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Automation and Chemistry

1.1 Introduction

The great advances in electronics and computing have revolutionized the way we work in the laboratory, freeing us from long and/or tedious and iterative tasks and allowing us to dedicate our time to more creative work.

Automation allows us to carry out new types of experiments, being especially of great help in those in which a large amount of data must be obtained in very short times, in those in which a large number of parameters must be controlled simultaneously, and in those in which the time of experimentation is very long.

Modern automatic analysis systems are based on the widespread use of electronic components and devices. At the beginning of automation, automatic systems were based on the use of mechanical devices, which were characterized by their lack of flexibility. They were designed to perform a specific task, and it was practically impossible to reconfigure them to perform a function other than that of the initial design. These major limitations changed dramatically with the appearance of microprocessors and computers, which have made possible the design of easily reconfigurable and highly flexible automatic systems.

With current automatic systems and with the introduction of chemometrics, which has been acquiring increasing importance thanks, again, to the ease of calculation and processing of computers, it is now possible to obtain and manipulate a large amount of data and extract maximum information from them to limits unsuspected just a few decades ago. Thus, multicomponent analysis techniques based on the use of multichannel chromatographs and spectrophotometers can be mentioned.

Miniaturization of increasingly sophisticated electronic components and systems – in an increasingly powerful development, with lower energy consumption and greater massive data storage capacity – is allowing one of the great aspirations of the analytical chemists to perform measurements in situ, with the minimum amount of sample and with sufficient sensitivity to be able to measure the fundamental parameters that characterize it. On the other hand, these developments are also making it increasingly feasible to incorporate analytical techniques into control processes, constituting part of the information feedback systems necessary for the system itself to change its operating parameters in accordance with the objectives of quality imposed on the processing plant.

1.2 Automation of the Different Stages of the Analytical Process

Depending on the objectives set and the type of sample, the analysis to be carried out and its corresponding automation can range from very simple to very complex. Thus, the control of the quality of boiler water can be based on systems as simple as conductimetric measurements to initiate the resin regeneration process alone, without the need for human intervention in the entire process that we want to control.

Those steps that require complex mechanical movements are especially difficult to automate, such as sample collection and preparation, dissolution, weighing, and dosing. Although the use of robots has been introduced to solve these mechanical processes, their use has not been widely introduced due to, in large part, the high cost of the robots and the accessories that must be at their disposal, and generally they must be specially conditioned to be used by the articulated arm. Therefore, most of the time, the processes are only partially automated, with the most complicated mechanical processes still being carried out manually very often.

Table 1.1 describes the stages of a general analytical process and the different alternatives used for its automation.

Each of the stages or devices can be controlled by its own microprocessor or dedicated computer, but in a globally automated system, the entire set is controlled in turn by a central computer, or host,

Table 1.1 Automation of the steps of an analytical control process.

Operation	Remarks	Equipment	Difficulty	Controller
Sampling	Solids	Robot	Unusual	Host or devoted microprocessors computers
	Liquids	Dosifiers	Easy	
	Gases	Pumps	Easy	
	Mixture of them	Robot	Uncommon	
Physical simple conditioning	Size reduction	Dosifiers	Easy	
	Drying	Robot and grinder	Unusual	
	Solving	Robot and oven or lamp	Unusual	
	Filtering	Robot and vortex Heater	Uncommon	
	Centrifuging	Robot and filtering	Unusual	
	Weighing	Robot and centrifuge	Unusual	
	Aliquot taking	Robot and balance	Unusual	
	Injection	Robot and balance	Uncommon	
		Dosifiers and valve	Easy	
Chemical sample conditioning		Robot and syringe	Usual	
	Extraction	Robot	Unusual	
	Adjust pH	Dosifiers	Easy	
	Masking	Dosifiers	Easy	
Calibration and measuring	Derivatization	Special sampler	Usual	
	Transduction	Transducer	Easy	
	Signal Conditioning	Noise filtering	Easy	
	Amplification	Amplifier	Easy	
	Data saving	Graphic records	Easy	
Calibration		Magnetic systems	Easy	
	Gases	Valves	Easy	
	Solids	Valves, dispensers	Easy	
Data treatment, results evaluation, and decision-making		Microprocessors and dedicated computers	Easy	

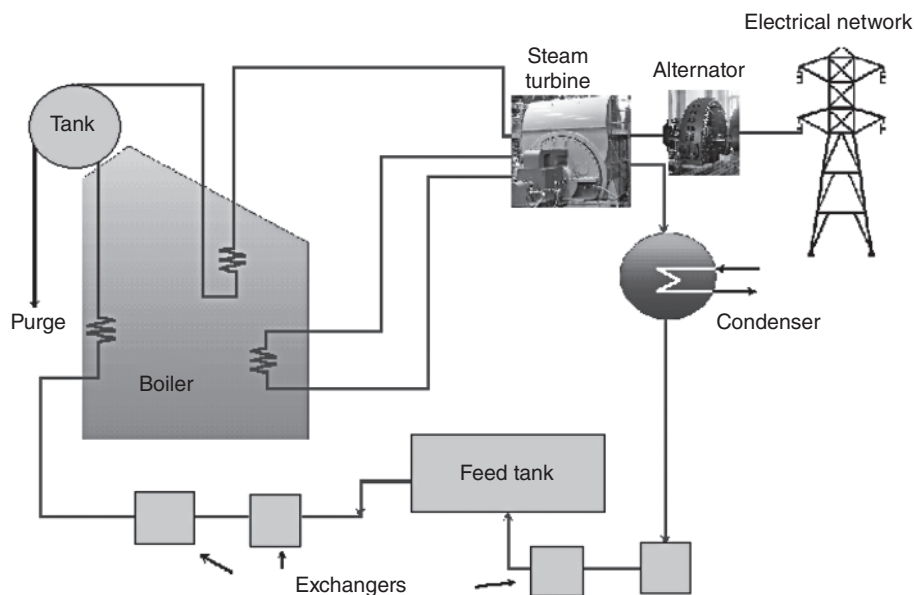


Figure 1.1 Energy cogeneration system of a municipal waste incinerator.

which harmonizes its operation. It can evaluate the results and even make decisions to modify the operation of the entire system. Systems capable of controlling or regulating their own functioning, using data or signals from any part of them, are called feedback systems.

Some stages may be easy to automate – such as fluid sampling, calibration, and taking measurements – but others are very difficult to automate. It is often preferred not to consider a total automation of the analytical process, with it being almost instinctive to carry out certain stages manually, to the point of stating that a process has been automated when, in reality, a very high percentage of it continues to be carried out manually, with the direct intervention of the analyst.

An example of the integration of an automated multiparametric chemical analysis in an industrial process is described in the following section. Figure 1.1 includes an energy cogeneration system of a municipal waste incinerator. Water supplied to energy cogeneration boilers usually comprises condensate or boiler steam passing through the turbine or heat exchangers and externally supplied water. The latter is usually subjected to various treatments, including filtering, decarbonation, and demineralization, in order to remove impurities. In fact, an appropriate treatment of the water in combination with efficient control of the recycled condensate and purge helps prevent corrosion, scaling, and other potential sources of deterioration and shortening of the useful life of boilers.

Corrosion is no doubt the detrimental phenomenon most strongly affecting maintenance costs. In order to minimize its impact, a chemical reaction inside boilers is forced prior to first obtaining a protective coating usually referred to as magnetite or ferrous–ferric oxide; this involves using pure or slightly alkaline water with a controlled oxygen content at a high temperature.

The parameters to be controlled in order to ensure proper functioning of a boiler system are SiO_2 , PO_4^{3-} , Fe, pH, N_2H_4 , NH_4^+ , conductivity, and acid conductivity. With the aim of minimizing the labor-intensive and time-consuming monitoring process, an automatic multiparametric system was developed for their joint determination. Sequential injection analysis (SIA) was chosen for this purpose on the grounds of its robustness and low reagent consumption (see Figure 1.2) [1].

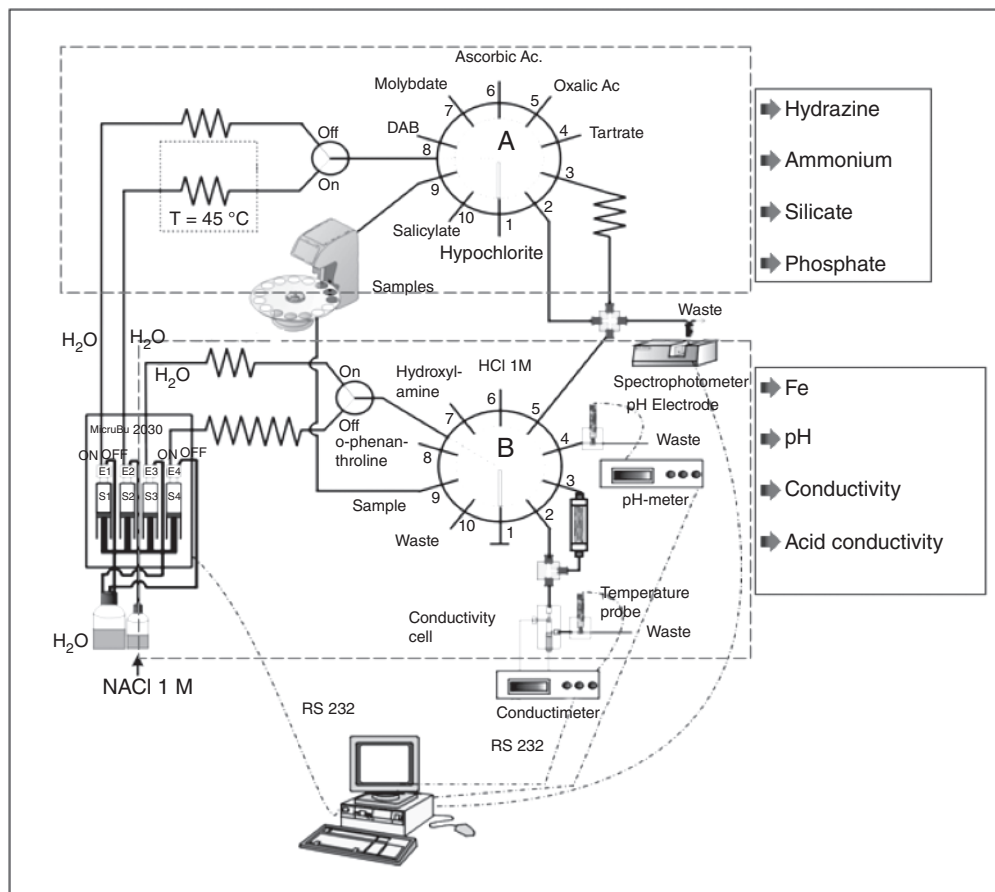


Figure 1.2 Dual SIA system for the determination of SiO_2 , PO_4^{3-} , Fe, pH, N_2H_4 , NH_4^+ , conductivity, and acid conductivity.

The analytical methods used to determine the previous eight parameters were as follows:

- Iron, hydrazine, and ammonium with *o*-phenanthroline, *p*-dimethyl amino benzaldehyde, and salicylate, respectively.
- Phosphate and silica by the formation of a molybdo heteropoly blue dye in the presence of ascorbic acid as a reductant – the former with an ammonium molybdate–potassium antimonyl tartrate mixture.
- Conductivity and acid conductivity by using a flow cell designed by our group – the latter parameter was determined following passage through a cation-exchange resin.

1.3 Computer Operating Modes

As already indicated, modern automation is based almost exclusively on the use of computers. There are several types of relationships between the experiments, the computer, and the user, as can be distinguished in Figure 1.3: offline, online, inline, etc.

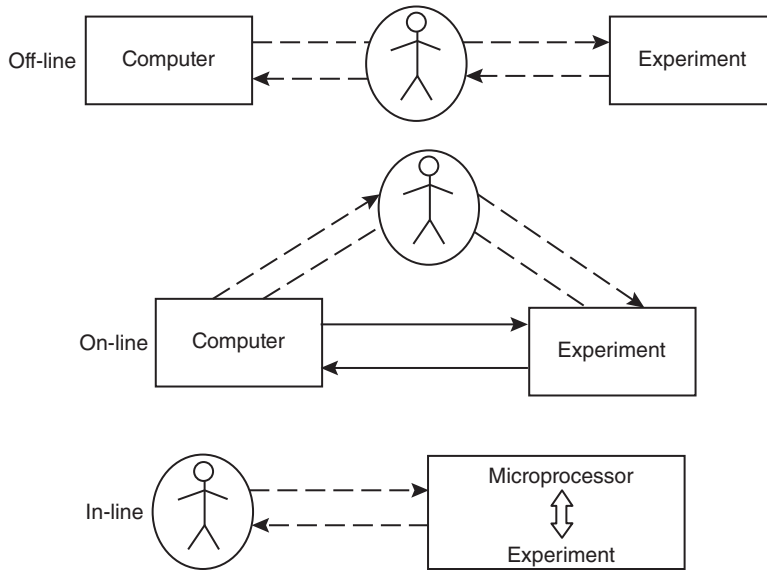


Figure 1.3 Computer operation modes.

In offline mode, the computer is practically used only as a computing element. The data are manually collected by the experimenter without help from the computer. These data are then manually transferred to the computer to carry out the relevant calculations.

In online mode, there is a link between the experiment and the computer. The data is transferred directly from the experiment to the computer, which can process it and make decisions based on the results obtained. The user can intervene or not in the process. Normally, the user will intervene to change the established specifications in order to launch new experiments under other conditions or objectives. The online work system has been acquiring increasing interest with the systematic incorporation of personal computers (PCs) in the management of instrumentation. The use of PCs allows the control of all types of operations and is especially useful for experiments of very short duration (milliseconds) and very long duration (hours or days). In this treatise, we are going to refer fundamentally to this type of online experiment. Manufacturers soon realized the advantages of online systems and have progressively incorporated computers into the instruments.

In inline systems, the computer and the experiment are completely integrated, which can mean certain disadvantages. Thus, manufacturers do not usually reveal the exact nature of this integration, data adjustment systems, or calculation forms, particularly with regard to corrections for interferences and nonlinearities; what is more serious, the programs can rarely be modified by users.

1.4 Approach to an Automation Problem

When considering the automation of a system, it is advisable to take into account a series of points:

- 1) Definition of the problem and objectives.
- 2) Available analytical methods.
- 3) Whether there is a need for control of mechanical systems and, consequently, whether appropriate computer interfaces are required.

- 4) Communication systems between the instruments and the computer, along with the protocols required for their use (RS232C and IEEE488).
- 5) Sensors and transducers required for the physical signals to be measured and analog/digital (A/D) and digital/analog (D/A) conversion systems.

In today's market, there are the required elements at very affordable prices. Thus, today it is easy to find cards on the market that can simultaneously perform several of these functions. Some of them, such as RS232C interfaces, are standard components in today's PC computers.

It is very important nowadays to properly select the instrumental offer on the market. Not only should the classic features of the instruments be kept in mind, such as the quality of the components, sensitivity, and resolution, but close attention should also be paid to whether they come ready to be connected to computers, whether through serial interfaces RS232C (or equivalent) or parallel, type HP-IB, or others. It is also very important when making a decision about the purchase to see if the manuals supplied with the device include the communication protocols and control commands of the instrument from a computer. Unfortunately, there are still instruments with a much more closed design and information that is very difficult to access, making their automation practically impossible or very difficult.

Every day, it is easier to automate your equipment yourself, adapting it to your experimental needs. It is possible, for example, to purchase programs in the current market under the Windows environment that, in a very graphic way, allow you to include the difficult instrumental modules necessary so that you can solve your problem yourself. Some of these programs include some of the most common instrumentation in order to further facilitate the automation of the equipment by the user. For this reason, it is convenient to insist again that it is of great importance that the instrumentation that is acquired meets the integration requirements, that is, suitable interfaces and known protocols.

Reference

- 1 Bauzá de Mirabó, F.M., Forteza, R., and Cerdà, V. (2009). A multisyringe sequential injection method for monitoring water in the energy cogeneration system of a municipal waste incinerator. *Talanta* 79: 1011–1020. <https://doi.org/10.1016/j.talanta.2009.02.037>.