THE DEVELOPMENT OF ANALYTICAL CHEMISTRY IN ROMANIA

GRIGORE POPA

Department of Analytical Chemistry, University of Bucharest, Romania

ABSTRACT

A brief history is given of the development of analytical chemistry in Romania. Aspects concerning the teaching of analytical chemistry in Romanian universities as well as the achievements of the scientific research in this field are presented.

The earliest beginnings of analytical chemistry in the territory of our country can be traced back to identify themselves with those of chemistry itself. The more so as analytical chemistry is one of the branches of chemistry with the widest range of applications in all fields of economic life.

Its theoretical character materializes in the study of the properties of materials in terms of concentration $P = f(c)$ and the development of analytical methods, whereas the practical character resides in the analytical techniques themselves. In fact, the study of materials with a view to using them has been the concern of man since the earliest times, a concern that was manifest in this country, too.

In the following I shall try to outline the major stages in the development of analytical chemistry and of its teaching in our country. Certain skills, such as the potters', the smiths' or metal workers' (with the Dacians), etc. requiring practical chemical knowledge have long been familiar to the country's inhabitants. But the lack of written documents would make it impossible in practice to state a precise date for the beginning of the development of chemistry in our country.

In feudal times, with the exception of boroughs, a number of trades sprang into being, closely connected with the processing of material products, which helped develop chemistry to a certain extent. Among the main trades at that time that are recorded in documents we can cite those of the 'păcurari'—fuel oilmen (from 'păcură, fuel oil, crude oil); potters; metal smelters and founders; 'slădniţari'—brewers ('sladniţă'—brewery); tanners, etc. All these trades required knowledge of chemical techniques.

Between the fifteenth and eighteenth centuries chemistry developed at a somewhat slower rate in the territory of our country, notwithstanding the steady efforts of the alchemists and chemists in these parts to improve the then existing primitive chemical processes. Thus, for instance, in the eighteenth century, Samuel Köleseri of Cluj the author of the famous *Auraria Romano-Dacia* printed in 1797 in Sibiu, was well-known for his work.

In Wallachia, the Frenchman Georges Flachat together with other chemists of the Principality used to discuss and elucidate chemical problems (an incipient school). The need for improved technological processes in the workshops and factories (wherein earthenware, metals, glass, leather and textiles were being processed or made) gave a strong impact to the development of chemistry and chemical practice in our country. The first analytical laboratories were set up, and with them the chemical control of metal quality in Transylvania (monetary gold titre, etc.).

With the advent of the bourgeoisie on our country, the new rising social class became interested in starting maximum-profit enterprises. Hence the growing number of breweries, bakeries, earthenware and glass makers, textile mills, and others. At the same time the bases of chemical education were laid by the courses of Gheorghe Asachi in Jassy and Gheorghe Lazăr in Bucharest.

The Society of Physicians and Naturalists in Moldavia founded in 1833 is an outstanding moment in the development of analytical chemistry. The society set out to record and render useful Moldavia's natural resources. Studies of the country's natural wealth were published in the journals concerned. It was in the *Albina Românească* magazine (1824) that the first studies on mineral water analyses performed by Zotta Gihoc jointly with the pharmaceutical chemists Abrahamfi and Humpel appeared. The studies were also published in *Buchner's Chemische Annalen* (1839).

In 1835 when the first higher school in Moldavia was founded, its programme included several courses in chemistry and experimental practice (T. Stamate – 1840).

The founder of the Bucharest Higher School of Medicine and Pharmacy—Carol Davilla (a Frenchman by birth), followed by Alfred Bernath (an Austrian), in 1855 introduced into their courses in chemistry experiments on foodstuffs and drug adulteration. Bernath was also the first reader of analytical chemistry at the same School. He it was who organized the first laboratories wherein foodstuff and drink analyses, forensic chemical and medical analyses were carried out.

Iacob Felix, Carol Davilla's successor in 1893, initiated a department for 'the chemistry and analysis of foodstuffs and beverages', which is actually the first department of analytical chemistry in our country; in 1897 it was taken over by Stefan Minovici (the first professor of analytical chemistry). Minovici wrote a number of works on analytical chemistry, among which were included quantitative methods for the determination of potassium, picric acid, manganese, etc.

A prominent figure of our nation in the field of analytical chemistry was Nicolae Teclu, professor at the Commercial Academy in Vienna (1880). By his over sixty publications in German and Austrian chemical journals he made a valuable contribution to analytical chemistry. His study of gas combustion and of the flames (19 notes) including development of the Teclu bulb, was essential for the understanding of flame reactions. Teclu tackled various problems of analytical chemistry, viz. the microscopic quantitative investigation technique, the use of a radiometer to measure light intensity, a zone assaying technique, etc.

In his later years Teclu was elected member of the Romanian Academy.

DEVELOPMENT OF HIGHER EDUCATION IN ROMANIA

The foundation of the Universities in Jassy and Bucharest (1860 and 1864, respectively) opened up a new chapter in the development of chemical higher education and of chemistry proper in this country. The Romanian chemical school was coming into being.

An outstanding contribution to the development of analytical chemistry was made by the two founders of the Romanian chemical school, Petru Poni and Constantin C. Istrati. The former was a follower of Stefan Micle in 1878 at the chair of Chemistry of the Jassy University, whereas the latter was professor at the newly established chair of analytical chemistry in Bucharest University (1887). Progressive patriots, both have strived against all kinds of difficulties for the progress of chemistry in our country. Upon his appointment as professor of chemistry, Petru Poni found a small room. a former kitchen, with several almost-empty flasks. That made him write the article 'It is the theory that we are lacking', whereas in a memorandum to the Ministry of Public Education (1878) he said: 'We do not know the nature and value of the minerals in our soil or the actual quality of our agricultural products, and the scientific conditions of our agriculture either, nor do we know our mineral waters—in a word we know nothing of what is the basis of our national wealth.'

That concern of Petru Poni's was equally manifest in his studies and analyses carried out during his life among which were: mineral water analyses, investigations of the minerals in the crystalline massif of Broşteni, research concerning Romanian mineral raw materials; and research on Romanian oil (chemical composition of the crude).

Like Petru Poni, Constantin Istrati started in Bucharest the campaign for the study of the chemical resources of the Romanian land; salt, ozokerite, amber and oil. With the development of chemistry, and particularly chemical higher education, as his primary concern, C. Istrati in his opening address to the Faculty of Sciences in Bucharest, pointed out the need for the following chairs within the Faculty (1887): general and inorganic chemistry, organic chemistry, analytical and preparatory chemistry, technological chemistry, and agricultural chemistry.

In support of his views Istrati argued that (I quote) 'one should not forget that such is the plight of our country that the immediate institution of these chairs would lend strong and wise support to agriculture and the development of our industries. There is nothing useful that will ever be possible, nothing liable to improvement or success, unless firmly rooted into the exact sciences from which the most useful applications stem and among which chemistry holds a leading position.' It was only much later that Istrati's wish came true.

After the chair of analytical chemistry was set up at the Faculty of Pharmacy (1897) the Conference in Analytical Chemistry of the Jassy University was changed to a chair (1932)—Radu Cernătescu.

Until the establishment of this chair in Jassy higher education in analytical chemistry came under the chair of inorganic chemistry, a situation that in Bucharest lasted until 1960.

The period after the foundation of the Romanian chemical school is characterized by steadier efforts in the study of analytical chemistry and chemical analysis.

In the university centres, the development of analytical investigation resulted in new analytical methods. In Jassy, N. Costăchescu, Petru Poni's successor, and later Radu Cernătescu, made significant contributions to analytical chemistry. Thus, Costăchescu directed his research along two main lines: (1) Utilization of natural resources (salt composition, correlation of salt-to-oil deposits); and (2) Complex combinations, a branch whose founder in our country he was.

Radu Cernătescu investigated new reactions for the study of nitric acid, nitrates, molybdates, vanadates, alkaloids, etc., established new methods for the determination of various cations (Ag^+, Cd^{2+}, Mg^{2+}, Cu^{2+}, etc.). He and his co-workers played a major part in the development of polarographic analysis and the analytical systematization of the polarographic reduction of cations.

The school of analytical chemistry in Jassy proved fruitful: today there is a chair of analytical chemistry both at the University and at the Polytechnic Institute in Jassy. The dream of the founder of the Romanian school of chemistry in Jassy – Petru Poni – materialized in the big chemical combines of socialism standing in Moldavia's beautiful fields in the new chairs and laboratories set up in this city and the Chemical Research Centre named after him.

INORGANIC CHEMISTRY AT BUCHAREST

In Bucharest, the first professor of inorganic chemistry of the Faculty of Sciences to institute a scientific activity in analytical chemistry, apart from the steady educational and cultural one, was G. G. Longinescu (1906–1938).

The scientific achievements in the field of analytical chemistry of the team headed by Longinescu can be summed up as follows: separation and identification of elements in the hydrogen sulphide group (lecturers G. Chaborschi, E. Petrescu and G. Theodorescu); separation, identification and determination of halogenated acids (G. Chaborschi, Th. Pirtea, M. Bădescu, and others); identification reactions for different ions (G. Chaborschi, E. Petrescu and Th. Pirtea); new practical experiments jointly with C. N. Teodosiu.

It is worth mentioning that Gabriela L. Chaborschi was appointed lecturer of analytical chemistry in 1927.

Both Longinescu and Chaborschi also wrote textbooks for the students attending courses in physical chemistry and engineering chemistry, dealing with such subjects as quantitative analysis.

In late 1940, G. Spacu from the University of Cluj was transferred to the chair of inorganic and analytical chemistry in Bucharest. In Cluj, where he was appointed professor in 1919, as well as in Bucharest, G. Spacu and his co-workers made big strides in the development of analytical chemistry. Working out new methods of qualitative and quantitative chemical analysis

and evolving new reactions and reagents were a constant concern of his staff. During his scientific research work carried out in Cluj, Spacu published a large number of studies in analytical chemistry jointly with his followers Raluca Ripan, L. Caton, E. Voicu, C. Creangă, T. Dick, G. Suciu, I. G. Murgulescu, C. G. Macarovici, V. Armeanu, Petre Spacu, E. Popper, P. Voichescu, M. Vancea, C. Drăgulescu, C. Dima, A. Pop, V. Nicolescu, M. Kuros and others. It is in these works that numerous analytical methods are developed, most of which are based on the formation of complex practically insoluble combinations to facilitate fast identification and assaying of a large number of metals, acids and various organic materials.

The gravimetric and potentiometric techniques for the assay of the Cu(II), Ni(II), Co(II), Cd(II) ions developed by Spacu and his co-workers involved the use of different organic bases such as pyridine, aniline, benzidine, etc. as well as alkali rhodanides. In collaboration with Kuros, Spacu used mercaptobenzthiazole as precipitation reagent for Cu(II) and other elements.

Analytical chemical works hold a significant place in Spacu's scientific research activity. By his over one hundred original scientific publications in the field of analytical chemistry, of which two are currently referred to as 'G. Spacu reaction' and the 'Spacu reagent', he made a valuable contribution to the development of analytical chemistry in our country and its recognition abroad.

The school of analytical chemistry headed by Spacu moulded many reputed scholars who in their turn were actively involved in the development of analytical chemistry; including Raluca Ripan, I. G. Murgulescu, C. Drăgulescu, C. G. Macarovici, C. Popper and V. Armeanu.

I. G. Murgulescu through his work in analytical chemistry mainly directed at evolving new methods for the assay of various metals, at using absorption indicators in volumetric analysis, studying redox reagents in volumetric analysis and developing new conductimetric techniques made an outstanding contribution to this branch of chemistry.

Raluca Ripan, today an eminent scientist of our country, worked in the domain of complex combinations and their use in analytical chemistry. Academician Ripan was able to discover and study new classes of complex combinations used in the determination of metals, as well as new methods of assay for thallium, lead, tellurium, selenic acid, selenocyanates, etc. Ripan and his co-workers have elaborated a valuable treatise of analytical chemistry.

It is worth noting that Ripan was able to continue Spacu's work in training analytical chemists who are today in charge of research teams in analytical chemistry in our country.

Thus, among Ripan's collaborators I would mention Candin Liteanu, Head of the Department of Analytical Chemistry in Cluj, Al. Duca, Head of the Department of Analytical Chemistry at the Polytechnic Institute in Jassy and myself leading the Department of Analytical Chemistry in Bucharest, and others.

C. G. Macarovoci, professor at the Cluj University, has published a good number of papers in analytical chemistry centring on: new methods for the assay of zinc, copper, cobalt and nickel, and on the study of some complex amines.

As early as 1933 Spacu in collaboration with E. Popper scored big successes

in the field of molecular refraction and refractometric analysis in general. Popper is concerned with the separation of heavy cations by a class of mercapto-derivatives and the indirect methods based on the excess reagents ratio in titrimetry, etc.

C. Drăgulescu, Head of the Department of Inorganic Analytical Chemistry at the Polytechnic Institute in Timişoara, has developed numerous methods for the assay of several metals and of some acid radicals (tin, bismuth, arsenates, sulphites, etc.) by potentiometric methods.

P. Spacu who was assistant professor at the Department of Inorganic and Analytical Chemistry of the Cluj University, later became a professor at the Department of Inorganic and Analytical Chemistry in Bucharest. From among the new analytical methods developed by him I quote those based on the formation of complexes for silver, mercury, bismuth, lead, copper, cobalt, etc.

V. Armeanu, professor at the Academy of Economic Sciences, continues his work in the field of analytical chemistry publishing a number of original scientific papers on methods for the determination of silver, copper, calcium and gallium, and a study on the substituents effect on the properties of complexing agents.

The followers of Cernătescu in Jassy, Margareta Poni, R. Ralea and Simon Fişel, in their works on polarography, kinetics, chromatography, colorimetric analysis, etc. have had their share in advancing analytical chemistry as a science.

RECENT ROMANIAN DEVELOPMENTS

After 1944, as a result of the wise policy of the Romanian Communist Party for the country's industrialization, the number of industrial units and scientific research laboratories rose steadily.

Industry raises numerous problems of analysis of both raw materials and end-products, analysis which not infrequently controls the technological flowsheet. I may safely state that the problems which industry, technology and science pose to analytical chemistry are responsible for the fast development of this branch of chemistry.

The advances in analytical chemistry, both at home and abroad, are largely accounted for by these requirements of industrial progress.

Life pushes analytical chemistry ahead.

Ever more numerous analytical chemists are employed by the analytical and control laboratories of the country's big industrial combines.

In recent years, new departments of analytical chemistry have been set up in higher education establishments for the training of analytical chemists to work in industrial and research laboratories. The Department of Analytical Chemistry of the Bucharest University founded in 1960 is the first of the kind, after the Education Reform in 1948. Stemming from an objective need, already emphasized by C. Istrati as early as 1887, a team was appointed within Bucharest University for the training of analytical chemists.

This team has produced over one hundred original scientific publications on the interaction of organic reagents with different metal ions, the stability

of complex combinations in various solvent media and new methods for the assay of various metal ions.

The Department of Analytical Chemistry created in 1964 at the Cluj University gathered a large number of research workers into a reliable team.

The teaching staff there have published valuable scientific studies on chelatometric titrations, determination of the equivalence points in titrimetric methods, the use of mathematical statistics in chemical analysis, frequentometric analysis and ion-selective electrodes using polymer plasticizer membranes, precipitate impregnated membranes and ceramic membranes.

In Jassy, the staff of the University Department of analytical chemistry direct their efforts to solvent-extraction, chromatography, spectrophotometry.

The Department of Analytical Chemistry of the Polytechnic Institute in Jassy focuses its attention on polarographic, chromatographic and ion-exchanging methods for the determination of some metal ions.

In the university centre of Timişoara, at the Department of Inorganic and Analytical Chemistry of the Polytechnic Institute and the University, the teaching staff, besides their educational tasks, are also involved in scientific research on new reagents for use in chemical analyses.

So far only the departments of analytical chemistry in the big university centres have been mentioned; but we should not assume that scientific research in analytical chemistry and chemical analysis is conducted by them alone.

These teams are primarily concerned with the teaching of this discipline, hence the training of specialists to fulfil the needs of industry and of scientific research.

The greater share in the progress of analytical chemistry as a science is the research workers' in scientific research, industrial and department laboratories.

As early as the first years of socialist construction, the Romanian Communist Party placed considerable emphasis on the development of chemical industry which was assigned a leading role in raising the degree of utilization of such natural resources as crude oil, natural gas, salt, non-ferrous metals, etc. Chemistry holds an important place in today's economic growth due to the ever wider use of the chemical products in industry, agriculture, and everyday life.

Illustrative of the upsurge of this industrial branch in the last five years are the production figures for every five-years period starting with 1950.

Taking 1950 as unit starting point, in 1960 production was 6.58 times higher, in 1965—21 times and in 1970—55 times that of 1950.

In keeping with the high rate of growth of the chemical industry, stronger emphasis was laid on scientific–technical progress, to the increased share of the individual in applied chemical research calling for an appropriate expansion of the existing network of industrial research laboratories and research institutes. The body of analytical chemists was enlarged to cope with the quality requirements of production. These requirements of the chemical industry acted as a strong incentive on the analysts' research work and were responsible for raising analytical chemistry in our country to an unprecedentedly high level.

The development, diversification and qualitative improvement of chemical industry, with automation as a means for raising economic efficiency, are the major concerns of scientific and technological research activity.

An outstanding part in the study of problems connected with increasing quality production to a level comparable with similar foreign products is played by analytical chemists working in the quality control laboratories of combines.

The present stage of development of analytical chemistry in our country and the advances made in recent years are largely accounted for by the use of improved automatic instruments in chemical analysis.

The physical constants that are the object of analytical chemical study and measurement are quite numerous ranging from weight and volume, density and colour to x-ray fluorescence, neutron activation or atomic absorption. The finding of new physical and chemical characteristics of materials but particularly the modern techniques to measure them are the future development trends of analytical chemistry.

Analytical chemistry today is a unified whole with a well-established theoretical basis that allowed for the shift from laboratory analysis to instrumental analysis—the chemical analytical control of production, automatic industrial analyses (automatic pH-meters, potentiometers, automatic industrial gas analysers, automatic on-line chromatographs etc.).

One of the tasks facing analytical chemistry and electronics experts is the improvement of the research instruments and of chemical analysis automation.

Considering the importance of analytical chemistry and of analytical chemical methods for the development of the chemical industry in our country, the approach of the theoretical aspects of analytical chemistry as well as the new organic or inorganic analytical methods worked out must be a major concern of analytical chemists in the future to cope with the development of our socialist technology and industry.