SOME TRENDS IN THE DEVELOPMENT OF
INSTRUMENTAL ANALYSIS IN HUNGARY

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Analytical chemistry developed earlier than the subject chemistry as
known today, and this analytical chemistry grew later into chemistry. When
the subject of chemistry grew too large and the process of fragmentation of
chemistry started in the last century, analytical chemistry became the first
independent branch of chemical science. This is well proved by the fact
that analytical chemistry has had its own journal for more than a hundred
years now. Then, as the younger branches of chemistry grew up to maturity,
they began, being proud of their performance, to despise their “elder sister”.
They often even denied that she was a sister, and looked at her as only a
maidservant. They forgot that analytical chemistry had helped to found
them all, and that they had always relied on it both during their growth
and subsequently as well. Later progress made by this specialized branch
showed that analytical chemistry is a truly independent branch on the
one hand, and is active in all branches of chemistry being omnipresent and
forming a link between the various fields of chemistry, on the other hand.
Being able to adopt this dual role analytical chemistry has often acted as
the vehicle of the universal advance of chemistry. All new chapters in
chemistry had analytical antecedents. On close examination of these
antecedents one can see that usually new analytical methods led to new dis-
covers. Among these new methods one can find procedures called collect-
evively physical or physico-chemical methods of analytical chemistry from
the beginning of the last century. The development of analytical chemistry
in modern times was characterized by an initiative which immediately made
use of the discoveries and results of physics, the storming party of natural
science, for its own purposes. This process started with the application of
electric current for the purposes of qualitative analysis in the first year of
the last century, and continued with the application of optics in spectroscopy
and has gone on ever since. A recent example of immediate analytical
adaptation of physical discoveries is perhaps the analytical application of
the Mössbauer effect. The new methods have not only increased the efficiency
and tools of analytical chemistry but have also affected its contents and
objects. In the beginning the analyst’s problem was: what is a sample com-
posed of? Later came the question: how much of the component is present?
Recently have arisen the questions: which way does a process proceed?
What is the structure of a compound like? Therefore, besides qualitative
and quantitative analysis, structural analysis was developed as the newest
branch of analytical chemistry. At the time of fragmentation of chemistry
the branches were separated more or less rigidly from one another, and the
research workers of a particular field often worked as if no contact would
exist with the other fields of chemistry. Analytical chemistry was nearly the
only link between them. The integration process of natural sciences started
in this century, in which the boundaries, so sharp half a century before, became indistinct. The new trends in analytical chemistry to which reference
has been made played an important part in this process.

While the methods of scientific analytical research receive increased
importance in this century, the importance of analytical research for
practical purposes did not show any decrease. In the time of the second
industrial revolution of our period, when the coal and iron epoch was
transformed into an epoch of "chemisation" based on the chemical industry
and that of plastic materials, the requirements of the rapidly developing
techniques, nuclear industry, automation and cybernetics set new problems
to analytical chemists, the resolution of which often necessitates a knowledge
of physics, chemistry, biology and other sciences. Analytical chemists should
have some knowledge of all these subjects and in addition be experts in
analytical chemistry. Analysts can perform their task effectively on this
basis. The new problems set to analytical chemistry could only be solved
by a further perfection of physical methods and by the development of
entirely novel methods. Looking back upon the period passed since the war
a unique progress can be seen. New methods such as: paper and gas chrom-
atography, $\gamma$-spectrometry, radiometric titration, atomic absorption
spectroscopy, x-ray fluorescence analysis, and new branches of thermal
analysis were introduced to mention only the most important ones, while
new, very important applications of old methods, such as electrometric and
activation analysis, photometry and others, were elaborated.

According to the statistical compilation of the American periodical
Analytical Chemistry [37, 27A (1965)] on publications on analytical subjects,
more than 10 000 papers appeared on chemical analysis, while the number
of papers on chemistry was about 170 000, i.e., every seventeenth paper
dealt with analysis. Sixty-four years before, in 1901, 1000 papers out of the
whole of 4000 papers on chemistry were on this discipline. While the number
of publications on chemistry increased 42-fold, the number of those on
analytical chemistry increased only tenfold, though this increase can be

<table>
<thead>
<tr>
<th>Method</th>
<th>In 1946 (%)</th>
<th>In 1955 (%)</th>
<th>In 1965 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical methods</td>
<td>34.1</td>
<td>26.0</td>
<td>14.2</td>
</tr>
<tr>
<td>Physical methods</td>
<td>60.0</td>
<td>71.8</td>
<td>81.5</td>
</tr>
</tbody>
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regarded as considerable. It is therefore easier to survey and systematize the
papers on analytical chemistry than those in other fields of chemistry. The
importance of physical methods in progress is given in Table 1. While in
1946 about 34 per cent of the papers dealt with the so-called classical
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analytical subjects, this percentage decreased to 26 in 1955, and even to 14·2 in 1965, and simultaneously the proportion of contributions on physical methods or their application increased from 60 per cent in 1946 to 71·8 per cent in 1955 and to 81·5 per cent in 1965. The comparison of data for 1955 and 1965 gives a picture of the most important trends of the development (Table 2). Optical methods diminished a little, the proportion for
table 2. Trends in the development of various analytical methods

<table>
<thead>
<tr>
<th>Method</th>
<th>In 1955 (%)</th>
<th>In 1965 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical methods</td>
<td>43·2</td>
<td>40·5</td>
</tr>
<tr>
<td>Electrometric titrations</td>
<td>4·8</td>
<td>4·5</td>
</tr>
<tr>
<td>Other electrometric methods</td>
<td>6·2</td>
<td>10·2</td>
</tr>
<tr>
<td>Radiochemical methods</td>
<td>2·0</td>
<td>7·4</td>
</tr>
<tr>
<td>Gas chromatography</td>
<td>?</td>
<td>9·5</td>
</tr>
<tr>
<td>Thermoanalysis</td>
<td>?</td>
<td>1·9</td>
</tr>
</tbody>
</table>

electrometric titrations was unchanged, while the number of publications on radiochemistry markedly increased during this period. Gas chromatography and thermoanalysis are not mentioned separately in this compilation for 1955, while more than 10 per cent of the publications appeared on these subjects in the last year.

What is the part Hungary played in this progress? How did Hungary, this relatively small country, which stands fortieth among the countries of the world as regards its population, contribute to the development of analytical chemistry? The above-mentioned compilation gives an answer also to this question, an answer we Hungarians need not be ashamed of.

It is clear that scientific publications are very different in value; there are papers of basic, sometimes even of revolutionary importance, and papers introducing little that is new, and (regrettably) others which, in the interest of science, should not have been written at all. Most of the publications fall between these two extreme cases, they are mostly simple bricks moulded by diligent work, from which the whole of science is built up. So far there is no compilation classifying publications into groups of very useful, useful and useless ones, and it is not probable that there will ever be such a compilation. But, according to the rule of great numbers, about the same distribution among the three groups can be expected for greater units, e.g. countries. Therefore a direct proportion exists between the number of papers published by chemists in various countries and the scientific activity of the particular country.

Hungary stood on the tenth place on the list of countries in 1965 with 2·6 per cent out of the total of analytical publications. This is a fairly good place for a small country like ours (Table 3).

It is interesting to compare the distribution of papers on analytical chemistry with that of all papers on chemistry. While the share of Hungary is 2·6 per cent in analytical literature, it is only 1·3 per cent in chemical literature [American Documentation, 159 (1962)]. It is surprising that with this 1·3 per cent Hungary takes nearly the same place as in analytical literature,
namely the eleventh. The reason for this is that the share of greater countries is higher, and that of the smaller ones is lower, in chemistry than in analytical chemistry. From this fact one can come to the conclusion that poorer countries can better approach the potentials and results of rich ones in the field of analytical chemistry than in other fields of chemistry. One of the reasons for this is obviously the fact that, although the costs of analytical research have markedly increased it is still possible to get high-standing results with limited means and lower costs than in many other fields of science.

<table>
<thead>
<tr>
<th>Country</th>
<th>Papers Published (%)</th>
<th>Analytical Chemistry 1965</th>
<th>Chemistry 1961</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.S.R.</td>
<td>21-8</td>
<td>19-1</td>
<td></td>
</tr>
<tr>
<td>U.S.A.</td>
<td>20-2</td>
<td>27-1</td>
<td></td>
</tr>
<tr>
<td>Germany</td>
<td>10-0</td>
<td>7-8</td>
<td></td>
</tr>
<tr>
<td>Japan</td>
<td>6-8</td>
<td>7-8</td>
<td></td>
</tr>
<tr>
<td>Poland</td>
<td>5-1</td>
<td>1-5</td>
<td></td>
</tr>
<tr>
<td>Great Britain</td>
<td>4-3</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>British Commonwealth</td>
<td>?</td>
<td>13-8</td>
<td></td>
</tr>
<tr>
<td>France</td>
<td>4-2</td>
<td>5-0</td>
<td></td>
</tr>
<tr>
<td>Czechoslovakia</td>
<td>3-6</td>
<td>2-0</td>
<td></td>
</tr>
<tr>
<td>Italy</td>
<td>3-0</td>
<td>3-2</td>
<td></td>
</tr>
<tr>
<td>Hungary</td>
<td>2-6</td>
<td>1-2</td>
<td></td>
</tr>
<tr>
<td>Switzerland</td>
<td>1-1</td>
<td>1-3</td>
<td></td>
</tr>
</tbody>
</table>

However, also the fact that Hungary has old and great traditions in the field of analytical research contributed indubitably to the distinguished place of our country in analytical research.

The past of analytical research in Hungary goes back to the middle ages. A national association for gold-testing was already organized in 1342.

It is also known that chemical laboratory exercises were first introduced in college education here in Hungary. In the famous Mining College in Selmecbánya, as early as 1735. Obviously, this laboratory training was purely analytical. This college earned such a fame that students came from all over Europe and even Latin-America to learn analytical chemistry.

The physical methods emerging in analytical chemistry soon attracted attention in our country. The famous professor of the University in Budapest, K. Than was very much interested in physical chemistry, still undeveloped at the time. K. Than was one of Bunsen’s students, so that it is not surprising that he applied emission spectroscopy in Hungary as early as 1862, and identified among other elements rubidium, discovered by Bunsen one year before, by emission spectroscopy in oak-ash. B. Lengyel (senior) delivered several lectures on spectroscopy in the seventies. It is appropriate to mention here that it was just one hundred years ago that K. Than was first to suggest that the elements found by analysis should not be combined into
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compounds, but that the results should refer to elements or groups, i.e. to ions. Obviously this latter term could not be used by him at that time, because the theory of electrolytic dissociation was elaborated only a quarter of a century later.

The absorption of various gases in water was determined by the Hungarian scientist L. Winkler, with very high accuracy, at the end of the last century.

In 1903, P. Szily conceived the idea of determining the acidity or basicity, i.e. hydrogen ion concentration of blood serum by means of an indicator series. By this he laid down the fundamentals of colorimetric pH-analysis. His other, perhaps even more important discovery was that solutions of known hydrogen or hydroxyl ion concentration can be prepared only up to a certain limit by dilution, but without any restriction by mixing primary and secondary phosphates. In this way, Szily discovered the artificial buffer solutions, which are indispensable in all kinds of pH determination. His work was further developed by Friedenthal and later by Sørensen.

The radioactive isotope tracer technique was discovered beyond the borders of Hungary, though not far from it by Hungarian, G. Hevesy and the Austrian, Paneth in Vienna. The method was very soon used in Budapest for the investigation of the self-diffusion of lead by tracer technique. These studies were carried out by Hevesy and G. Gróh in 1918 and 1919.

As is known, the isotope dilution method and also the neutron activation analysis was discovered by Hevesy, abroad again, in 1932 and 1936, respectively.

Although the history of adsorption chromatography goes back into the last century, the method became important only in the thirties of our century. The fundamental research work of Zechmeister and Cholnoky at the University of Pécs, as well as their pertinent book, were important contributions to the development of the method.

L. Szébellédy, the very talented professor of the University of Budapest, developed two important methods of physical-chemical analysis before the second world war during his short life-time. He enriched, with the discovery of several reactions, the field of the sensitive catalytic analysis, and elaborated together with Ajtay a chrono-photometric catalytic method for the determination of trace elements.

The other important method of Szébellédy is coulometric titration. His coworker in this work, L. Somogyi was a victim of the second world war.

It is very sad that we have to mention already Professor E. Schulek among the dead Hungarian scientists who worked in the field of analytical chemistry, while only a short time ago he took a vigorous part in our conferences. His work embraces nearly half a century of the history of Hungarian analytical chemistry, and more than 450 publications report on the results of his indefatigable scientific activity. His research work covered the application of nearly all physico-chemical methods.

From his works within the scope of the present conference special mention should be made of his method for the determination of alcohols in the presence of other volatile compounds by means of pumice stone columns which can be considered as a forerunner of gas chromatography.

His activity in the field of structural analysis is also of great importance.
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He determined the structure of Caro's acid, bromo phenol derivatives and other compounds. Also his studies on indicators are well known. His gas-analytical works are also of great importance. In his last work he reported on the application of oxy-cellulose as an ion-exchanger.

We do not intend to give a picture of the whole of Hungarian research work, it would be too long. We only wish to give an outline of some of its trends. First we should like to survey the development of methods the introduction of which was also helped by Hungarian scientists, then some of the methods we are more closely concerned with.

In the field of catalytic analysis very good results were obtained in Hungary on the determination of numerous ions, e.g. iron, cobalt, copper, manganese, molybdenum, etc. Several institutes, namely the Institutes for Inorganic and Analytical Chemistry of the Universities of Budapest, Szeged and Debrecen, the Institute for Chemistry of the Technical University for Heavy Industries Miskolc, and also the Institute for General Chemistry of the Technical University, Budapest participated in these results.

Although the fundamentals of radiochemical analysis were laid by Hevesy more than four decades ago, it is a rather new field in Hungary. It is true that the importance of the method increased suddenly all over the world only after the second world war. Our backwardness in this field is partly due to the fact that a great variety of radioactive isotopes are necessary for radiochemical analysis. The analytical research in this field could start therefore only after the production of isotopes had started in Hungary. Simultaneously, the production of instruments for radiochemical analysis was developed, so that now Hungary can supply instruments for all types of radiochemical analysis, even the most modern ones. This is primarily due to the work of the Central Research Institute for Physics.

The most highly developed branch of the Hungarian radiochemical research, looking back upon a past of about 10 years, is neutron activation analysis. This method was used in the ion-exchange chromatography of rare earths, for the determination of trace contaminants in semi-conductors and in substances used in telecommunication, for the analysis of biological and medical samples for purity tests of high purity water and pharmaceutical ampoules, for the determination of vanadium in oils, for the analysis of germanium, metals and luminescent substances in the Central Research Institute for Physics, the Research Institute for Heavy Chemical Industries, the Research Institute for Telecommunication, and in the institutes for physical chemistry of the Technical University of Budapest.

Absorption and reflection of radioactive radiation were used for studying oils and alloys in the Research Institute for Oil and Natural Gas Products, and on the Technical University of Budapest. The method was utilized in Hungary also for testing red pepper.

Among tracer methods the techniques, initiated in Hungary, based on the change in solubility of radioactive precipitates caused by the substance to be determined offer opportunities for various sensitive determinations on the micro scale. The increase in solubility of mercury iodate and mercury iodide precipitates was used for the determination of halide, cyanide and rhodanide ions in the Institute for General Chemistry of the Technical
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University of Budapest, while the decrease in the solubility of silver chloride precipitate for the determination of chloride ions at the Institute for Inorganic and Analytical Chemistry of the University of Budapest. The first results in Hungary in the field of radiometric titrations and of the very sensitive substoichiometric dilution methods were also achieved in the latter institute.

An interesting development of the coulometric method is polaro-coulometry, worked out in the Institute for Inorganic Chemistry of the Technical University of Budapest. The method is a combination of polarography and coulometry, in which, though a dropping mercury electrode is used for concentration determination, only the charge transported by the diffusion current is measured in a special hydrogen coulometer.

Mention should be made of the excellent theoretical and practical results obtained in connection with glass electrodes in the Institute for General and Inorganic Chemistry of the University of Budapest, and the promising research work on ion-specific rubber membranes in the Institute for Analytical Chemistry of the Technical University of Veszprém. Without going into details, Hungarian research work in the field of oscillometry must also be mentioned; here the Institute for Inorganic and Analytical Chemistry of the University of Budapest and the Institute for Analytical Chemistry of the Technical University of Veszprém can be considered as important centres for research work on oscillometry.

Statistical data reflect the recent remarkable increase of the importance of thermoanalysis. In this field considerable research work has been done in our country. In the congress five years ago we reported how, starting from a study of the precision gravimetric method of L. Winkler and with the objective of a general survey of gravimetric determinations, on the one hand, and with the aim of developing further thermodenimetry, on the other hand, derivative thermodenimetry was developed, and by combining its principles and instrumental features with those of differential thermal analysis, derivatography was evolved. The derivatograph was used to great advantage in several fields. The derivatographic study of analytical precipitates made possible a modern completion of gravimetric analysis, by detailed informations on the crystal structure and thermal stability of the compounds. Thus, analytical reagents and chromatographic eluents were studied from a new point of view. By the derivatographic treatment of organic compounds new, previously unknown, compounds were prepared. The method has a wide range of application in the alumina, silicate, pharmaceutical and plastics industry, in electrotechniques, in the investigation of catalysts, and recently even in medical practice. We do not wish to speak about these applications in detail, we would like to mention only recent fundamental developments of the method. The derivatograph can be successfully used in fields other than analysis and structural analysis. Thus, the method can be applied advantageously to reaction kinetic measurements.

The use of a novel type of sample holder of great surface increases the selectivity of the method and also makes possible the separation of overlapping processes. The analysis of the gaseous decomposition products can also facilitate the interpretation of derivatograms, especially if the products are determined in function of the temperature. The automation of the
continuous titrator designed for this purpose, is under way. If instead of titration the derivatograph is connected to a continuous gas analyzer, e.g. a gas chromatograph, the thermal decomposition process and decomposition products of organic compounds can be studied more closely. By combining the derivatographic and dilatometric methods, transformations of the crystal structure, dislocation processes etc. can be better studied.

Research work on the history of the development of analytical chemistry, a field neglected incomprehensibly for such a long time, resulted in a compilation of the history of the progress of our science, physical-chemical methods included. This research unearthed many unknown facts and slighted merits, and brought to light the work of undeservedly forgotten authors.