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Important Figures of Analytical Chemistry from Germany in Brief Biographies

From the Middle Ages to the Twentieth Century

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Acknowledgments

This volume arises from the wish to fulfil the ideals set out by the Working Party on Analytical Chemistry of the Federation of European Chemical Societies after EUROANALYSIS I in 1972 and continued to the present by the Division of Analytical Chemistry of the European Association for Chemical and Molecular Sciences for the organisation of EUROANALYSIS conferences.

That there should always be an opening ceremony where the host country makes a contribution describing the history and development of Analytical Chemistry in the respective country.

A listing of the publications of such lectures and other materials on the history of analytical chemistry in Europe resulting from the activities of the Study Group History is available via the DAC-EuCheMS website.

Germany has been the host country on two occasions for EUROANALYSIS I, Heidelberg, 1972 and for EUROANALYSIS XII, Dortmund, 2002. However due to the nearly impossible task to provide the historical review lectures for Germany, within the time frame of an opening ceremony, no such lectures were presented. The present work seeks to complete series of these accounts by dealing with the previous gap, that for Germany.

The authors wish to record their thanks and appreciation to their wives, Cecilia Mary Burns, Ursula Hanni Müller, Gloria Salzer and Sigrid Werner, for their tolerance and support during the many years of research and preparation of this text.

Contents

Chapter 1
Introduction and Overview

D. Thorburn Burns, R. Klaus Müller, Reiner Salzer and Gerhard Werner

The contributions of chemists of and who worked in Germany are vast and any account must deal with three main problems: define what specifically is analytical chemistry within the whole corpus of chemistry, determine the geographical area to be designated as Germany from the variable areas occupied by the German speaking states and the country as unified over the ages and selection of the system for the periodization of developments in chemistry and their subdivisions over time.

The formulation of an agreed definition of analytical chemistry was first considered by the Working Party on Analytical Chemistry (WPAC) of the Federation of European Chemical Societies (FECS) in 1975. Following an international competition and further debate, the WPAC agreed in 1993 the definition to be:

> Analytical chemistry is a scientific discipline which develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter in space and time [1].

This definition could with advantage, at the present time, be further refined by replacing *analytical chemistry* by *analytical science.* An "Inventory of Definitions in Analytical Chemistry" is available to provide assistance with the categorization of topics within the diverse subdivisions of the subject that have arisen particularly from the development of instrumental methods [2].

An additional essential problem was the logical choice of the persons to be included, who had to be dealt with not only based on their services for analytical chemistry, but also by their national background. Our survey aimed not to boast the importance of the country, but to express the feeling of obligation towards essential contributions to our scientific area by persons correlated with Germany, as it had been done similarly for other countries. But who is a German chemist? Birthplace alone may mislead, for example, when somebody was born abroad, but studied, lived or worked mainly in Germany. The place of the most relevant analytical studies might be considered as a criterion, or the language of their most relevant publications (although then hardly any German researchers would remain on this criterion). In a political sense, the changing borders between Germany and

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neighbouring countries such as Sweden, Poland, Czech Republic, Austria and France let some chemists commonly considered as Germans become Foreigners (or vice versa), and depending on personal points of view on their nationality.

The selection of the included scientists has been decided by best intention and knowledge of the authors, but is certainly incomplete. Nevertheless, it provides examples for a broad development, which was one of the preconditions for our current state of the art. The articles are intentionally focused onto the analytical contributions of the authors. Some of the articles on especially well-known people are certainly rather short, but this is often more balanced by the high number of available biographical publications about them.

For a number of reasons, we chose 1920 as the final year of birth for important analytical scientists to be included in this compilation. None of the scientists appreciated in this book is living anymore. Data Protection Acts prevent archives from permitting access to non-published personal information. This could lead to severe imbalances between biographies of those who died earlier and whose documents are available, those who died more recently and whose documents are not accessible, and those still alive and grant all information about their personal data.

During the period of existence of the "Iron Curtain", the role of the IUPAC via its commissions and many of its members acting individually and their National Societies was important in developing and maintaining close relationships between numbers of analytical chemists across the divide. Assistance was also given by analytical chemists on either side, which ensured scientific contacts at least on a minimal level. Of the figures mentioned in this book, Wilhelm Fresenius, played an outstanding role also in this respect.

Hufbauer in his scholarly monograph, *The Formation of the German Chemical Community* took a reasonably broad geographical view of the extent of the community but used a relatively narrow time frame, 1720–1795 [3]. He discussed in detail, the role of Lorenz Crell (1745–1816), the chemical journalist, in the formation of the community, the various differences of opinions between the German and French chemists during the period of the demise of the phlogiston theory and the "notorious reduction experiment" that of mercury(II) oxide. The book concludes with three most useful appendices, which deal with biographical profiles, institutional histories and a list of Crell's subscribers.

Interestingly, Partington in his monumental *History of Chemistry* [4], following a historical time sequence, dealt with the subject primarily by persons, then by locations and to a lesser extent by theories. Many German contributions were described within broad topics, such as iatrochemistry, however, a specific chapter on *Chemistry in Germany* [4a], covering the contributions from Johann Christian Wiegleb (1732–1800) to those of Johann Wolfgang von Goethe (1749–1832), a time span from the mid-1700s to 1840 which includes Crell's activities, by the end of the which German community was quite well developed. In Volume 4, accounts were given of the history of the subdivisions of chemistry, physical, organic, inorganic, radioactivity and atomic structure of atoms but not that of analytical chemistry.

Thomas Thomson in his *History of Chemistry* gives considerable details under the heading *Progress of Analytical Chemistry* of the period of the development what are now called that of classical methods. From the progress made in the late eighteenth century by Martin Heinrich Klaproth (1743–1814) by his substitution of silver crucibles for the iron crucibles used by Bergmann to that made in the early nineteenth century by William Hyde Wollaston (1767–1829) by his introduction of platinum crucibles [5]. This account was followed by von Meyer in his now classic, *A History of Chemistry: From the Earliest times to the Current Day* [6] who divided his account of analytical chemistry as follows: qualitative analysis of inorganic substances, quantitative analysis of inorganic substances, volumetric analysis, methods of gas analysis and finally, the analysis of organic substances [6a]. He reviewed the chemical literature, the manuals, textbooks and journals. Concerning the most recent textbooks of technico-chemical methods, he noted, in particular, the development of methods for the analysis of articles of food and drink, the importance of which is shown by the increasing provision for instruction in it [6b]. The significant contributions to the growth of chemical instruction in the nineteenth century by German chemical institutions and their influence abroad were well recognized by the end of the nineteenth century [6c].

The first comprehensive free-standing account of the history of analytical chemistry as such is that due to Szabadváry [7, 8] in 1966. Starting with the earliest knowledge of analysis in antiquity, followed by those in the middle ages, the periods of iatrochemistry and of phlogiston, he continues to the establishment of the fundamental laws of chemistry, qualitative and gravimetric analysis and volumetric analysis. The material in the modern period focussed on instrumental methods of organic analysis, of electrochemical and of optical methods and briefly on radiochemical and chromatographic methods. This seminal account was followed by Laitinen and Ewing's monograph in which the editors chose to de-emphasize the early work covered in the general histories of chemistry and focus on the more modern period [9]. The topics covered are developments in chemical methods of analysis, analytical spectroscopy, electrochemical chemistry, separations and lastly the common features of instruments and signal processing instrumentation. Overall this is an excellent, well-illustrated account but suffers from the serious omission of all biographical data, which was made available at the time of publication via a set of microfiche cards, but which now cannot be acquired. The development of chemical instrumentation in the twentieth century was the subject of a conference in 2000 which resulted in an interesting multi-authored volume *From Classical to Modern Chemistry: The Instrumental Revolution* [10]. In addition to describing the development of specific techniques and many of the personalities involved, this volume places the techniques in their social, economic and political contexts. Furthermore, the impact of instrumentation on all branches of chemistry and on the biomedical and environmental sciences is outlined. Since these three accounts, Hudson has listed the reviews of the development of analytical chemistry in specific countries and further expanded the number and variety of instrumental methods to include thermal methods [11].

Homburg has recently discussed *The rise of analytical chemistry and its consequences for the development of the German chemical profession* [12], focusing on the changes in the chemical laboratory rather than the changes over time in the theoretical basis of chemistry. Particular attention was paid to social developments in Germany which led to the separation of practical chemistry from the arts, the distinction perceived between chemists trained at the Universities and Polytechnics and those "empirically trained", and to the emergence of courses in practical analytical chemistry and a new profession. However, academic analytical chemistry and industrial analysis went their separate ways in Germany until the 1840s. This division is described more detail in the article *Two factions, one profession: the chemical profession in German society 1780–1870* [13]. Wetzel in outlining the social effects of the revolution in Germany 1848 on the "*Origins of and education and career opportunities for the profession of 'chemists' in the second half of the nineteenth century in Germany*", expands further on the dualism that existed within the German formal and professional education systems [14].

Vershinin and Zolotov have drawn attention to the problems that exist in the periodization of developments of the history of chemical analysis [15] which have arisen from the semi-independent developments of analytical chemistry in industry and in academic science. Both moved apart as different people worked in these two fields. However, as the problems they solved were closely related, the historical development of academic analytical chemistry and industrial chemical analysis shows considerable synchronicity and similarity in periodization. They proposed four periods, namely: (1) before the middle of the seventeenth century; (2) late seventeenth century to second half of the nineteenth century; (3) late nineteenth century to second half of the twentieth century; (4) from the 1979–1980s till the present time. This classification broadly fits with the approach taken herein, where we have split the earlier period's alchemy and assay, iatrochemistry and analysis in solution, the phlogiston period, the demise of phlogiston and rise of stoichiometry and lastly the period of the development of text books of chemical analysis. Our subsequent Chapter is termed *The growth into a scientific discipline* and covers the period of 1800–1920 (birth of the personalities 1800–1870). The book is concluded by the Chapter *The development of instrumental techniques* that includes scientists born between 1870 and 1920.

There is no comprehensive account of analytical chemistry in Germany, from the precursors of science in the early middle ages to the present era, either before or to follow on from Szabadváry and Chalmers' brief overview produced to celebrate the centenary of Carl Friedrich Mohr's death in 1879 [16]. Merely a few specialized areas have been reviewed such as that on metallurgical analysis in Habashi's *Chemistry and metallurgy in the German Empire 1740–1918* [17] and Possehl on the development of analytical and quality control laboratories in the German pharmaceutical industry [18].

Improvements on the simple classical chemical methods of analysis were the extensions and systematization of "wet analysis" by Kühn [19], Erdmann [20] and Fresenius (separation schemes, mineral waters, [21]), Reinsch [22] and Behrens (microchemical analysis) [23]; the invention of volumetry or titrimetry, extended and improved by Anton Friedrich Robert Behrend, Fritz Förster, Walther Hempel, Justus Liebig, Mohr [24], Schwarz [25], Volhard [26], Winkler [27]; and the development of chromogenic reagents with selectivity and other broad applicability by Otto [28], Fehling [29], Nessler [30], Dragendorff [31], Griess and Leibius [32] and Ehrlich [33].

The measurement of physical parameters for analytical purposes was introduced by Ernst Otto Beckmann (ebulliometric and cryoscopic determination of relative molecular masses, [34]), and the application of optical phenomena from the Lambert-Beer Law [35] to spectral analysis (Kirchhoff and Bunsen [36, 37]), to the use of electrochemical principles such as electrolytic separations (Classen [38]) through contributions of Förster [39] and LeBlanc [40] to Robert Bunsen, Walter Hermann Nernst and Ostwald [41].

Implementation of chemical analysis from mainly metals, minerals and mineral waters to categories of other analytes and other economical areas led to significant advances. For example, Justus Liebig's extensive analyses of biological samples [42] led to a significant increase of agricultural productivity, and Julius Nessler's and Stöckardt's [43] work in agricultural and forestry chemistry has had similar impacts. The forensic-toxicological procedures and analytical systems of Erdmann [44], Mohr [45], Otto [28], Sonnenschein [46], Autenrieth [47] and Gadamer [48] produced substantial advances in poison and other crime detection, and Hoppe-Seyler [49] opened up the extremely wide new field of clinical chemistry, which has included many of the aforementioned methods initiated in the outlined time frame.

Theoretical advances such as the Lambert-Beer Law [35], the Nernst Equation for ionic equilibria or his Partition Law [50] had general importance for analytics as well as for technical processes and in the interpretation of biological phenomena. The detection of new elements has been more or less a side effect of the analytical advances, equally to the sometimes surprising technological applicability and success of—originally more academic or purely analytical—results such as the invention of azo dyes by Griess and Leibius [32] or the separation of rare earth elements.

When what became known as chemistry was still in its basic evolution stages and comprised all its later branches in the centuries before 1800, special chemical fields of activity developed more and more from the turn to the twentieth century and created experts focusing onto smaller sectors of chemistry including that of analytical chemistry. In the nineteenth century, one could contribute essentially to analytics even from neighbouring disciplines such as medicine, pharmacy and biology (e.g. work of Autenrieth [47], Dragendorff [31], Ehrlich [33], Hoppe-Seyler [49], Otto [28], Sonnenschein [46], Gadamer [48]). Considering chemical analytics in a broad sense, it seems appropriate to also include aspects on those steps forward, which finally contributed to the present tremendous knowledge and methodologies in biochemistry, biology and medicine and to the fascinating improvements of our insight into nature.

The image of analytical chemistry at the outgoing nineteenth century is still dominated by wet-chemical methods (Fig. 1.1), but the measurement of physical

Fig. 1.1 Grand lecture hall of the Chemical Laboratory at Universität Leipzig, opened in 1868. *Photo* Archive Faculty Chemistry and Mineralogy, Universität Leipzig, with permission

parameters and the application of physico-chemical techniques start to complement the picture. The vast development of analytical chemistry as a sub-discipline is illustrated by the progress shown by Remigius Fresenius' *Anleitung zur qualitativen chemischen Analyse* (Instruction for qualitative chemical analysis) [51], which grew from the little booklet of the first edition in 1841 to a volume of considerable size by the 16th edition in 1895 [52].

Around the same time, Wilhelm Ostwald published his book *Die wissenschaftlichen Grundlagen der analytischen Chemie* [53] (The scientific foundations of analytical chemistry treated in an elementary manner [54]). One sentence of the author's preface is still quoted today:

> Analytical chemistry thus fills the subordinate but at the same time indispensable position of handmaid to the other branches of our science.

Commonly neglected is Ostwald's sequel remark:

> While we everywhere find the liveliest activity with regard to the theoretical arrangement of scientific material, and observe that questions of this kind always arouse far more interest than purely experimental problems, analytical chemistry is content with fashions of theory which have long been discarded elsewhere, and sees no harm in presenting its results in a shape which has really been antiquated for the last half century.

The young generation of analytical chemists at the time eagerly obeyed Ostwald's demands to combine advanced analytical techniques with the theoretical foundation of their data. Due to Ostwald's worldwide reputation, these developments were adopted in all developed countries (e.g. [55]). The improved understanding of the chemical mechanisms behind the analytical determinations permitted an increasing accuracy of quantitative determinations. Initial steps were based on electrochemical titrations (e.g. Erich Müller, Wilhelm Böttger) and extended to the anticipation of fuel cells (e.g. Kurt Schwabe). The developments were supported by the early miniaturization of the analytical equipment, which provided not only access to low concentrations but also to smaller sample sizes (e.g. Georg Lockemann, Max Boëtius).

Another area of impressive developments was in the separation and determination of elements (e.g. Otto Hönigschmidt, Robert Grießbach, Wilhelm Geilmann, and Werner Fischer). Here, it was not only the access to advanced technical equipment but also the need for painstakingly executed chemical operations that limited progress. Progress was facilitated by early radiochemical trace analyses (e.g. Ida Noddack-Tacke, Otto Hahn, Fritz Straßmann), the progenitors of modern environmental analyses and even cosmochemistry. In due course, the capability for trace analysis needed to be complemented by fast chemical determinations for the detection of short-lived species.

Many important industrial processes and new chemical products required innovative approaches in analytical research (e.g. Hermann Staudinger, Karl Fischer). In the production processes, more and more analytical controls were used (e.g. Erwin Lehrer, Hermann Kienitz). Of great impact to process control were the developments in spectroscopy (e.g. Josef Goubeau, Erwin Lehrer, Arthur Simon, Reinhard Mecke, Kurt Laqua, and Hans Massmann). From about 1965, chromatographic techniques became popular (e.g. Robert Grießbach, Reinhard Mecke, and in particular Gerhard Hesse). The large amount of data available from analytical instruments that became available then required the careful consideration of the data quality (e.g. Heinrich Kaiser and Wilhelm Fresenius).

The top advances in analytical chemistry between 1935 and 1985 have been summarized in a list of the 500 most-cited papers [56]. Of these, 133 papers (27 %) belong to analytical chemistry, clear evidence for the growing importance of the sub-discipline. By 1980, the overwhelming majority of these papers dealt with bioanalytical tasks. The dominating techniques used in the research are spectroscopy and spectrometry (45 %), chromatography (37 %) and immunoanalysis (13 %), whereas nuclear analysis (3 %) and electroanalysis (1 %) lost much ground compared to the beginning of the century [56]. The lives and contributions of the major contributors in Germany to this period of progress are summarized in Chap. 4.

Some ideas that were prophetic at their time and have since been shown to have prognostic value, so suggests a paper of Fresenius and Babo [57], to compare several published analytical procedures for the same purpose for effectivity prior to their application, because authors often claim imaginary advantages for their proposal. Only a late understanding, a few decades ago, lead to the obligation