REVIEW

The anfractuous pathways which led to the development of electrochemical stripping techniques

Fritz Scholz

Abstract Stripping voltammetric techniques provide the most sensitive electroanalytical determinations. Although the idea to combine an electrochemical (or non-electrochemical) preconcentration step with an electrochemical detection step is very simple, the technique needed an astonishing long period to mature. A number of people, who deserve remembrance, have made smaller or larger steps toward the establishment of that kind of analysis. In some cases, the motivation for its development was indeed the search for higher sensitivity, but in other cases it obviously was sheer scientific curiosity. Some scientists who made advancements in electrochemical stripping analysis did not even realize the full importance of their work, and only in the retrospective we can now rightly value their work. Indeed, it was Geoffrey Cecil Barker who must be credited for having published for the first time the complete protocol of stripping voltammetry, unfortunately without presenting the experimental details.

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Do we need to care for the history of science?

This is an old question, and there are enthusiastic apologists of a historical view, as well as furious opponents. The first refer to the better understanding of the contemporary state of knowledge and experience, when knowing the history and deriving current knowledge from ancient. They also argue that a complete ahistorical perception of science aggravates the comprehension of many terms used in modern science; however, rooting in a gone by world of ideas. The apologists also praise the beauty of contemplation upon the fight of ideas, the fight for proving and disproving theories by more and more elegant and elaborate experiments, and the profound personal insight that we thus gain into human thinking. On the other side, the opponents of a historical view on science, normally rate history as useless for solving current problems, and accuse the apologists of being nostalgic. I do not think that this question should be answered in an apodictic way. Everybody needs to find his own answer. My personal experience is that the history of science helped me considerably to understand its current state. From history, we learn how new ideas grow, what resistance they often face, and what facilitates the acceptation of new ideas. To view science not merely as a collection of current theories, techniques, and data, but as a grown body, is as necessary as to understand the present human societies as the result of historical developing processes. It is especially intriguing to discover

when and why scientists made their discoveries, and when and why they missed their chances for discoveries, and to try to learn from these pitfalls. It is for all these reasons that I attempt to answer here the question, why the most sensitive electroanalytical technique developed as it did, both with respect to time and people. In attempting to follow the historical pathways, it is also extremely important to go back to the original sources and data, and not to rely on second sources and later testimony—a rule already stressed by the great empiricist, John Locke, in his essay concerning human understanding, where he wrote:

> This is what concerns *Aſſent* in matters wherein *Teſtimony* is made uſe of: concerning which, I think, it may not be amiſs to take notice of a Rule obſerved in the Law of *England*; which is, That though the atteſted Copy of a Record be good Proof, yet the Copy of a Copy never so well atteſted, and by never ſo credible Witneſſes, will not be admitted as a proof in Judicature. … This practice, if it be allowable in the Deciſions of Right and Wrong, carries this Obſervation along with it, *viz*, That any *Teſtimony*, the farther off it is from the original Truth, the leſs force and proof it has.… I would not be thought here to leſſen the Credit and uſe of *Hiſtory*: 'tis all the light we have in many caſes; and we receive from it a great part of the uſeful Truths we have, with a convincing evidence [1].

We shall see also in case of stripping techniques that the historical surrender needs some corrections when studying the original papers.

What is electrochemical stripping analysis?

According to a IUPAC suggestion [2], "(1) Electrochemical stripping methods are methods involving the preconcentration of a determinand onto the working or indicator electrode, before it is determined electrochemically. (2) Stripping voltammetry (SV) involves the determination of an accumulated determinand by monitoring the faradaic current during a potential scan." The authors of that report also suggest the term stripping tensammetry for the determination of an accumulated determinand by monitoring the capacitance current produced by a desorption process during a potential scan, and the term stripping chronopotentiometry for the determination of an accumulated determinand by measuring the change of electrode potential with time during the stripping of the accumulated determinand either chemically or electrochemically. It became customary to distinguish anodic SV, cathodic SV, and adsorptive SV for solution studies [2–6], according to the electrochemical process occurring during stripping in case of anodic and cathodic SV, and according to the

accumulation step for adsorptive SV. All these techniques have been developed for trace analysis of solutions. For the electrochemical studies and analysis of solid materials, the term abrasive stripping voltammetry has once been introduced [7]. That term is still used, but it is advisable to call the technique "voltammetry of immobilized particles" [8]. Although electrochemical preconcentration steps are strongly dominating stripping analysis, it should be mentioned that non-electrochemical methods of preconcentration have also been developed [9].

Stripping voltammetric methods of determination are the most sensitive electroanalytical techniques reaching detection limits down to 10^{-12} mol L^{-1}, and even less. Several monographs have been published detailing the methodology and applications [10–15]. According to a recent metrological survey of electroanalytical publications [16], between 1999 and 2004, roughly 20% of papers in the leading analytical journals concerned electroanalysis, and 30–50% of them dealt with voltammetry. This is a rather large percentage for electroanalysis, probably overestimating its share in analytical praxis, but clearly indicating that electroanalysis is still an active research field.

Electrogravimetry, coulometry, and polarography—forerunners of electrochemical stripping analysis

Electrogravimetry

Although the deposition of metals on the negative pole of an electrolysis cell is known since the beginning of
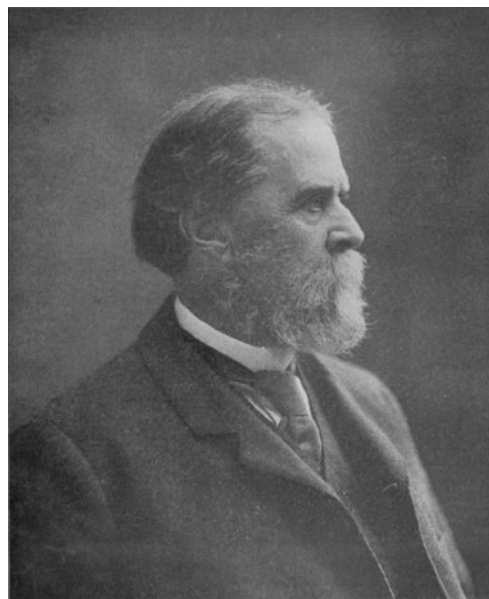

Fig. 1 Oliver Wolcott Gibbs (February 21, 1822, New York–December 9, 1908, Newport (Rhode Island), USA). Reproduced from [26]

nineteenth century (1800: William Cumberland Cruikshank [17] and Humphry Davy [18]), it took 60 and more years until this phenomenon was utilized for quantitative analysis by the German chemist Carl Luckow [19] and the American chemist Oliver Wolcott Gibbs (Fig. 1) [20]! Luckow has performed the electrogravimetric determination of copper since 1860, but has published it only in 1865 [21, 22]. He was a chemist with the "Köln-Mindener Eisenbahngesellschaft" (Cologne-Minden Railway Society) in Deutz [23]. The 60 years between Cruikshank/Davy and Luckow/Gibbs are a long time, taking into account that all necessary experimental prerequisites, i.e., batteries and balances were available much earlier, as well as the necessary basic ideas of electrochemistry. A possible explanation may be that analytical chemists were traditionally trained to perform only chemical operations, and they may also have lacked knowledge and practice of electrolysis. Another, probably, more important point is that there was no real need at that time to search for more sensitive and faster methods of analysis. The slowly developing industry did not yet demand methods with a better performance than the classical analytical chemists could provide at that time. A look in the classical text books of Heinrich Rose (Fig. 2) [24] and Carl Remigius Fresenius (1818–1897) [25] gives a clear picture of what were the high-performance analytical methods of the mid-nineteenth century. The deposition of metals by electrolysis followed by weighing the deposit with an analytical balance is now called electrogravimetry. Until the emerging of all the modern varieties of electrochemical analysis techniques, it was customary to call it simply electroanalysis because

Fig. 2 The analytical chemist Heinrich Rose (August 6, 1795, Berlin, Germany–January 27, 1864, Berlin, Germany). © Humboldt-Universität zu Berlin, Universitätsbibliothek

Fig. 3 The mineralogist Carl Friedrich Rammelsberg (April 1, 1813, Berlin, Germany–December 28, 1899). © Humboldt-Universität zu Berlin, Universitätsbibliothek

electrogravimetry was the only known electroanalytical method. Oliver Wolcott Gibbs [26] has worked with the eminent mineralogist Carl Friedrich Rammelsberg (Fig. 3) and the famous analytical chemists Heinrich Rose and Justus von Liebig in Germany and with Jean-Baptiste Dumas in Paris, France. In 1848, he became assistant professor at the College of Physicians and Surgeons; in 1849, full professor of chemistry and physics at the Free Academy in New York (now College of the City of New York); and in 1963, professor of applied sciences at Harvard University, Massachusetts and head of the chemical laboratory at the Lawrence Scientific School, New York. It is said [26] that among his teachers it was Heinrich Rose who impressed him most and who gave his work a strong bias towards analytical and inorganic chemistry.

Electrogravimetry has been strongly developed in Germany by Alexander Classen and in the US by Edgar Fahs Smith.

Alexander Classen [27] (Fig. 4) started his studies of chemistry at the University of Gießen in 1861, where he was a student of Heinrich Will (1812–1890) [28], Theophil Engelbach (1823–1872) [29], Johann Heinrich Buff (1805–1878) [30], and Hermann Franz Moritz Kopp (1817–1892) [31]. He later moved to Berlin where he was a student of Franz Leopold Sonnenschein (1817–1879) [32], Heinrich Rose, Eilhard Mitscherlich (1794–1863) [33], and Emil Heinrich du Bois-Reymond (1818–1896) [34]. Classen received his Ph.D. in 1864 in Berlin, was an assistant of Sonnenschein from 1865 to 1867, then moved back to Aachen where he worked as "Privatchemiker" (private chemist), and in 1870, he was given a teaching assignment at the newly founded "rheinisch-westfälische polytechni-
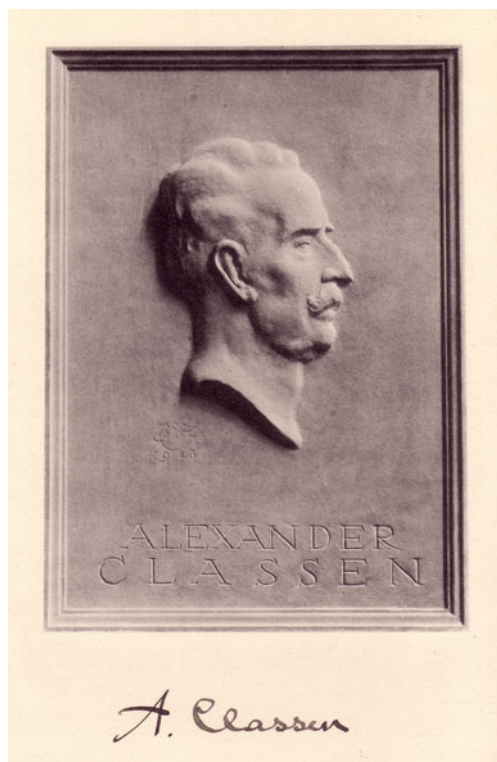
Fig. 4 Alexander Classen (April 13, 1843, Aachen, Germany–January 28, 1934, Aachen, Germany). The lithography with original signature is the property of the author

sche Schule" (now Rheinisch-Westfälische Technische Hochschule Aachen). Since 1878, he was a professor at that institution. He published many original papers on electrogravimetric analyses, and he wrote a very influential book on electrogravimetry, which was published in numerous editions [35].

Edgar Fahs Smith (Fig. 5) made his Ph.D. ("Philosophiae Doctorem et Artium Liberalium Magistrum" diploma, which was renewed 50 years later as a sign of special recognition) with Friedrich Wöhler (1800–1882) [36] in Göttingen, Germany. The topic of his thesis was organic chemistry of benzene derivatives [37]. Smith was a talented organizer, a co-founder of the American Chemical Society's History of Chemistry division, three times president of the American Chemical Society, and president of the American Philosophical Society and the History of Science Society (1928). In 1926, he was awarded the Priestley Medal. It is interesting to cite here from the American Chemical Society web page "The Edgar Fahs Smith Memorial Collection in the History of Chemistry": "Edgar Fahs Smith and many other aspiring scientists of his time completed their doctoral training at the University of Göttingen. Their time in German laboratories gave them a new vision of scholarly research, programs for institution building, and a commitment to the moral and cultural value of university study that permeated German academe. Smith and his colleagues,

Theodore W. Richards at Harvard, Charles F. Chandler at Columbia, and Ira Remsen at Johns Hopkins, played leading roles in the transformation of American academic life at the turn of the century. They were comfortable with the production of new Ph.D.s and the publication of research, yet still sensed that graduate study in chemistry in the United States was thought to lack the moral value of studies in the traditional liberal arts." Smith was deeply interested in the history of science and a great collector of historically significant books and autographs. His library formed the core of what is now "The Edgar Fahs Smith Memorial Collection in the History of Chemistry" of the ACS. In 1935, Meeker writes in his biographical memoir about Smith [38]: "Perhaps his most important contributions were those he made to electrochemistry, a domain in which he was a pioneer and soon became a recognized leader of international reputation. In the hands of this master craftsman, the electric current became a tool of undreamed-of usefulness and possibilities, opening up wholly new methods of analysis, separation and determination. About half of all the research papers he published were based upon new applications of the electric current. His introduction of the rotating anode together with the employment of currents of high amperage and high voltage, marked a new epoch in the development of electroanalysis." Edgar Fahs Smith has written a monograph on

Fig. 5 Edgar Fahs Smith (May 23, 1854, York, PA, USA–May 3, 1928, Philadelphia, PA, USA) in 1878. University of Pennsylvania Archives

electrogravimetry [39], which was published in several editions and translations. It very much helped to popularize this kind of electroanalysis. Smith used rotating electrodes (either the anode or the cathode) and demonstrated that the convection shortened the analysis significantly. A good example of the successfulness of solution agitation is a paper of his Ph.D. student F. F. Exner, the results of which have been published in 1903 [40]: The Pt spiral anode was rotated by an electric motor with 500–600 revolutions per minute. Cu, Ag, Hg, Zn, Co, Cd, Pb, Mo, Sn, Au, Sb, and Bi were deposited on the inner surface of a Pt dish. The current density denoted as $N.D_{100}$ (normal current density for 100 cm^2 electrode surface area [41]) was rather high, in the range of 2–10 A. The combination of solution stirring (by the rotating anode), high current densities, and hot solutions (during electrolysis kept hot by the high current only) assured the short electrolysis times. The range of precipitated metals was 200–500 mg with errors of ±0.2 mg (in some cases some mg). People like Classen, Smith, and the many other pioneers of electrogravimetry have compiled a huge amount of experimental knowledge about electrolytic precipitations of metals (and also oxides and hydroxides), as well as knowledge about the most favorable electrolysis conditions, which later turned out to be very useful in the development of the modern electroanalytical methods. Meeker [38] writes about Smith: "As a scientist he ranks with those of high distinction, though not with the few of recognized greatness." And later "As is true of most scientists of note, his discoveries, investigations and inventions possess recognized distinction, but have not epochal quality." This judgment is certainly also true for Classen. The life span of Smith and Classen (middle of the nineteenth to the first third of the twentieth century) encompasses the last period of classical analytical chemistry, for which Heinrich Rose and Carl Remigius Fresenius are two archetypes—and the beginning of the development of instrumental methods of analysis in the twentieth century, with Jaroslav Heyrovský (1890–1967) [42] as the first and most notable figure. Following Classen and Smith, the next generation of scientists developing electrogravimetry may be exemplified by William Dupré Treadwell [43, 44], the son of Frederic Pearson Treadwell, the author of once famous textbooks of Analytical Chemistry. The son William Dupré Treadwell (Fig. 6) studied in Zurich, where he also received his Ph.D. (1909), for which he partly worked with Fritz Förster in Dresden. Shortly after obtaining the Ph.D., he moved to the *Technische Hochschule Berlin-Charlottenburg* (now Technical University of Berlin). There he habilitated in 1914. In 1915, he published a monograph on electrogravimetry, which very much helped to make popular this rather new technique [45]. This book was essentially his habilitation thesis. From 1911 to 1913, the professor of electrochemistry at that

Fig. 6 William Dupré Treadwell (March 25, 1885, Zurich, Switzerland–July 25, 1959, Zollikon (Kt. Zurich), Switzerland). ETH-Bibliothek Zurich, Image Archive

Fig. 7 Franz Josef Emil Fischer (March 19,1877, Freiburg i.B., Germany–December 1, 1947, Munich, Germany). © Humboldt-Universität zu Berlin, Universitätsbibliothek

institution was Franz Josef Emil Fischer (Fig. 7), who himself published on electrogravimetric techniques, who, however, is best known for the Fischer–Tropsch synthesis of gasoline from coal. Further down, we shall see that László Szebellédy, one of the fathers of coulometry, worked with W. D. Treadwell when the latter was back to Zurich.

Coulometry

Nowadays, it is usual to refer to Faraday's law as expressed by $q = nF \frac{m}{M}$ (q—charge, n—number of electrons appearing in the electrode reaction, F—Faraday constant, m—mass of the oxidized or reduced substance in grams, M—molar mass). However, it should be remembered that Faraday formulated it as follows: the masses of two compounds (or elements) deposited by electrolysis are related to each other in the ratio of their equivalent masses. It needed the determination of the charge of a single electron (elementary charge) and the determination of the Avogadro number to calculate what we now call the Faraday constant, i.e., the charge of 1 mol of electrons. In the nineteenth century, it was already possible to measure a static electric charge (Coulomb's torsion balance); however, the physical determination of the charge that is caused by a constant or varying current would have been a problem, e.g., in electrolysis experiments because it was not possible to keep the current sufficiently constant, neither it was possible to register the current time curves with sufficient precision to perform an integration. Hence, the only possibility was to measure the charge by weighing the amount of silver deposited in a second electrolysis cell in series with the one in which the reaction to be studied was performed. The silver electrolysis cell was called a "silver coulometer." The term coulometer was suggested by Theodore W. Richards [46] (1868–1928, Nobel Prize for Chemistry in 1914). Earlier, the instrument was called a voltameter or coulombmeter. Similarly, so-called copper coulometers have been used, although they were inferior with respect to precision. With these coulometers, electrogravimetry has been performed for the sake of measuring the electric charge that passed through the electrochemical cell; however, unlike in electrogravimetry, great care had to be taken that only one well-defined electrode reaction proceeds at the electrode the weight of which was measured. It is also possible to perform water electrolysis and to measure the volume of produced detonating gas (oxygen–hydrogen mixture) for the sake of charge determination [47] or to electrolyze a hydrazine solution forming H_2 and N_2 [48]. For a review of historic coulometers, see [49] and [50]. The "chemical coulometers" (like the silver, copper, or detonating gas coulometers) are in fact very elegant integrators of the current–time relationships as the mass of precipitated metal, or the liberated volume of gas,

were ideally directly proportional to the charge. These coulometers were the state of art instrumentation until the middle of twentieth century, when electric charge counters and mechanical integration (e.g., by the so-called ball and disk integrator of Lingane and Jones [51]) were introduced. Still, in the 60th of last century, constant current coulometry was performed with the help of devices providing a highly constant current and having a stop watch, which was automatically coupled to the circuit switch, so that the interruption of the current also stopped the time counting [52]. This allowed a facile charge calculation by multiplying current by time. The electronic revolution, including the revolution in computation, which took place in the second half of the twentieth century, has made current integration a very simple task, implemented in almost all electrochemical instruments. However, the digital data processing, including the digitalization of the potential ramps, also produced new complications: Not all the displayed or calculated charges of electrochemical reactions are the true values, unless special care is taken that the data evaluation is performed in such way that the time gaps between the current integrations will not affect the overall charge.

Now, we shall turn our eyes to the introduction of coulometry as an analytical tool for chemistry: That happened with the seminal work of the two Hungarians László Szebellédy (Fig. 8) and Zoltán Somogyi (1915, Budapest–1945, Budapest). Szebellédy was a pupil of the Hungarian analytical chemist Lajos Winkler (1863–1939) who invented a famous method to titrate oxygen (Winkler

Fig. 8 László Szebellédy (April 20, 1901, Budapest, Hungary (Austro-Hungarian Empire)–January 23, 1944, Budapest, Hungary)

titration). From his list of publications, one can see that Szebellédy was a devoted analytical chemist who was striving for developing highly reproducible analytical methods that provide true values, the ultimate goal of all quantitative analyses. In 1938, Szebellédy and Somogyi published eight papers in German language in the then leading analytical journal "Zeitschrift für Analytische Chemie" (later called "Fresenius' Journal of Analytical Chemistry," and currently being published as "Analytical and Bioanalytical Chemistry"). These papers are an excellent introduction of the new technique: in the first paper [53], the authors describe the general features of a coulometric determination, discussing the importance of having only one single electrode reaction, discussing the use of a silver coulometer, etc. In the second paper [54], the authors describe the coulometric analysis of a hydrochloric acid solution with the purpose of establishing exactly the titre for titrations. For that purpose, they performed the hydrogen evolution on the cathode and the oxidation of silver to silver chloride at the anode. Rightly, they realized that it is necessary to prevent the evolution of chlorine gas at the anode as that would partially dissolve in the solution and disproportionate, giving rise to wrong results. In the third paper [55], they report a coulometric titration of sulfuric acid. It is interesting how they understood the electrolysis of sulfuric acid: at the cathode they assumed the discharge of protons leading to hydrogen gas evolution, and at the anode, they assumed a discharge of sulfate ions according to $SO_4^{2-} \rightarrow SO_4 + 2e^-$, followed by the reaction $2SO_4 + 2H_2O \rightarrow 2H^+ + 2SO_4^{2-} + O_2$, i.e., they did not yet know that the water oxidation is an electrochemical reaction preceding the sulfate oxidation. To get rid of the oxygen evolution, they simply added an excess of potassium chloride and used a silver anode, so that the formation of silver chloride prevented the regeneration of protons at the anode. In the following papers of that series, these authors described the coulometric determination of thiocyanide [56], hydrazine [57], sulfite and hydrogen sulfite [58], and hydroxylamine [59] by electrochemical generation of bromine from bromide. Szebellédy and Somogyi are frequently credited for having invented coulometric analysis [60–62]. Without diminishing the importance of their contribution, this is not the complete truth: others have used coulometers before (e.g., Grower [63] for the analysis of tin coatings). Szebellédy and Somogyi have introduced the principle of coulometric titration and opened the view of analytical chemists how to use coulometers for their tasks.

Polarography and voltammetry

Polarography was the first technique utilizing current versus potential recordings, which were applicable for analytical determinations and electrochemical characterization of the properties of dissolved species. The history of polarography has been described elsewhere, e.g., [64], and it is the subject of two papers in this special issue [65, 66]. Therefore, it may suffice to remind the reader here that since 1921, when Jaroslav Heyrovský published his Nobel prize winning papers on the new technique, polarography was a well-known and vividly developing measuring technique, which not only conquered the analytical laboratories but also those of physical chemists, and even those of other branches of chemistry, of biology, and of physics.

The first electrochemical stripping experiments

As early as in 1917, G. G. Grower [63] published in the "Proceedings of the American Society of Testing and Materials" a congenial method to determine the amount of tin on tinned copper wires, and also the amount of tin in the tin–copper alloy that forms between the copper core and the surface layer of tin. Although that publication is frequently cited in reviews on electroanalytical techniques, it seems that only from today's perspective we can fully value its significance: Fig. 9 depicts the used circuitry, which consisted of two gas coulometers, the electrolysis cell, a voltage source, and a relay. The electrolysis cell hosted the tinned copper wire, a platinum counter electrode, and a third electrode, which was a pure piece of tin connected via the relay to the same positive terminal as the tinned copper
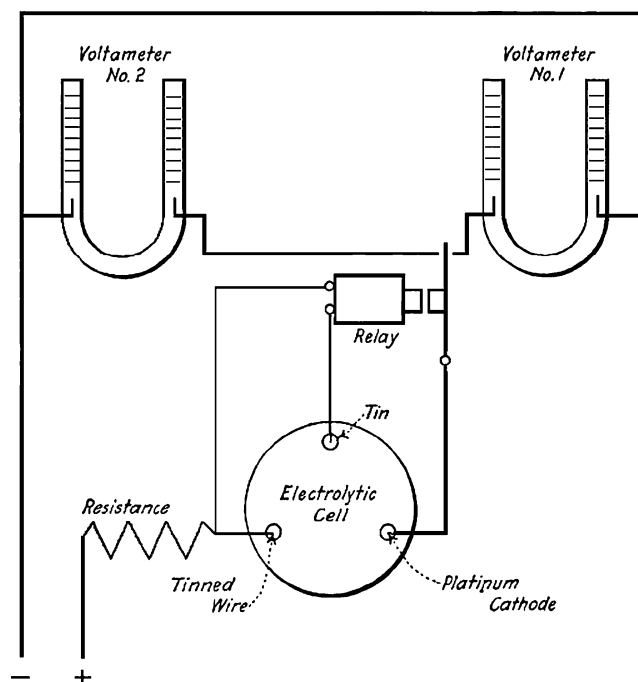
Fig. 9 Circuit used by Grower in 1917 for the stripping of tin from copper wires. Reproduced from [63] and electronically reworked

wire. When the cell is switched on, the dissolution of the tin on the copper wire starts. As long as there is still only tin on the surface, the tinned wire and the tin electrode form a galvanic cell with zero potential difference and the relay is connecting only coulometer 1 (called by Grower "voltameter 1") with the electrolysis. When the pure tin phase is dissolved and the tin–copper alloy is exposed, that galvanic cell attains a certain emf, and the flowing current causes the relay to switch off the coulometer 1 and switch on coulometer 2. The electrolysis is continued until the tested wire assumes the color of metallic copper. At this moment, the electrolysis is manually switched off. Coulometer 1 has counted the charge for dissolving the pure tin phase, and coulometer 2 has counted the charge to dissolve the tin of the tin–copper alloy. Grower mentions that the charge quantity measured by coulometer 2 must have some relation with the amount of tin–copper alloy and admits that he does not know what the exact relation is. Doubtless, Grower's work is the first example of quantitative coulometric measurements for the purpose of analysis, and it is also a first example of a stripping analysis, in the sense that a deposit was electrolytically stripped off, although the preconcentration step (the deposition)—which is now regarded to be an essential part of what we call stripping analysis—was not necessary. Unfortunately, the author was not able to get any information about the life and other activities of Grower.

After Grower's publication, it took another 14 years until the next step was made, i.e., a metal was first electrochemically deposited on an electrode, followed by anodic stripping and coulometric evaluation of the data: This step was made by the Swiss analytical chemist Christian Zbinden (Fig. 10).[1] He studied at the University of Lausanne, where he obtained his "diplôme d'ingénieur chimiste" on May 23, 1929, and his "doctorat ès sciences" on November 28, 1929. The title of his doctoral thesis was "Recherches spectrographiques sur des cendres de sangs et d'organes humains" ("Spectrographic studies of the ashes of blood and human organs") [67, 68]. The supervisor of his Ph.D. thesis was Paul Dutoit (1873–1944), a pupil of Philippe-André Guye (1862–1922). Dutoit had established physical chemistry as a teaching subject at the University of Lausanne, and during his career, he had carried out extensive electrochemical research for both analytical and industrial applications [69]. Most likely, Dutoit shaped Zbinden's education and introduced him to electrochemical techniques. Zbinden joined the Nestlé company in 1930 where he held different positions, first in the research laboratory and later in senior management. He

Fig. 10 Christian Zbinden (February 29, 1904, Bern, Switzerland–August 31, 1983, Moudon, Switzerland). Courtesy of Olivier Zbinden, Pully, Switzerland

ultimately became head of the infant food section. In 1935, he proposed the establishment of a company nursery ("Pouponnière Nestlé"), which was rather novel at that time. He retired in March 1969. Whilst still at the University, Zbinden developed a new method of determining copper [70, 71], which was a key step in the evolution of anodic stripping voltammetry. Using a simple two-electrode electrolysis cell, a lead battery, and a Wheatstone bridge to control the current, he exhaustively electrolyzed a dilute Cu^{2+} solution so that all the copper was deposited on a Pt electrode. He then reversed the polarity of the two electrodes, dissolving the copper metal while keeping the current constant by manually adjusting the sliding contact of the Wheatstone bridge. The time (in s) at which the current could no longer be kept constant was then multiplied by the steady current value (in mA) and by a conversion factor ($0.0003294\ \mathrm{mg\,mA^{-1}\,s^{-1}}$) to yield the amount of copper in milligrams. From a modern point of view, this was an example of stripping coulometry under constant current conditions. By this very clever method, Zbinden had removed the need to weight the deposited copper as necessary in electrogravimetry. In 1947, Elema published several improvements of the Zbinden method, including an apparatus and circuitry for an assembly of cells [72].

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[1] It is my great pleasure to acknowledge the kind provision of personal information from the son Olivier Zbinden and the grandson Sébastien Zbinden.

The 50th of last century: stripping techniques

The 50th of last century is characterized by a rapid development of electroanalytical measuring techniques, partly benefiting from the war-time developments in electro techniques (especially in case of Barker's contributions). In several laboratories, it has obviously been realized that the very successful dropping mercury electrode has also disadvantages, and people have thought about the construction of stationary electrodes, which still keep some of the positive features of the mercury electrode. Thus, G. C. Barker (Fig. 11) and I. L. Jenkins write in the paper where they introduced square-wave polarography in 1952 [73]: "As regards any further improvement in sensitivity, it is believed that the useful concentration range of the present instrument might be extended to lower values by a factor of 10 or more by paying more attention to the purity of chemicals, to the noise level of the electronic circuits and to the design of the capillary. The experimental technique would then become somewhat specialized and it may be doubted whether it would be acceptable for analytical purposes. Indeed, there is some doubt in the authors' minds as to whether there is any real need for higher sensitivity. If there were, one might mention a recent development that can lead to a large increase in sensitivity for the detection of many of the species that form metallic amalgams. Briefly,
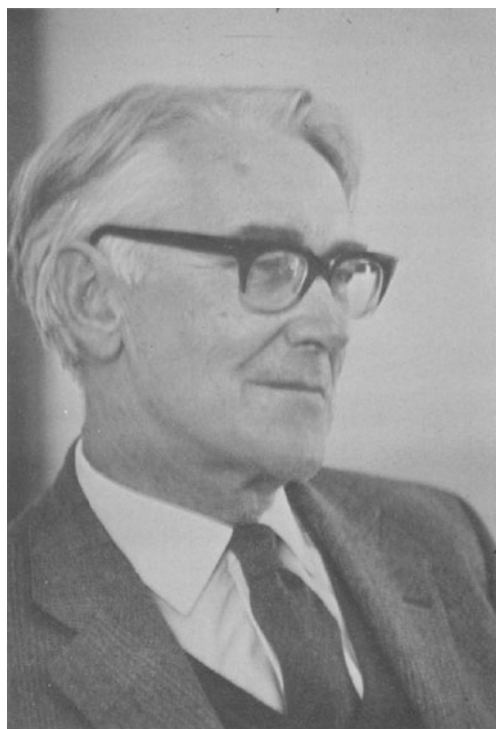

Fig. 11 Geoffrey Cecil Barker (October 2, 1915, Belper, Derbyshire, UK–March 31, 2000, Oxford, UK). Reprinted from *Journal of Electroanalytical Chemistry* 75(1977)1, Copyright (1977), with permission from Elsevier

this involves the use of a single mercury drop in place of the dropping-mercury electrode, and a special cell is used that permits the circulation of the solution past the surface of the drop, the circulation system being such that the diffusion system in the vicinity of the drop can be reproduced. At the start of an experiment the drop electrode is polarized to as negative a potential as is possible without depositing the cations of the supporting electrolyte and is held at this potential for a suitable time. Metallic impurities in the solution then tend to be concentrated in the drop and, after 15 minutes have elapsed, the concentrations of the electro-deposited ions in the drop may well exceed their concentrations in the solution by a factor of a hundred or more. After a suitable amount of concentration has been effected, the circulation of the solution is stopped and a derivative polarogram is recorded with a relatively rapid rate of change of the mean potential of the drop. If the conditions under which the experiment is carried out are correctly chosen, the heights of the waves observed on the polarogram are determined by the concentrations of the various metallic ions in the drop at the start of the polarogram, and these concentrations consequently can be determined from the measured wave heights. If the system is calibrated in some way, the concentrations in the drop can be used to estimate the original concentrations of the various ions in the solution. The accuracy of the method is probably not better than 6 to 10 per cent but the method is of interest as it is readily applicable to the estimation of concentrations as small as 10^{-9} M and, if pressed to its limit, one might expect the smallest amount of a single species that could be detected to be of the order of 10^{-11} moles. The method has been found useful for studying the purity of the supporting electrolyte."

This is a most remarkable text, as it is (1) the formulation of the complete protocol of stripping techniques and (2) the introduction of the idea of a static mercury drop electrode! *These two facts suffice to see Barker as the real inventor of modern stripping techniques*! The fact that this achievement escaped very much the attention of his contemporaries and historians may be partly ascribed to Barker's modest formulation, which shows that he did not realize what a great and important thing the development of so sensitive techniques would be. This is certainly very surprising because he developed square-wave and pulse techniques to improve the sensitivity of Heyrovský's classical direct current polarography. Obviously, it was shear scientific curiosity that prompted him to develop the idea of stripping voltammetry and the use of a static mercury drop electrode. Unfortunately, he obviously rated the improvements in sensitivity, which he achieved by electronic means as being sufficient. One can certainly learn from this story that it is a mistake not to advance something when one sees the opportunity to do so, even when one

does not has the requirement from industry or research. It can safely be assumed that W. Kemula has read the Barker/Jenkins paper. In 1956, i.e., 4 years after Barker and Jenkins, W. Kemula (Fig. 12) and Z. Kublik (Fig. 13) have published in Polish language a paper in the Polish journal "Chemia Analityczna," introducing the hanging mercury electrode for oscillopolarography and stripping analysis [74]. In 1958, they published a similar, but expanded paper in French in the journal "Analytica Chimica Acta" [75], and in 1959, together with Głodowski, another analytically oriented paper in English in "Journal of Electroanalytical Chemistry" [76]. In 1959, on the 2nd International Congress of Polarography in Cambridge, UK, Kemula has presented in a plenary lecture the results of his group in applications of the hanging mercury drop electrode (that type was later called Kemula electrode) for mechanistic studies and stripping analysis [77]. Certainly, these publications supported very much that he was recognized as the father of the static mercury drop electrode and stripping analysis. The idea to use a static mercury drop simply matured in the 50th and in various laboratories attempts have been made in that direction. According to a private communication of M. Heyrovský (private communication, 2010), the pioneers of a static mercury drop electrode in Prague were Jiří Vogel and Vladimír Čermák. In 1962, Yakov Peysachovich Gokhshtein (Fig. 14) published the construction of a static mercury drop electrode [78], the electrode which turned out to be the most

Fig. 13 Zenon Kublik (January 6, 1922, Warsaw, Poland–November 9, 2005, Warsaw, Poland)

Fig. 12 Wiktor Kemula (March 6, 1902, Ismail, Bessarabia, Russian Empire, now Ukraine–October 17, 1985, Warsaw, Poland)

Fig. 14 Yakov Peysachovich Gokhshtein (September 23, 1906, Golendry, Ukraine/Russian Empire–November 29, 1996, Moscow, Russia)

versatile renewable mercury electrode for stripping analysis, following its technical improvements in the 70th and 80th, esp. by the companies Princeton Appl. Res. Comp. (USA) and Methrohm (Switzerland). In the 50th, there have been also publications on stripping coulometric and stripping voltammetric determinations from US laboratories, e.g., from the groups of L. B. Rogers (1917–1992; Ph.D. 1942, Princeton [79]) at MIT and P. Delahay (1922, [80]) from Louisiana State University [81, 82].

The 60th and 70th of last century: a time of maturing for stripping techniques

The stationary mercury drop electrode developed in the 50th was a substantial improvement as it allowed performing electrochemical measurements with an electrode having a constant electrode surface area. This is of course most beneficial for stripping techniques, which afford a finite accumulation time. Later, there have been attempts to use extremely slow dropping mercury electrodes for that purpose, and these electrodes exhibited very high accuracy in reproducing the electrode surface area, but their use and maintenance was too tedious to be a real competition to the static mercury drop electrode [83]. The 60th were dominated by a very wide development of stripping analytical techniques. It is impossible to mention here all scientists who have made contributions.[2] Instead, only two analytical chemists will be considered because of their outstanding work: the German Rolf Neeb (Fig. 15) and the Australian Trevor Mark Florence (Fig. 16). Neeb's scientific genealogy can be directly traced back to Johann Wolfgang Döbereiner (1780–1849) [84]. After 1959 Neeb published several seminal papers on the development and application of stripping voltammetry (e.g., [85–87]) and stripping voltammetry remained central to Neeb's work for the rest of his life. His papers on stripping techniques are a tremendous resource for anybody working in this area. His opus magnum is a monograph on stripping techniques [88], which, unfortunately, has never been translated to English. Trevor Mark Florence [89] is best known for the introduction of the in situ plated thin mercury film electrode [90, 91]. The advantages of thin mercury film electrodes are

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[2] The following list is incomplete, but it may give an impression of how many scientists worked in this field: G. E. Batley (Australia), E. Beinrohr (Slovakia), H. Berge (Germany), S. van den Berg (UK), A. Bobrowski (Poland), A. M. Bond (Australia), M. Branica (Croatia), Kh. Z. Brainina (Russia), J. Golimowski (Poland), G. Henze (Germany), P. Jeroschewski (Germany), R. Kalvoda (Czech Rep.), M. Lovrić (Croatia), Š. Komorsky-Lovrić (Croatia), H. Monien (Germany), E. Neyman (Russia), H. W. Nürnberg (Germany), W. W. Slepushkin (Russia), A. G. Stromberg (Russia), K. Štulik (Czech Rep.), P. Valenta (Germany), F. Vydra (Czech Rep.), J. Wang (USA), N. F. Zakharchuk (Russia), and J. Zarębski (Poland).

Fig. 15 Rolf Neeb (January 7, 1929, Mainz, Germany–March 18, 2006, Mainz, Germany)

manifold: (1) the μm-size mercury droplets forming the film, keep the diffusion gradients large during stripping, and thus provide high currents; (2) the thin film mercury electrode combines the reproducibility of conventional mercury electrodes with the stability of solid electrodes; (3) it provides the high hydrogen overvoltage of mercury
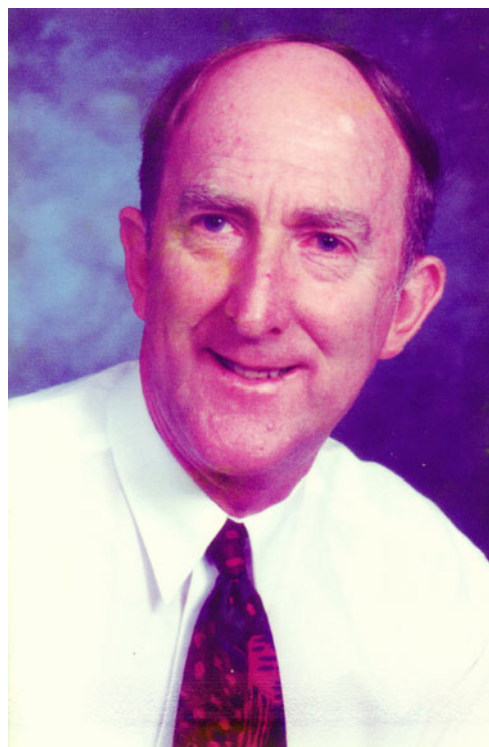

Fig. 16 Trevor Mark Florence (June 5, 1934, Mareeba, North Queensland, Australia–April 19, 2003, Syndey, Australia)

electrodes, etc. In combination with the most advanced electronic measuring techniques, the thin film mercury electrode (especially when using glassy carbon as substrate) lead to the most sensitive stripping determinations in the range of 10^{-10} to 10^{-12} mol L^{-1}.

Stripping voltammetry, however, is much more than only an extremely sensitive technique for quantitative determinations: In 1973, S. Bubić and M. Branica published [92] a paper in which they have shown that a plot of anodic stripping currents versus deposition potentials can be successfully used to determine the state of the metal ions in solutions. The technique that has later been named "pseudopolarography" because of the wave-shaped nature of these plots, which indeed resemble the polarographic curves at much higher metal concentrations, has been extensively developed by the research group of M. Branica in Zagreb, Croatia, and also by H. W. Nürnberg and P. Valenta in Jülich and also in a cooperative program between these groups [93].

Conclusions

The electroanalytical stripping techniques are the result of a long and anfractuous way of developments. The historical main road has been paved by the prime figures of electrochemistry, H. Davy, M. Faraday, W. Nernst, and J. Heyrovský. Scientists like C. Luckow, W. Gibbs, A. Classen, E. F. Smith, G. G. Grower, L. Szebellédy, Ch. Zbinden, G. C. Barker, W. Kemula, R. Neeb, T. M. Florence, and many others have build second and third order roads, have build bridges crossing some turbulent rivers, and they have cultivated the vast plains of analytical practice. It needs special emphasis that it was G. C. Barker who formulated already in 1952 the complete protocol for stripping analysis with a stationary mercury drop electrode, viz., he deserves a prime position in the history not only of pulse and square-wave techniques, but also of stripping voltammetry. Unfortunately, in this review, I could not trace back the historical development of the theory of stripping techniques, and I must leave that for a later occasion.

From the perspective of now, it is surprising that certain steps in the development of stripping techniques have not been made earlier. The reasons can be seen in (1) a lack of requirements (impetus) from outside, (2) in objective hindrances, or—we shall never know this—a lack of realization of opportunities, and finally, (3) because ideas must mature, and must be distributed in the scientific community. This historic survey is a good example of how both the personality of the researchers and the practical requirements determine the pathways of a practice-oriented science like analytical chemistry.

References

1. Locke J (1706) An essay concerning human understanding, 5th edn. Awnsham and Churchill, London, p 562
2. Fogg AJ, Wang J (1999) Pure Appl Chem 71:891–897
3. Wang J (2006) Analytical electrochemistry, 3rd edn. Wiley-VCH, Hoboken
4. Bond AM (1980) Modern polarographic methods in analytical chemistry. Marcel Dekker, New York
5. Brett ChMA, Oliveira Brett AM (1998) Electroanalysis. Oxford chemistry primers. Oxford University Press, Oxford
6. Kopanica M, Opekar F (1987) Electrochemical stripping analysis. In: Kalvoda R (ed) Electroanalytical methods in chemical and environmental analysis. Plenum, New York, pp 58–84
7. Scholz F, Nitschke L, Henrion G (1989) Naturwissenschaften 76:71–72
8. Scholz F, Schröder U, Gulaboski R (2005) Electrochemistry of immobilized particles and droplets. Springer, Berlin
9. Scholz F, Nitschke L, Henrion G (1988) Zh analit khimii 43:1166–1169 [(1988) J Anal Chem USSR 43: 929–931]
10. Haase HJ (1996) Elektrochemische stripping-analyse. Eine Einführung für Praktiker. VCH, Weinheim
11. Neeb R (1969) Inverse Polarographie und Voltammetrie. Neuere Verfahren zur Spurenanalyse. Verlag Chemie, Weinheim (also: Akademie-Verlag, Berlin)
12. Brainina KhZ (1974) Stripping voltammetry in chemical analysis. Wiley, New York
13. Brainina Kh, Neyman E (1993) Electroanalytical stripping methods. Wiley, New York
14. Brainina KhZ, EJa N, Slepushkin VV (1988) Inversionnye elektroanaliticheskie metody. Khimija, Moskva
15. Brainina KhZ, EJa N (1982) Twërdofaznye reakcii v elektroanaliticheskoi khimii. Khimija, Moskva
16. Budnikov GK, Shirokova VI (2006) J Anal Chem 61:973–984
17. Cruikshank WC (1800) Nicholsons Journal 4:187
18. Scholz F (2008) Davy, Sir Humphry, Baronet. In: Bard AJ, Inzelt G, Scholz F (eds) Electrochemical dictionary. Springer, Berlin, p 137
19. Luckow C (1865) Dinglers Polytech J 177:231–235, and 296–302
20. Gibbs W (1864) Fresenius' Z anal Chem 3:334 [(1865) Amer J Sc 39:64–65]Luckow C (1880) Z Anal Chem 19:1–19
21. Luckow C (1880) Z Anal Chem 19:1–19
22. Stock JT (1990) Bull Hist Chem 7:17–19
23. Fresenius R (1913) Z Anorg Allg Chem 81:4–23
24. Rose H (1851) Ausführliches Handbuch der analytischen Chemie. Vol 1: Die Lehre von den qualitativen chemisch-analytischen Untersuchungen. Vol 2: Die Lehre von den quantitativen chemisch-analytischen Untersuchungen. Fr. Vieweg & Sohn, Braunschweig
25. Fresenius CR (1862) Anleitung zur quantitativen chemischen analyse. Fr. Vieweg & Sohn, Braunschweig
26. Clarke FW (1910) Biographical memoir of Wolcott Gibbs. National Academy of Sciences VII:3–22, Washington, DC
27. Anonymous (1913) Z Anorg Allg Chem 81:1–3 (editorial of a special issue dedicated to the 70th birthday of Alexander Classen)
28. Pötsch WR (1988) Will, Heinrich. In: Lexikon bedeutender Chemiker (1988) Pötsch WR, Fischer A, Müller W (eds) VEB Bibliographisches Institut, Leipzig, p 454
29. Oppenheim A (1877) Allgemeine Deutsche Biographie (1877) Historische Kommission bei der Bayerischen Akademie der Wissenschaften (ed) 6:119
30. Scholz F (2010) J Solid State Electrochem.
31. Bredig G (1910) Allgemeine Deutsche Biographie, Historische Kommission bei der Bayerischen Akademie der Wissenschaften (ed) 55:820–826

32. Müller W (1988) Sonnenschein, Franz Leopold. In: Pötsch WR, Fischer A, Müller W (eds) Lexikon bedeutender Chemiker (1988). VEB Bibliographisches Institut, Leipzig, p 401

33. Müller W (1988) Mitscherlich, Eilhard. In: Pötsch WR, Fischer A, Müller W (eds) Lexikon bedeutender Chemiker (1988). VEB Bibliographisches Institut, Leipzig, p 306

34. Scholz F (2008) Bois-Reymond, Emil Heinrich du. In: Electrochemical dictionary. Bard AJ, Inzelt G, Scholz F (eds) 54

35. Classen A (1882) Quantitative analyse auf electrolytischem wege. Mayer, Aachen; (1908) 5th ed. Springer, Berlin; Engl Transl: Classen A (1913) Quantitative analysis by electrolysis. Wiley, New York

36. Müller W (1988) Wöhler, Friedrich. In: Pötsch WR, Fischer A, Müller W (eds) Lexikon bedeutender Chemiker. VEB Bibliographisches Institut, Leipzig, p 460

37. Smith EF (1876) Über trisubstituierte Benzolverbindungen und über die Einwirkung von Chlor auf Benzyltrichlorid. PhD thesis. Göttingen, Huth

38. Meeker GH (1935) Biographical memoir of Edgar Fahs Smith. National Academy of Sciences XVII, Washington, DC, p 149

39. Smith EF (1890) Electrochemical analysis. Blakiston, Philadelphia (Reprinted by Kessinger Publishing, Whitefish 2007) 2nd ed 1894, 3rd ed 1902, 4th ed as 'Electro-Analysis'. 1907, 5th ed 1912, translations to German and French were also published)

40. Exner FF (1903) J Am Chem Soc 25:896

41. Smith EF (1907) Electro-analysis. Blakiston, Philadelphia, p 11

42. Katz E (2008) Heyrovský, Jaroslav. In: Electrochemical Dictionary. Bard AJ, Inzelt G, Scholz F (eds), p 332

43. Craig GW, Kauffman GB (2009) Helv Chim Acta 92:217–229

44. Craig GW, Kauffman GB (2008) Chem Educ 13:111–116

45. Treadwell WD (1915) Elektroanalytische Methoden. Borntraeger, Berlin

46. Richards TW, Heimrod GW (1902) Z Phys Chem 41:302–330

47. Sawyer DT, Sobkowiak A, Roberts JL Jr (1995) Electrochemistry for chemists. Wiley, New York, p 97

48. Lingane JJ (1958) Electroanalytical chemistry. Interscience, New York, p 456

49. Kremann R, Müller R (1931) Elektromotorische Kräfte. Elektrolyse und Polarisation. In: Walden P, Drucker C (eds) Handbuch der allgemeinen Chemie. Vol VIII, 2nd part. Akadem Verlagsges, Leipzig, p 8

50. Delahay P (1954) New instrumental methods in electrochemistry. Interscience, New York, p 398

51. Lingane JJ, Jones SL (1950) Anal Chem 22:1220–1221

52. Dobos D (1966) Electronic electrochemical measuring instruments. Terra, Budapest, p 427

53. Szebellédy L, Somogyi Z (1938) Z Anal Chem 112:313–323

54. Szebellédy L, Somogyi Z (1938) Z Anal Chem 112:323–331

55. Szebellédy L, Somogyi Z (1938) Z Anal Chem 112:332–336

56. Szebellédy L, Somogyi Z (1938) Z Anal Chem 112:385–390

57. Szebellédy L, Somogyi Z (1938) Z Anal Chem 112:391–395

58. Szebellédy L, Somogyi Z (1938) Z Anal Chem 112:395–399

59. Szebellédy L, Somogyi Z (1938) Z Anal Chem 112:400–404

60. Kies HI (1962) J Electroanal Chem 4:257–286

61. Szabadvary F (1964) Talanta 11:593–599

62. Szabadváry F (1966) History of analytical chemistry. Pergamon, London, p 316

63. Grower GG (1917) Proceedings Amer Soc Testing Materials 17:129–155

64. Zuman P (2001) Crit Rev Anal Chem 31:281–289

65. Heyrovský M, this issue

66. Heyrovský M, Marecek V, Samec Z, this issue

67. Zbinden Ch (1930) Recherches spectrographiques sur des cendres de sangs et d'organes humains. Impr Commerciale, Lausanne

68. Dutoit P, Zbinden Ch (1930) Compt rend 190:172

69. Haenny Ch (1944) Helv Chim Acta 27:1414–1422

70. Zbinden Ch (1931) Bull Soc de Chim Biologique 3:35–46

71. Zbinden Ch (1932) Lait 12:481–489

72. Elema B (1947) Antonie Leeuwenhoek 12:243–256

73. Barker GC, Jenkins IL (1952) Analyst 77:685–696

74. Kemula W, Kublik Z (1956) Chem Anal 30:1005–1008

75. Kemula W, Kublik Z (1959) Anal Chem Acta 18:104–111

76. Kemula W, Kublik Z, Głodowski S (1959/60) J Electroanal Chem 1:91–100

77. Kemula W (1960) Voltammetry with the hanging mercury drop electrode. In: Longmuir IS (ed) Advances in Polarography. Pergamon, Oxford, pp 105–143

78. Gokhshtein YP, Gokhshtein AY (1962) Zh Fiz Khim 36:651–655

79. http://www2.chemistry.msu.edu/Genealogy/chem_gene.shtml

80. Chemistry News, University of Oregon, 2007, pp 6

81. Lord SS Jr, O'Neill RC, Rogers LB (1952) Anal Chem 24:209–213

82. Mamantov G, Pand Papoff, Delahay P (1957) J Am Chem Soc 79:4034–4040

83. Scholz F, Roloff R, Henrion G (1983) Coll Czechoslovak Chem Commun 48:2721–2727

84. Scholz F (2009) Anal Bioanal Chem 395:1571–1573

85. Neeb R (1959) Fresenius Z Anal Chem 171:321–339

86. Neeb R (1961) Fresenius Z Anal Chem 180:161–168

87. Neeb R (1962) Angew Chem 74:203–213

88. Neeb R (1969) Inverse Polarographie und Voltammetrie. Weinheim, Verlag Chemie

89. Batley GE (2004) Aust J Chem 57:899–902

90. Florence TM (1970) J Electroanal Chem 27:273–281

91. Batley GE, Florence TM (1974) J Electroanal Chem 55:23–43

92. Bubić S, Branica M (1973) Thalassia Jugoslav 9:47–53

93. Branica M (1990) Environmental research in aquatic systems. Forschungszentrum Jülich GmbH, Zentralbibliothek. Jülich