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Historic Chemical Instrumentation: From the Cellar Upwards

John T. Stock, University of Connecticut

To begin this address, I need to offer both thanks and an apology. My thanks are to my fellow members of the Division of the History of Chemistry and to the Dexter Corporation, for granting me the 1992 Dexter Award. The apology is simply because I cannot hope to reach the level of erudition of the addresses given by many earlier awardees. My account is merely of my progress towards some understanding of the history of chemistry, especially of its instrumentation.

Becoming a Chemist

When I was about eight years old a neighbor, who was taking his son to the London Science Museum, invited me to join them. We youngsters rushed from exhibit to exhibit, pushing all the buttons that we could find. I had never seen anything like this! At once, I pestered my mother to make many other visits; unaccompanied kids were not exactly welcome in those days. Inevitably, the wardens found her a chair in some quiet corner, while I vanished, to reappear an hour or so later. I got into the Chemistry Gallery, but was not impressed; at that time, there were showcases with lengthy descriptive cards, but no pushbuttons. All of this left me cold; I knew no chemistry. However, a balance with a long cone-like beam caught my attention and I even read the label. After a few more visits, I resolved to become a scientist. How little did I realize the long and tortuous path that lay ahead! Soon after, another neighbor gave me a few monthly-issued parts of a general encyclopedia. As I read my first article on chemistry, I suddenly felt that I had been here before. This sort of feeling has never occurred again.

My 15th birthday passed, so my classmates and I were soon to finish school. We sat for the Schools Certificate examinations, for which the grading scale was "credit" (a very good pass), "pass," and "fail." I got four credits, but two fails. University entrance required five passes, so I was out of the running. This did not seem to matter very much at the time; we were anything but wealthy, so I looked for a job. I could not find any science-related opening, and was finally hired by an accountant partnership. I thought that this was due to my proficiency in arithmetic, but later learned the real reason; I was a teetotaler! The main concern of the business was with licensed premises—pubs, if you like—and I was judged safe to work in the cellars. At least I got to know what goes on behind the bar, as well as underneath it!

After about two years, I took a job in the planning division of a large engineering works. If not exactly scientific, the work certainly involved technology and brought me into close contact with skilled craftsmen. Today, I cannot look at an historic instrument without beginning to visualize how it was made. Before shifting from accounting, I became an evening student at Norwood Technical Institute (now South London College). The fees at institutes like this were very small, sinking to zero if one's attendance had been good. I soon had the run of the laboratories. Although I was awarded both the Ordinary and the Higher National Certificates in Chemistry during the next few years, I still was ineligible to enter a university, even as a part-timer.

Although not very old, the University of London is both large and liberal. Provided that a candidate went through the proper steps and took the examinations, he or she could obtain a degree. Before the War, several

British colleges were unchartered, so their students were examined in London. I believe that Southampton College, now a celebrated university, was one of these. The University of London had realized that some who missed out at school might still make the grade. Thus arose the Special Entrance examinations, open to anyone aged at least 23. I took these examinations as soon as I could and fortunately passed. During my final year at Norwood, I passed the University Intermediate Science examinations and transferred to the Sir John Cass College (now City of London College) which was recognized for degree-level training. Not being able to get time off, I took my annual vacation to coincide with the final examinations, and obtained my bachelor's degree in the summer of 1939. Almost at once, war broke out.

What a change! Anyone professing even a little science was in great demand. I was placed on the National Register and, after many years, my evening studies ended. I was soon on plant control in a wallboarding factory, then moved to a Ministry of Supply establishment in southern England. Initially, we were concerned with possible gas warfare, but later went on to other areas such as smoke screening. With the closing of colleges and the seconding of the faculty, I rubbed elbows with some of the leading scientists of the land. The more fortunate did work that led to post-war publications; with my background, I was assigned to "technical chemistry" and engineer liaison. These were polite terms; for example, I spent a good deal of time hanging on to the turret of a tank while it bumped its way across the countryside, duly emitting its smokescreen. When this was based on the vaporization of oil, I was sometimes involved in spectacular fires! Of course we had laboratory work, usually involving highly unpleasant substances or trying to trace the reasons for the failure of a smokescreen.

I shall never forget the kindness of Professor Neil K. Adam, of Southampton College, some 30 miles south of my location. He gave me the run of the College laboratories on Sundays. The College was some two and one half miles from the railroad station, and the streetcars were not running. Fortunately, I like walking. I wanted to study the polarography of quinoline compounds, but had neither recorder nor pH meter. Nevertheless, by point-by-point plotting, I managed to get the curves at one-half pH intervals over the range 1.5 to 12.0 units. Fortunately, I was well acquainted with the vagaries of the hydrogen pH electrode. After more than a year of Sunday work, the writeup was accepted for publication in the *Journal of the Chemical Society* (1).

Then came another switch, to take over the laboratory of a London food factory. With evenings free, I

used the quinoline work and some other studies to compose a thesis, for which I was granted a London master's degree. I also started teaching in the evenings at, of all places, Norwood Technical Institute. The war was nearing its end and educational establishments were beginning to return to their normal activities. I liked teaching, so became full-time at the Institute in the fall of 1946.

With veterans pouring out of the armed services and numerous groups of students from the soon to be independent African colonies, we were overrun. We taught five and a half days a week, plus two or three evenings. My colleagues and I had little time for research, but we developed a lot of simple apparatus and wrote a couple of texts on small-scale laboratory methods (2, 3). One of these ran through five editions. Because we were short of space, equipment, time, and funds, we used small-scale techniques wherever practical. I also began to study the history of some electrochemical techniques (4, 5).

When things quietened down a bit, I managed to keep Fridays free. So I resumed my electrochemical studies in a corner of the Institute and then wrote a thesis which gained me a London Ph.D. I had become head of department and eventually gained an award for overseas study with Professor I. M. Kolthoff at the University of Minnesota. He fixed me with speaking dates across the country when my wife, small daughter, and I were traveling back home. I was surprised to be offered several jobs. I accepted the offer from the University of Connecticut, arrived there in January, 1956, and have been there ever since.

Chemical Balances

Eventually, I introduced a course on the history of chemistry, but unfortunately this lapsed when I became emeritus. I progressively increased my London contacts, especially with the Science Museum. During my 1965 sabbatical leave, I examined the Museum's fine collection of historic balances. Balances were certainly known to the ancient Egyptians. Quite sensitive small balances, needed for trading in gems, coins, and the like, were in use in the 15th century. The demands of the tax collector may have influenced the design of balances. The British Government needed a means to assess the excise duty on spirituous liquors, and the means chosen required the accurate determination of the specific gravities of standard alcohol-water mixtures. This required a sensitive balance capable of handling a quite heavy load. The famous instrument maker Jesse Ramsden (1735-1800) (Fig. 1) fulfilled this requirement. He was fond



Figure 1 Jesse Ramsden (reproduced by permission of the Trustees of the Science Museum, London)

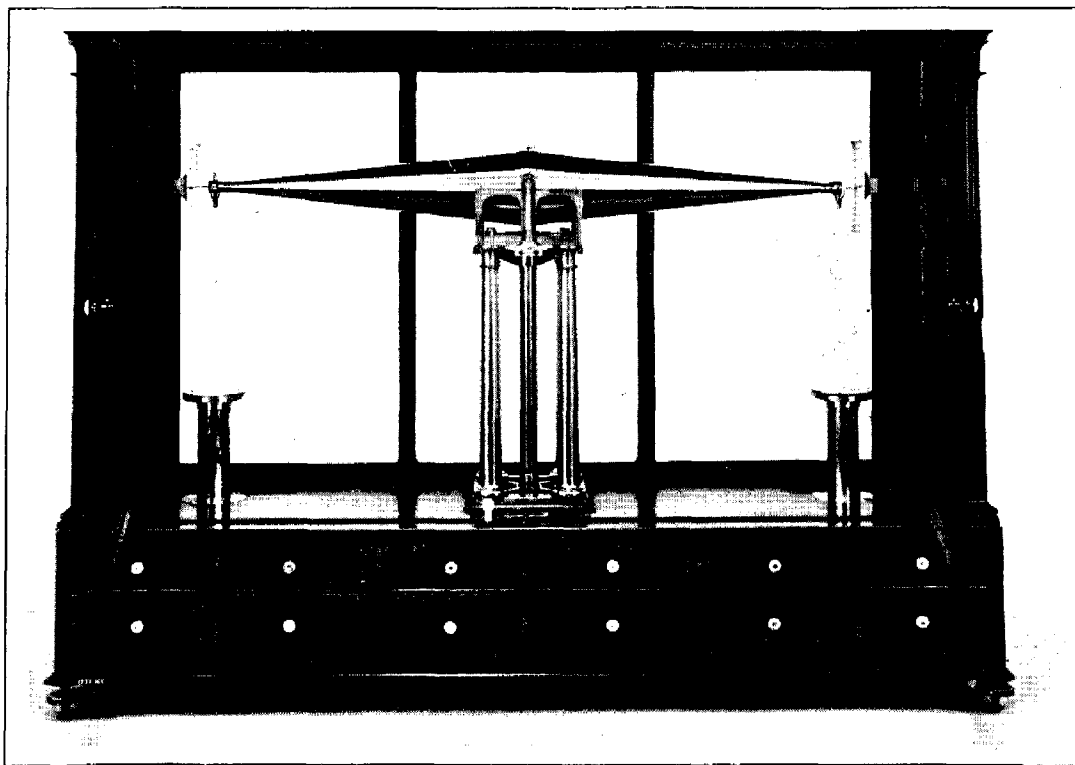


Figure 2 The Ramsden balance (reproduced by permission of the Trustees of the Science Museum, London)

of the rigidity provided by the use of hollow cones; some of these can be seen in the astronomical instrument in the background of his portrait. He made the cone-beam balance shown in Fig. 2 and it was used to make the determinations in 1789. This was the instrument that had caught my eye during my first trip to the Science Museum as a boy. When examined in 1965, the pans were missing, but I reckoned that the sensitivity was better than to one milligram.

Other makers followed Ramsden's design. Actually, the lateral rigidity provided by the cones is quite unnecessary; the beam-bending force is entirely vertical. Hence the triangulated flat beam came into being. A major figure in this development was Thomas Charles Robinson (1792–1841) (6). In 1967, I examined the Robinson balance in the Chemistry Department of the University of Edinburgh. The assumption was that the balance had belonged to Joseph Black (1728–1799). This was, of course, impossible, because the maker was less than ten years old when Black died. A more likely owner was Thomas Charles Hope (1766–1844), Black's successor. This balance, along with a near-copy made by the Scottish firm Adie & Son, is now in the Royal Museum of Scotland.

The intriguing history of the precision balance, described in the Science Museum's account, is too long to go into here (7). I would, however, like to mention a fact and an error. The British standard troy pound was destroyed in a fire of 1834. Three balances, two by Robinson and one by his successor, Henry Barrow (1790–1870), were used in the lengthy work of reestablishment. I know the location of one Robinson balance and the fate of the other. But, after 25 years of searching, I have yet to find the "balance of extreme delicacy, procured from Mr. Barrow" (8). The error concerns the chain balance, in which an adjustable chain eliminates the need for small weights. In company with several others, I had described this type of balance as an American invention of 1916. We now know that the chain principle was introduced in France a quarter of a century earlier (9).

Galvanometers

I had long realized that progress in electrochemistry depended largely on electrical instrumentation. The account by Michael Faraday (1791–1867) of how he made

his own galvanometer intrigued me, so I spent part of my sabbatical leave of 1972 working under Professor Ronald King at the Royal Institution in London. Here Faraday had worked and lived. This was an exciting time, because King was setting up the Faraday Museum in the basement. He suggested that I should write an account of the developments that arose from Faraday's simple instrument.

Around this time, I had been appointed Honorary Research Fellow of the Science Museum and was fully aware of the Museum's outstanding collection of electrical instruments, some on view and some in the Museum stores. Here I must remark that I have seen some interesting instruments in the cellars of various foreign museums. When in Czechoslovakia, I noticed a German copy of an early type of Robinson balance. However, the curator could not tell me how, or when, this had been acquired. In Australia I saw some instruments that had been made locally because of wartime unavailability from overseas. Historic indeed, as examples of instrument-making under stress! However, I must return to the "galvanometer project." After writing a paper or two on limited aspects of current measurement, I joined forces with Denys Vaughan, of the Museum's Department of Physics. It took about ten years of our combined part-time work to get the overall account into print (10).

The siphon recording galvanometer designed by William Thomson (1824–1907), later Lord Kelvin, has always amazed me. It made possible the paper-tape recording of transatlantic telegraph signals. The tiny force available could not possibly drag a pen across paper. Thomson solved the problem by maintaining an imposed potential between the tape and the nearby jet, which moved laterally in response to the incoming signals. Tiny drops of ink were thus projected onto the traveling tape in a frictionless manner. I often wonder if the inventors of the modern ink-jet computer printer were inspired by this device. There is a little electrochemistry associated with the testing of another of Thomson's galvanometers. In 1866, when two cables were working, they were joined at the far end. Thomson transmitted intelligible signals through this total length of 3700 miles, using as a power source a silver thimble containing a little acid and a slip of zinc.

Chemical Automation

Nowadays the automation of laboratory processes is quite common. Attempts to do this are by no means new. I would like to give one example that I noted when

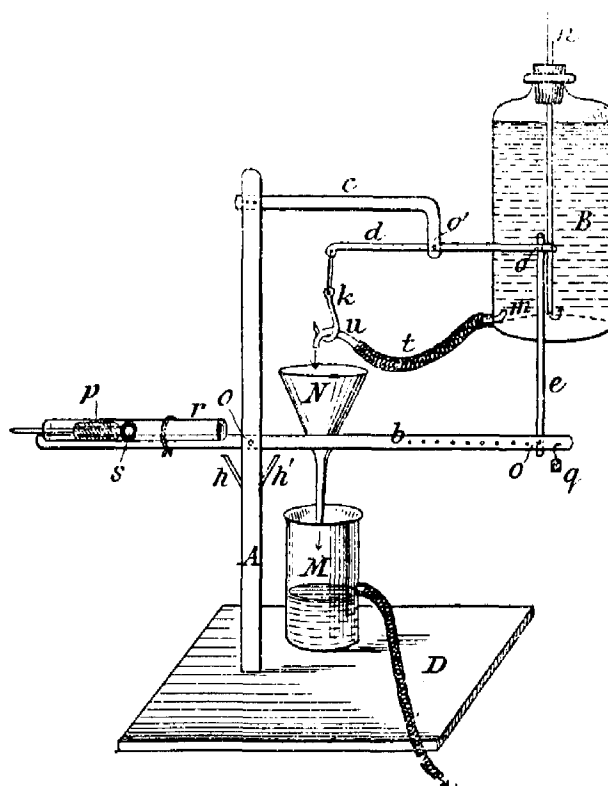


Figure 3 Automatic precipitate washer

surveying this topic some years ago (11). Although not much used today, gravimetric analysis was once a major technique. The washing of a precipitate on a filter paper is a tedious operation; each wash portion should be allowed to drain away before the next portion is added. A method for the automation of this washing, illustrated in Fig. 3, dates from 1893 (12). Suppose that funnel N, carrying the precipitate on its filter paper, is essentially dry. Counterpoise tube P, closed at the end nearest the upright, carries ball S in the position shown. The lever system has depressed the tip of jet U below the level of the bottom of control tube in wash liquid reservoir B. Liquid runs into the funnel until the increased mass tilts the lever system. This raises the jet and stops the flow. At the same time, the ball rolls right, to the bottom of P, thus reducing the counterpoising force. Not until N has drained is this reduced force strong enough to reverse the tilt. The flow restarts, the ball rolls back to its original position, and the cycle continues as long as desired.

My varied career has left me with an interest in the history of industrial automation (13). Purely mechanical automation was well known to the ancients, as in the magic opening of temple doors. A somewhat more mod-

ern example is the Falcon loom of 1728, which was controlled by punched cards.

Traditionally, the fuel for steam-raising was coal, which is still in use today. Although the production of carbon dioxide cannot be avoided, there is the obvious need for obtaining good energy efficiency. To achieve complete combustion, somewhat more than the stoichiometric amount of air must be supplied. With too little air, a smoking chimney will soon get the stoker into trouble. To avoid this, he is likely to be over-generous with the air supply. Efficiency is lost in heating the excess air. Efficient operation can be achieved by monitoring at least one component of the flue gases. Some modern devices measure the oxygen content; traditionally, the percentage of carbon dioxide was involved. Gas analyses are possible by the Orsat or similar apparatus. However, boilers run continuously, so any method requiring an operator is virtually impossible. Here we have an excellent case for automation, usually involving flue gases aspirated directly from the chimney (14).

Figure 4 shows the "Oekonometer" of 1893. The density of the gas is continuously indicated by what is

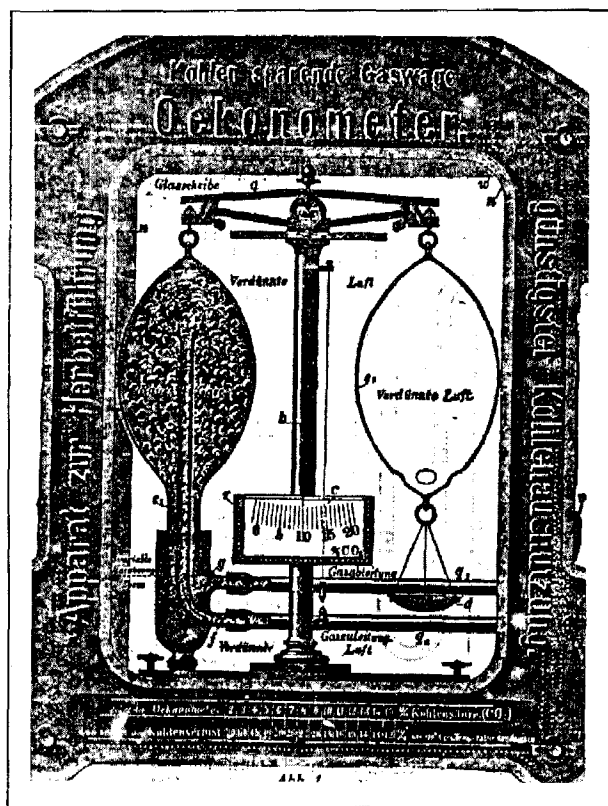


Figure 4 Oekonometer carbon dioxide monitor

essentially a balance in an iron case. The instrument is adjusted so that the pointer scale gives the percentage of carbon dioxide. Another approach is to measure a portion of gas, absorb the carbon dioxide, then measure the residue. A good example of this approach is in the Cambridge Bimeter, introduced in 1910. After passing through a cooler system and a meter, the gas enters an absorption chamber containing slaked lime (calcium hydroxide). With the carbon dioxide now removed, the gas again passes through the cooler to equalize temperatures and then escapes through a second meter. About every two minutes, the differential rates of the meters cause the slowly rotating chart to be marked with a vertical pen stroke of length proportional to the percentage of carbon dioxide.

For use in boilers, the "hardness" of water must be removed. The classical lime-soda treatment requires the titrimetrically controlled additions of calcium hydroxide and of sodium carbonate. The 1906 German patents for the photometric automation of this process were found by sheer luck (15). Looking through early *Chemical Abstracts*, I was puzzled by an entry describing regulated additions "especially to drinking water." In that prefluoridization era, why dose water? The abstractor did not realize that the term "Speisewasser" in the patents, meaning "feed water," is exactly the term used by boilermen. I have never found any reference to the installation of this ingenious but complicated equipment. Only the poorly-responding selenium photocells were then available, and electronics was not yet in sight. The idea was probably before its time.

One Thing Leads to Another

In the study of the history of chemistry an interest in one aspect inevitably leads into another. Perhaps I should give a few examples. I have mentioned the "missing" Barrow balance; I thought that if I found out a little about Barrow himself, this might help in a future search. I was unlucky here; however, I was intrigued to learn that Barrow had been associated with the Great Survey of India. In fact, George Everest (1790-1866) had arranged for Barrow's appointment as survey instrument maker. However, the association eventually broke down, owing, it seems, to the clash of the two strong personalities.

Like most schoolboys, the availability of the celebrated "burner" made me aware that we owed this device to a gentleman named Bunsen. Much later, my interest in electrochemistry turned to the Bunsen cell, another invention by Robert Bunsen (1811-1899). Bat-

teries of these cells were often used by early experimenters; Bunsen himself used them in his experiments on arc-lamp lighting. This got me interested in illumination, both by the gas mantle and by the Edison lamp bulb. A chemist's interest in gas lighting can be readily excused; success was reached through Welsbach's expertise in what we now term lanthanide chemistry (16). But what of electric lighting? Sufficient to say that Edison used electrolytic meters to fix the bills for his customers (17).

In reviewing my long interest in potentiometry, I realized that I knew little about the history of potentiometric titration, except that it had been introduced by Behrend in 1893. On inquiring, I found that Robert Behrend (1856–1926) (Fig. 5) began by studying law, quickly changed to physics, and then decided to become a chemist (18). In 1877 he went to the University of Leipzig, where he was interviewed by the celebrated or-

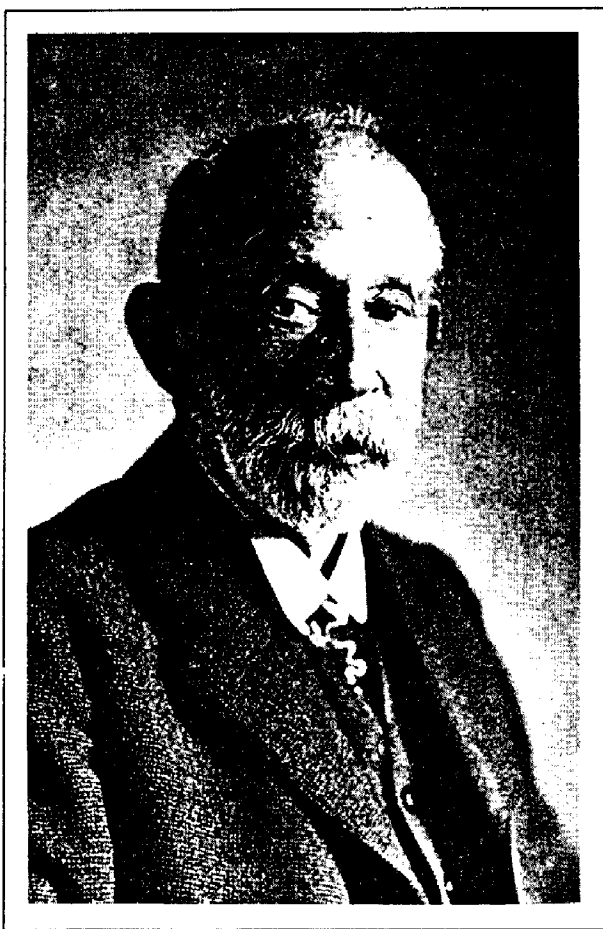


Figure 5 Robert Behrend

ganic chemist, Herman Kolbe (1818–1884), who turned him down. This was because Behrend did not even know the formula of saltpeter! However, he was accepted by a physical chemist and, four years later, obtained his doctorate, *summa cum laude*. Behrend went on to publish some 100 papers. With one exception, these dealt with various topics in organic chemistry. The exception was his 1893 paper which ended with his description of the first potentiometric titrations. Apparently, Behrend did this work because of apparatus made available to him by his colleague Wilhelm Friedrich Ostwald (1853–1932).

Stock's Law

The conservation of historic instruments is a major concern of mine. I collect nothing; anything offered is steered to a museum, where it will be safe for all time. My experience in searching has led to the conclusion "If an historic item can disappear, it will." The lost Barrow balance that I mentioned has a double importance. First, it must have been a superb instrument. Second, it was the principal balance in the trio used to restore a national standard, thus affecting society in general. Concerning another of the trio, I found the remains of this Robinson instrument, offered restoration at my own expense, but could find no taker for the difficult job.

This leads me to another conclusion, which has almost blossomed into "Stock's Law." This is "A scientist's instruments are his successors' junk." I have just mentioned a sad example of this. For years, I have been urging anyone thinking of scrapping an instrument to check before execution. The item in question may be the last of its kind; if it is a prototype, it is historically unique! A species can be numerous but can still face extinction. Thousands of flue-gas analyzers were, and are, in use. Some years ago, a leading British engineering journal published my request for news of the whereabouts of a pre-1930 analyzer. I still await the first response. I suppose that I should go hunting in boiler houses when I travel around. However, I want to push on with other projects, so I think that I will let this one go. I may yet stumble upon the needful when looking for something else!

REFERENCES AND NOTES

1. J. T. Stock, "The Reduction of Quinaldonic Acid at the Dropping Mercury Cathode," *J. Chem. Soc.*, 1944, 427–430.

2. J. T. Stock, and P. Heath, *Small-Scale Inorganic Qualitative Analysis*, University Tutorial Press, London, 1953. (5th ed., 1963).
3. J. T. Stock, and M. A. Fill, *Introduction to Organic Chemistry*, University Tutorial Press, London, 1955.
4. J. T. Stock, "Microchemical Applications of Potentiometry," *Analyst*, **1948**, *73*, 321-326.
5. J. T. Stock, "Microchemical Aspects of Electrolytic Conductivity," *Analyst*, **1948**, *73*, 600-604.
6. J. T. Stock, "Thomas Charles Robinson and his Balances," *J. Chem. Educ.*, **1968**, *45*, 254-257.
7. J. T. Stock, *The Development of the Chemical Balance*, Science Museum, London, 1969.
8. J. T. Stock, "Henry Barrow, Instrument Maker," *Bull. Sci. Instrum. Soc.*, **1986**, *9*, 11-12.
9. J. T. Stock, "Victor Serrin and the Origins of the Chainomatic Balance," *Bull. Hist. Chem.*, **1990**, *8*, 12-15.
10. J. T. Stock, and D. Vaughan, *The Development of Instruments to Measure Electric Current*, Science Museum, London, 1983.
11. J. T. Stock, "Early Automation in the Chemical Laboratory," *Educ. Chem.*, **1983**, *20*, 7-10.
12. P. N. Raikow, "Ein selbstthige Vorrichtung zum Filtrieren und zum Auswaschen von Niederschlägen mit kaltem und heissem Wasser," *Chem. Ztg.*, **1893**, *17*, 1565-1566.
13. J. T. Stock, "Early Automation in the Chemical Industry," *Amer. Lab.*, **1984**, *16(6)*, 14-21.
14. J. T. Stock, "Flue Gas Monitoring: An Early Application of Mechanized Analysis," *Trends Anal. Chem.*, **1983**, *2*, 14-17.
15. J. T. Stock, "Lime, Soda and Selenium: An Early Example of Chemical Process Automation," *Trends Anal. Chem.*, **1983**, *2*, 261-262.
16. J. T. Stock, "Carl Auer von Welsbach and the Development of Incandescent Gas Lighting," *J. Chem. Educ.*, **1991**, *68*, 801-803.
17. J. T. Stock, "Coulombs for Customers," *J. Chem. Educ.*, **1989**, *66*, 417-419.
18. J. T. Stock, "Robert Behrend's Foray into Electrochemistry," *J. Chem. Educ.*, **1992**, *69*, 197-199.

ABOUT THE AUTHOR

John T. Stock, winner of the 1992 Dexter Award in the History of Chemistry, is Professor Emeritus in the Department of Chemistry of the University of Connecticut, Storrs, CT 06269 and is especially interested in the history and preservation of chemical instrumentation.