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ANALYTICAL ASPECTS OF CHEMICAL PROCESS CONTROL. PART 1. FUNDAMENTALS

(Technical Report)

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Analytical aspects of chemical process control. Part 1. Fundamentals (Technical Report)

Abstract: The aim of this report is to present recommendations for reporting results concerning chemical process control and to deal with terms most relevant to the viewpoints of both analytical chemists and process engineers. Part 1 gives a brief description of the fundamentals involved in the basic analytical system. After formulating and explaining the operating system, approaches to process control are classified, followed by the planning, design and sample manipulation of dynamic systems as well as measurement and detection modules. The position of different components in the analytical system and the relation to the operating system should be clearly indicated when presenting results concerning process analytical chemistry.

INTRODUCTION

In the last few years, a growing number of papers in analytical chemistry have contained references to the possible use of techniques or methods described for the monitoring and control of chemical production processes. This illustrates the awareness of many analytical chemists of the great need for the development of methods for the control of processes and the determination of the composition of process streams. There are at least three factors driving these developments:

- better quality of products required by the consumer.
- more stringent regulations by the authorities in relation to production and production processes; and
- greater economic competition, which requires a minimization of energy consumption, a reduction of the amount of raw materials used in reactions and process operations and a decrease in the production of waste.

Although the term process analytical chemistry (PAC) seems to indicate a specific relationship with industrial processes, PAC is not (or should not be) merely restricted to the control of industrial processes. PAC is indispensable in *all cases* where chemical information is needed for the examination (or control) of an *operating system*. Examples of *operating systems* are a patient from whom blood and/or urine is taken for diagnosis, a plant in industrial processes, effluent streams, dams, rivers, etc. PAC is used in environmental studies and monitoring (for example air, water and effluent streams), in medicinal practice in the clinical treatment of patients, in agriculture, for the regulation of living systems and for quality assurance of various supplying, provisioning systems such as food and water.

APPROACHES TO PROCESS CONTROL

In industrial chemical reactions [1,2], PAC is an application of analytical science to monitor and control chemical processes. The information generated may be used to both control and optimize the performance of a chemical process in terms of variables such as capacity, quality, cost, consistency and waste reduction [3]. PAC plays a very important role in the efficient management of industrial processes, in mining and refining of raw materials and minerals, in agriculture, in food and animal feedstuff manufacturing, in fertilizer processing, in the medical field (clinical and pharmaceutical), and forms the cornerstone in the quality of daily life and sustainable environments. Depending on the specific application involved (which may vary slightly for different fields), there are two basic approaches to process control. In the so-called traditional approach, samples from the process environment are obtained manually, transported to a centralized analytical laboratory and analysed by highly qualified technical staff; the staff evaluate the data obtained and report the results to those involved in the operating system (plant in industry); corrective action is taken if required by adjusting conditions of the operating system

accordingly. In the more modern PAC approach, analysis is performed at or inside an *operating system* (plant site) with an *analytical system* (*process analytical system or process analyser*), where corrective action is immediately taken. These two approaches are shown schematically in Figs 1 and 2.

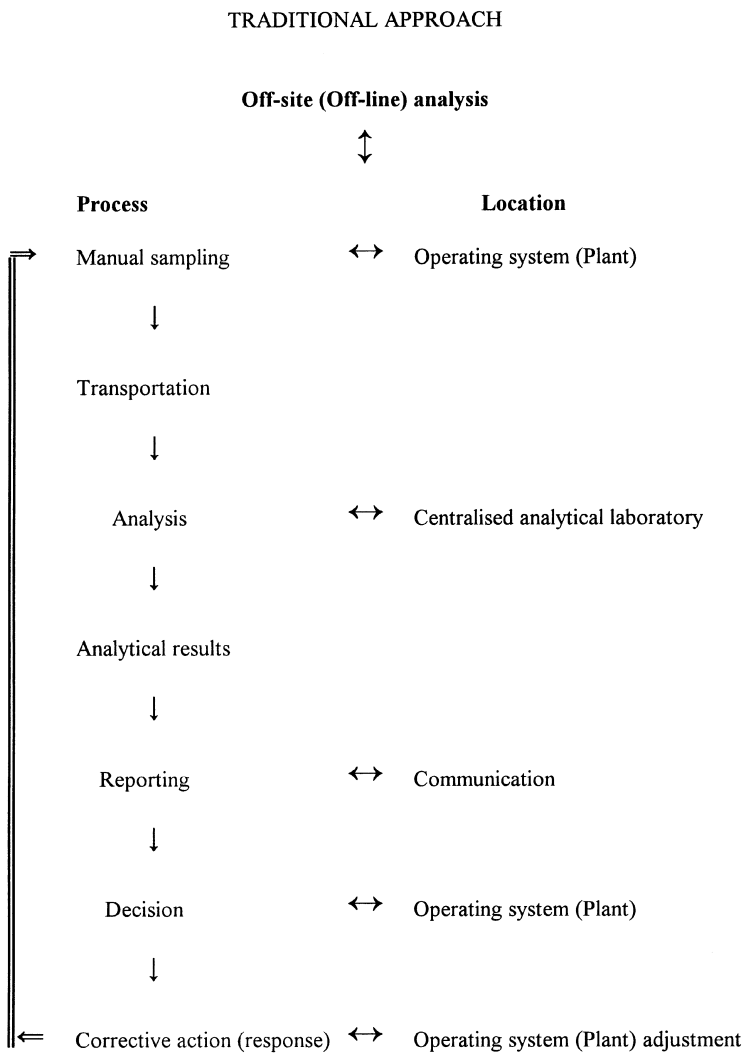

Fig. 1 Traditional approach to process control.

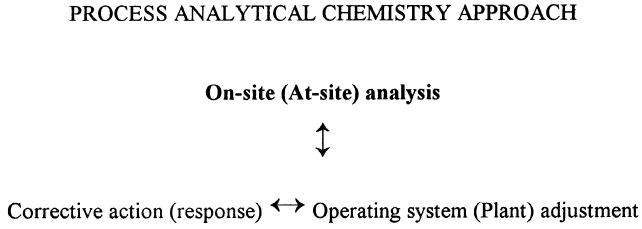

Fig. 2 Process analytical chemistry approach to process control.

There is not always a direct two-way communication in the traditional approach to process control, and a typical operation from sampling to corrective action may take several hours. This feature is known as *time-delayed monitoring*. Processes in, for example, chemical manufacturing plants are usually designed to accommodate this time delay, at a cost of longer cycle times and reduced plant utilization compared to

when using a PAC approach. Two-way communication is a very important part of the PAC approach of process control where corrective action is immediately implemented once results are computed, i.e. results of analysis are evaluated and chemometrics on results applied. The term *real-time monitoring* has been coined for this type of operation.

This report is not designed to give a detailed description of the mechanics of PAC, but aims to provide recommendations for presenting results concerning PAC. Detailed and comprehensive descriptions of PAC are given in monographs [3–7] and a number of reviews [1,2,8,9].

There are, however, some definitions and terms that currently need attention. The following terms and approaches have been described in depth [1–3] and the pros and cons of each highlighted [3], and only brief basic descriptions are given here. *Off-site* (*off-line*) *analysis* involves the manual removal of samples from the sampling site, and transportation to a measurement instrument located in a specialized central laboratory, where the analysis is performed by highly qualified technical staff who acquire and process data and report the results obtained to the people directly involved with the operating system (for example, a plant in industrial chemical processes). A decision is then taken by operating system management, sometimes in collaboration with laboratory personnel, and corrective changes made to the conditions of the operating system. *On-site* (*at-site*) *analysis* is divided into three categories. In *at-line analysis*, the sample is still manually sampled, but the measurement is carried out on a dedicated analyser located at the sampling site. Sample preparation is simplified and the measurement technique modified to permit the use of robust, reliable instrumentation to cope with the production environment. The term *close-time monitoring* (*near real-time monitoring*) is used to describe this type of operation. In *on-line analysis*, the sample is automatically sampled and fed into a dedicated analysing system where analysis is automatically performed with an automatic feedback to the operating system (for example, process stream for industrial chemical processes) for adjustment and corrective action. In *in-line analysis*, the analysing probe is situated inside the operating system (or plant) as part of the operating system (or process stream). Transduction is performed inside the operating system with a feedback to the processor outside the operating system with facilities for automatic adjustment and corrective action. *Real-time monitoring* or a good approximation to real time is attained with *on-line* and *in-line analysis*.

PLANNING, DESIGN AND SAMPLE MANIPULATION

In the planning and design of instrumentation for dynamic systems, the following points should be considered very carefully [8,10,11].

- selection of the *process variable* (characterizing the quality of the process);
- *quantitative relation* between the measured and controllable properties; these relationships are not obvious in every case;
- *places* of sampling (or analysing) points;
- *frequency of the measurements and correlation time of the process* required; for continuous measurements, the *time constant* of the measurement system;
- *duration time* of the measurements; measurement time could be short, calculation time longer (time elapsed from sampling until result, $t_{\text{elapsed}} = t_{\text{sample}} + t_{\text{measurement}} + t_{\text{calculation}}$);
- *tolerance limits* (upper and lower) of the measured variable;
- selection of sensing or analysing instrument(s);
- cost and maintenance of instruments;
- *calibration frequency* of the instruments used;
- *total cost* of the measurements and regulations involved; and
- reliability, ease of operation and simplicity.

The system should be fully computerized, which includes computer control of pumps, valves, data acquisition, data processing and data transfer to a central bank with automatic feedback.

A process analyser system normally contains seven main parts [3,4]:

- the sampling point;
- the preconditioning system;
- the sample-transport line;
- the sample-conditioning system;
- the analyser (analytical measurement or sensor unit) itself;
- the analyser control unit or the programmer; and
- the associated output equipment.

The equipment which penetrates the operating system's (for example, plant's process envelope in industrial chemical processes) envelope is called the sampling probe. The *sampling probe* must ensure that the sample taken is *truly and fully* representative of the *entire* operating system (process stream in chemical processes). Once a sample has been extracted from the operating system, it must be transferred to the analyser. A *preconditioning system*, situated close to the sampling point, may be used to treat the sample in such a way as to eliminate problems, for example by solid particles, droplets or condensate, which may lead to blockage or fouling of the sample-transport line and to regulate the pressure and temperature of the sample provided to the system.

The *sample-transport line* must transport the sample from the preconditioning system point to the analyser in an *acceptable time* and without the *composition* of the sample being affected appreciably. *Speed* and *representativeness* are the key issues. The *sample-conditioning modules* are designed to ensure that the sample is *acceptable* to the analyser and that it is still *truly representative*. The analyser accepts the conditioned sample, senses or processes the analyte into a product that is measured, and produces an appropriate output signal.

MEASUREMENTS

Measurements in process analysers are based on physical properties which can be transformed into chemical quantities expressing chemical information. These may be classified as follows.

(A) Methods based on the measurement of process streams with intensive physical properties (density, light absorption, refraction, etc.).

(B) Methods based on the measurement of intensive properties after using chemical reaction(s) for increasing selectivity and sensitivity (spectrophotometry using colour-forming or chromogenic reagents, etc.).

(C) Measurement of extensive physical properties using chemical reaction(s) (for example gravimetry, titrimetry, coulometry, etc.).

(D) 'Two-dimensional' analytical methods. One coordinate is related to the quality (nature), and other to the quantity of the components (for example polarography, chromatography, spectroscopy, etc.).

The procedures of class (A) are preferred on the grounds of simplicity in process control, but they are not applicable if high selectivity or sensitivity is required.

DETECTION SYSTEM

The detection system in a process analyser can be a destructive or non-destructive sensor. In a *destructive* mode the sample is destroyed, for example in inductively coupled plasma (ICP) spectroscopy where the sample is eventually fed into a plasma. With *non-destructive* detection, the composition of the original sample is maintained, for example when using a pH probe as detector; although a change at micro level occurs at the electrode surface–solution interface, the bulk of the process stream remains unchanged.

The scope of the PAC approach has been broadened with the introduction of a new generation of devices, accompanied by new terminology, in process analysers. The terms non-invasive and non-intrusive are widely used [1,3,12]. With a *non-invasive* technique, the sensing probe does not physically come into contact with the process stream and all non-invasive measurements rely on the transmission of information through the wall of the vessel. Non-invasive techniques have almost entirely focused on the measurement of physical parameters. At present, there are only a small number of chemical measurements that can be made in this way. A *transducer*, in this context, is a device for converting a

chemical or physical parameter into an electrical signal. *Non-invasive* therefore means that, in all cases, the transducer does not come into contact directly with the process medium. A familiar example of this is a thermowell, which is simply a piece of tubing welded into the wall of the vessel and closed at the innermost end. To measure the process temperature, a thermocouple or platinum resistance thermometer is inserted into the tube. To be able to make a reasonably representative measurement of the process fluid temperature, this tube needs to extend some distance into the fluid. It is therefore *intrusive*. An obvious disadvantage of an intrusive technique is that the probe may disturb the flow of process fluid or may be eroded by the passage of entrained abrasive material.

A pH probe is an example of an *invasive intrusive analyser*. For this to function, the pH-sensitive element needs to be in intimate contact with the process fluid, preferably where there is some kind of flow. This suffers the disadvantage of an intrusive monitor.

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