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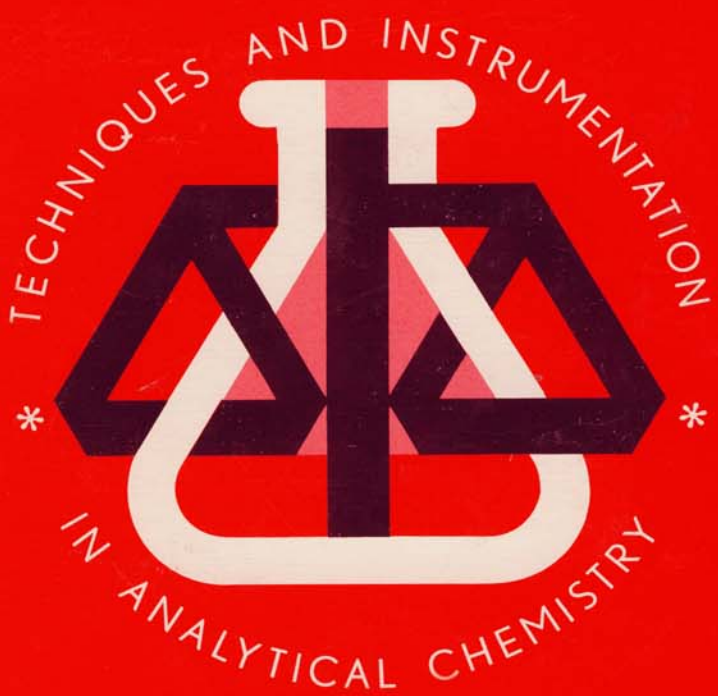

AUTOMATIC METHODS OF ANALYSIS

M. Valcárcel and M.D. Luque de Castro

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AUTOMATIC METHODS OF ANALYSIS

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Preface

Miniaturization and the reduction of human intervention are two clear trends in the technological developments which characterize the last years of this century. Analytical chemistry has not ignored these trends, as has been reflected in most of the innovations introduced in this discipline for some time now.

For a variety of reasons, the automation of laboratory processes is an aspect of growing theoretical and practical interest. This was one of the reasons for us to write a monograph on the subject with the aim of presenting a rational overview of the areas most strongly influenced by the advances in automation. It was not our aim to present an exhaustive review of the large variety of alternatives reported and applied in the field of automatic methods of analysis, which would have been the subject of an encyclopaedia rather than a single volume.

The different topics dealt with were chosen according to various criteria such as the degree of consolidation, scope of application and most promising trends. The monograph consists of four parts. The first, after dealing with the basic principles behind the automation of laboratory processes (Chapter 1) and the role of computers in this context (Chapter 2), describes automatic systems for sampling (Chapter 3) and sample treatment (Chapter 4). The second part discusses the principles and commonest components of the principal types of analysers, namely continuous (Chapters 5-7), batch (Chapter 8) and robotic (Chapter 9). The third part is devoted to the automation of analytical instrumentation: spectroscopic (Chapter 10), electroanalytical (Chapter 11) and chromatographic (Chapter 12) techniques, and titrators (Chapter 13). The last part presents some examples of the application of automation to three of the most representative areas of chemical analysis: clinical chemistry (Chapter 14), environmental pollution monitoring (Chapter 15) and industrial process control (Chapter 16).

The authors wish to acknowledge the aid of the many others who contributed their work to this book. Thus, Drs Angel Ríos and Fernando Lázaro wrote Chapters 2 and 16, respectively; Antonio Losada, MSc, translated and typeset the

manuscript to its final form and Francisco Doctor drew the numerous figures in the book. Finally, the warm reception of the project by Elsevier Science Publishers also deserves due acknowledgement, as does the financial support received from the Spanish *Comisión Interministerial de Ciencia y Tecnología* (CICyT), which allowed us to acquire the experience in the field of laboratory process automation materialized in this book.

THE AUTHORS

Córdoba, April 1988

1

Fundamentals of laboratory automation

1.1 INTRODUCTION

The partial or complete replacement of human participation in laboratory processes is a growing trend that started in the 1960s and consolidated in the next decade [1-3]. So much so that, in the course of time, the distinction between modern and classical analytical chemistry will predictably be closely related to that between automated and non-automated analytical procedures.

This trend is the result of a variety of causes. On the one hand, automation relies on the spectacular advances in micromechanics, microelectronics and microcomputer science [4,5]. Microcomputers, whether or not used as microprocessors, are by now as commonplace as balances in laboratories, whether devoted to routine control or research and development. On the other hand, society's needs, frequently turned into demands, have grown to the extent of posing problems unimaginable a few years ago [6]. Such demands are not only the need for greater and more rapidly obtained analytical information, but also the laboratory's need to respond to new, pressing questions. All areas of social interest (health, ecology, industry, nutrition) are profoundly affected by the need for increasingly stricter control of a growing number of samples in which a large number of analytes are to be determined at increasingly low concentrations. Developing new products and solving problems previously not encountered are other aspects strongly dependent on laboratory work.

Cost reduction is yet another aim of the growing trend towards automation. The progressive elimination of human participation in laboratory processes or stages, wherever feasible and sensible, improves economic yields and reduces the cost of performance. Surveys carried out by many private and public US laboratories show the need for automation. It is interesting that most of such studies also show that automation does not necessarily result in redundancy as the growing number of problems encountered require new sections or even specialized laboratories to be started by the same organization. This results in retraining or even in the engagement of further employees. Obviously, automation affects unskilled workers to a greater extent on account of their more difficult retraining. Unmanned laboratories are as yet an utopia: there

is a series of tasks, both intellectual and manual, still reserved for humans. Although the number will probably decrease in time, there will always be a limit to complete automation, a limit that will probably have been established by the end of the century.

Automation, as shown later, offers undeniable advantages. Thus, it is hardly surprising that most analytical instrumentation manufacturers are tending to increase the degree of automation of their commercial ranges; the trend of laboratory managers to invest increasing funds in these automated instruments is also not surprising. However, as with any technological innovation, automation frequently meets with reluctant attitudes from those who think that adherence to a given change will invariably give rise to a variety of complications —a reactionary attitude in this respect can only result in more serious problems in the future. The complete opposite of this attitude is that of those who, with the sole worry of not falling behind in the technological race, unthinkingly purchase highly automated instruments (e.g. spectrophotometers or electroanalytical systems featuring built-in microprocessors) and lay aside conventional instruments which are in good working order and perfectly suited to their actual needs. It is also relatively frequent for some laboratories to purchase automatic analysers with a high throughput and capable of performing simultaneous and sequential determinations and then exploit only 10–20% of their potential capabilities.

Laboratories can be automated in one of two ways, either by purchasing new instruments or by adapting those already available with the aid of different units (modules). Which way is chosen is a matter of convenience. Thus, the determination of amino-acids in protein hydrolysates calls for a new instrument based on HPLC principles and known as a sequencer. However, in many instances, one or several of the stages of some analytical procedures can be automated by use of one of the large number of modular elements available. Thus, an FIA system fitted to a conventional photometer considerably reduces human participation in the preliminary stages (sampling, interference removal, transport to the detector, etc.). The on-line incorporation of electronic integrators or microcomputers allows the acquisition of the analytical signals provided by the detector, and also their appropriate treatment in delivering the required results with the human involvement only in the computer programming.

1.2 OBJECTIVES OF AUTOMATION

The objectives pursued in partly or completely automating analytical laboratories are varied. Thus, the automation of non-routine work (e.g. research) is chiefly aimed at facilitating a laboratory process that otherwise is not

feasible owing to the limitations of manual operators. Such is the case with the manipulation of radioactive materials, the need to carry out a large number of repetitive experiments in a continuous fashion or those situations where vast amounts of data are generated at a high speed or over long periods.

TABLE 1.1
Basic objectives of laboratory process automation

. Processing of a large number of samples
. Determination of several components in the same sample
. Reduction of human participation to:
- Avoid errors
- Cut costs
. Increasing sample throughput
. Process (industrial or otherwise) control
. Lowering consumption of sample and/or reagent(s)
. Facilitating an anaytical technique or method

The basic objectives of automation of the analytical laboratory, summarized in Table 1.1, tend to solve a variety of problems related to one or several of the following aspects:

(a) *Samples*, occasionally dealt with in large numbers or too scarce or valuable to be handled manually.

(b) *Analytes*, which are sometimes present in very dissimilar (macro components, traces) or low (ultra-traces) concentrations in the sample.

(c) *Reagents*, some of which are scarce or expensive (e.g. enzymes), or even unstable.

(d) *Rapidity*, frequently essential in large laboratories such as those in hospitals, urgently requiring the analytical results (e.g. clinical parameters in acute crises or shock treatments), and of industrial and other laboratories requiring constant availability of data for process control.

(e) *Economy* in personnel and material expenditure.

(f) *Precision*, closely related to the elimination of both definite and indefinite errors arising from the so-called 'human factor' (tiredness, mood, prejudice, pathological complaints and so forth).

(g) *Data generation*. Some analytical techniques are based on the acquisition of a large number of data. Even if these are generated at a rate hand-

able by a manual operator, the tedious nature of their acquisition and manipulation makes it advisable to entrust them to an automated system, obviously indispensable when data are generated at a high rate (e.g. in stopped-flow methods).

(h) *Data processing* is better performed automatically when a large number of data are generated by the same or many different samples, or when their subsequent treatment is complex and liable to error if human participation is involved in the process (e.g. in transcriptions, transfers, recordings, etc.).

(i) *Analytical technique* or *method*, occasionally unfeasible with the involvement of an operator —this book abounds in illustrative examples of this kind. Thus, electrothermal vaporization atomic absorption spectroscopy demands the automation of the sample thermal treatment in the graphite tube via a microprocessor programming the different heating stages involved (automation of methodology). Likewise, the use of image detectors in spectroscopy calls for computerized data acquisition, impossible with manual operators.

1.3 DEFINITIONS

The definitions given below are aimed at clarifying a series of concepts related both to the analytical process and to its automation used throughout this book.

The analytical literature abounds with references to different concepts, facts or processes by the same name. It is therefore advisable to establish a clear, hierarchical distinction of such frequently confused terms, based on that reported by Taylor [7] and including:

(a) *Analytical process*, namely the series of analytical operations between samples and results. It usually involves a large variety of stages which can be summarized in three groups: preliminary operations, measurement of the analytical signal and data treatment.

(b) *Analytical technique*, *viz.* a scientific principle adapted to one or several instruments to obtain information about diverse material and methodological aspects. Gravimetry, atomic absorption spectroscopy, coulometry, etc. are all representatives of analytical techniques.

(c) *Analytical method*. This is the actual application of a given analytical technique in the analytical process. Thus, in gravimetric analysis, the precipitation stage can be carried out traditionally or by precipitation in a homogeneous solution; the atomization in atomic absorption can be effected by aspiration of the sample solution into the flame or by electrothermal vaporization; coulometry has two basic methodological varieties, namely constant intensity and constant potential. The nature of the method also varies with the manner in which the sample is manipulated or the data are treated. Thus, the

determination of sulphur dioxide based on the photometric monitoring of the product yielded in the reaction between the analyte, formaldehyde and p-rosaniline differs methodologically depending on whether environmental (acid rain water) or wine samples are concerned. The different ways in which the data provided by the signal-time kinetic curve can be treated give rise to as many methodological alternatives to determinations based on reaction-rate measurements.

(d) *Analytical procedure*. This term should only be used to refer to the set of precise instructions followed in implementing an analytical method and aimed at the determination of one or several particular analytes in a given type of sample. In his original hierarchical distinction, Taylor also includes the term *protocol*, subsidiary to and even more specific than procedure.

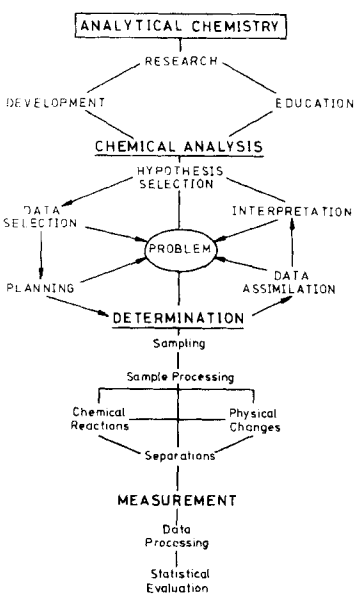

Fig. 1.1 Major functional processes in Analytical Chemistry according to Pardue. (Reproduced from [8,9] with permission of the American Chemical Society).

'Analysis', 'determination' and 'measurement' are a triad of also readily confused terms which, according to Pardue [8,9], can also be defined in a hierarchical way. Thus, *chemical analysis* is just one of the four chief components of Analytical Chemistry —the other three are research, development and teaching. The *determination* is one of the stages of chemical analysis, which also

comprises the investigation of the unknown —one of whose components is the sample itself—, selection of the hypothesis to be applied and data to be used, interpretation of the data obtained, etc. The *measurement* is a sub-stage of the determination, which also includes sampling, separations, data acquisition and treatment, etc. Pardue's hierarchical view of Analytical Chemistry is illustrated in Fig. 1.1. According to him, samples (unknowns) are *analysed*, analytes are *determined* and parameters qualitatively or quantitatively related to these are *measured*.

The IUPAC Commission for Analytical Nomenclature laid down a series of definitions which distinguish and specify the essential features of Automatic Methods of Analysis [10]. *Not all the instruments, systems or methods designed to reduce human intervention can be regarded as automatic*. Thus, IUPAC clearly distinguishes between 'mechanization', 'instrumentation' and 'automation'. *Mechanization* is related to the production of motion and is defined as "the use of mechanical devices (machines) to replace, refine, extend or supplement human effort". A *mechanism* is "a combination of parts, of which one at least is moveable, capable of producing an effect." A *machine* or *apparatus* is a system made up of one or several mechanisms which perform one or more actions. *Instrumentation* is related to information production and transmission. An *instrument* is a device used to observe, measure or communicate a property (parameter), which replaces, refines or supplements human action. The terms 'instrument' and 'apparatus' are often used erroneously as synonyms. The essential difference between the two lies in whether or not they provide information. Thus, a centrifuge is apparatus, whereas a photometer is an instrument. While a centrifuge can indeed offer an analogue or digital read-out of its rotation speed (rpm), this information is not related to the analyte concentration. The transmittance or absorbance provided *can* be considered to be information as it is used to calculate the aforesaid concentration.

Automation involves the use of systems (instruments) in which an element of non-human decision has been incorporated. It is defined as "the use of combinations of mechanical and instrumental devices to replace, refine, extend or supplement human effort and faculties in the performance of a given process, in which at least one major operation is controlled, without human intervention, by a feedback system. A *feedback system* is defined as "an instrumental device combining sensing and commanding elements which can modify the performance of a given act.

According to IUPAC's recommendations, a clear distinction should be made between 'automatic devices' and 'automated devices'.

Automatic devices are those which "cause certain required actions to be performed at given points in an operation, without human intervention". The

system makes no decisions and the operation sequence is always the same. They possess no feedback system.

Automated devices are defined as those enacting automation. They are conceived to make decisions with the aid of a feedback system, without human intervention. There is a different operational sequence for each situation (sample). These systems are self-monitoring and self-adjusting, have greater independence than automatic devices and are sometimes called 'completely automatic'.

The distinctions established by IUPAC are clear-cut. Thus, the speed of titrant addition is always constant in an automatic titrator, whereas it is adjusted by a feedback system according to the nearness of the equivalence point in an automated titrator. However, some workers [11,12] acknowledge the accuracy of these definitions but consider them too stringent. Very often, the term 'automatic' is used to refer to systems with and without feedback indistinctly. In any case, whenever the concept 'automatic process' is referred to in this book, it will be meant in its widest connotation, namely that involving partial or complete elimination of human intervention not related to instrumentation.

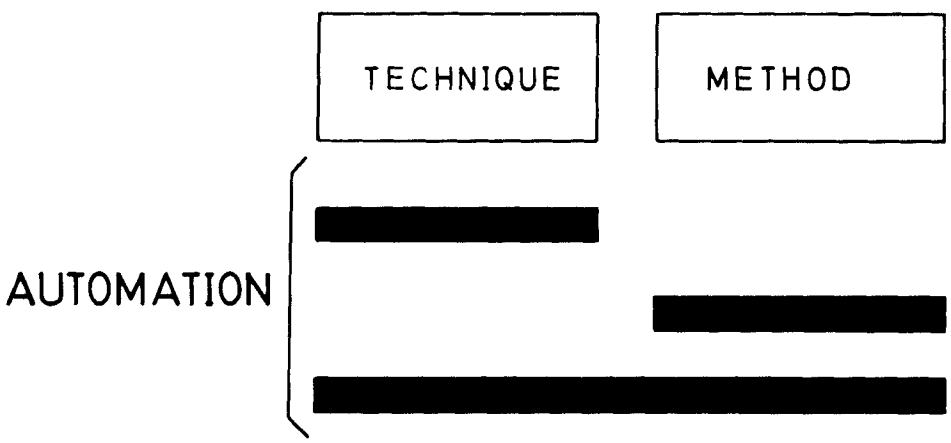

Fig. 1.2 Ways to automate chemical analysis.

According to the definitions laid down above, both the analytical technique and the analytical method are liable to automation, either individually or jointly (see Fig. 1.2).

1.4 AUTOMATIC ANALYSERS: CLASSIFICATION

An *analyser* can be defined as a series of elements —modular or not—, of which at least one is an instrument, which operate with different degrees of automation and have been designed for the qualitative or quantitative determination of one or several analytes in a single or a series of samples based on changes in its physical, chemical or physico-chemical properties. It can provide results in the required form or simply offer raw data [13].

TABLE 1.2
Classification of analysers

According to the degree of automation	Automatic	
	Semi-automatic	
According to the way in which samples and reagents are transported	Batch (discrete)	
	Continuous	Segmented
		Unsegmented
	Robotic	
According to the number of analytes per sample	One-parameter	
	Multi-parameter	
According to flexibility	Specific	
	Flexible	
According to source	Commercial	
	Home-made	
According to state of aggregation of sample	Gas analysers	
	Liquid analysers	
	Solid analysers	
According to foundation	Based on physical principles	
	Based on physico-chemical principles	
According to sampling frequency	One-off	
	Periodic	
	Continuous	

Table 1.2 shows several classifications of analysers according to different criteria. Thus, a first classification is based on whether automation is *partial* or *complete*. Because of the difficulty involved in correctly applying the terminology in this respect, establishing clear distinctions is understandably difficult on account of the variety in the degree of automation. A *(completely) automatic analyser* is defined as an analytical processor receiving one or a series of untreated, unquantized (weight, volume) samples to provide the analytical results sought in the required form without the need for the operator's intervention at any point in the intermediate stages of the process. If any of such stages is carried out manually —the commoner case—, the analyser is said to be *semi-automatic*. It should be noted that, despite its widespread use, the term 'semi-automatic' is not supported by IUPAC. This differentiation is also somewhat stringent and, in practice, the adjective 'automatic' is applied to analytical processes in which some major stage is carried out manually: such is the case with highly computerized centrifugal analysers in which the sample tray is transferred manually from the automatic dispensing unit to the reaction-measurement unit (see Chapter 8).

Analysers can also be classified according to the way in which samples are transported and manipulated into:

(a) *Discrete* or *batch analysers*, where each sample preserves its integrity in a vessel (cup) which is mechanically transported to various zones of the analyser where the different analytical stages (sample quantitation and reception, dilution, reagent dispensing, mixing, heating, etc.) are carried out in a sequential manner. Each sample is finally led to the detector (instrument), where signals (one per analyte) are recorded. As can be seen from Fig. 1.3a, the functioning of these analysers, described in greater detail in Chapter 8, resembles the operations carried out by a manual operator.

(b) *Continuous analysers* are characterized by the use of a continuous stream of liquid or —much less often— gas. The samples, usually liquid, are introduced sequentially at regular intervals into a channel carrying a liquid that can merge or not with other channels carrying reagents, buffers, masking agents and so on. Upon reaching the detector —generally furnished with a flow-cell—, the resultant reacting mixture yields an analytical signal which is duly recorded. This signal is transient in nature and its height or area is used to calculate the analyte concentration. The baseline between signals represents the time over which no sample zone is passing through the detector. There are two types of continuous analyser, namely:

- Segmented-flow analysers (SFA), originally developed by Skeegs [14] and first commercialized by Technicon under the name 'AutoAnalyzers', in which the flow is segmented by air bubbles aimed at preserving the integrity of samples

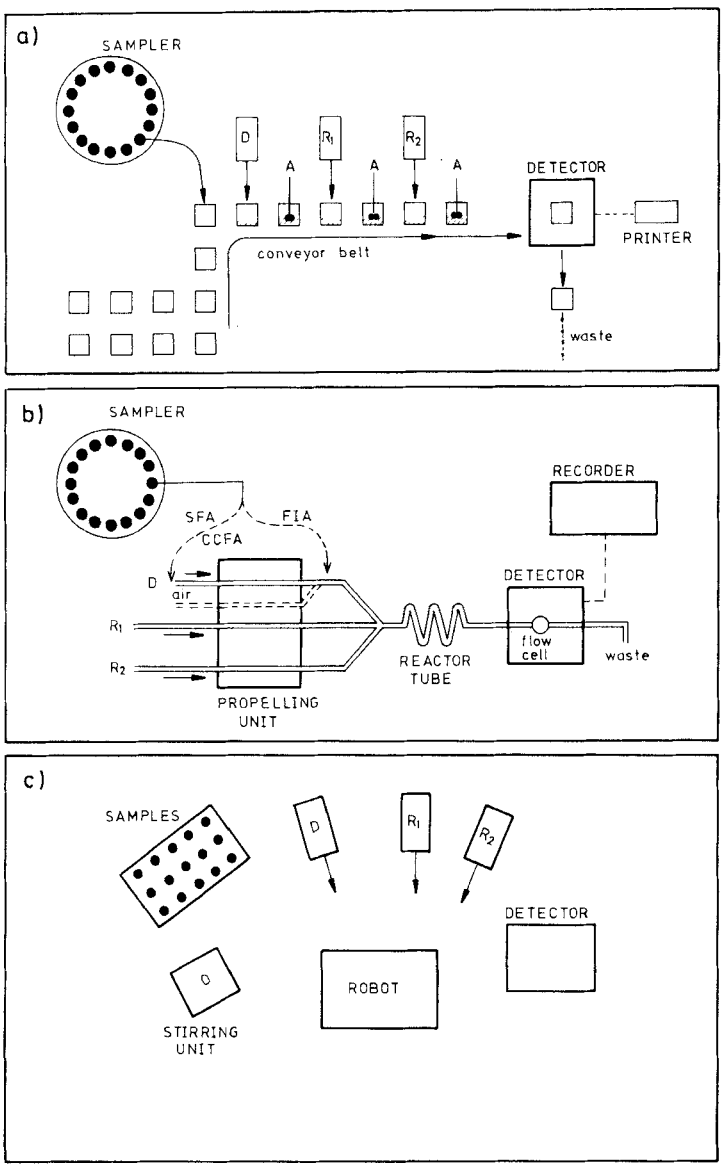

Fig. 1.3 Scheme of the different types of automatic analysers, classified according to the way in which sample transport is effected. The examples illustrate the determination of a single analyte in a liquid sample requiring dilution (D) and sequential addition of two reagents (R_1, R_2) for the analytical reaction to develop. (a) Batch analyser. (b) Continuous analysers (SFA, segmented-flow; FIA, flow-injection; CCFA, completely continuous flow). (c) Robot station. Note that agitation is carried out by independent units in (a), is not required in (b) and is effected by a single unit in (c). (Adapted from [17] with permission of Ellis Horwood).

and removed prior to reaching the detector. They are discussed in Chapter 5 [15].

- Unsegmented-flow analysers (Fig. 1.3b) can be classified according to whether samples are injected or continuously inserted into the system, into 'flow-injection analysers' (FIA) [16,17] and 'completely continuous flow analysers' (CCFA) [18], respectively. Both are described in detail in Chapters 6 and 7, respectively.

(c) *Robotic analysers*, which should rather be referred to as 'robot stations', are based on the use of a high-precision minirobot whose movements mimic the actions of a human operator (Fig. 1.3c). By means of a hand (grip), the robot takes the sample and the products resulting from the different stages of its processing to a series of apparatuses (dilutor, liquid dispensing units, extractors, centrifuges, heaters) and instruments (balance, photometer, chromatograph). A single microprocessor usually controls the robot's motion and the operation of the different apparatuses and instruments, from which it receives the corresponding signals to be treated in order to obtain the final results [19]. Chapter 9 is devoted to the use of robots in the analytical process.

Depending on the number of analytes that can be assayed per sample, analysers can be classified into *one-parameter* (e.g. centrifugal and flow-injection analysers) and *multi-parameter*. The latter are of special use in clinical assays, usually requiring the determination of several parameters in blood or urine —the SMAC, an extremely powerful analyser manufactured by Technicon allows the determination of up to 20 parameters (analytes) per sample. Because of reminiscences of former times, some workers still use a parallel nomenclature (single-channel and multi-channel) to refer to these analysers. This is acceptable as the earliest commercially available continuous segmented flow analysers (Technicon AutoAnalyzers) carried out one determination per channel into which the sample was split. Hence the equivalence between 'channel' and 'parameter', exclusive to this type of analyser.

A classification of great practical interest divides analysers according to their *flexibility* for adaptation to different situations or needs (i.e. different types of sample or analyte) into 'specific designs' and 'flexible designs'.

(a) *Specific designs* are aimed at determining a single analyte or a few in the same type of sample. Their adaptation to other applications is normally unfeasible or requires major modifications. The automated assemblies for the determination of nitrogen by the Kjeldhal technique are a representative example, as are the analysers marketed by Leco for a variety of determinations: carbon and sulphur analyser (CS-244), nitrogen and oxygen determinator (TC-136) for ferrous and non-ferrous materials, etc.

(b) *Flexible designs* are characterized by their ready adaptation to different needs (types of sample or analyte) by merely changing one or several modular elements. They generally allow for changes in the reagents, configuration, detector, methodology and even the sub-stages of the process. Obviously, the flexibility of these designs will vary from one to another.

Semi-automatic analysers can also be classified according to other less relevant concepts such as the state of aggregation of the sample, the way in which the signal is measured and the sampling frequency.

(a) Depending on the state of aggregation of the sample, analysers can be classed as *gas*, *liquid* and *solid*. Obviously, the analyser design strongly depends on the type of sample to be handled. A solid analyser is usually much more complex than a liquid or gas analyser unless it is based on direct physical measurements; in fact, weighing is difficult to automate in all but robotic analysers, as are preliminary operations such as dissolution, disaggregation, extraction and so forth. The collection and treatment of liquid samples is much more affordable by most analysers. On the other hand, gas analysers are more frequently employed in industrial continuous process control and pollution monitoring.

(b) Depending on the way in which the signal is measured, one can distinguish between analysers based on *physical*, *chemical* and *physico-chemical* principles. Those based on physical properties of the sample or the analyte (e.g. density, refractive index, thermal conductivity, magnetic susceptibility) are characterized by their simplicity and by their notorious lack of selectivity; in addition, they are sensitive to pressure and temperature changes. Analysers based on chemical and physico-chemical principles are commoner and offer clear advantages over those mentioned above. The use of optical (photometric, fluorimetric) or electroanalytical (potentiometric, voltammetric) detectors among others, and also the occurrence of one or several chemical reactions, considerably increase the selectivity and sensitivity of measurements.

(c) Depending on the sampling frequency achieved, analysers can be classified as 'one-off', 'periodic' and 'continuous'.

- *One-off* analysers are conceived for sporadic determinations. They are used when the number of samples to be analysed is not too large and delivery of results is not too urgent.

- *Periodic* analysers are aimed at analysing a series of samples received at given intervals. Such is the typical case with clinical samples. They are also employed in industrial control of mass production lines involving a relatively consistent process.

- *Continuous* analysers, typically represented by 'process analysers' [20, 21] use the continuously generated results to adjust an industrial process *in*

situ. Environmental monitors, exposed in strategic places to send data continuously to a surveillance station, are another representative example. These analysers are described in greater detail in Chapter 16.

Finally, analysers can be classified according to their source or construction into *home-made* and *commercial*. Although there is a vast range of commercial analysers available to the potential user, some workers develop their own 'home-made' systems, which occasionally exceed the former in performance. While FIA configurations can be readily assembled from available parts, batch or SFA configurations are difficult to customize and are best purchased as supplied by the manufacturers.

1.5 DEGREES OF AUTOMATION

As can be seen in Fig. 1.4, every analytical process consists of three essential stages, namely:

(a) *Preliminary operations*, the most complex and varied of the three stages. They include sample collection and treatment, which will vary with the state of aggregation (dissolution or disaggregation, centrifugation, filtration, gas entrapment) and the potential interference from the matrix (different separation techniques); the development of the analytical reaction and the transport of the reacting mixture to the detection system.

(b) *Measurement and transduction of the analytical signal* by means of the detector used (optical, electrochemical, thermal) and on which calculation of the concentration of the analyte(s) is based.

(c) *Data acquisition* and *treatment*. This final stage can be implemented with a straightforward y-t recorder or with a microcomputer which can not only treat the acquired data and process them, but also pass them on to a central computer governing the analytical operations of a large industrial or hospital laboratory.

The main levels of automation in the analytical laboratory were defined recently [22]. As stated above, the concept of automation is still confusedly applied to analytical processes, techniques and methods. Therefore, against IUPAC's recommendations, it is worth establishing different degrees of automation in order to refer more accurately to the extent of replacement of human intervention in the laboratory. According to this criterion, analytical processes can be classified into (Fig. 1.4):

(a) *Semi-automatic* (I), namely those with *one* automated stage. There are five types of analyser used to implement this type of process.

(b) *Semi-automatic* (II). Processes with *two* stages requiring no human intervention. They are carried out by three types of analyser.

(c) *Completely automatic*, where the analyser —commonly given the name 'analytical black box' [23]— totally replaces the human operator.

The differences between the nine types of analyser referred to above are not clear-cut; in fact, the scheme in Fig. 1.4 is not exhaustive and could be expanded —yet, it is representative of automation in Analytical Chemistry. Below are described the nine alternatives to automation following the scheme in Fig. 1.4.

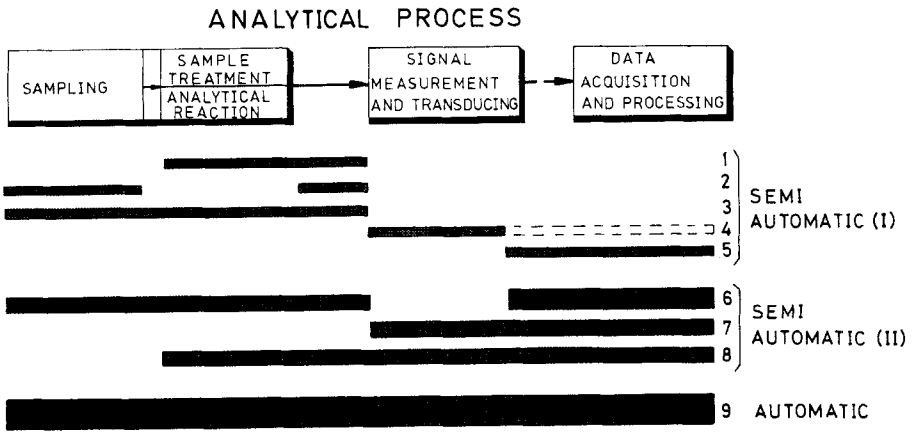

Fig. 1.4 Degrees of automation of the analytical process, assumed to consist of three analytical stages. Numbers 1 to 9 denote the different levels at which human intervention is replaced.

Type 1. This involves automation of the developent of the analytical reaction and the transport of the reacting plug to the detector (generally continuous in nature and furnished with an optical or electroanalytical flow-cell. A representative example of this alternative is presented in Fig. 1.5, namely the flow-injection determination of aluminium in silicate rocks based on the formation of a coloured chelate between the metal and Xylenol Orange (λ_{max} = 560 nm) [24]. The sample collection and dissolution (disaggregation) stages, which are tedious, are done manually, as is the injection of an accurately measured volume of treated sample. However, the main analytical reaction and removal of interferences (addition of ascorbic acid to reduce Fe^{3+} to Fe^{2+} and EDTA to form soluble chelates with a large number of potentially interfering metal ions) are carried out in a continuous fashion, as is the transport to the photometric detector used. An ordinary recorder acquires the transient signals yielded upon passage of the reacting plug through the flow-cell. Data treatment is also performed manually.

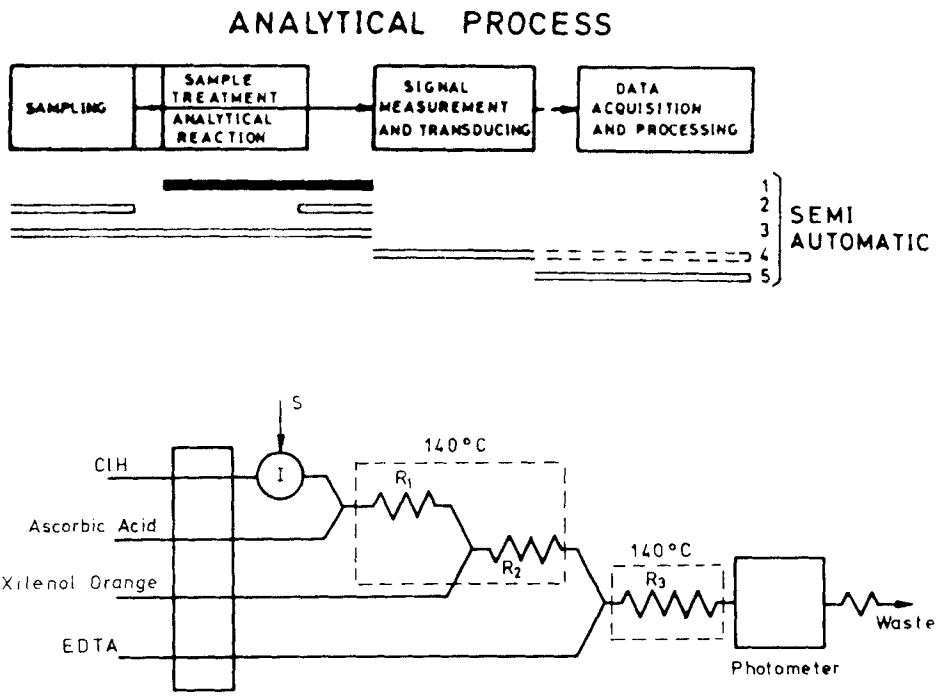

Fig. 1.5 Automation of the first few stages (preliminary operations) of the anlytical process in a Type 1 analyser, an FIA assembly for the determination of aluminium in rocks. (Reproduced from [24] with permission of Pergamon Press).

Type 2. This involves partial automation of the first stage of the analytical process: the accurate measurement of a sample volume (sampling) and its transport to the detector without human intervention. However, sample treatment (e.g. dissolution) and the analytical reaction development —if required— are carried out manually. Figure 1.6 shows a representative example: the incorporation of an automatic sampler in a thermal-vaporization atomic absorption spectrometer. This instrumental configuration is representative of those where the automation of one stage is highly recommendable —in this instance to ensure reproducible results.

Type 3. The implementation of all the preliminary operations in the analytical process without human intervention represents a remarkable degree of automation. By incorporating a sampler in ordinary FIA assemblies or the classical AutoAnalyzers, the first stage of the analytical process could be regarded as automated. However, it should be noted that the sampler holds pre-treated samples, so that the automation of the first stage is only apparently complete.

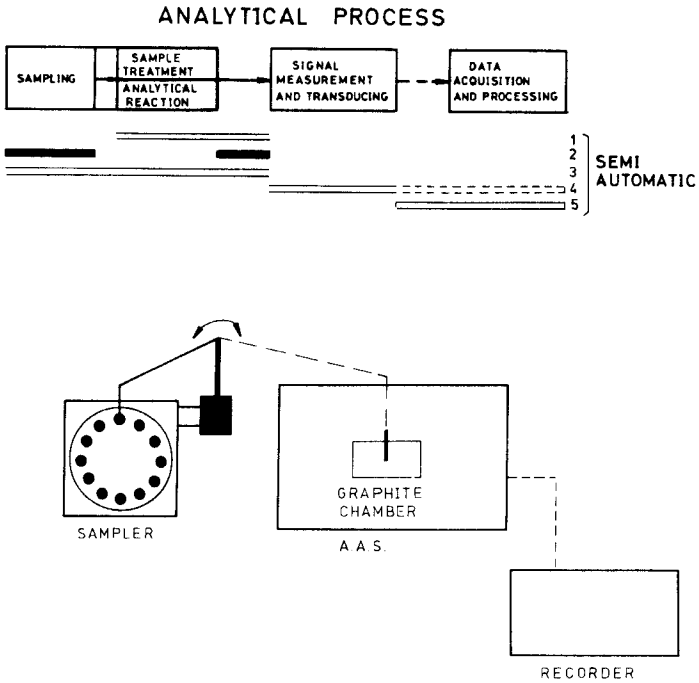

Fig. 1.6 Automation of the first few stages (preliminary operations) of the analytical process (Type 2 analyser). Automatic system for introduction of samples in electrothermal-vaporization atomic absorption spectroscopy.

Type 4. The automatic control of an instrumental analytical technique — whether optical, electroanalytical, magnetic or thermal— by means of a microprocessor has become commonplace in commercial instruments in the last few years. Thus, the control of the parameters governing the functioning of a conventional molecular absorption spectrometer (lamp selection, monochromator movement, change of slit width, movement of the cells in the measuring compartment, etc.) is carried out via the keyboard of a microcomputer linked to the system through an active interface. Figure 1.7 depicts an example of automation of the second stage of the analytical process. However, this situation is currently uncommon as the microcomputer used can also deal automatically with data acquisition and treatment as in Type 7 analysers.

Type 5. This involves the automation of data acquisition and treatment in a traditional analytical instrument —even a balance can be the subject of automation. As shown in Fig. 1.8, a microcomputer connected on-line with the analogue output of the instrument ensures the automation of this stage of the