

MORAL AGEING OF ANALYTICAL METHODS

George E. Baiulescu

Department of Analytical Chemistry, National Institute of Chemistry, Splaiul
Independentei 202, 77208 Bucharest, Romania

Abstract - The lecture is based on progress, development and optimisation of analytical methods. On the basis of the examination of three kinds of correlations, the method-instrument, the man-instrument and the man-method-instrument correlations, the best conditions to diminish the moral ageing of analytical methods are proposed.

INTRODUCTION

One of the features of modern analytical chemistry as a science is its continuing improvement, both as such and in its close co-operation with other disciplines such as physics, automatics, data processing and others.

Lately, the rank-and-file analytical chemist has found that it becomes increasingly difficult to characterise a sample objectively, particularly when the sample belongs to a material with a very complex structure and composition or when one's aim is to determine traces of a particular component in a matrix.

The introduction, for objective reasons, of novel physical methods of analysis, which need not be detailed here but are responsible for the explosive advance in the methods of analysing surfaces, and which are ultra-rapid because of their non-destructive and easily automated character, has brought to the analyst a wide spectrum of analytical methods, some of which are highly sophisticated.

Competition among instrument manufacturers is of course responsible for the fact that an up-to-date instrument may become outmoded overnight as far as its operational parameters are concerned, or else the method of analysis itself may become impracticable in some cases. This way, it becomes harder and harder to make an educated choice of the most adequate method for analysing a certain material and of the most suitable instrument available on the market.

When considering the evolution of the analytical methods and of the analytical instrumentation, we may see that from time to time, as required by the chemical-analytical control of the industrial output or by the necessities of new fields in the scientific research, new techniques of analysis occur which complement the older ones. Under such conditions, the older analysis methods, which are no longer appropriate with reference to sensitivity, selectivity, accuracy and rapidity for the considered scope of the particular problem, may be regarded as being morally aged. The degree of moral ageing depends on the very nature of the method, but the analytical methods preserve nonetheless, within certain limits, their viability and validity. These limits are set by the nature and composition of the sample. No matter how much the analytical methods may be improved, a degree of the operational parameters with which we could know the exact composition of the sample would never be reached. We might say that "no analysis is better than the sample itself."

During the latter decades of this century, in order to get satisfactory results, an analyst who investigates various materials from a compositional or structural point of view must be an excellent connoisseur of analytical chemistry as a science and of chemical analysis as a technique.

To get a high degree of confidence, an analytical chemistry specialist must be aware, in our opinion, of three groups of correlations:

- a) the method-instrument correlation;
- b) the man-instrument correlation; and
- c) the method-man-instrument correlation.

These correlations are simple repercussions of the modern development of science and technology. The analytical chemist is aware that by his activity he contributes both to the advancement of science and to the optimisation of the industrial processes by the chemical-analytical control of its output.

As early as during his undergraduate studies, the future analyst should be made aware of the necessity of a great correlation between teaching, research and industrial production, which could be schematised by a triangle (Fig. 1), which may become equilateral under proper conditions.

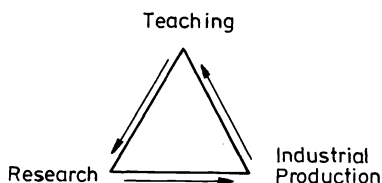


Fig. 1 The *great correlation*

This may only happen if a perfect optimisation of the whole informational system exists, the informing moving in the sense indicated by the arrows. Only that man who can be integrated into this cycle can eradicate gradually, step by step, his own degree of moral ageing.

As Professor Laitinen appropriately shows in a recent editorial of *Analytical Chemistry* (Ref. 1), "the essence of the modern approach is a quest for the fundamental understanding of a problem rather than an empirical determination of composition."

Before proceeding to scrutinise the three types of correlation, let us consider for a moment the notion of moral ageing insofar as the operator is concerned.

The continuing increase in the amount of information, in analytical chemistry as a whole, and in its various branches may cause the man, its beneficiary, to be overwhelmed; he must therefore readapt himself continuously to this informational universe. To avoid his own moral ageing, the analyst has to embrace the most efficient information system, a system which he would use in accordance with the complexity of the analytical system.

The most difficult problem apparent today is that of the mentioned correlations, particularly of the method-man-instrument correlation. The appearance of new synthetic materials, the demands associated with substances of higher and higher purity, the needs of biochemical, biomedical and clinical research have caused this triple correlation to become the most difficult to preserve within normal parameters.

Horwitz appropriately remarks (Ref. 2) that "as the level of measurement goes down, analytical methodology and instrumentation become increasingly complex and sophisticated, operations may become too expensive and results too unreliable for practicability", and which is still more important, "a practical method will always be practicable, but a practicable method is not necessarily practical."

These facts, which may seem very clear to many people, are nevertheless by their nature very complex and have implications upon the general analytical process itself. The progress, development and optimisation of the analytical methods would have to take account of these correlations and to investigate them within their interdependence. This is the only way to ensure that the notion of moral ageing would be understood; that means would be eventually found to harmonise older analysis methods with the new requirements and that entirely novel methods would be continually devised.

In what follows we shall discuss this group of three correlations, based on the daily practice of the analyst and on pure analytical research.

THE METHOD - INSTRUMENT CORRELATION

It is the personal opinion of the author, always conveyed to his students, that any great scientific discovery in chemistry in general, and in analytical chemistry in particular, is based on facts which, once shared by the general public, may appear as extremely simple. A certain phenomenon is noticed by most of the specialists in a certain field, but it takes a certain type of person or research team to think somewhat differently as to how this phenomenon could be applied.

The history of analytical chemistry provides us with a large number of such instances, one need only remember polarography and atomic absorption. Perhaps the discovery of these techniques is the surest proof of this method-instrument correlation. The polarographic technique was introduced by Heyrowsky in the early '20s and it developed explosively mainly because of improvements in instrumentation.

A method of analysis is really good when it may develop horizontally, i.e. when it is applicable to a wide class of compounds. Application of polarography to systems of organic compounds was made possible by a knowledge of the mechanisms of the organic reactions in general and of the electrode reactions in particular. However, the polarographic technique began to show signs of ageing after only a few decades; it could no longer face the sensitivity requirements of the modern age science and practice. Polarography had to be revived - but how? It revived by itself, not through such palliatives as oscillopolarography (a technique which may well be more sensitive but which surely is much more demanding), but by renewing the principle itself. By analogy with the concentration by extraction or by chromatographic techniques, an increase in sensitivity was sought by electrochemical preconcentration. "This is the principle of electrochemical stripping methods, in which the substance to be determined is concentrated electrolytically on the measuring electrode (in the form of an amalgam or of a film on the surface of a mercury or solid electrode) and is then transferred back into the solution by the reverse electrolytic process." (Ref. 3).

Anodic stripping voltammetry has now become a technique of prime analytical importance, which equals by its performance, especially with respect to its sensitivity, flameless atomic absorption spectroscopy and is comparable with many radiochemical and radiometrical methods. Owing to instrumental improvements, it has become a current working method for trace analysis. It has, over atomic absorption, the advantage of allowing multielement determinations in a single run, and in addition it is possible to determine elements in several of their different valence states.

Atomic absorption spectroscopy emerged as a necessity at a precise time, when any medical care given to flame photometry could no longer maintain it in a better shape than at a level of moral ageing. It is to the merit of all those who had studied the flame - Kirchoff, Bunsen, Teclu as predecessors, Mavrodineanu and others - that they opened the way to Walsh to initiate that analytical informational explosion which is atomic absorption. A very simple idea indeed, but highly efficient, that of using the atoms in their ground state and not in their excited states. If you wish, this is a problem of atomic statistical population.

Introduced in late 1954, this technique revived by itself. A short time thereafter, L'vov, T.S. West and Massmann improved it, bringing it to spectacular performances as sensitivity (10^{-14} g for some elements, e.g. Cd and Zn) and a high degree of automation. The modern instruments, provided with microprocessors, can carry out hundreds of analyses per hour in a totally objective manner.

We cannot overlook however, not even in the framework of this general presentation, a technique which has not become morally aged, at least formally, although its age is the same as of our century. This is mass spectroscopy, which has developed so far in three stages: isotope separation, organic structural analysis and, through adaptation of the spark sources, an invaluable integral, high sensitivity technique for analysing traces at the ppb levels. Every aspect of this technique still preserves its viability and validity. By modernising and computerising the instrumentation, mass spectrometry has become a highly efficient detector for GC and HPLC. Spark mass spectrometry is today an un superseded weapon in analytical cosmochemistry and in the investigation of high purity materials.

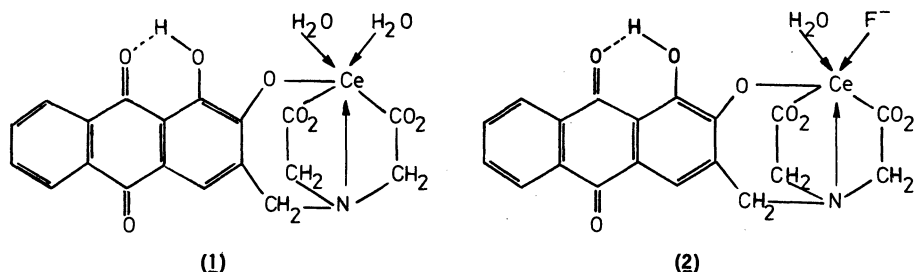
We cannot however discuss the method-instrument correlation without mentioning the moral support which we, the analysts, have - namely the reaction itself. The chemical reaction is our stronghold which, no matter how highly automated or ultrasophisticated is the instrument (and we mean instruments of various generations, even those provided with self-servicing), will always remain viable. The most perfect instrument, even when totally automated, will never be able to do what the man can do, what he thinks and imagines. The researcher in the field of analytical chemistry will never be replaced by an automaton - and this is what gives us some hope.

Knowledge of the reaction mechanisms in solution, in flame, etc., is a chief problem, which can affect ultimately the advance of analytical chemistry as a science and of chemical analysis as a technique.

We will illustrate this with a few significant examples taken from the domain of chemical reactions in solution. We shall refer to some studies carried out on organic reagents. Perhaps the most significant example on these lines is the introduction by Belcher et al. (Ref. 4) of the Alizarin Complexan 3-di(carboxymethyl)aminoethyl-1,2-dihydroxyanthraquinone or 1,2-dihydroxyanthraquinon-3-ylmethylamine-N,N-diacetic acid. This reagent

(ALC-Ce) has the very interesting feature of giving a direct colour reaction for the fluoride ion.

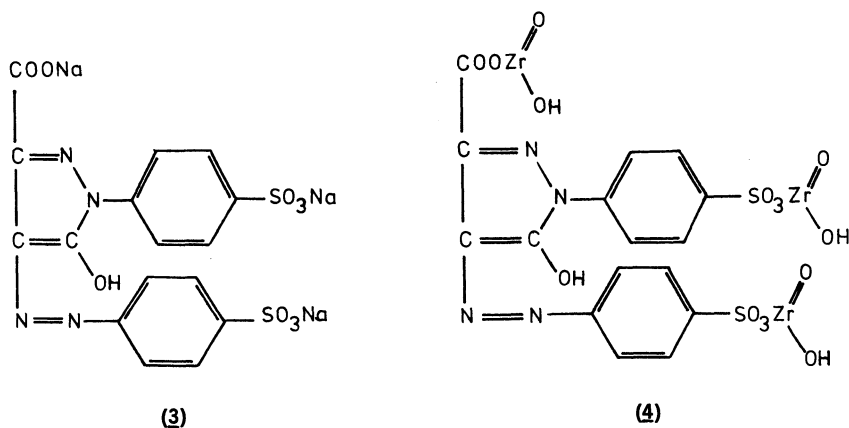
Leonard and West (Ref. 5) believe that the blue complex formed by ALC-Ce with the fluoride ion is a ternary complex. The ALC-Ce complex has the formula (1), whereas the ternary complex the formula (2):



Can anyone say why must we determine the fluoride ion in this way, when we have today on hand an electrode which is particularly selective to this ion, the LaF_3 electrode, as a single crystal if you wish? Let us not forget however that these solid-membrane electrodes themselves owe their existence to a study on the mechanism of the precipitation process. We can see that, at certain moments, the analytical research grows by itself and that new fields start development from some field which had beforehand appeared outmoded.

We may draw from this the very interesting conclusion that the degree of moral ageing of a particular method depends on a particular period of time, that any analytical method remains potentially valid provided that it adapts itself as well as possible to the increasing demands of the analytical process.

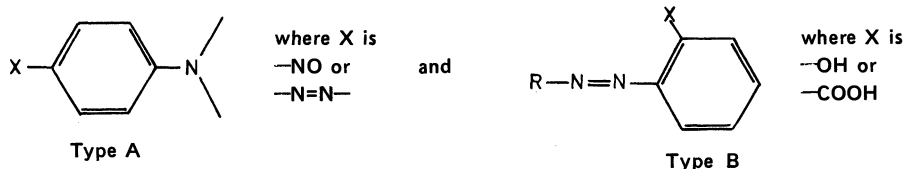
Let us argue the importance of the study of the reactions by two examples picked up from our own practice. We shall refer first to an element whose ions have an extremely pronounced tendency of hydrolysing and of forming inorganic polymers. This is zirconium, which forms very strong bonds with oxygen, accounting thereby for its hydrolysing and polymerising capacities. For these reasons, a very limited number of organic reagents are known which form unitary compounds with zirconium, detectable as such by a physical method. We had begun this study of the organic reagents for zirconium more than 20 years ago, based on the examination, statistical if you wish, of a wide group of reagents; we concluded that a reagent containing a pyrazolonic nucleus, namely Tartrazine (3), used as a dye and indicator in volumetry, forms an unitary compound with zirconium (Ref. 6), whose formula, tested by EM, IR, NMR and MS studies, is (4):



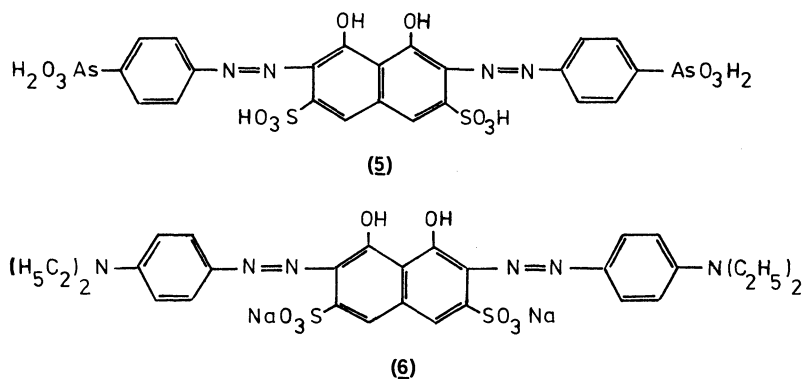
The reagent allowed the zirconium compound to be directly weighed and the method turned out to be highly selective. Due to this selectivity, it was used for determining zirconium both in our country and in the United States, Poland and the USSR.

Our second example will belong this time to the analytical chemistry of palladium. While zirconium is a difficult element to study analytically, palladium is, on the contrary, too submissive - to such an extent that its analytical chemistry is very rich. We proposed ourselves, also many years ago, to systematise the reactions of this element with organic reagents used to detect and determine palladium.

We concentrated on the study of the analytical functional groups and of the analytical active groups (a terminology we believe is still valid today). As a consequence of our study, it became clear that palladium (II) reacts with organic reagents containing two general types of analytical functional groups (A and B), shown below:



By noticing (Ref. 7) the fact that reagents which contain both A and B groups in their molecule, e.g. Methyl Red, give a very sensitive reaction with palladium (II), we synthesised a new reagent, a derivative of chromotropic acid which contains symmetrically both types of groups (Ref. 8). This way, we obtained the reagent (6), which is very sensitive and selective for palladium. Its performance is comparable to that of the Palladiazoreagent (5), (Ref. 9). As a matter of fact, by examining the formula of Palladiazoreagent we may see that this reagent belongs to the class of those reagents containing analytical functional groups for palladium:



We believe that these examples show to a sufficient extent the importance of studying reactions in solution and the contemporary relevance of such studies. It is appropriate to repeat that our main role as analysts lies in doing basic research in the framework of analytical chemistry as a science; the most sophisticated instrumentation merely serves the analytical goal of this science, i.e. the chemical analysis and control of the industrial production.

We do not deny that for a series of analytical research such as the study of some kinetic reactions or of some enzymatic reactions, we need sophisticated instruments. Let us not forget however that all major discoveries in analytical chemistry were made based on knowledge of the essence of the phenomena and, moreover, using fairly primitive instrumentation.

A very fashionable field of modern analytical chemistry, that of chemi- and bioluminescence (CL and BL) may well illustrate this point; it based to a great extent on the study of the nature and mechanisms of these reactions and makes use of less sophisticated instruments.

At the 11th Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, held in Oak Ridge, Tenn., April 26-27, 1979, Seitz, from the University of Durham in New Hampshire, suggested, in connection with the instrumentation available today for CL analysis, that "the instrumentation for the most part is not fully automated; I'm not convinced that if you operate manually you're going to get the kind of operator-to-operator precision you'd like for a clinical instrument. Also, if you do the firefly or bacterial reactions, you have to have some provision for not using up too much of your reagents."

Seitz continues: "My prediction is - and this is my personal belief - that you won't find the present instruments used on a wide scale in the clinical laboratory. My feeling is that someone will either adapt some of the present automated equipment so it can measure chemiluminescence, or come out with some special instruments dedicated to specific analyses. The whole instrument will be much more automated - you'll put a sample in a tube and the instrument will do everything else" (Ref. 10). These are opinions only. What is positive is that the complexity of this kind of reaction (the CL and BL reactions), their restricted number, ought to guide forcibly the research in this field, in order to discover new reactions of this type and, what is still more important, in replying to Seitz - to find the optimum method-instrument correlation. After that, the problem would be left in the hands of the electronic people and of the automation specialists to optimise the system.

It is certain that, in some period of time, explosive processes occur, which finally lead to a very fast advancement of some laboratory techniques and in which new methods of analysis appear. Do these appear randomly? Of course not. Let us think of the ultimate beneficiary; this is solely industrial production or is, in other words, the control of industrial output. That great Teaching-Research-Industrial production correlation closes in upon itself for a while, having to be developed thereafter on another, higher level, once new necessities of the production demand it. The general analytical process is therefore dependent on production and the information explosion in analytical chemistry has, as its eventual purpose, the very progress, development and optimisation of the analytical methods in order that they be taken over by the beneficiary, which is chemico-analytical control, and terminally the optimisation of the industrial process by and with analytical chemistry.

Several fields, every one implying a large number of analyses, have contributed to a great extent in the improvement of the method-instrument correlation; in what follows we shall refer to only three of these fields - environmental pollution, clinical analysis, and forensic science. Since every one of these fields has particularities of its own, the analytical systems had to be adapted to the specific purpose of each field.

The necessity for continuous determinations, for automatically recording the analytical information given by the study of the air and water pollution imposed a selection of the analysis methods and their harmonisation with the monitors. Not every method of analysis has withstood this shock. The methods used today for selectively determining air pollutants, for example, have to depend on high sensitivity, selectivity, accuracy and rapidity (the rapidity being mainly determined by the rate of the involved reaction). Only a limited number of analytical methods passed such a test. Although manufacturers have produced various portable instruments for controlling the atmospheric pollutants (O_3 , SO_2 , NO_x), most of these instruments, while being sufficiently sensitive, do not have the desired selectivity (we have especially in mind the electrometric analysers). The only selective and accurate method for determining SO_2 in the atmosphere is, for example, the method proposed by West and Gaeke (Ref. 11), although it has the drawback of being slow in transmitting the signal. The circle closes again, after all, and we return to the necessity of a method based on a principle which is adaptable to some empirical requirements, the analysis of pollutants in this case. Only those methods based on chemical reactions or the entirely physical methods of analysis which give due credit to the operational parameters of the analytical process will be adaptable on the new, automated and computerised instrumentation. Horwitz (Ref. 2) is right again: "A practical method will always be practicable, but a practicable method is not necessarily practical."

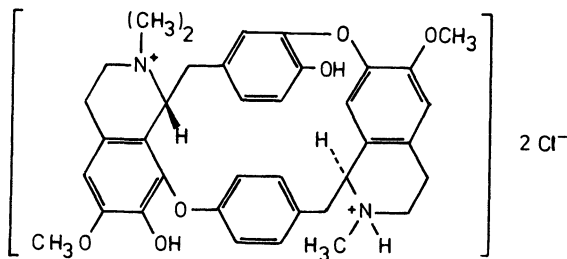
The problem becomes markedly difficult when we have to analyse a complex mixture. A typical example is the analysis of the organic pollutants in the environment. Their large number and great diversity require a previous separation and a suitable detector. It is in this field that the efficiency of the separation techniques, such as GC, and the necessity of exigent and expensive detectors, such as the MS, can be verified. The modern GC-MS-Computer systems turn out to be very suitable for resolving complex mixtures of air pollutants. Their acceptance avoids the use of a large number of individual instruments; due to their lack of selectivity, these would be morally aged starting from the very moment of their manufacture (see the unsuccessful attempts at producing separate analysers for various groups of hydrocarbons).

Clinical analysis has also imposed a selection of those methods of analysis which are sufficiently sensitive, selective and fast, and have an advanced degree of automation. A substantial contribution to the understanding of the method-instrument correlation in this very important field has been made by the study of the enzymatic reactions. Broadly speaking, the classical analysts were afraid of using enzymes, maybe due to the uncommon working conditions required by their manipulation. The instability of the enzymes caused their application in analytical practice to be difficult. A technique was then developed for immobilising the enzymes by bonding them to an inert support; their stability thereby increased, while their catalytic activity was preserved. Based on the study of the enzymatic reactions, on the one hand, and on the progress made in the enzyme immobilisation techniques, on the other, a series of instruments was soon developed for determining glucose, lactose, sucrose, galactose, etc. Immobilised enzymes have evolved from simple chemical determination to more complex fields, where they do remarkable work. For instance, the immobilised cholinesterase is successfully used in the analysis of pesticides.

We can see from all these examples that, willy-nilly, the fundamental basis is again the study of the reactions; the instrumentation is merely an annexe which is necessary and sufficient to the general analytical process insofar as it is adequately selected. By contrast to biology, this selection is not natural, but is directed by laws suitably formulated (by man) to reach the optimisation parameters of the method-instrument correlation.

Use of the chemical analysis in criminology and forensic science is an interface connecting the broad group of methods specific to clinical analysis with proper forensic procedures; this is valid in the large number of cases in which components of an organic nature are involved. Forensic science has got rid, to a great extent, of the older research techniques. The electron microprobe replaced microscopy, the atomic absorption spectroscopy, particularly the flameless one, replaced almost completely the classical emission and absorption spectroscopic techniques. Radioimmunoassay (RIA), a technique developed by Rosalyn S. Yalow and Solomon A. Berson in the 1950's has become a current technique in the modern forensic laboratories.

The achievements of analytical chemistry in forensic science are spectacular indeed. We mention here only two examples: the detection of curare in the Jascavevich Murder Trial (Ref. 12) and the detection of drugs of abuse in hair by radioimmunoassay (Ref. 13). The Jascavevich case could only be solved by close co-operation between several high performance analytical techniques such as RIA, HPLC and MS. You can see how many things analytical chemistry can do, and all this merely to identify a substance such as d-tubocurarine (7):



(7) (+) tubocurarine chloride

Analytical chemistry is practically a field without frontiers, the analytical techniques revive by themselves, they are apparently inoculated against moral ageing, they complement and supplement each other. Let us consider now the second of our correlations:

THE MAN-INSTRUMENT CORRELATION

Discussing this correlation means practically discussing the process of teaching in chemistry in general and in analytical chemistry in particular. The problem of teaching and education in analytical chemistry is a perpetually open problem, a problem of today!

In teaching analytical chemistry, special attention must be given to correlating the specific knowledge with that of other related fields, to get rid of some obsolete data, to acknowledge simultaneously the tradition and the innovation. As far back as 1970, Professor Laitinen (Ref. 14), concerned by the prospects of education in analytical chemistry, had

said: "It appears to me that there is now starting a period of re-evaluation of curricula, and that there is real hope for achieving balance both in theory and experiment between tradition and innovation."

Teaching analytical chemistry in Universities has to follow a logical, pedagogical and stimulative line. The theoretical concepts have to be balanced and related to the practical laboratory activity. This is the only chance for the future analytical chemist to become a good teacher and a good researcher as early as during his undergraduate studies.

One of the aspects generally overlooked by many teachers in chemistry in general, and in analytical chemistry in particular, is the necessity of shaping a specialist who must be cultured in the field of analytical chemistry. Let us outline what we mean by this kind of culture. As shown in the frame of the first correlation, a good analyst is only he who understands the relation between method and instrument; in other words, he who realises the necessity of having a profound knowledge of the various chemical disciplines and, in addition, of some other disciplines which might interfere.

We shall try to figure this problem graphically by a simple geometric body, an octahedron (Fig. 2). This geometric picture of analytical chemistry might seem naive to some specialists in chemistry. In our opinion, it tells the whole story. Let us see how things stand, step by step. The first instrument which the analytical man meets, which incidentally will also be the last to disappear, is the balance. As Stock notices in an outstanding paper, "Weighed in the Balance" (Ref. 15), "the modern precision balance has an ancestry that goes back beyond recorded history."

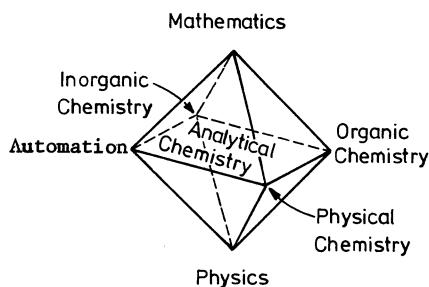
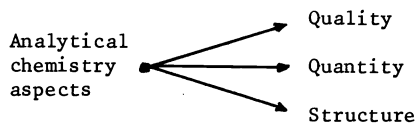


Fig. 2 The octahedron of analytical chemistry

You might rightfully consider that use of the balance has originated the qualitative jump from chemical analysis as a technique to analytical chemistry as a science. Our reasoning behind this statement is that analytical chemistry can only exist as a science through a close interdependence among its three aspects as far as the produced information is concerned:



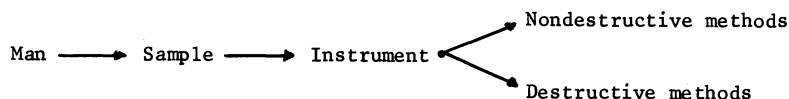
Any analytical determination is based on a very simple relationship:

$$P = f(C) \quad (1)$$

that is on setting up a dependence between a physical property and the concentration of the substance to be determined. Hence the most proper name for the methods used in analytical chemistry: Physical Methods of Chemical Analysis. Any other names, such as physico-chemical methods or instrumental methods, are either incomplete or biased, or sometimes even confusing. It might be recommended that we define our own speciality in very precise terms, at the very least in order to be in a position to promote it. The name of physico-chemical analysis methods was much appreciated by some physical chemists who, wishing to appropriate these methods and being somewhat ignorant of the matter, believed them to belong to physical chemistry. They were nevertheless willing to concede that gravimetry and volumetry, regarded as classical methods of analysis, rightly belong to analytical

chemistry. They overlooked the obvious fact that these methods also make use of a physical property in their measurements, hence the validity of the above-mentioned name.

The man-instrument correlation is carried out by the intermediary of the sample. By its very nature, the sample to be analysed is the culprit in the division on the analysis methods into nondestructive and destructive:



Let us go back to our octahedron; in fact, the sample itself leads us to it. On this occasion we can solve a much discussed, generally valid problem, the competition among specialists in acquiring increasingly more sophisticated laboratory instruments. When (inorganic and organic) samples with comparatively simple composition, especially in solution, are analysed, emphasis is given to the analytical chemist as a performer of the chemical analysis. An altogether different situation is met when the sample has a more complex composition (biological samples or synthetic materials), or when trace analysis is necessary (ultrapure and nuclear materials, or semiconductors); such cases require more and more advanced nondestructive methods (let us only mention the surface analysis techniques) and the analytical chemist is in many cases excluded or replaced by a physicist.

For this reason, in order to make an efficient use of the complete arsenal of physical methods, nondestructive or destructive, the analytical chemist must know the nature of the sample, to get the utmost information about it. This knowledge of the nature of the sample implies, in turn, being well informed horizontally in three corners of the parallelogram: inorganic, organic and physical chemistry. This is the reason why we used this particular geometric representation; in our opinion, these branches play perfectly equal parts in the formation of a good analyst. The fourth corner of the parallelogram representing the horizontal development of the analytical chemist, is automation.

The analytical chemist of the '80s and the future analytical chemist must take as an undisputable fact that a compulsory prerequisite for using the new microprocessor- and micro-computer-equipped instruments is to know, at least at an elementary level, the basic problems of automation.

This parallelogram, which connects the sample to automation by means of the three fundamental chemical disciplines, accounts for the fact that today the analytical chemist is no longer a simple performer, but also a thinker, a man who solves problems - by using an automated instrument if you so wish. As Jeanette Grasselli aptly remarks in a recent paper (Ref. 16), "the modern analytical chemist no longer just answers questions, but rather solves problems or suggests solutions."

Though equivalent, each of the four disciplines represented on the parallelogram has a decisive role in the formation of the analytical chemist. He will have to get, in the first place, a sound basic knowledge of inorganic and organic chemistry; this is the way for him to understand and approach any kind of sample; he will understand many mechanisms of reaction in solution or the complexation (masking and demasking) processes. As shown above, knowing the nature of the sample is almost an unmistakable sign that the analysis would be successful. Understanding the solution chemistry, the equilibrium reactions, the reactions in partially aqueous or in nonaqueous media requires the analytical chemist to possess a deep knowledge of physical chemistry.

Several high performance analytical methods such as the kinetic and enzymatic methods, in order to be understood and thereby used at their best parameters, also require a thorough study of physical chemistry. Similarly, the analytical chemist cannot carry out thermal analyses, not even the simplest thermogravimetric one, if he has not a solid knowledge of chemical thermodynamics. If the parallelogram has equivalent corners, this means that the analytical chemist has got a sound instruction in the horizontal direction, that he has got a scientific foundation. This scientific base is furnished by the school and by the teacher; if good himself, the teacher injects him with the creative spirit needed by research. It is commonly known that a good science teacher can only be a person who has worked in the scientific field and who continues to do so; to put it into our terms, one who can understand the man-instrument correlation. From their very beginning all chemical sciences, and especially analytical sciences, have progressed as a result of some instrumentation.

The man-instrument correlation is however much more complex than it appears to be at first sight. To illustrate this we shall replace the plane parallelogram with a solid body and shall consider the two apices of the octahedron, that is the development of the analytical chemist on the vertical direction. This development involves physics and mathematics. The very name of physical methods of chemical analysis is an argument for the necessity of having a sound knowledge of physics in order to be able to use laboratory instrumentation and to understand the physical significance of the various phenomena which occur in a chemical interaction or reaction. On the other hand, cleaning of the analytical signal, its conversion and transmission in a suitable form, requires a deep knowledge of mathematics, and not only of mathematical statistics for data processing as some analytical chemists still believe. The efficient use of computer terminals or of microcomputers needs a basic knowledge of the programming methods and of data processing, particularly in cases where a large amount of analytical information is involved; this is the case of tandem techniques such as GC-MS-Computer or of transform techniques such as the FT-IR or FT-NMR spectroscopies.

Owing to the complexity of data to be interpreted, the structural analysis branch is the user of an ample mathematical apparatus. Many undergraduate students who just begin to acquire the bases of the qualitative analysis in their first year of study, regard themselves as detectives who try to identify a number of ions in a solution. The true detective is however that analytical chemist who deals in structural analysis. Let us take the example of a complex mixture resolved by the GC-MS-Computer tandem system or, still more convenient, merely the MS analysis of some organic components. The analytical chemist has to reconstitute the original molecules by only knowing the mass fragments. You might call it a new chemistry. In most cases he cannot solve this problem by his own means and he calls for the computer. This might be very helpful, but only if the analyst knows enough chemistry to be able to interpret the results. As Kowalski, a specialist in a new field, Chemometrics (which includes the application of mathematical and statistical methods to the analysis of chemical measurements), rightly remarks (Ref. 17), "computer pattern recognition methods extend the ability of human pattern recognition but, in the end, it is the chemist who must do the chemistry."

Looking again at the "Octahedron of Analytical Chemistry" we can be in some measure satisfied, having specified every corner of the octahedron. Some people will ask nonetheless, where is electronics? Is it necessary for chemists? In my opinion, electronics, in spite of its impressive recent development and of its being a rather separate discipline, is too close to physics to elude being included in it. An analytical chemist who has a sound knowledge of physics can also understand electronics and can be the beneficiary of the information given by the most up-to-date physical methods of analysis.

We shall refer in what follows to one of the most recent physical methods in surface analysis, solid state photoelectron spectroscopy with synchrotron radiation. This is the only one of the many techniques of modern science benefiting from the synchrotron radiation. As Weaver and Margaritondo show (Ref. 18), "Synchrotron radiation sources, providing intense, tunable, polarized and stable beams of ultraviolet and X-ray photons, are having a great impact on biology, physics, chemistry, materials science, and other areas of research. Synchrotron radiation has revolutionised solid-state photoelectron spectroscopy by enhancing its capabilities for investigating the electronic behaviour of solids and solid surfaces."

The new techniques of analysing surfaces can only be used through a healthy knowledge of physics. As so appropriately Hercules remarks (Ref. 19), "one of the new frontiers in analytical chemistry is the chemical analysis of surfaces." We benefit today from a wide spectrum of techniques for analysing surfaces, techniques which often allow trace analysis on surfaces. We cite here ESCA (X-ray photoelectron spectroscopy), AES (Auger electron spectroscopy), SIMS (Secondary ion mass spectroscopy), ISS (Low-energy ion scattering spectroscopy). These techniques have emerged to supplement X-ray fluorescence spectroscopy, an old surface analysis method which, though morally aged at a certain moment, has revived by automation and computerisation. XRF and its grandsons are successfully used today for studying a large variety of inorganic, organic and biological materials.

Perhaps the most spectacular field which proves the involvement of physics in analytical chemistry is however the development of ICP-AES (Inductively coupled plasma-atomic emission spectroscopy). Research in this domain has led to the emergence of a powerful technique for chemical analysis. To give history its due, we shall quote Professor Fassel (Ref. 20), a specialist not in physics, but in physical chemistry: "For the past 17 years my associates and I have devoted a fraction of our efforts to the development of the basic science, the

investigative methods and the hardware for an analytical approach that would eventually provide the capability of determining the chemical elements selectively, at all concentration levels, i.e. major, minor, and trace constituents, simultaneously if so desired, or in a rapid sequential manner, with a single analytical technique, and with accuracy and precision. A new analytical approach, usually identified as inductively coupled plasma-atomic emission spectroscopy (ICP-AES) has emerged from these studies."

This technique has necessarily appeared as an addition to, a revival of emission spectroscopy, a technique which had become morally aged from several points of view. The highest ageing coefficient of the classical emission spectroscopy concerned its sensitivity. Together with flame and flameless AA, ICP-AES furnishes today the best high performance instruments in the hands of analytical chemists. Discovery of ICP-AES and its use in modern analytical chemistry are one of the best proofs of the existence of a man-instrument correlation. In order that this technique could emerge, the octahedron had to work perfectly on both directions in space. Development of such a technique needs a sound knowledge of chemistry (organic and inorganic), physical chemistry, physics, mathematics and automatics.

Let us now take up the last, and perhaps most important correlation:

THE METHOD-MAN-INSTRUMENT CORRELATION

This correlation is closely related to the method-instrument and the man-instrument correlations.

Whereas in discussing the first correlation, we emphasised the role of the reaction and of the reaction mechanisms and, in the framework of the second, the role of the teaching process in analytical chemistry, this third correlation will have as a pivotal term the chemico-analytical control of industrial production. In most cases, this control is carried out today with automatic analysers and has as its final purpose the optimisation of the industrial output.

Does this mean that, within this last correlation, the man is included in an inflexible tandem, that he becomes a one-man instrument, a man ultraspecialised in a certain field? Perhaps many of those who are not familiar with the education problems in analytical chemistry would tend to believe that this is so. The problem must however be stated in totally different terms. To adapt himself to this correlation, to interpose himself between method and instrument for optimising the analytical process, the analytical chemist of the future must be a cultured man in his own speciality, and indeed be generally cultured. This will only be ensured by the continual improvement of the teaching process in chemistry in general and in analytical chemistry in particular. This is one of our common problems, but it is solved differently from case to case and from country to country.

In an editorial entitled "Education for the 21st Century", published in Science (Ref. 21), Abelson states that: "Whatever the changing shape of society, scientists and engineers will have essential roles. The uncertainties, though, make it advisable to caution against excessive specialisation. In contrast, it seems desirable to adopt policies of maximum flexibility, of preservation of options, of being prepared to pursue lifelong learning."

It is certain that in order to preserve his form, a good specialist must continuously read, must have a good development on the horizontal - but of course not only on the surface.

The chemico-analytical control of industrial production could have brought both the analyst and analytical chemistry itself to a virtual standstill. Fortunately, basic analytical research has solved and still solves the method-man-instrument correlation. Man has to adjust himself to the necessities of the continuous control required by the production process. To the analytical chemist, the necessity of knowing the problems of automation and of analytical sciences has proved to be a necessary and assertive forward step.

In this way the analyst has learned to operate automatic analysers, but not to become part of them. We must realise once and for all that analytical chemistry as a science used automation for doing chemical analyses and does not automate itself. As Whalley correctly remarks (Ref. 22), "now in industry, and in the chemical industry in particular, we are swinging over more to automation of analytical control, and by this I do not mean doing analytical chemistry automatically."

Analytical chemistry is substantially involved in the control of the product's quality and this by the very observance of the method-man-instrument correlation. Taking account of the intended purpose and of its implications, this correlation must be considered very seriously. This action of the correlation upon the control process, hence ultimately upon

the optimisation of quality control, may be pictured by a triangular pyramid (Fig. 3):

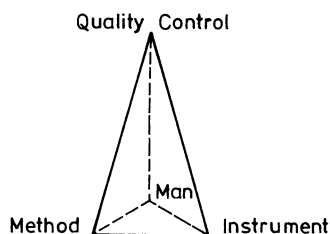


Fig. 3 Optimisation of quality control

It would be interesting to consider quality control from a historical point of view and from which the analytical chemist sees it. In a first stage, the instrumentation used by the analyst was rather primitive and many of us can recall the time when the quality control in steel mills was still carried out by rapid volumetric methods. Today, volumetry has become morally aged in this branch of industry, where it was replaced by automatic emission spectroscopy or X-ray fluorescence spectroscopy. The current requirements of quality control in industry have led to an extremely fast progress of the automatic control instrumentation. The presence of a process chromatograph in an industrial installation is now regarded as commonplace.

Two domains of prime consequence, air and water pollution, are perhaps among those for which the necessity of automation and of the automatic quality control appears as most obvious. A formidable competition has existed and still exists among instrument manufacturers to come out with more and more new devices, new analytical automata for continuous measurements. The control of the quality of air and of water is however, by the very nature of the determinations involved, very pressing. Analytical chemistry had to co-operate with a series of related disciplines in order to work out novel principles, new analysis methods. These had to be provided with optimised operational parameters which could make them adaptable to automatic systems.

In this sense, a spectacular example of method-man-instrument correlation is perhaps the use of piezoelectric sensors as continuous monitors of the atmospheric pollutants. The piezoelectric crystals, coated with various adsorbent materials, have been used as sensors for a number of pollutants, including sulphur dioxide, nitrogen dioxide, ammonia, etc. Cooke et al. have recently proposed (Ref. 23) such a piezoelectric sensor as a continuous monitor of the atmospheric pollutants.

Even if, as in any new field, these sensors still have drawbacks, we are certain that in a not too distant future analytical chemistry will prove the possibilities of such devices being incorporated as parts of an automatic system of controlling the quality of air. This point of view is based on the theoretical feasibility of such a system and on the relatively simple way of building up the necessary instrumentation.

Investigation of the water pollutants, in other words the analysis of waste waters, has been a main beneficiary of the research carried out in connection with the electrochemical sensors. The ion-selective electrodes originally proposed for analysing some anions (a branch of analytical chemistry which had been previously ignored) have found today practically unlimited applications in the analysis of organic and biological compounds. They are now a highly efficient means in the continuous analysis in many industrial branches, especially in the control of the quality of water. As early as the '60s, research in the field of ion-selective electrodes carried out worldwide by various analytical chemistry groups has led to an advancement of the theory and practice of this prominent technique. The research progressed at an unexpectedly quick pace, if we take into account that, in the analysis of waste waters, most of the pollutants which could be potentially determined are organic. The references found in the literature are so rich that this led us to publish in 1977 a monograph (Ref. 24) on the application of the ion-selective electrodes in organic analysis. There are today a lot of electrochemical sensors for on-line process monitoring, using a variety of techniques such as potentiometry, conductivity measurements, voltammetry, etc. (Ref. 25).

In order that the method-man-instrument correlation is able to lead us to an automatic quality control, the man factor has to ensure a perfect matching of the operational parameters of the method with those of the instrument, that is the adaptation of the most suitable method to the most suitable instrument. Let us picture this fact in the form of the most perfect spatial body, a sphere (Fig. 4). Following the choice of the most suitable

method for analysing a certain material, simple or complex, in order to get most out of it the analyst will have to choose from the great variety of instruments available, the most appropriate to his actual analytical problem. In the case of on-line analyses, he would have to get and process the analytical information continuously.

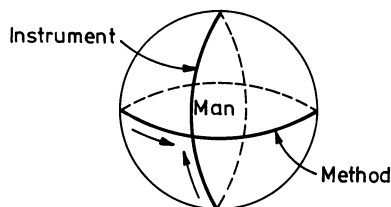


Fig. 4 Adaptation of the method to the instrument

A very significant problem which arises in the case of the automatic on-line analysers is that of the reproducibility of the analytical signal. Instruments which are able to self-calibrate periodically have to be designed. These devices should be extremely reliable. An automatic device is up to the expected task insofar as the angle between the two great circles (one standing for the method and the other one for the instrument) approaches zero, that is when one great circle superimposes the other. A method-instrument symbiosis is then ensured, which remains valid for a practically unlimited time with no need for man to interfere. The analytical chemist is the only one in a position to judge, or assess, when this "couple" is no longer necessary and to decide which other "couple", operationally more favourable, should replace it.

Besides providing the automatic control systems used directly in the industrial process, chemical analysis becomes an indispensable weapon in a string of public services, among which is the quality control of food. In this field of direct concern to us, since it is related to public health, the contribution of analytical chemistry is tremendous. All the examples already given in this short lecture, as well as the many others which could not be enclosed, prove that analytical chemistry, by the intermediate of the chemical analysis, is of great consequence to our daily life. This is mainly because we seek products of better and better quality; quality means quality control which, in turn, implies chemical analysis, which has to rely on analytical chemistry in order to get from it the best quality control system. This is perhaps why Markland (Ref. 26) believes that "analysis includes any process for determining any fact as to the nature, substance or quality of any material."

Let us look now, in the framework of this third correlation, at the general analytical process. To do this we should take into account, as shown above, the operational parameters of the method and the functional parameters of the instrument. To become competitive, any analytical method must meet the following requirements: (a) The highest possible sensitivity (also dependent on the concentration of the analysed component). In other words, a method which is suitable for trace analysis should be used in this field only, and not for major components; to do otherwise would mean impairment of the method-instrument correlation; (b) The best possible selectivity. We should be able to determine a chemical species, immaterial of its concentration, in the presence of a complex matrix; (c) Good accuracy, a parameter which depends on both method and instrument and which varies as a function of the concentration of the analysed component. However advanced the laboratory instrumentation, in going down to lower and lower concentrations, to ppm, ppb, ppt or even lower levels, the accuracy of the determination decreases; (d) The rapidity of obtaining the analytical information which, in the case of the destructive analysis methods, depends on the reaction mechanisms in solution and, for nondestructive methods, is to a great extent affected by the functional parameters of the instrumentation.

In order to be correlated with the most adequate method, the analytical instruments should also perform in the optimal range of their functional parameters. In today's so-called third generation instruments, the high degree of automation is provided by a micro-processing core. We might say that our discussions today about miniaturised and automated analysis instruments would not have been possible without the invention of microprocessors. In most analytical fields, the modern instrumentation is almost completely automated, starting with sample positioning (automatic sample switching) and ending with remote information transmission if you wish. The most typical example is that of the totally automated instruments for analysing the Moon's soil, placed on the Lunar Module and directly sending the analytical information to Earth; but let us not forget that an automaton does not think, that it is an artefact of the human mind, whom it may in some measure mimic, but whom it could never substitute.

CONCLUSIONS

Following this general inquiry into the correlations involved in the analytical process, we have gained a clear understanding of the role of analytical chemistry in education, in research and in the quality control of the industrial products (by means of the chemical analysis). The analytical process can be thus schematised as in Fig. 5.

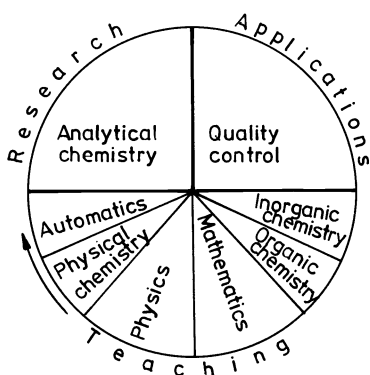


Fig. 5 The analytical system

We are using the name of Analytical System because it is a comprehensive notion, including all the stages of the analytical process (Teaching-Research-Applications). All stages have to be maintained at optimal parameters in order that the system be viable. If not, moral ageing of the whole system sets in. The system is cyclical, but the circle never closes upon itself. Improvements in teaching lead to an amplification of the research which, in turn, benefits the industrial production, and the present and future production needs to use men and instruments which should be adaptable to its optimisation, therefore having a reduced degree of moral ageing. We saw above how we can partly reduce the degree of moral ageing of the laboratory instrumentation (for research and control) and of that used in the automatic on-line control, but the task is much more difficult with regard to the operator, the man. Man cannot be bettered but within a continuous educational process. In chemistry, in particular in analytical chemistry, education can be carried out as a continuation of the teaching process. The possible educational forms are very diverse, but a principle which always holds is that the best form of education is the steady team work in the laboratory. No modern large-scale analytical investigation can be carried out except by a well blended team, consisting of persons equal as far as their scientific background is concerned or, as often happens, by mixed, interdisciplinary team. The most significant example is that of the new physical methods of chemical analysis, which owe their emergence to a continuous, often long-term research effort of a mixed team. This is the only way in which the automatic analysis and control systems could appear, in which the existing instrumentation can be improved. This is the only way in which we can steer clear of moral ageing.

Any analyst who can understand this truth will become persuaded that:

1. Analytical chemistry is a science which will always remain young.
2. Research in analytical chemistry is required not only by chemistry, but also by a wide series of other frontier scientific fields whose name begins with bio: biophysics, biochemistry, biology, bioenergetics, biochemical engineering, etc., to mention but a few of the beneficiaries.
3. Chemical analysis - the applicative side of analytical chemistry - has now become a constituent, integral part of the production process; it contributes to the optimisation of the process of controlling the quality of the industrial products.

In order that all this becomes true we will have to believe in the boundless possibilities of this science, Analytical Chemistry.

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