

ANALYTICAL CHEMISTRY AND AUTOMATION

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INTRODUCTION

To describe the relationship between analytical chemistry and automation is at the same time to describe the present position of both these fields, each of which strongly influences the other. We must give each its proper terms, and define the limits of their application. In so doing, we are considering not only the present position of analytical chemistry in its relationship to other branches of science, but also its own inner structure.

If we consider, as the first stage of our approach, the overall view of the subject, the underlying difference between chemical analysis and analytical chemistry is quickly apparent to use. We find that today's analytical chemistry is a co-ordination of chemical analysis with physical, biological and statistical methods, to name some of the more important. Therefore I cannot follow the statement of Liebhafsky made about two years ago: "like it or not—chemistry is going out of analytical chemistry!" If we consider the steady changing of every branch of science and knowing that physics had already been in — in analytical chemistry since the first balance was used — I prefer to say, in answering Liebhafsky "Happy enough, physics more and more is going into analytical chemistry without knocking out chemistry".

Analytical chemistry may be considered the general approach to the study of materials whose properties we wish to investigate and understand, and it is of little consequence which methods we use to attain our end. Furthermore, it is apparent that the current division of analytical chemistry into only two groups is now insufficient, and the following four groups should at least be considered, in answer to the following questions¹:

(a) *WHICH* components does the sample contain?

Qualitative Analysis

(b) *HOW MUCH* of each component is present? Quantitative Analysis

(c) *IN WHAT WAY* are the components related?

Co-ordinative Analysis

(d) *HOW MUCH* do the former three points influence process control?

Kybermatic Analysis

Only the correlation of these individual pictures can give us the true solution to the composition and structure of a product, and this reflects at the same time on the true nature of analytical chemistry; and only with a full acceptance of this fact is there any point in speaking of Analysis and Synthesis.

When we consider the union or the "equilibrium" of analytical chemistry, i.e. analysis, with synthesis, with regard to the four main branches of the natural sciences, namely, chemistry, physics, biology and mathematics, then we get the scheme shown in the *Figure 1*, which shows that there is an equilibrium-like relation between analysis and synthesis.

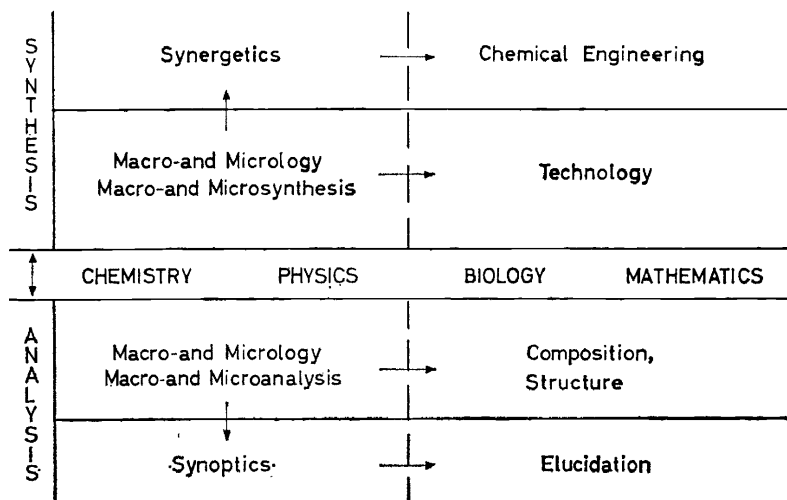


Figure 1. Relation between synthesis and analysis

With the steadily improving resolution, in both two and three dimensions, of the newer analytical methods (mass spectrometry, electron-probe microanalysis, etc.) and the associated penetration into the finer structure of matter, we become able to analyse smaller and smaller entities, both qualitatively and quantitatively. Thus the question of sample homogeneity comes very much to the fore; a question which can only be answered in connection with the possible "resolution-power" of the analytical methods used. The solution to this problem emphasized the next sore point in analytical chemistry, namely, the still widely accepted value of average analysis. This is in contrast to the rapidly advancing use of the substance-characterizing methods of co-ordinative analysis. Obviously, a correlation between the results of macro-methods (mostly giving average analyses) and of micro-methods (mainly point-analyses giving) is very important. Thus the data obtained from small particles of substances often give quite different pictures to those to which we have been accustomed from the analyses of "large samples".

The deeper we delve into the micro-region the less certain a definite reaction can we predict, simply because of statistical reasons. These as yet unformulated relationships will undeniably lead to a new branch of science—"micrology", the study of small phenomena and their interpretation. But if we are to have "micrology" (to which would belong the scientific disciplines of microchemistry, microphysics, microbiology and microtechnology) then we must also have a corresponding "macrology". The mathematicians

have long since solved this problem with the concept of differentiation and integration as summarized in *Figure 2*.

MACROLOGY	MICROPROCESSES
1. MACROPROCESSES 2. statistically guaranteed CAUSALITY 3. <i>common</i> consideration of INTER- and INTRA-RELATIONS 4. DETERMINITY 5. obvious	1. MICROPROCESSES 2. statistically <i>not</i> guaranteed CAUSALITY 3. <i>particular</i> consideration of INTER- and INTRA-RELATIONS 4. INDETERMINITY 5. <i>less</i> obvious

Figure 2. Relation between macrology and micrology

Not infrequently, a mean analytical value for a sample represents that of a quantity 10^8 – 10^{10} times as big as the sample, and especially in connection with the aims of automation, there arises, the question of how small may, or how large must, the sample be in order that the results produced be meaningful.

In general, an analysis comprises the following consecutive steps:

Sampling + sample preparation + (physical or/and chemical) reaction + measurement + calculation = Result

All these steps are subject to both determinable and indeterminable errors, the elimination of which will of course be important and desirable in automation.

Alimarin² has put forward in his discussion on trace analysis, the term *analytically active concentration* of a substance. This is of importance in our context since (a) many modern instruments can only handle relatively dilute solution, and (b) during preparation, a sample is often subdivided or diluted to reach a suitable concentration or size for the measuring stage.

The full 100 per cent of all the atoms, ions, or molecules of a substance to be analysed cannot all be analysed by every method, since not all particles are present in a form suitable for the determination. This may depend, for example, on a limited solubility of the compound, on polymerization of polyvalent cations, on the dissociation of complex compound, on the incomplete ionization of atoms in a plasma, or on incomplete radiation in a neutron beam, and so on. On the other hand, a substance may be stable for only a short time, e.g. due to radioactive decay of short-lived isotopes, decomposition of unstable compounds, photochemical effects, instability due to "hot" atoms, and catalysis. Such an incomplete or unstable state of a substance can affect, to a considerable degree, the sensitivity and accuracy of an analysis depending on some particular measurement, such as of absorption or of emission. The experimental error can be eliminated by the use of standards or by the addition of isotopes under the same conditions.

In spectrophotometric analysis, the analytically active component is also a product of complex-forming cations (metal ions). For many compounds, more than 90–99 per cent of the ions are bound as the desired complexes. From this point of view, the analytically active concentration is the greatest in spectrophotometry.

In emission spectroscopy, the number of the analytically effective particles is very small in comparison to the inactive ones. Many scientists believe that about 1–7 per cent of atoms in an electric arc are in the excited state, and only for a very short time (10^{-7} – 10^{-8} sec). Distinctly fewer atoms are active in flames. We should take into consideration the observation that a much greater quantum yield is obtained by the use of photographic plate than by tubes.

In atomic absorption analysis, more than 99 per cent of the “element-flame-radiation” are absorbed. The sensitivity of atomic absorption analysis is higher than that of flame photometry. The ideal case is that of luminescence of gases in an enclosed vessel which makes possible the use of a “cumulative detector”. Methods of increasing the sensitivity and accuracy in spectroscopic analysis are closely connected with the development of new excitation sources in which nearly all of the atoms present, desired or otherwise, become active.

In mass spectrometric analysis the yield of ions is somewhat greater than in spectrographic analysis, but a rough calculation shows that from a sample of 5–10 mg, about 1.5–2 mg are vaporized, a smaller part is ionized, and only about 10^{-1} per cent of the atoms reach the detector finally.

In the modern laboratory, more and more instruments are being used which, though outwardly simple to use and handle, are in fact very complex machines. Measuring techniques have undergone great changes in the last few decades. Two decades ago the main instruments of the analytical chemist were relatively simple in mechanism and construction, and their theoretical principles were quite well understood by their users. Such instruments as photometers and potentiometers are still in use today.

The development of vacuum tubes and electronics brought about a major change in analytical instrumentation. Three fields of greater interest to the analyst are those of high-input resistance amplifiers (and d.c. amplifiers), stabilization of systems through negative feedback circuits, and the use of servo-mechanism in data presentation devices. The analyst now has a range of sensitive and precise pieces of equipment based on these electronic units, but the rate of progress in the design of instruments has been so great that it has not been possible for him to keep up to date. As soon as a new machine had been designed, it was available on the market, was bought and put into service and the methods worked out for it. The working principles of the instrument were, however, often only vaguely understood.

So as to make the best use of such instruments the basic sequence of steps within the instrument must be understood.

1. A detector accepts the input signal (temperature, pressure, concentration, pH or some other parameter of interest to the chemist) and converts it to another form such as an electric current or voltage.
2. The signal from the detector is accepted and modified so as to give the output signal. The modification can be in the form of amplification, either in terms of voltage or of power; or the d.c. form could be chopped to facilitate amplification, and afterwards rectified. The signal may be compared with a reference so as to provide a difference signal, or it may be differentiated or integrated. This corresponds to mathematical handling of the information.

3. The data presentation device makes the information available to the user. A chart recorder, an oscilloscope and a galvanometer are common examples.

These functions are clearly separated in some instruments, but in others they may be combined into one physical component. In the more modern instruments the middle section usually has more sophisticated circuitry than was the case in the earlier instruments. This is the modern "Black Box" component. Also, the information is handled with a much greater degree of precision by the more advanced techniques. Many chemists are satisfied when they have mastered the knobs and switches.

When we come to the second step to deal with automation, we must, so as to set out limits, ask ourselves the question "Automation in analytical chemistry or automation with analytical chemistry?" The former being in the laboratory and the latter is concerned with process control. The reasons why there should be automation will in both cases be much the same, and may be divided under the following headings:

1. Analysis become more rapid

(a) Many technical processes require control-analysis of materials during the process itself as in steel production. Here the situation is such that the material in the furnace must be analyzed, and the results made available in seconds. Of course plant and laboratory are often some distance apart, the problem of transmitting the sample (e.g. by means of a compressed air line) is also a question of time. Properties of the melt in the furnace may have changed in the few minutes it takes to provide the analytical data. (b) In a clinical laboratory, the question is not so much the speed of an individual analysis, but of the large number of samples requiring analysis, and the amount of material to be handled.

2. Elimination of subjective errors

This point is quite clear. However, automation itself is nevertheless capable of introducing systematically false information.

3. Saving in working time and man-power

This point, which has caused no little concern to mankind, is of general significance and three possibilities shall be pointed out. (a) Because of the greater rapidity of analysis, it is possible to carry out a set amount of analyses either with fewer people, or in shorter time. (b) Working staff can be spared the often tiring and boring repetitive work (which in quantity often leads to greater errors in results). (c) Since the working staff need not be increased, the problem of the enormous amount of extra space required by extra staff is also solved. One need just consider how much space is required when doing the same number of analyses manually as compared to mechanically.

4. Special cases

Automation is of great value in, for example, the handling of short-lived radioactive isotopes, or for carrying out analyses by remote control, as in space travel.

Automation does, of course, bring its associated disadvantages, as for example (i) High capital costs, (ii) Need for specialist service engineers,

(iii) Restricted flexibility, (iv) Requirement of teaching or education in new fields.

RELATIONSHIP BETWEEN ANALYTICAL CHEMISTRY AND AUTOMATION

It is certainly not only the chemical industry which depends on the information from analytical chemistry for control and regulation of automated processes. In order to facilitate further the discussion of the relationships between analytical chemistry and automation, we shall divide the subject under five headings.

1. Definition of terms: nomenclature

It is certainly difficult to make definitions in such a complex field as automation in which not only mechanisms, machines and instruments, but also reaction kinetics and measurement of physical quantities play important roles. The term "automation" is now widely used and misunderstood in analytical chemistry, to mean either complete or partial replacement of a manual operation or sequence in or during analysis. This loose application of the term robs it of any precise meaning and results in it being in many cases a synonym for mechanization and instrumentation.

So that we can distinguish the following four terms, we should try to see first what it is they all have in common: the transfer of analytical procedures out of human hands and beyond human capabilities. *Mechanization* is concerned with the production and transmitting of movement (guidance of a burner, filling of burettes, setting of relays, etc.). *Instrumentation* is concerned with the producing and transmitting of signals to obtain data. Very often a signal can become immediately an information. *Automation* is concerned with the use of systems in which at least a part of the human power of decision is eliminated—by a combination of mechanization and instrumentation. In other words, here both movement and information must be used and combined in order to get a programme.

This train of thought may be extended further, and we come to the evaluation and transfer of measured data, which can be used for the control of a chemical process, or the automation of an analytical procedure. When next it deals with the processing of measured data from a chemical or physical process, the field of Kybermation has been entered.

A rationalization of each of these stages may enable the present situation in an analytical system, or in the organization of an analytical laboratory, to be more practically and more economically arranged.

The Division of Analytical Chemistry of IUPAC has been making great efforts to clarify these terms and definitions. Without wishing to anticipate the outcome of this work, I would like to show the schematic relationships in *Figure 3*.

A machine does not give a signal in our sense (see below) an instrument must not give a movement in the sense of dislocation, e.g. as long as a balance is only used for finding the rest point it is a machine but if the deflection point is to be found it becomes an instrument, especially if the balance is loaded. Because from the deflections we get the signals needed.

machines instruments W machines programm W instruments W machines transfer W programm W instruments W machines	MECHANIZATION INSTRUMENTATION AUTOMATION KYBERMATION	movement movement W signal movement W signal W result movement W signal W result W self-regulation
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Figure 3. Relation between mechanization and kybermation [**W** = closely related with]

The following explanation of the terms signal, message and information should help for a better understanding of automation. *Signal* is, in general, the relative change in a condition, referred to a definite level. The unit may be, for instance, 1 bit (a binary bit). *Message* is a succession of signals, i.e. a sequence of bits. *Information* is the decoded content of a message. *Table 1* shows the relationships more clearly. Without doubt, this occupation with the problem of automation and analytical chemistry also demands a study of information theory.

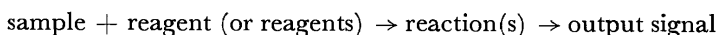
Table 1. Relationship between signal, message and information.

<i>Stimulus</i>	<i>Representation</i>	<i>Morse</i>	<i>Chemistry</i>
Signal	Bit	.	Current or voltage pulse
Message	Sequence of bits	· · · - - - · · ·	Millivolt (digital)
Information	Decoded message	S O S	1 mV = 0.1 pH etc.

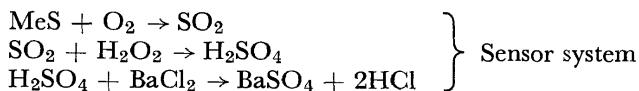
2. Sensor-Transducer-Detector-Black Box

The difficulties arising in this section are not only those of choosing a suitable heading, but also those of arranging the content, with its possibilities of interpretation.

By *sensor* we mean some kind of a system delivering an analytically useful signal corresponding to measured quantities; by *transducer*, a means of conveying the signal to the receiver, and by *detector*, the signal receiver. These three components, together with signal-changer, amplifiers, etc. are usually designated as a simple—but in analytical circles often not sufficiently highly regarded—Black Box. This unit (the Black Box), however, represents the heart of each automat in analytical chemistry. A sensor can in many cases correspond to a simple proton (or electron) transfer according to the chemical reaction (e.g. neutralization or redox reaction) but it may depend on a complex reaction going through a number of intermediates. A sensor system could also depend on the absorption on electromagnetic radiation, e.g. x-ray fluorescence analysis. In all cases, however, it must deal with a chemical or physical reaction giving a measurable signal. An exact correspondence of specific signals is essential to the system:



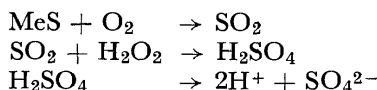
As an example, let us consider the determination of sulphur in steel by the combustion method in a stream of oxygen followed by measuring the SO_2 thus produced with a suitable reagent. As sensor, we have then the following reactions:



in which BaSO_4 is the signal for the sulphur. The sensor here comprises all the reactions leading to the formation of BaSO_4 . The carrier, the transducer (this should not be mixed up with transducer) is simply the water, where the BaSO_4 is suspended and the receiver (detector) comprises the crucible and balance. Only the difference in crucible weights gives, by means of calculation factor and sample weight the real amount of sulphur. Therefore the system Balance + crucible is an instrument.

The BaSO_4 can also be used as a signal if the S-content will be determined by turbidimetric methods. Here we can see that in effect BaSO_4 is the signal and not the difference, e.g. in crucible weights.

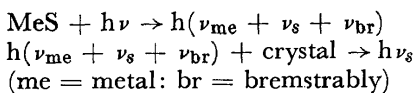
The situation is somewhat different when the sulphur determination is carried out with a conductometric finish. Here the important reaction mechanism is the one concerning the absorption of SO_2 in, for example, peroxide containing dilute sulphuric acid. The signal comes, then, from the sensor-system:



in which the signal is the increase in the concentration of protons from the dissociation of the newly formed sulphuric acid, leading to an increase in the electrical conductivity of the solution. The absorption solution, with all the ions in it, serves as the carrier (transducer) and the receiver (signal detector) is the Wheatstone Bridge circuit with which the conductivity of the solution is measured. The measured parameter is electric current which lends itself to easy measurement. Instead of measuring the conductivity before and after the absorption, one can use two identical measuring cells, one with original absorption solution and one with the same solution after absorption, in two arms of the bridge circuit and measure the difference in conductivity. With such a differential method, using suitable circuitry to transform the ratio measured, and taking always the same weight of sample, it is possible to have direct read-out as a percentage.

As yet another possibility we may consider the determination of sulphur by x-ray fluorescence analysis, in which case the sensor system is the reaction between the sample and the electromagnetic radiation, and the measured parameter is the intensity of x-radiation. Since the primary beam encounters other atoms besides those of sulphur in the sample, the emitted radiation contains components due to all the other constituents of the sample, and must be "purified" with the help of an analyzing crystal so that the detector (counting tube) receives as signal only the x-ray quanta characteristic of sulphur. The signal carrier in this case is the radiation itself.

The sensor system may be described as:



Now it appears that however simple a measuring technique seems, the classification of the steps of the whole system may still be very difficult. When for example, the original measured parameter is a potential which in itself is capable of being changed and transformed in a number of ways. Figure 4 gives an idea what a Black Box may contain.

BLACK BOX		
<i>Sensorsystem</i>	<i>Transducer</i>	<i>Detector</i>
$\text{MeS} + \text{O}_2 \rightarrow \text{SO}_2$ $\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$ $\text{H}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + 2\text{HCl}$	water	crucible + balance
$\text{MeS} + \text{O}_2 \rightarrow \text{SO}_2$ $\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$ $\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$	absorption-solution	Wheatstone-bridge
$\text{MeS} + h\nu \rightarrow h(\nu_{\text{s}} + \nu_{\text{me}} + \nu_{\text{br}})$ $h(\nu_{\text{s}} + \nu_{\text{me}} + \nu_{\text{br}}) \rightarrow \text{crystal} \rightarrow h\nu_{\text{s}}$	radiation	counting tube

Figure 4. Sensor-transducer-detector system in a black box

These few examples of the determination of sulphur certainly show how important these considerations are, and also that the analyst has an important word to add in that matter.

3. Inventory of methods suited for automation

One need only try to give a short survey on this topic, or take part in a brief discussion on it, to realize the magnitude of the problem. We have at our disposal already some literature, including books on automation, but scarcely anything on the relationship between analytical chemistry and automation. Analytical chemistry is the "nerve system" of each automat, and in every case the measured quantities result from chemical or physical reactions.

One cannot do an analysis if one does not know what kind of material is to be handled, and similarly, one cannot use automation without knowing exactly what material is being used and for what. Waste water, for example, to be discharged from a plant after automated control analysis, must be handled differently from water which is to be recirculated. Hence it is also worth remembering the distinction between automation in analytical chemistry, and automation with analytical chemistry, since the second lies more in the field of cybernation.

To the first group belong the methods which can be used in the laboratory, and which may be in use frequently or only at times, and to the second

belongs the employment of methods of the first type for independent regulation and control of chemical processes. In either case we are dealing with a chain-system, in which the first and last links represent the material or the phase in the process, and which always has the general structure of three links, namely Input—Black Box—Output. What is of interest to use here is the choice of means at our disposal for the analytical process, i.e. for the middle link.

To hope to find a generally and universally applicable model for this system is both senseless and pointless, because it is primarily the nature of the sample which dictates the choice of method, and so, to be able to construct any useful system whatever, we must, before making a choice from the numerous methods available for each material, first clarify just what information is wanted. The number of points to be considered in this connection are shown in *Figure 5*.

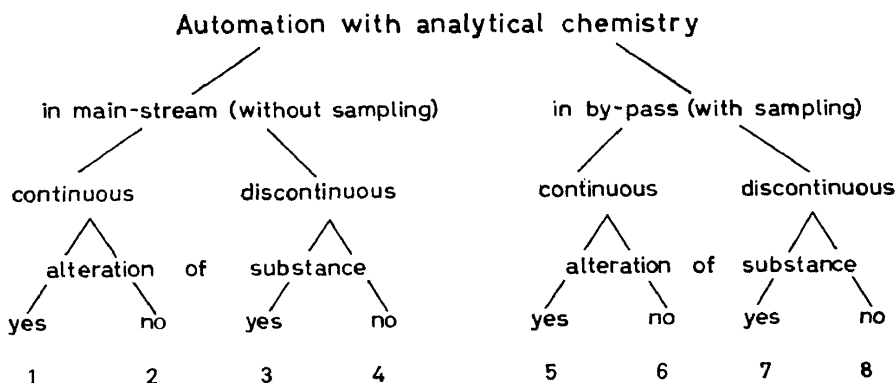


Figure 5. Automation with analytical chemistry

In *Figure 5* the numbers given refer to the following examples.

1. Determination of SO_2 in air by Liesegang's method, as BaSO_4 .
2. Level indication in a storage bunker, using a radioactive isotope, and detector.
3. Bringing down measuring sondes based on chemical reaction in lakes or at sea. Measuring the content of NO_2 in the stratosphere via ballon-sonde and a chemical reaction.
4. Determination of chlorine in rain water by ion-specific electrodes.
5. Measurement of electrical conductivity after absorption of a component to be determined.
6. General conductivity methods.
7. Microchemical C and H determination (according to Pregl).
8. X-ray fluorescence analysis of samples from the furnace.

Such "inventories" can be drawn up from many points of view, but the important considerations will always be the nature of the sample, and the method of measurement.

Just what can be automated, and that it can be done, has been shown by many people, from the ancient Egyptians, and Leonardo da Vinci, to the present day. The question of what is pointless and what is not is just a

question of the time and generation in which one lives. For our purposes an inventory of automation-oriented methods in and with analytical chemistry must cover two groups: (i) those producing a direct electrical signal, e.g. electrometric methods; and (ii) those doing so only indirectly.

An important requirement of the methods should be that they involve a minimum handling of the sample, and wherever possible, leave the sample unchanged. It would seem better, rather than giving a general inventory of automation-oriented methods, to ascertain the requirements so that the most suitable method may be chosen before a start is made. Therefore, the programming of automatic analysis is very tightly connected with the planning of the necessary analyses, coupled with the obtaining, handling and output of the data. This is schematically presented in *Figure 6*.

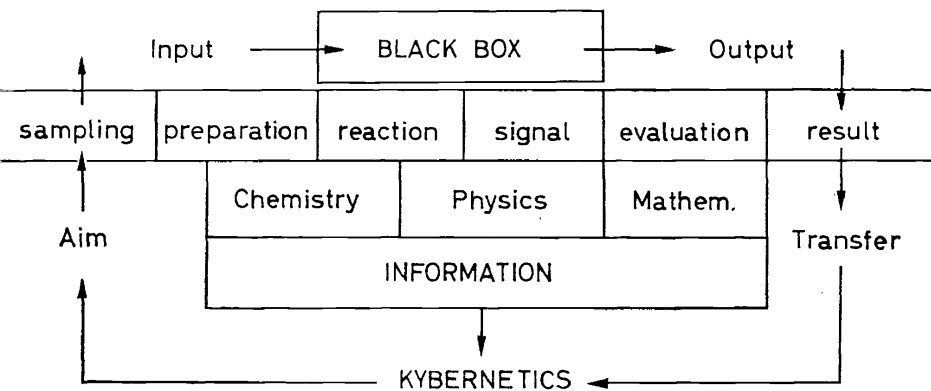


Figure 6. Kybermatic analysis

In the simplified language of automation, this means that the taking and preparation of the sample, which also may be done mechanically, is a part of the system, and may be called the *Input*. It means also that the analytically useful reaction forms the basis of the measurement and that the real measurement is done by instruments, either directly or indirectly—all this being called the *Black Box*, and may be a series of instruments or just one. Finally, this system includes the *Output* of the analytical results. It is clear that such a procedure involves a dependence on mechanics, chemistry, physics and mathematics, of which chemistry plays an important role in determining the choice of the reaction mechanism used and the preparation of the sample.

Physics plays an important role in the measurement and the transformation of the signals into corresponding physical quantities. Mathematics is important for the correlation of data and units of measurement, and lead via applied physics to the information needed for control and via kybernetics to regulation. This includes the last link of the chain—the transfer of the analytical results, in most cases in the form of feed back.

When automation is discussed these days, most of the basic facts, such as the nature and state of the material in question, are either just assumed, or, as is more often the case, are just neglected for the sake of simplicity. It is of course much easier to develop a line of thought in automation when the

information required for directing the working processes is assumed to be as simple as possible. Unfortunately this information is not always so simple.

What we have seen is that to consider or attempt the automation of just one of these links is pointless. These days we hear more and more often of so called "automatised sampling machines" or "automatised laboratory places". Quite apart from the fact that these are only concerned with the mechanisation of particular stages, they do not fulfil the purpose of automation as long as they are limited to only sampling or only analyzing. We shall go into this briefly.

Both the sampling and the analyses are each subject to unavoidable uncertainties. Not seldom, one sees in practice that the steadily improving analytical methods are subject to smaller errors than the sampling. It seems that either too much attention has been paid to the analytical methods or else too little to sampling techniques.

Similar considerations should also be given to the analytical results, which should be more strongly stressed than they have been up till now. If for the control of a process, analytical results with an accuracy of 0.1 per cent are sufficient, then a method yielding an accuracy of 0.001 per cent should not be used. The temptation arises, as Zettler has said long ago, to use more accurate methods so that one is allowed a greater degree of carelessness. It is much more to the point and sense of analysis to solve the problem with the help of a method which gives the required accuracy, is simple, and at the same time satisfies the requirements. There is therefore no sense in carrying out the analysis with greater accuracy than the sampling, or than that demanded by the process control.

We need not only high precision methods of analysis, but also others with lower precision, but which offer greater speed and simplicity.

It is more valuable to have a larger margin of error and a higher degree of certainty, than a small margin of error and low certainty, i.e. a 99 per cent certainty is in automation much more important than a 60 per cent one.

Because standard deviation and degree of certainty are interdependent we must demand (i) No method should be used, the standard deviation for which is not known. (ii) In the case of automatised methods, the standard deviations should not be greater than for the original methods. (iii) Three times the standard deviation should be taken for automated analyses, and the variance quoted as well, in order to give a margin of safety for the analysis.

4. Symbolism

Every analytical procedure consists of a series of single steps, e.g. sampling, addition of reagent, obtaining the signal of measurement, and calculation.

Especially in the field of automation, and more so in that of Kybermation, one can do without longwinded descriptions of analytical processes, and deal instead with block- and flow-diagrams. The use of symbolism is thus unavoidable. It will also be soon necessary to make use of the related disciplines of semiotics (dealing with graphical symbols), semantics (relation to pictures), syntactics (relationships between symbols), pragmatics (relationships to mankind), and sigmatics.

From these considerations, two main groups will emerge: (a) those con-

cerned directly with calculating and computing systems (e.g. *Algol*), and (b) those that may be used in connection with analytical and control systems. We should find for (b) symbols which do not duplicate those already in use, which are not complicated, and which have a high information content. The first steps of proposals will be given by Jellinek and Malissa⁵ during the course of the congress. As for point (a), G. Gottschalk³ has already written about the use of symbols in connection with statistics and analytical chemistry, and point out which symbols from *Algol* may be used. With computer techniques, he was able to cut computing time from 8 hours to 5 minutes for one special problem.

Very important, and for the future quite essential, will be the coupling of computing techniques with analytical techniques yielding data in the form of high impulse rates (such as x-ray fluorescence or electron-probe microanalysis). In *Figure 7* is shown the *Fortran* programme for determining the mutual solubility of calcium and magnesium oxides⁴.

After the *Read* statement that follows the read-in of statement cards, the constants (b) and (c) are calculated from data from the standard samples. The next step—the actual calculation of the percentage of calcium oxide and of magnesium oxide at all measured points—is done with the aid of a *Do* statement, beginning with a *Do* command and finishing with a 1. The *Fortran* statements lying between these two are run through as many times as there are sets of data, and finally the programme runs on to the end. After the *Do* statement, the percentage contents are calculated, and there follows an *If* statement. This controls that all percentage compositions falling below 93 per cent are not considered in the calculation of the mean value (as being statistically not valid). If the composition comes to less than 93 per cent, all the following operations are skipped and the *Do* statement run through again for the next set of data. If greater than 93 per cent, the sum is recorded and the values are added up for averaging.

To calculate the standard deviation, a further summation is necessary, and this is also contained in a *Do* statement, and includes an *If* statement as before. When this summation has been carried out for the required number of sets of data, the standard deviation is calculated with the help of a set of square-roots held in a part of the store. Finally, after a *Write* statement, the constants, the desired results and other information, are printed out on the high-speed printer.

After the programme *Stop* card has been read in, the programme is checked by the computer itself for errors of syntax. When it finds the programme to be correct, the pulse-rates are read in from data cards, and the programme run through for each set of data. Using this procedure, we were able, with the help of the IBM 7040 in our computing centre, to determine the solubility of the components in the calcium–magnesium–oxygen system, and the associated standard deviations, from data obtained with the electron-probe microanalyser.

In the near future it may be necessary to alter the computer languages at present in use, and perhaps also to develop a new one for the purposes of analytical chemistry, such a language might be called *Analchel* (*Analytical chemistry language*), or for process control, *Chemprol* (*Chemistry process language*).

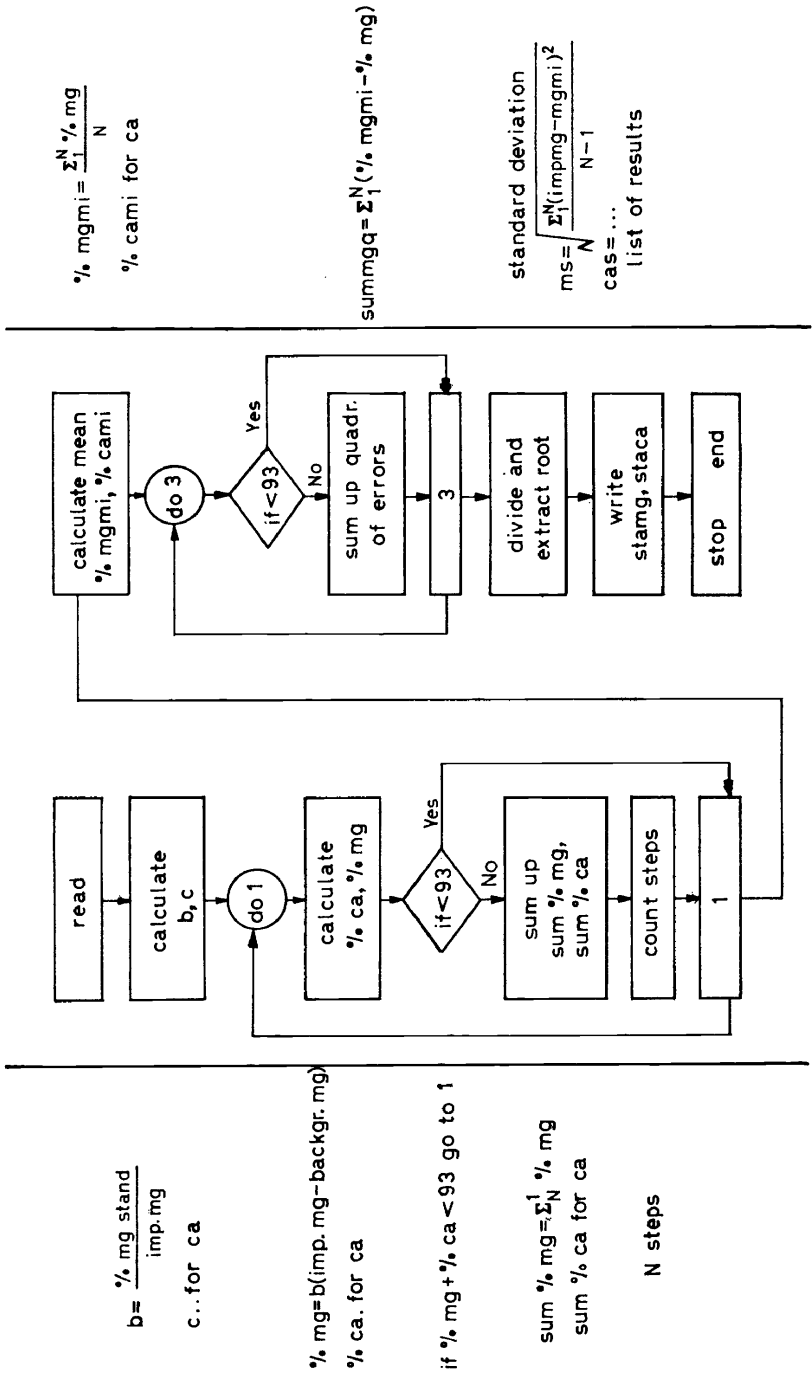


Figure 7. Fortran programme for determining the mutual solubility of calcium and magnesium oxides

An example of point (b) is provided in *Figure 8*. We see in the upper part of the figure a description of the individual steps in a block diagram for the gravimetric determination of barium, and in the lower part, the same determination represented as a flow diagram with symbols partly based on those contained in DIN 7091. This problem is also being investigated in our Institute.

Summing up, the following points should be remembered when considering the use of symbolism in analytical chemistry:

(i) Possibilities in the plant control. (ii) Simplification of exchange of ideas between disciplines. (iii) Simplification of documentation. (iv) Possibilities in the field of automatized translating of scientific literature. (v) Possibilities in programmed teaching.

5. Automation in analytical chemistry

Automation in analytical chemistry means the rationalization of the research and the service laboratories. We should consider two points of view: (i) automatic analytical procedures, and (ii) automatic collection and transfer of data. Each further step is automation with analytical chemistry, and leads to Kybermation. In the second group a high degree of perfection has been reached—there is an excellent paper by Karau and coworkers⁶ on electronic data handling.

In a large laboratory, both collection and transfer of data is a problem. A research group of Gulf Research and Development Co. has developed a distribution system that fulfils the following requirements:

Speed: continuous input and output with minimum delay in the system.

Accuracy: greatest possible diminution of errors during transmission and handling.

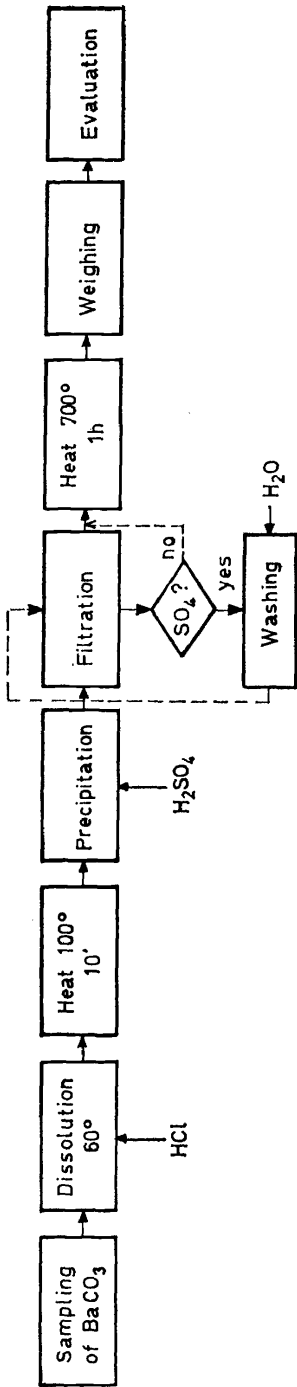
Simplicity: applies both for the laboratory assistant who provides the information and also for the person who wants the information.

Control: stored data are available in connection with samples, procedures, work load, etc.

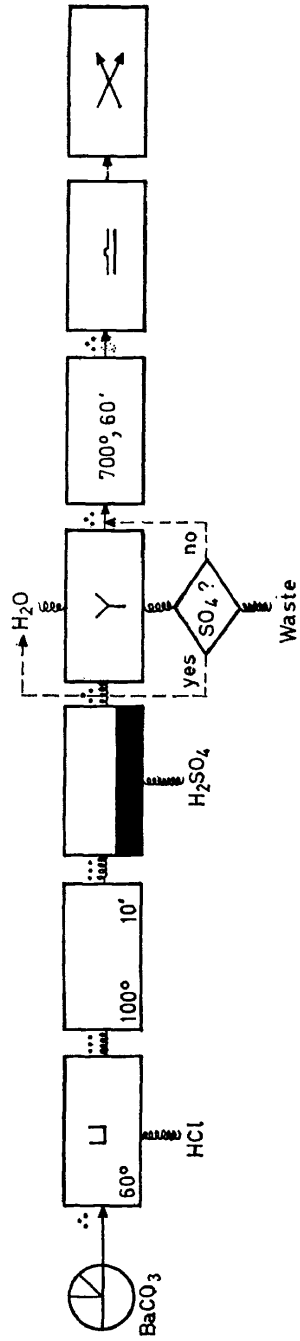
Economy: the administrative and office work is reduced, and the system is also capable of being expanded to cope with an increased work load, and the need of a larger organisation.

All of these requirements have been met to some degree, and efforts at completely meeting them are being made. The procedure is as follows.

To each sample is attached a numbered two-part card, the top part of which is punched with the initial information about the sample, and everything is sent to the laboratory. Each analyst uses the punched card for the registration and transmission data, thereby minimizing errors which could be cumulative during the handling time. The initial information is sent right away to the computer centre (over an IBM 066 data transmitter) and the analyst transfers his results using a Master Card, giving also the test number, procedure, his name and number and a code. Each separate result is individually given to the computer centre, and the sequence in which the results arrive is quite unimportant. At regular intervals the data that has arrived is collated and stored on magnetic tape. A Sponsor Card is punched



①



②

Figure 8. Determination of barium

for each set of results, and from the completed analysis programmes, an analytical report is printed for each sample, containing also the initial information. It is not possible to withhold data from a partially completed report.

This system involves procedures for sorting, comparing, completing and collating of information. The cost of the computer and the development was offset by the large volume of work being handled. The main advantage of the system lies in the facility for handling large quantities of data and converting them into report as a summary of the stored data. A survey of the stored data is made daily, indicating the missing information, and three reports give summaries of: (i) work distribution over all the laboratories—in a general report; (ii) work load and distribution of each section, in more detail—report for section leaders, and (iii) work load and distribution of each smaller laboratory unit.

These three reports have various points of interest. Information about the timing facilitates a reduction of throughput time for analyses, and helps to avoid bottlenecks. Section leaders can plan the working of their staff better, and re-arrange the use of equipment.

The publication of the stored data can act as an impersonal control system for the laboratories, and the saving in time previously for paperwork by the section leaders can be profitably used to obtain a more personal contact between the staff and improve working relationships.

The monthly reports have an added interest in that they give a real idea of the turnover of analyses, and can indicate changes in the requirements, and can also indicate when a method is possibly becoming too slow and should be changed or improved. The quantities and the origins of the samples are listed, and the work load of each laboratory can be seen from the Laboratory Index, in which each of 2000 tests are included. The work done for any one project can also be easily seen from these indexes, and the costs incurred by the project can be calculated. When a new project is contemplated, a good estimate of the analytical costs can also be provided.

The work load of each analyst is checked by the control report on him, and his work output can be investigated with the help of the index. As improvements are still being made on this scheme, it is preferred to use these theoretical indexes to the "Standard Production Hours".

I have mentioned in some detail just one system that has been shown to be workable and worthwhile as a means of controlling analysis of materials on a large scale. The main difficulties and the advantages are the same for all establishments so concerned, and only the details are different. The most outstanding and successful combinations of mechanical or automated analytical techniques with modern information and data handling equipment are to be seen in the field of clinical analysis, as described by several firms manufacturing equipment.

To sum up, and to go back once again to the topic of this paper, we should remind ourselves that

Automation *in* analytical chemistry is when, after *handing* in the sample for analysis, no further work is done by human workers until the results are printed out, and

Automation *with* analytical chemistry is only when the measurements by

the analytical instrument are used, either directly or after processing for the control and regulation of processes or plants and may be called *Kybermation!*

CONCLUSION AND SUMMARY

In order to try to clarify the situation in the field of automation and analytical chemistry the following statements have been made.

1. Terminology

- (a) Mechanization: for production and transmitting of movements.
- (b) Instrumentation: for machines which are mainly producing useful signals but can also include movements.
- (c) Automation: a system in which a part of the human power of decision is removed by a combination of machines and/or instruments.
- (d) Kybermation: is when the (final) result of the (analytical) control-step is used to the regulation of the (chemical) process concerned, without further human decision.

2. An instrument shall, but an automat or kybermat must consist of

- (a) a sensor: i.e. a system delivering an analytically useful signal corresponding to measured quantities.
- (b) a transducer: a means of conveying the signal to the receiver (transducer is not the same as transducer)
- (c) a detector: a means which is able to receive the signal.

3. Automation in and automation with analytical chemistry

There is a great difference in "automation in analytical chemistry" and "automation with analytical chemistry". The former is usually connected with a high degree of instrumentation plus the strong use of computers for getting analytical results; the latter—which leads doubtless to kybermation—is using the analytical signals and/or results in order to get via transfer (feedback or feedforward) a self-regulation (without human decision) of the process.

To achieve a real automation in and with analytical chemistry the proper use of chemical and/or physical reaction, the knowledge of kybernetics and other disciplines is necessary. It may be that a new kind of language and symbolism must be developed (a) for automation in analytical chemistry: *Anachel* (Analytical chemistry language); (b) for kybermation: *Chemprol* (Chemistry processing language).

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