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A Short Course on the History of Analytical Chemistry and the Related Sciences

There is no doubt that the keeping-up with advances in techniques, processes, and instrumentation is an ever-increasing problem in the teaching of almost any branch of science. Because of the more-or-less inflexible maximum imposed upon allotted hours, the inclusion of the new inevitably requires the rejection of more and more of the traditional. In some respects this is good, because it offsets natural tendencies to cling to the well-established. However, it is easy to over-react to this tendency, thereby sacrificing traditional material that is really educative. In any case, the historical aspects of science seem to be suffering the most.

Apart from minimizing the risk of presenting a distorted perspective of science, the inclusion of a modest survey of the past can provide guidelines for the future. Fundamental discoveries sometimes take a long time to become exploited fully. Oft-quoted examples are the powerful techniques of coulometric titration and of controlled-potential coulometry, the groundwork for which lies in the laws of electrolysis formulated more than a century earlier by Faraday. A piece of his apparatus is shown in Figure 1. The presently preeminent techniques of chromatography took an amazingly long time to emerge from their quite humble beginnings. Although a wider appreciation of the history of science would not eliminate such delays, these should be lessened by such an appreciation.

Quite early in the study of the practical aspects of the history of science, two phenomena of the past become increasingly apparent. One is the accuracy achieved by our scientific ancestors with their often very limited facilities and simple equipment. The other is the beautiful workmanship of many of the early instrument makers.

Figure 1. Voltammeter (coulometer) used by Faraday (by permission of the Director, Royal Institution of Great Britain).

The term "short course" in the title of this paper needs a little explanation. As actually given, the course extends over an entire 14-week semester. However, only one credit is awarded, because there is only one 50-minute meeting per week. Obviously, the "shortness" could be real if meetings were more frequent. In our particular program, we have this type of "special topics" course that may be taken for credit more than once. This is reasonable, because both instructor and topic change every semester. Occasionally, the course will deal with the contents of a series of current papers, but usually a single topic is chosen. Examples of such topics are mechanisms of electrode reactions, aspects of the design of analytical instruments, and chromatographic detectors. Although this type of course carries a graduate number, it is not unusual to have several Honors undergraduates as participants.

Included in the description of this particular "special topic" is a statement that the treatment will lean towards the history of apparatus and techniques. However no course of this kind can be given without adequate reference to the makers of science and the backgrounds to their working conditions. Limited class time necessitates considerable individual reading. This is not limited to the "recommended text" (*1*), but includes more general works (*2–4*), as well as original papers.

The treatment of events before approximately 1750 is, in general, very limited, so that students have to "fill in" right from the start. However, enough is said to indicate that operations that are recognizably "analytical" were going on several thousand years ago. The phlogiston period is given modest treatment. Here we have a classic example of a "wrong" theory that served as a useful guideline for the development of chemistry.

Lack of time permits only scanty treatment of qualitative analysis, but care is taken not to "undersell" it. The activities of Joseph Black, Joseph Priestley, and Henry Cavendish are among those outlined in order to introduce gravimetry, gas analysis, and, in the case of Cavendish, refined measurements made in these early times. Then follows the first real plunge into instrumentation—the development of the precision balance (*5–7*).

The theme next taken up is the determination of atomic weights. Berzelius and Stas naturally figure largely here. The treatment then blossoms into a miniature "portrait of a scientist," who in this case is Theodore William Richards (1868–1928), and the devices (Fig. 2) and techniques that he introduced (*8*). This, with an indication of the work carried

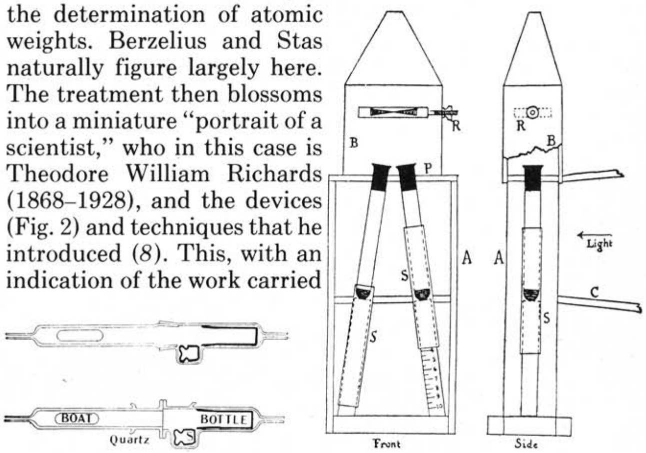

Figure 2. Apparatus devized by Richards (a) bottling apparatus (b) nephelometer.

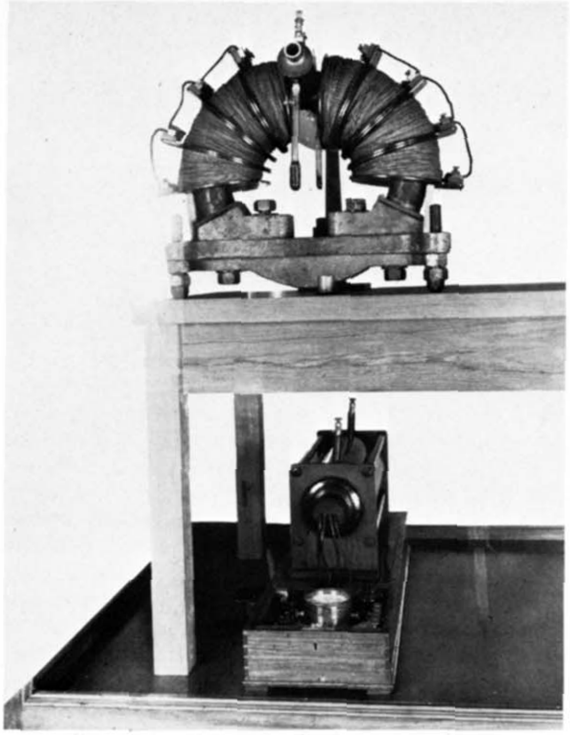

Figure 3. Aston's first mass spectrograph (by permission of the Director, Science Museum, London).

out by such notable associates as Baxter and Hönigschmidt, serves to illustrate the apotheosis of classical quantitative analysis.

Before anyone can comment that modern atomic weights are based on mass spectrometry, a switch is made to this subject. Entry is by an indication of the phenomenon of electrical discharge through gases, when Michael Faraday is mentioned for the first time (the "dark space"). Eventually, this leads to Thomson's positive ray apparatus, the concept of isotopes, and to Aston's first mass spectograph (Fig. 3) which is now in the London Science Museum. Naturally, other courses give specific instruction in mass spectrography, so the "history" stops with an indication of the contributions made by American workers such as Dempster and Bainbridge.

Volumetric analysis is introduced by a thumbnail sketch of industrial chemistry in the 1750's—sulfuric acid, "potash," washing soda, bleach liquor, etc. Gravimetric processes were too slow for control purposes and too difficult for the unskilled. Joseph Louis Gay-Lussac (1778–1850) is one of the workers introduced at this stage. His apparatus, that of workers such as François Antoine Henry Descroizilles (1751–1825), and the stopcock burets of Friedrich Mohr (1806–1879) naturally receive attention. However the members of the class are not historians but aim to become practicing chemists. Therefore the item shown in Figure 4 is considered relevant. This is an electromagnetically operated buret valve described in 1928 (*9*). Actually, the treatment of volumetric analysis ends with a comment that *automatic* titrations, useful in routine analyses, date back more than 60 years (*10*).

One cannot conduct electroanalytical measurements without electrical measuring instruments. Many of these are electromagnetic in nature. Electrical and magnetic phenomena have been recognized since ancient times, but our knowledge of the interrelationships of these phenomena is of much more recent origin. The breakthrough was the discovery made by Hans Christian Oersted (1777–1851), during a lecture given in the winter of 1819–1820.

Students are painfully aware of the almost explosive present-day growth of scientific knowledge. They may not realize that such "explosions" have occurred in the past. Only a few weeks after Oersted had announced his discovery, André Marie Ampère (1775–1836) produced the first of his rapidly succeeding series of papers that enunicate much of our understanding of electromagnetic effects. Within approximately one year, at least three independent workers had found a way to convert Oersted's simple device into a quite sensitive detector of an electric current (*11*). At the same time, Faraday produced what is really the first electric motor (*12*). Shortly afterwards, we have the discovery of the thermoelectric effect and the establishment of Ohm's law.

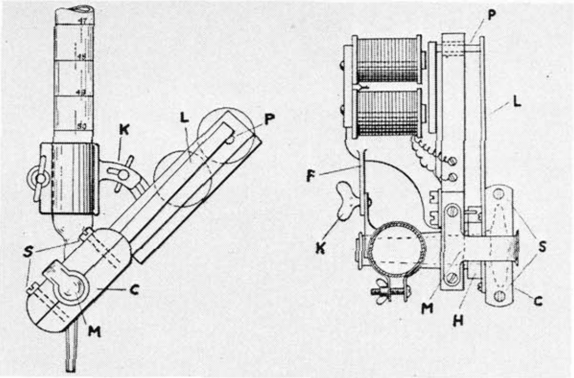

Figure 4. Early electromagnetic buret valve.

Although the contributions by American scientists to modern electrical instrumentation are fully recognized, it is easy to overlook the ideas of their scientific ancestors. In the Obach galvanometer, variable sensitivity was achieved by tilting out of the vertical the coil that deflected the magnetic needle (*13*). Actually, this principle was described several years earlier by the Harvard scientist John Trowbridge (*14*). The beginnings of the moving-coil galvanometer, usually attributed to D'Arsonval, are envisaged in the simple instrument shown in Figure 5. This was described in 1838 by Charles G. Page (*15*). Several other galvanometers were also developed by Page, who was Professor of Chemistry and Pharmacy at Columbian College, Washington, D.C. (now George Washington University).

Because the concept of electrode potentials underlies so much of electroanalytical chemistry, comments on potentiometry open the study of this field of analysis. A point made is that although the glass electrode was devised in 1909, 30

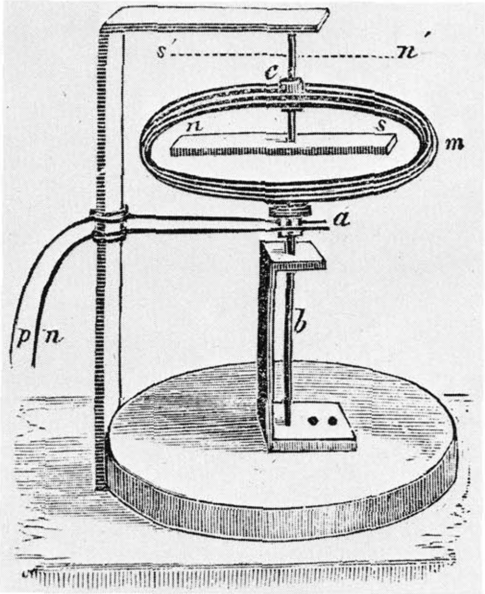

Figure 5. Page's moving-coil "galvanometer."

Figure 6. Henry J. S. Sand (1873–1944), (Courtesy, D. W. Wilson.)

years or more elapsed before this pH-measuring device became a common laboratory object. We had to wait for the development of reasonably inexpensive and reliable electronics!

As an introduction to conductometry, Cavendish's experiments of 1776 are pointed out. His method involved making adjustments until two successive electric shocks were judged to be of equal intensity. Yet Cavendish's results are within 15% of present-day values! The extensive use of conductometry in monitoring the purity of water and, in particular, in studies in nonaqueous systems is used to indicate that our oldest electroanalytical technique is by no means obsolete!

The roots of electrogravimetry lie in such events as the electrolysis of water, by Nicholson and Carlisle, in 1800, and in the isolation of potassium and other highly reactive metals, by Davy in 1808. However, the first real electrogravimetric determinations were not made until the early 1860's, by Wolcott Gibbs, later Professor at Harvard and, independently, by C. Luckow, a German industrial chemist. The many contributions to electroanalytical chemistry made by H. J. Sand (Fig. 6) include controlled-potential electrolysis. This survey leads on to the invention, by A. Hickling in 1942, of the potentiostat. Natural follow-on topics are controlled-potential coulometry and coulometric titration. Here one cannot do much better than to amplify the remark made near the beginning of this paper: "Faraday's laws of electrolysis, 1834; put to systematic analytical use, 1939."

Current-potential curves had been plotted long before Jaroslav Heyrovsky's time. However, his invention of polarography in the early 1920's gave the analytical chemist a valuable new tool and eventually gained the inventor the Nobel Prize for Chemistry (*16*). He also invented the technique now known as amperometric titration, but the development of the technique occurred largely in this country, especially in the University of Minnesota laboratories of Izaak M. Kolthoff, now Emeritus Professor.

Optical methods are extensively studied in our regular curricula, so that treatment here is rather limited. An account of the discovery of basic principles is followed by brief surveys of emission methods up to the work of Bunsen and Kirchoff, and of absorption methods as illustrated by colorimetry. However, the role of advances in instrumentation does not escape some mention. The modern spectrophotometer is one of the analyst's most versatile tools. Refractometry is particularly valuable for monitoring flowing systems, including those involved in liquid chromatography (*17*).

In the program actually described, we run out of time around this stage. Obviously, there are large areas of analytical chemistry available for exploration. Examples are separation methods, especially chromatography, microchemical techniques, on-line instrumentation (which might even include a thumbnail sketch of the development of the computer from or before the time of Charles Babbage), organic ultimate analysis, and radiochemical methods. Some coverage can be provided by assigned reading and by the preparation of term papers. In any case, a course of this kind is never repeated slavishly, so that at least one or more of the "omitted topics" is certain to get in at each time around.

Literature Cited

(1) Szabadváry, F., "History of Analytical Chemistry," Pergamon Press, Long Island City, N.Y., **1966.**

(2) Idhe, A. J., "The Development of Modern Chemistry," Harper and Row, New York, **1964.**

(3) Leicester, H. M., "The Historical Background of Chemistry," John Wiley & Sons, New York, **1956.**

(4) Partington, J. R., "A Short History of Chemistry," 3rd Ed., MacMillan & Co., New York, **1957.**

(5) Stock, J. T., J. CHEM. EDUC., **45,** 254 (1968).

(6) Stock, J. T., "Development of the Chemical Balance," Science Museum, London, **1969** (Pendragon House, Inc., Palo Alto, Calif. 94303).

(7) Stock, J. T., *Anal. Chem.*, **45,** 974A (1973).

(8) Hartley, H., *J. Chem. Soc.*, **1930,** 1937.

(9) Mueller, R. H., and Partridge, H. M., *Ind. Eng. Chem.*, **20,** 423 (1928).

(10) Lingane, J. J., "Electroanalytical Chemistry," 2nd Ed., Interscience Publishers, Inc., New York, **1958,** p. 158.

(11) Stock, J. T., J. CHEM. EDUC., **53,** 29 (1976).

(12) King, R., "Michael Faraday of the Royal Institution," Royal Institution, London, **1973,** Figure 8.

(13) Obach, E., *Nature*, **18,** 707 (1878).

(14) Trowbridge, J., *Amer. J. Sci. and Arts*, 3rd series, **2,** 118 (1871).

(15) Page, C. G., *Amer. J. Sci. and Arts*, 1st series, **33,** 376 (1838).

(16) Zuman, P., and Elving, P. J., J. CHEM. EDUC., **37,** 562 (1960).

(17) Maley, L. E., J. CHEM. EDUC., **45,** A467 (1968).