THE ROLE OF ANALYTICAL CHEMISTRY IN THE DEVELOPMENT OF MODERN CHEMICAL INDUSTRY

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ABSTRACT

On the basis of rich documentation, the paper defines the place of analytical chemistry in process control as well as the contribution of this science to the development of modern industrial chemistry.

At present, analytical chemistry plays a decisive role in the control of technological processes, and becomes one of the sciences bringing a particular contribution both to the production of goods required by modern society and to scientific research.

The important contribution of chemistry to the scientific and technical revolution of the last decade leads implicitly to the development of analytical chemistry too, as an indispensable instrument both in scientific research and in the raw materials processing industry in general and chemical technology in particular.

Modern analytical systems, based on the introduction of apparatus working directly in production process plants, as well as on the use of automatic equipment for laboratory analyses, have created conditions of rapid and efficient control of the carrying on of technological processes, starting from the raw materials and continuing to the final products, throughout all the manufacturing stages.

It is characteristic of modern analytical chemistry that the elaboration of new methods of analysis implies a more and more active participation, in addition to chemists, of skilled men from the most varied branches of science: physicists, mathematicians, electronics experts, cyberneticians, etc. Analytical chemistry is also characterized by its ever closer ties both with fundamental and applied research and with commercial production.

Some years ago, our well-known scientist C. D. Nenițescu gave the following appreciation of the role of analytical chemistry:

'Analytical chemistry is the universal and infallible control of every production process, in any field of chemical industry itself, also in metallurgy, in the fuels industry, in metropolitan or industrial plants for water supply, in agriculture, in medicine, etc. The quality, and to some extent, the quantity of our output, the efficiency of our technological equipment, our health, all depend upon the accuracy and promptitude of analytical control, effected at the appropriate time and place'.

The modern trend in applied sciences to turn wholly to profit in a complex

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way our raw material resources, in order to obtain new products of specially high grade and often of high purity, has also demanded an increased contribution from analytical chemistry.

The particular merit of this discipline is to have risen theoretically and practically to the level of modern scientific and technological requirements, resulting largely in increased quality and quantity of contemporary production.

The fact is recognized on a worldwide scale that the development of analytical chemistry as a separate scientific discipline has facilitated creation in schools the world over, and in the commercial practice of well-known companies, of specialized works and publications of a high scientific level which make a remarkable contribution to the contemporary development of science and technology.

The use of the raw materials, the carrying on of the technological processes and the qualitative control of the final products cannot be imagined under present conditions without the direct help of analytical chemistry.

From this point of view, modern practice confronts analytical chemistry with a great variety of chemical, petroleum, metallurgical, electrotechnical products, foodstuffs, agricultural products, textile goods etc. which require rapid and particularly accurate analytical tests.

It is sufficient to cite in this respect the case of high purity metals and the products required by the electronics industry, which have imposed the elaboration of methods of a particular finesse based on techniques of elevated scientific refinement.

HEALTH AND WELFARE

Besides industry and agriculture, medicine and public health also raise major problems relating to pollution of the environment (water and air) that also need rapid determination of various noxious substances, sometimes present only in trace amounts.

The chemical analyst now has to extend his sphere of activity, ensuring by interstage control the efficient performance of technological processes in order to attain the accelerated rhythm characteristic of modern production. Modern industry is not conceivable without permanent, rigorous and rapid analytical control.

It is of course well-known that there exists in our country an old tradition in the chemical, petroleum, paper and pulp industries, in ferrous and non-ferrous metals, in the textile and leather industries.

The programmes elaborated in the last twenty-five years by the Romanian Communist Party and the Government of the Socialist Republic of Romania regarding the economic development and the country's industrialization, have given our chemical industry a prominent place, being situated as it now is among the basic branches of our national economy. Thus, at the end of 1970, the production of the chemical industry represented 10.5 per cent of the overall industrial output of our country.

During the period 1950–70, the output of the Romanian chemical industry has increased by 54 times, the average yearly rate of increase reaching above 22 per cent. Thus Romania ranks among the countries having old traditions in this field, both from the point of view of the volume of output and from the point of view of the diversity and quality of the resulting assortment.

The petrochemical industry, a basic branch of modern chemical industry, has seen marked development in Romania, representing at present about 75 per cent of the organic chemical industry, which means 43 per cent of our total chemical industry. This branch turns to profit almost all the crude oil production and a large part of our natural gas production, converting them into products of high commercial value.

We manufacture, both for internal needs and for export, a varied set of polymers, plastics and synthetic resins, of chemical fibres and yarns, and of synthetic rubber. We also produce important amounts of chemical fertilizers, pesticides, drugs and dyestuffs, reagents and solvents, etc.

Particular attention has been given to the fertilizer industry, which has increased about 3.5 times during the last five years, adequate at present for all the needs of our agriculture, and for the export of important amounts.

The drugs industry has been increased by 1970 37.5 times with respect to 1950 and twice with respect to 1960, satisfying almost all internal consumption. The dyestuff industry also covers about 75 per cent of the requirements of our textile industry.

Having at its disposal modern works and plants, provided with high capacity and efficient equipment, Romania is at present an important producer of chemicals.

In the 1971–75 five-year period, over 300 new chemical plants will be built, based for the most part on technologies studied in the country or reproduced from those existing in earlier plants.

The future for our constructors and chemists will bring important and difficult tasks that can be accomplished only by highly organized work, sustained by a young and enthusiastic staff, guided by the desire to conquer new heights in this magnificent science and production field with its practically unlimited possibilities which offer the satisfaction of the synthesis of products with new structures and properties, unknown in nature, and helping to raise mankind to a new level of civilization and culture.

ANALYTICAL CHEMISTRY IN ROMANIA

The Romanian school of chemistry has been distinguished in recent years by the contributions of some world-renowned men of science: N. Teclu, Petru Poni, Constantin Istrati, I. Longinescu, Lazăr Edeleanu, Radu Cernătescu, Petre Bogdan, Gheorghe Spacu, Costin D. Nenițescu, Eugen Anghelescu, whose activities closely blended professorship with scientific research and industrial application.

The scientists, teachers, researchers and specialists that constitute the new Romanian school of chemistry continue to raise to the summit of modern science the chemistry of our country and have active participation in the performance of the ample development programme planned for the present ten-year period.

On this occasion, we want to express our appreciation of the chemistry schools of the universities in Bucharest, Cluj, Iassy, Timişoara, in which analytical chemistry plays a great part and which stimulate in their work researchers and specialists from our big chemical works, as well as from other fields of the national economy.

There have been many great difficulties to be overcome in the field of analytical chemistry, because the conception used to prevail that it was an auxiliary branch having only a secondary role in production processes, which we frequently could dispense with, because there were no skilled men, no chemicals of analytical purity and no corresponding equipment.

At present, the part played by analytical chemistry in the carrying on of modern production of material goods is well delineated, and it continuously extends its sphere of activity both with regard to the characterization of the raw materials and final products and to the control of the technological processes, in their automatic regulation and monitoring.

Analytical chemistry employs at present the most up-to-date achievements in mathematics, physics, electronics, cybernetics; new procedures and better and better instrumentation; it continuously extends its sphere of activity, successfully finds access into the fine and superfine metals industry, into nuclear technology, in the drugs industry, in hydrobiology, health control etc.

The spheres of atomic and molecular structure to which the present methods of analysis have to refer lead to the fact that the analyst becomes an indispensable factor in the study and characterization of final products both of chemical industry and of other industrial branches.

The development in recent years of stereochemistry, a discipline dealing with the three-dimensional structure of molecules and the relation between the structure and the properties of matter, as it has been recently defined by G. Natta and M. Farina, the introduction of stereospecific polymerization into industrial practice, require at the same time structure analyses in the complex macromolecular sphere that can lead to the preparation of well-defined products, having specific qualities.

Having to solve new problems, of ever-increasing complexity, the analyst has found new and more efficient methods, such as: solvent extraction, spectroscopy, photometry, roentgenometry, magnetometry, ion exchange, potentiometry, conductometry, polarography, amperometry, chromatographic technique and others that maintain their qualities when passing from the analytical laboratory to the industrial scale.

On this occasion at the Third National Meeting of Analytical Chemistry in our country, I wish to point out that there are meeting here with the same purpose, of being reciprocally informed of achievements, of discussing the problems raised and of tracing out in common the direction of their future activity in the service of our country's progress, analytical chemists from all fields of activity: from universities, research, industry and agriculture.

There are present at this Meeting persons of note from many countries of the world, with a remarkable activity in this field of chemistry, and I consider that the exchange of ideas and information with regard to new methods and working techniques, having various applications in science and technology, new apparatus and reagents used in the different fields of analytical chemistry, will be particularly useful and will effectively bring its contribution to the progress of this science in our country.

The impetuous development of our industry has required analytical chemistry to keep pace with the latest performances of science, and to adapt itself in a dynamic way to this rhythm.

The progress registered by physical chemistry and electrochemistry, together with the latest achievements in spectral techniques, in electric and electronic measurements, have resulted in essential changes in this discipline, leading to generalization of the physical methods of analysis, known at present everywhere under the name of instrumental methods.

Analytical methods based on modern equipment are in current use in the laboratories of our works and research institutes, which have at their disposal a strong material base, being provided among other things with: spectrophotometers for molecular and atomic absorption, refractometers, x-ray diffraction and fluorescence instruments, nuclear magnetic resonance and electronic resonance spectrometers, thermal analysis instruments, polarographs, chromatographs and, more recently, quantometers.

These up-to-date optical, electrical and electronic pieces of apparatus oblige the chemical analyst to resort more and more to physical and mathematical methods.

The application in our country of the abovementioned methods has contributed decisively to the reduction of the time required for analysis, to increasing accuracy, and also to the performing of analytical determinations inaccessible to classical methods.

Modern laboratory equipment facilitates more rapid and accurate knowledge of the elements required for determining the chemical properties of matter.

But instrumental analysis was the highest achievement of analytical

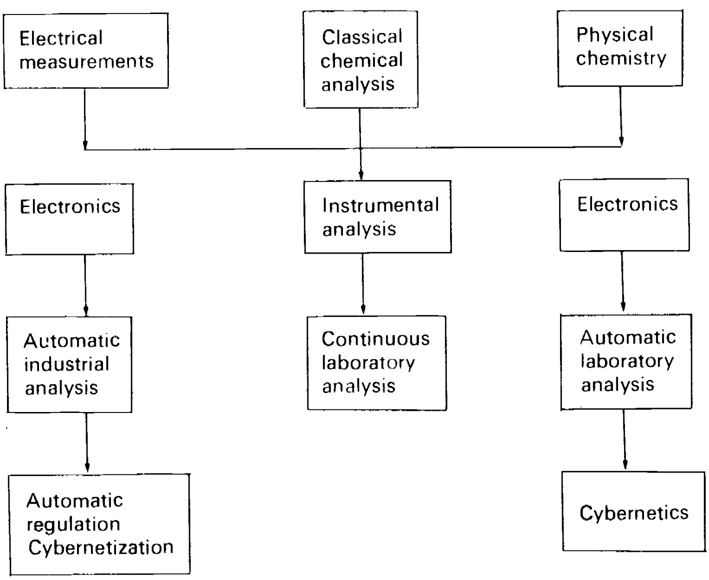

Figure 1. Development of chemical analysis

chemistry only for a short time. The step immediately following was transfer to automatic analysis, followed closely by the control of industrial processes by means of automatic analysers.

Automatic industrial analysis associated with automatic control have created the possibility of accurately regulating industrial processes with a higher degree of security, especially those processes with very rapid chemical kinetics, and of governing with deeper certainty the catalytic processes at high pressures and high temperatures, so widely used in recent years in the petrochemical industry.

Use of laboratory control for the operation of modern plants would only give rise to retarded conclusions regarding the process run and would have as a consequence either its delay or simply the lack of scientific criteria in appreciating the manner of its running or the impossibility of intervening in the normal course of the process, interventions that sometimes occur within a range of seconds.

Automation, as completing instrumental analysis in the present stage of development of analytical chemistry, has put at the disposal of the chemical analyst not only the apparatus for effecting rapid determination of a certain measure, but also the automated device replacing him, more or less, both in the operating of the apparatus and in computing and using the results for the correction of operational factors in the industrial plant.

The control of industrial plants is based on analytical determinations which are carried out in the different stages of the process upon a limited number of factors, considered to be essential for the characterization of the way it is running. This control has been developed steadily during the last decade together with improvement both of the analytical methods and apparatus and of the information transmission and processing systems, wherein we must distinguish the following stages: (1) surveying and recording, (2) control and regulation, and (3) automation and cybernetization.

Surveying and recording have constituted the most primitive methods of following the process, while complex regulation allows in large measure the optimization of an industrial process based on instrumental analytical control.

Automation can lead to complete optimization of the process, giving the highest yield at the lowest cost and of a specified purity.

In the case of control, the information obtained by the measuring instruments from the instantaneous state of the process is converted by the operator into the corresponding commands. The process is hence under supervision, the quality of the product and the efficiency of the production depending upon the capacity and working power of the operator.

With automation of the process, the same information used for control is transmitted to the information converters which process it according to a pre-established programme, or, in a simpler case, use it just to maintain certain parameters constant, transmitting the necessary commands to the devices regulating the running of the plant.

This evolution is suggestively represented in *Figure 2*, from which can be seen the role of surveying and regulating played by the operator in the first stage, which is reduced to control and regulation in the second stage and to general surveying in the third stage.

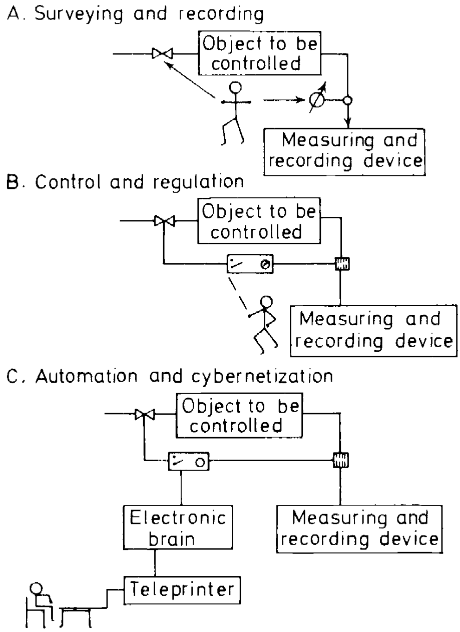

Figure 2

An obvious condition for good regulation is that of converting into commands, in a fixed or programmed manner, the information received relating to the running of the process, in such a way that the desired action shall appear as quickly and accurately as possible.

Although it replaces an important part of the physical labour of man, effecting more surely and constantly the established analyses, the regulating device cannot, however, perform the control function, make a decision and adapt itself to modified states.

Concomitantly with the increasing complexity of process monitoring, the role of automation and cybernetization is becoming more widespread. By automation, a higher step is understood of man activity replacement by devices that comprise both the control and the decision and adaptation functions. While control is possible by comparison of information, making a decision and adaptation require the observing and evaluation of the variation with time of information, the objective interpretation of data by scientists and specialists.

A characteristic of automatic regulation in chemical industry is hence constituted by the process computer, provided that it compares the analytical information, follows its variation, interprets this latter and gives a resolution, from this latter deriving the commands for monitoring the process. It is most important of course that it shall work as designed on the basis of the scientific thinking of the specialists.

Every analytical measurement starts with sampling or has to be effected in a stream derived from the main stream of the chemical products, since in general, the substance to be measured must first correspond to a certain physical state, before it can be measured.

For proper direction of the process, from the chemical point of view, it is particularly important to make an accurate evaluation of the concentrations of certain substances. The measuring devices used for this purpose depend on a function (calibration function) relating the concentration to certain settled measurable parameters. This involves the use of sure calibration data and a high validity in comparing the standards.

FUTURE REQUIREMENTS

For certainty of information, a control cannot be avoided and, based on the latter, a correction of the measurement and a re-controlling.

Since the automation of process monitoring has sense only if the information output is also automated, it is necessary for the control and correction of the information output to take place automatically. Thus obtaining the data by means of the measuring technique has to reach an automation stage even higher than the automation of the chemical process itself. Based on this conclusion, it is necessary to examine to what extent the chemical and physical measuring technique corresponds to these requirements.

We can consider the measuring process in analytical chemistry on the basis of the same scheme as that for process monitoring, because they are developing in a similar way, especially when they relate to chemical processes.

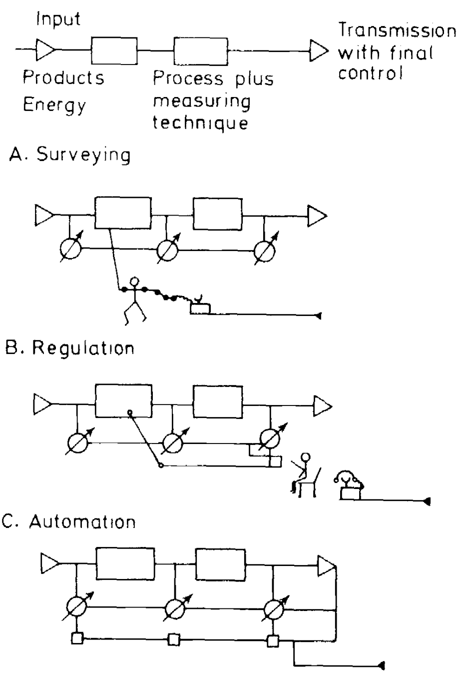

Figure 3

Manual analysis, in which a sample is subjected to conversion and measuring, fulfils the conditions to reach the regulation step only when a complex apparatus is used to obtain data, because the analyst has to control the sample quality and, if required, to correct the latter.

With regulation only analytical measurements are compatible that are performed by means of automatically working devices. Frequently, these devices are called analysis automatons. However, this expression must be used only when the respective instruments satisfy all the conditions of automation: control, correcting, decision, adaptation.

In *Figure 3* there are schematically represented, for a two-step chemical process, the three stages: (1) surveying, (2) regulation, and (3) automation (monitoring the process by instruments).

The three stages reached by automatic analysis are represented in *Figure 4*: manual analysis, mechanized analysis in which control, research and evaluation are made by man, and automated analysis in which man no longer participates directly.

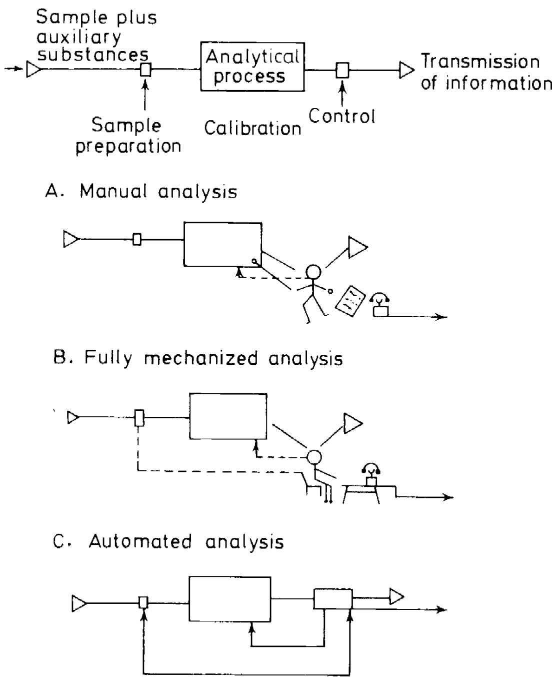

Figure 4

Regulation and automation with the aid of analytical measurement in comparison with regulation based on physical measures or manual regulation are schematically represented in *Figure 5*.

Automation in chemical industry cannot be attained without automation of the measuring technique, including automation of sampling. From instrumental control of chemical processes and chemical kinetics, we have

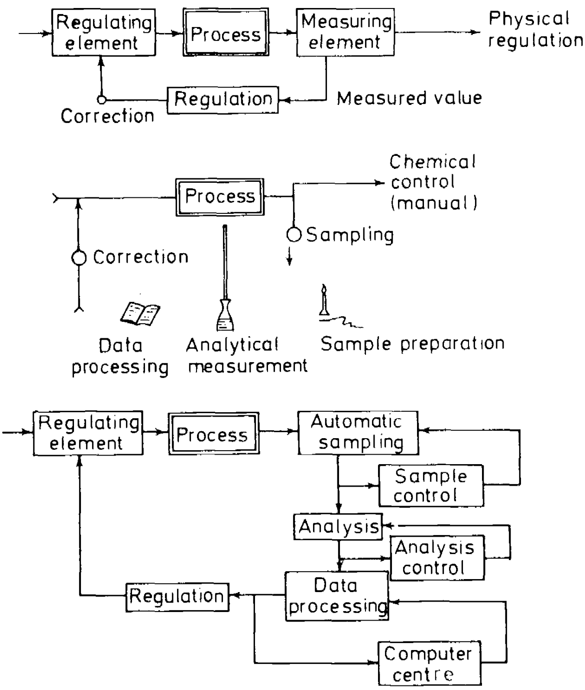

Figure 5

passed to automated control of chemical structures, as they result from the development of production processes in their intermediate and final stages. The final product of a chemical process must be obtained by the most economical way, while it must of course have also the purity required for subsequent use.

The control of product quality is another particularly important field, in which analytical chemistry finds ample application.

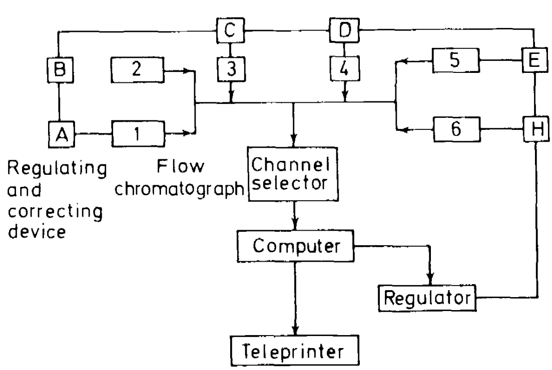

Figure 6.

The introduction of modern methods of analysis, the procurement of the corresponding equipment, and the gathering together of skilled and highly qualified staff have constituted important aims of the activity developed during the last two decades in our country for the creation of Romanian chemical industry.

Concrete results of this activity can be found in the continuous rise in the quality of our products, conditioned by their utilization in many different fields of economy both in our country and abroad.

Among the many methods of analysis that lend themselves to automation (autocontrol, autoresearch, autocorrection and adaptation) can be cited the chromatographic and spectrometric methods of analysis. Such a chromatographic control can be exemplified (*Figure 6*) by a schematic representation (flow chromatography–channel selector–computer–regulator–regulating and correcting device).

Flow chromatographic analyses, having an influence on certain technological parameters, are carried out at present at the olefin plants in Ploieşti and Piteşti and at the acrylonitrile plant in Piteşti.

The use of the automated analyser has led to a considerable reduction of the response time, to an increase of the control frequency, and the effect has been a reduction in the number of faults and finally a substantial increase in plant efficiency.

For the control of various industrial processes, continuous measurement of the concentration is used with the aid of electrochemical transducers, also the determination of polymer quality by rheological measurements etc.

In parallel with the automation of control and regulation of industrial processes, plant laboratories and laboratories for analytical research have installed instruments with a high degree of complexity which, besides replacing classical methods, have allowed the accomplishment of large-series analyses with increased accuracy and rapidity.

These instruments have made it possible at the same time to measure parameters that could not even be approached by classical methods.

To characterize polymers, there are used at present rapid methods of determining molecular weight distribution, such as: gel chromatography, rheological methods and molecular absorption spectroscopy. To characterize synthetic fibres, x-ray diffraction instruments with automated recording are used.

The analytical control of catalysts would be at present inconceivable without the utilization of modern methods of spectroscopy, especially of atomic absorption spectrometry, because only spectral methods permit the simultaneous achievement of the three desiderata of modern analytical control: sensitivity, accuracy and rapidity.

Spectral methods have also facilitated entry to the particularly interesting, I should say fascinating, field of the determination of trace elements, having important application in the manufacture of catalysts, of semi-conductors, in nuclear technology, in biology etc.

Our metallurgical industry is equipped at present with spectral instruments with a high degree of automation (quantometers) which coupled with computers permit the simultaneous analytical determination in some minutes only of 21 elements in a metal sample, thus permitting extremely rapid intervention in the process; sometimes this intervention can even be carried out automatically.

In parallel with the aforementioned preoccupations, in order to achieve analytical control directly on the process flow, our research institutes, research laboratories and sections of the industrial management and engineering groups have made a sustained effort to adapt old and create new analytical methods to given even better utilization of the up-to-date and complex arsenal of instruments with which they have been provided.

Thus, for example, thermogravimetric analysis coupled with chromatography is used to characterize synthetic polymers, catalysts and other products. The use of various types of spectrophotometers (atomic and molecular absorption, emission spectrophotometers) allows determination of the structure of newly synthesized substances. The use of preparative chromatography coupled with infra-red absorption spectrometry or with mass spectrometry allows identification with a high degree of certainty of the complicated organic substances resulting from such syntheses. This series of examples could of course be continued with other instrumental methods, no less spectacular, currently in use in industrial laboratories.

I consider that for the chemical analysts of our country, the fact must appear like a guiding star that only by highly accurate analytical control can the rationalization of each industrial process occur to yield high-grade products.

One of the tasks that analytical chemistry has to face at present is to apply most completely, competently and perfectly, instrumental analysis, because this represents a basic factor in the automation of technological processes.

The chemical analyst must at the same time keep pace with the newest achievement in science, in order to become a universal and infallible controller of any production process.

The more accurate and precise the result of an analysis, the more rapidly it is supplied, the higher will be its value and the effect upon process efficiency.

The further development of chemical industry is also conditioned by the competent introduction of the most up-to-date scientific methods of analysis for production control, this fact being well understood and appreciated by most of the chemical analysts working in our national economy.

This fact is also demonstrated by your participation at this Meeting wit a great number of high quality papers that will be presented here.

The modern analytical chemist is held in high esteem and consideration in the great family of chemists. He cannot be a skilled man in a narrow field and has to appeal more and more to achievements in other fields of science: mathematics, physics, electronics, cybernetics etc., combining fundamental with applied research and laboratory activity with that in industrial plants.

In conclusion, allow me to express my appreciation of the very important role played by the present Meeting with regard to further improvement of activity in the field of analytical chemistry in our country, to the rich and useful exchange of experience it brings about with persons of note from other countries, working in this field, to the contribution it will more particularly bring to the rapid introduction into industrial process monitoring of automatic analytical control methods, as well as of analytical methods in determining the molecular structure in the different production process stages.

On the other hand, having as much importance as the aforesaid, chemical and physicochemical analysis will facilitate control of raw materials, the intermediate and final products, and ensure a high quality level of goods required for material and spiritual life in modern society.

This will mean an important contribution to the achievement of the vast development programme for the chemical industry during the five-year plan 1971–1975, promulgated at the Tenth Congress of the Romanian Communist Party.

REFERENCES

[1] G. Natta and M. Farina, *Stéreochimie: Molécules en 3-D*, Masson: Paris (1971).

[2] F. C. Nachod and W. D. Phillips, *Determination of Organic Structures by Physical Methods*, Academic Press: New York (1962).

[3] C. D. Neniţescu, *Contemporanul, Bucureşti*, No. 51 (1958).

[4] C. Liteanu, *Analiza Chimică Cantitativă Volumetrică*, Ed. V, Editura Didactică şi Pedagogică: Bucureşti (1969).

[5] D. Bîrcă Gălăţeanu, M. Giurea, I. Iova, V. Sahini, V. Truţia and R. Tiţeica, *Introducere în Spectroscopie Experimentală*, Editura Tehnică: Bucureşti (1961).

[6] C. Duval, *Inorganic Thermogravimetric Analysis*, 1st ed. Elsevier: Amsterdam (1953).

[7] I. Bănăţeanu, A. Căluşaru and Z. Slabu. *Metode Fizico-chimice de Analiză*, Editura Technică, Bucureşti (1961).

[8] W. West, *Chemical Application of Spectroscopy (Technique of Organic Chemistry)*, Interscience: New York (1961).

[9] G. W. Ewing, *Instrumental Methods of Chemical Analysis*. McGraw-Hill: New York (1960).

[10] H. H. Willard, L. L. Merritt and J. A. Dean, *Méthodes Physiques de l'Analyse Chimique*, Dunod: Paris (1965).

[11] I. Robin, *Introduction aux Méthodes Electrochimiques*, Masson: Paris (1967).

[12] A. A. Babuşkin, P. A. Bajulin, F. A. Korolez, L. V. Levşin, V. K. Prokofev and A. R. Striganov, *Metodî Spectrolnovo Analiza*, Izdatelstvo Moskovskovo Universiteta: Moscow (1962).

[13] V. M. Ciulanovski, *Vvedenie v Moleculiarnîi Spectralnîi Analîz*, Moscow.

[14] Margareta Giurgea, *Spectroscopia Experimentală*, Editura Tehnica: Bucureşti (1966).

[15] E. Lederer, *Chromatographié en Chimie Organique et Biologique*, Masson: Paris (1959).

[16] H. van Olphen and W. Parrish, *Progress in Analytical Chemistry*, Plenum: New York (1968).

[17] F. J. Welcher, *Standard Methods of Chemical Analysis*, Van Nostrand: Princeton, N.. (1968).