. For instance, he added one drop of hydrochloric acid to increasing amounts of distilled water, then added one drop of a silver solution and observed whether the formation of a precipitate was visible. Citing his own words: "... one grain of spirit of salt had a manifest operation, tho' not quite so conspicuous as the former, upon above three thousand grains of saltless water ..."

Another of his important achievements was the design of a hydrostatic balance for determining the density of liquids.

In the 18th century, the blow-pipe was an important instrument of ore analysis. The discovery of many metals is the result of its application. It is interesting that although the state of development of metallurgy was highest in Great Britain, less memories of the use of blow-pipes for analysis have survived in this country than on the continent. This might be the reason why less elements were discovered at that period in Great Britain than, for instance, in Sweden or Germany. Among metals, only titanium was discovered in Great Britain (by GREGOR in 1791), and CRAWFORD recognized strontium as a new earth. In the first years of the 19th century, however, WOLLASTON

and TENNANT rapidly made up for this lag, by their discovery of the platinum metals. This was then followed by the series of alkali and alkali earth metals prepared electrolytically by DAVY.

On the other hand, British scientists deserved much credit in the 18th century for their gas studies. It is very interesting how many British researchers were attracted by this new field. Maybe, because there were so many breweries where large amounts of gas were evolved. The discoveries, in Great Britain, of the gaseous elements oxygen, hydrogen and nitrogen brought about the great turning-point in chemistry during the last decade of the 18th century — though, as a matter of fact, in France. The successes in the discovery of gases were due to the invention of the basic instruments of gas analysis.

The first gasometers were designed by BOYLE, WREN and MAYOW. HALES first succeeded in collecting gases separately from their place of evolution. The principle of the apparatus for gas development most currently in use in laboratories up to our days is linked with the name of PETER WOULFE (1767). This apparatus was later improved by GRIFFIN. CAVENDISH invented the eudiometer. The scientific achievements of BLACK, PRIESTLEY and CAVENDISH are common knowledge. Their activities form one of the most significant chapters of the history of universal chemistry. One of the factors that contributed to their success was their remarkable sense for analysis. In particular, CAVENDISH remained unmatched for a long time in the accuracy of measurements of gas compositions and densities, as demonstrated by the discovery of argon 100 years later, by RAMSAY. It is generally known that Cavendish's experiment gave the clue for this discovery. CAVENDISH converted a mixture of nitrogen and oxygen into nitrogen oxide by means of an electric spark. He then removed excess oxygen with liver of sulphur. In his paper, he mentioned that a small bubble, the 120th part of the initial nitrogen volume, was always left over. What a marvellously exact observation! When RALEIGH, in 1894, stated that a small difference between the densities of nitrogen obtained from air and from ammonia, respectively, is always observed, RAMSAY remembered CAVENDISH's bubble and concluded that some other substance must be present in atmospheric nitrogen.

The statement that CAVENDISH got as far as the determination of analytical equivalent weights is met rather frequently. However, this is not true, though he actually did use the word "equivalent". It was MAXWELL, arranging Cavendish's posthumous papers, who gave his results this additional interpretation. Of course, CAVENDISH was a good analyst, and you can always calculate equivalent weights from good analytical results, but obviously only if you know the stoichiometry.

However, the first logarithmic table of analytical equivalent weights, intended for researchers and industrial chemists, was published by the Englishman WOLLASTON in 1814. As a matter of fact, this publication further in-

creased the confusion that arose after DALTON from mixing up the concepts of atomic weight and molecular weight. This was all the more so because the values given by WOLLASTON were correct equivalent weights in some cases and atomic weights in other cases. He wrote: "I have not been desirous of warping my numbers according to an atomic theory, but have endeavoured to make practical experience my sole guide." WOLLASTON designed the first analytical slide rule in 1816, for the purpose of rapid stoichiometric calculations of analytical results. These slide rules were sold by Newman in Regent Street. It was also WOLLASTON who developed a method for preparing malleable platinum. He dissolved platinum in aqua regia, precipitated it in the form of ammonium chloroplatinate, decomposed the precipitate by heating, pressed the obtained platinum powder and hammered it into an ingot. This process, allowing to manufacture platinum vessels and utensils, was kept secret for a long time. The platinum equipment was sold exclusively by Johnson, Matthey and Co. until 1829. Platinum vessels increased the reliability of ore analyses to a great extent.

The world of minerals became known by means of gravimetry. For a long time, separate tests had to be made to determine the weight of the ash of filter paper. Ash-free filter paper made analysis much easier. This was the invention of AUSTEN, around 1870.

The first specialized manual of analytical chemistry was written by the German chemist LAMPADIUS in 1801. In its introduction he wrote: "For work in all natural sciences persistency is needed, but especially in analytical chemistry . . . Those who cannot wait weeks and months for the results should never begin analytical work . . ." However, already in the 18th century industry could not wait weeks and months. The developing textile industry used potash and sulphuric acid, later hypochlorite for bleaching. Determination of the concentrations of these solutions was very important, since too strong solutions would destroy the fabric. Volumetric analysis came to life in order to perform this task. The prehistory of volumetric analysis is found in Great Britain. The book of Francis HOME, professor in Edinburgh, appeared in Dublin in 1756 under the title *Experiments of Bleaching*. In this book, he proposed the following method for testing potash: "In order to discover what effect acids would have on these ashes and what quantity of the former the latter would destroy, from which I might be able to form some judgment of the quantity and strength of the salt they contained, I took a drachm of blue pearl ashes and poured on it a mixture of one part spirit of nitre and six parts water which I shall always afterwards use and call the acid mixture. An effervescence arose, and, before it was finished, 12 teaspoonfuls of the mixture were required. This effervescence with each spoonful of the acid mixture was violent, but did not last long." This was indeed a true volumetric method: a standard solution, namely nitric acid, an indicator, namely the

effervescence phenomenon, and a burette, namely the teaspoon were used. However, the method yields no absolute result. When less than 12 teaspoonfuls were consumed, the solution was too dilute, when more were consumed, it was too concentrated for bleaching purposes. The first example for an absolute determination is found in W. LEWIS' book that appeared in London, in 1767, entitled *Experiments and Observations on American Potashes with an Easy Method of Determining their Respective Qualities*. He used hydrochloric acid standardized with sodium carbonate. Instead of the teaspoon, he weighed the amount of standard solution consumed. For indicating the end point, however, he already used paper impregnated with lithmus. This is what he wrote: "Pour gradually some of the acid from the vial into the solution of salt of tartar, so long as it continues to raise a strong effervescence: then pour or drop in the acid very cautiously, and after every small addition, stir the mixture well with a glass cane and examine it with the stained papers. So long as it turns the red side of the paper blue, more acid is wanted . . ."

Moreover, an example of precipitation titration is also found in HOME's cited book. He writes: "Let a certain quantity of alkaline salt be dissolved in a certain quantity of soft water. Into a certain quantity of hard water in a glass pour in the solution gradually, so long as the milky colour is on the increase . . . Let the water stand till it becomes pellucid. Try it again with a few drops of solution: if no whiteness arises in the water, it is then soft . . . By this means it is known what quantity of salts is necessary to soften that quantity of water."

KIRWAN, in 1784, first used potassium hexacyanoferrate(II) as a standard solution for the determination of iron.

Further progress in titrimetry then moved to the continent, above all to France, where its apparatus took final shape. Between 1820 and 1850, various substances, in rapid succession, were proposed to prepare standard solutions. Most of these are still being in use. Among these, PENNY, professor at Glasgow University, proposed potassium bichromate as standard solution in 1850, and CLARK, professor at Aberdeen University, recommended soap solution, in 1847, to determine the hardness of water. The results were expressed in Clark degrees of hardness. Degrees of hardness of water have remained in use up to our days, but this is rather unique at present. At that time, however, the results of titration were often given in degrees for other substances too, that is, the concentration of the standard solution corresponded to a particular purpose. The Scotsman ANDREW URE was the first to consider that a chemical unit, namely atomic weight, should be applied as the basis of the concentration of standard solutions. In 1839 he wrote an encyclopedia entitled *Dictionary of Arts, Manufactures and Mines*. In its Appendix, under the heading Alkalimetry, he argues that such a standard solution should be prepared whose unit amount neutralizes just one atomic weight amount of the acid.

In his own words: "1000 grain measures of it neutralize exactly a quantity of any one real acid, denoted by its atomic weight upon either the hydrogen or oxygen scale: as for example 40 grains of sulphuric acid. Hence it becomes a universal acidimeter: after the neutralization of 10 or 100 grains of any acid, the test tube measures expanded being multiplied by the atomic weight of the acid, the product denotes the quantity of it present in 10 or 100 grains."

This was a recognition of high importance that led to the generalization of titrimetry and to the application of the stoichiometric mode of calculation in volumetric analysis. However, this principle was realized only at a later date, in 1855, when FRIEDRICH MOHR, in his celebrated manual *Lehrbuch der Titriermethode*, repeated and systematically applied Ure's suggestion. Presumably Mohr's success was partly due to his use of the decimal metric system. And — although you will perhaps find it difficult to agree — analysts all over the world found metric units more convenient than British units.

The expression "normal solution" in the sense that we use it today was already applied before Mohr, namely by GRIFFIN, Ure's pupil, in 1846. He wrote: "I prepared normal test liquors . . . by dissolving one test atom of the substance in so much water as produces one decigallon of solution at 62 °F."

The first reference to a burette equipped with a tap is found in URE's cited book. However, the tap was not fitted to the lower end of the burette where the liquid runs out, but to its upper end.

The electric current was born in March 1800, when VOLTA, in Pavia, built his first Volta pile. It is quite amazing how rapidly — even by present standards — scientific information spread at that time. Volta wrote a letter to London about his experiment. As early as May of the same year, CARLISLE and NICHOLSON, on the basis of this information, decomposed water, utilizing a Volta pile, and CRUIKSHANKS also stated that under the effect of an electric current, metals will be deposited from their solution on the negative pole. He immediately proposed to utilize this phenomenon for the detection of copper. This was the first analytical application of the electric current. It is surprising that the idea of quantitative electrogravimetric determination of metal was conceived only 60 years later, by the American WOLCOTT GIBBS.

Spectral analysis is connected with the names of BUNSEN and KIRCHHOFF, but this, too, did not come out of nothing. Its prehistory is long, and British scientists played an important part in it. WOLLASTON was the first to observe, in 1802, that the spectrum of the sun is not continuous, but contains lines. TALBOT, one of the inventors of photography, constructed a device, in 1826, for the examination of flame spectra. He dipped a wick into the substance to be examined, and after drying it, he lit it and passed the light from the flame through a slit and a prism, and examined the emergent spectrum on a screen. This was a very primitive spectroscope, but TALBOT succeeded

to distinguish, for instance, strontium from lithium by means of their respective lines. He wrote: "I do not hesitate to state that by optical analysis the smallest amounts of these two substances can be distinguished at least as well, if not better, than by any other methods." Professor MILLER, at King's College in London, described and published in figures the spectra of different inorganic substances in 1845. SWAN, professor of physics at St. Andrew's University, wrote in 1856 that the R line of the spectrum is yielded by sodium, and that, by its means, sodium concentrations as low as 2.5 ppm can be detected. As a matter of fact, reference was made to SWAN in the fundamental paper of KIRCHHOFF and BUNSEN published in 1859. They did not, however, mention their other precursors and were duly blamed for doing so.

One of the pioneers of colorimetric analysis was JOHN HERAPATH in Bristol. He determined iron in 1852 from the colour of iron thiocyanate, by simple visual comparison of the colour, using a colour series containing known amounts of iron.

Herewith, we have arrived at the time when the Society for Analytical Chemistry was established, at the great age of classical chemical analysis, and at the still very modest beginnings of instrumental analysis.

Summary

British achievements in analytical chemistry preceding the establishment of the Society for Analytical Chemistry are reported. In the 17th century works by Jordan and Witty already contain references to indicators. Boyle used them systematically, he was the first to apply hydrogen sulphide, and to introduce the expression "chemical analysis". Pioneers of gas analysis are Hales, Black, Priestley and Cavendish. In the middle of the 18th century, Home and Lewis discovered the volumetric analysis. Ure introduced the use of the standard solutions. The first British scientists dealing with electrogravimetry and spectroscopy are also mentioned.

References

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