Process Analytical Chemistry, necessity for the modern industry and environment

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Abstract

Technological development in the chemical industry has gone towards automation and computer control of manufacturing processes. Monitoring and control of emissions to the environment are also automated to a large extent. This is valid for both continuous and batch processes. Computer control is applied to optimize the use of the processing capacity of the plant, raw materials and energy. With proper control even processes that without control would be unstable can be stabilized. All these operations require monitoring the material and energy streams as well as measurement of concentrations of the compounds that are involved in the process.

During the recent years process automation has developed considerably. However, the analytical measurements required to perform all the automatic operations are often rather simple compared with the used automation and information technology. Many of the analytical methods still used are based on the same technology that is used in laboratory environments and therefore are not well suited for measurements in harsh process environments. Therefore development of the analytical methods for process industry is of great importance and has led to development of a new scientific discipline: Process Analytical Chemistry, which is in the crossroad of Chemistry and Chemical Engineering. Process analytical chemistry is based on traditional analytical chemistry but it uses process technology, electronics, mathematics and information technology in developing analytical methods for in-line and on-line methods for continuous analysis of the main and by-products as well as process and effluent streams. Especially the use of chemical sensors will be more important in the future.

Introduction

Computers are nowadays frequently used in the chemical industry to control both batch and continuous processes. Computer control allows optimal use of raw material, energy and the capacity of the process plant resulting in a higher yield and a more even quality of the final product. Better quality normally means higher price on the product. On the other hand low quality products have to be sold for a lower price, reprocessed or discharged. Dumping into land or sea which means dilution is not a solution to pollution any more. By using computer control it is also possible to automate processes with narrow stability range or which are unstable without control. This requires accurate measurements of the material streams and concentrations of the active compounds in the process. Continuous analysis of main and by-products is also important. The environmental authorities require continuous monitoring of discharges and effluent streams. Analysis of poisonous and radioactive materials has also to be done automatically. All these requirements have given new problems and challenges to analytical chemistry and to the analyst. A new branch in analytical chemistry has been developed: Process Analytical Chemistry, which is in the crossroad of Chemistry and Chemical Engineering. Process analytical chemistry is based on the traditional analytical chemistry but it uses process technology, electronics, mathematics and information technology in developing analytical methods to be used in continuous analysis in chemical processes and in environmental monitoring. The process analytical methods give quantitative and qualitative information of the state of the process or the environment.

Process analyzers

Figure 1 shows an analyzer in a feed-back control circuit. The state of the project is described by the output of the analyzer. This value is then compared with the set-value which is the value the process should have in stable conditions or the target value the process should have. Difference between these values is then observed by the control element, e.g. a valve, heating element etc., to take the proper action to bring the process to the desired state or to keep the process within the specified limits.

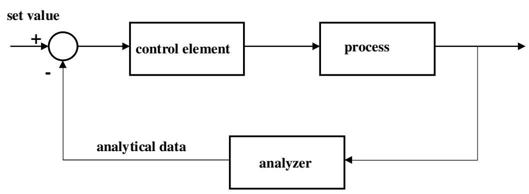


Figure 1. Analyzer in a feed-back system

Process analytical chemistry has its own special features and therefore it differs from the traditional analytical chemistry. The analyses have to be performed in industrial environment putting specific requirements on instrumentation. Analyzers have to work continuously 24 hours per day and they have to stand to chemical and mechanical stress. They have also to be easy to maintain. The result of the analysis is used to describe the state of the process and is used to control it. The analytical methods used have to be simple and easy to automate. Sometimes methods that are less accurate than the corresponding laboratory methods can be used with advantage. Reproducibility and repeatability are in most of the case more important than the absolute accuracy of the method. In process analytical applications the change of the process is often the main concern.

In developing process analytical methods the analytical problems often have to be seen from a completely new point of view. A method that works well in laboratory environment does not necessarily be the best method for process analytical applications. To use a laboratory method in the process is seldom a good solution. In comparing different analytical alternatives for process measurements it may turn out that it is more practical to monitor a physical property of the process that varies with the key compound.

Process analytical methods

There are several ways to perform analyses in the chemical process industry. The first and oldest way is to use **off-line** methods, Fig.2a. In those methods samples are taken manually and then transferred to a central laboratory serving the whole plant or even several plants. The samples are then analyzed by the staff of the laboratory who reports the results to the people in charge of the operation of the process. The advantages of this approach are the economy and efficiency in time sharing of the use of expensive instrumentation and the availability of analytical expertise in consulting, method development and instrument maintenance. The main disadvantage is the delay between sampling and reporting of results.

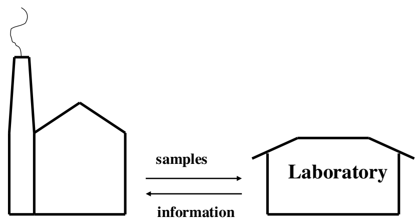


Figure 2a. Off-line measurement

Next stage towards more automation of analytical work in chemical processes is the use of **at-line** methods, Fig. 2b. In these methods samples are still taken manually but analyzed in close proximity to the process line in a plant laboratory by plant operating staff. The advantages are faster sample processing and closer control of the analysis by the process staff. To the disadvantages can be counted lower level of maintenance and that the analytical work is often performed by persons having only limited analytical training.

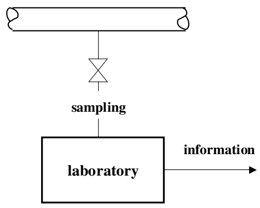


Figure 2b. At-line measurement

To further minimize the dead time in connection with analysis, the instruments can directly be connected to the process for monitoring the key component in reactors, process streams and gases. These **on-line** methods can be divided into two groups depending on the sampling procedure as shown in Fig. 2c. In the continuous methods the sample is led by a side tube directly to the analyzer. Most of the gas analyzers are working according to this principle. Such methods are, e.g. measuring IR-absorption, chemiluminescence and fluorescence. In the other type of on-line methods the analysis is done on discrete samples withdrawn automatically from the main stream by a sampling system. The sample is then processed by an automatic analyzer. The results are not received continuously but at discrete time intervals. Methods belonging to this category are, e.g. gas chromatography, titrations and flow injection methods. It should be pointed out that modern process gas chromatographs and titrators are rather reliable although they are complicated in their constructions.

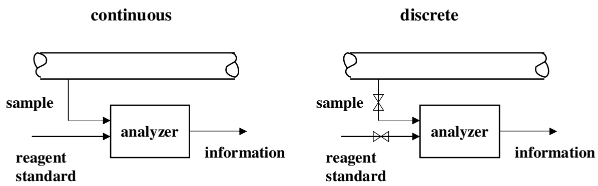


Figure 2c. On-line measurement

Analyses without dead-time can be done by **in-line** methods where the sensors are placed directly in the process steam as shown in Fig. 2d. By using these methods the state of the process is continuously monitored. Such in-line methods are measurement of pH and activities of other ions by using ion selective electrodes, measurement of conductivity and concentration of dissolved oxygen. There are chemical plants and power stations where several chemical sensors are connected to make a network to monitor the key components in the plant. The main problem with in-line methods is calibration and maintenance of the sensors. Certain intelligence can be build in the sensor system by using microprocessor technology. In these systems calibration, correction of the base line and tests of the sensors performance are done automatically. An intelligent sensor can also do some data processing such as averaging of the signal or even more complicated operations like Fourier transform of acquired data.

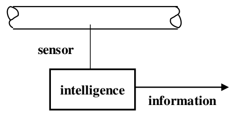


Figure 2d. In-line measurement

Analyses without dead-time can also be performed with methods where the instrument is not in physical contact with the sample. These **non-invasive** methods, Fig. 2e, are based on energetic interaction between the excitation signal and the material to be analyzed. As examples of theses methods can be mentioned measurement of IR-absorption directly through the process gas, use of IR-ATR method in monitoring liquid process streams, measurement of diffuse reflection of solid samples, X-ray fluorescence measurements in metallurgical industry and electrode-less conductivity measurement in monitoring concentrations in process streams.

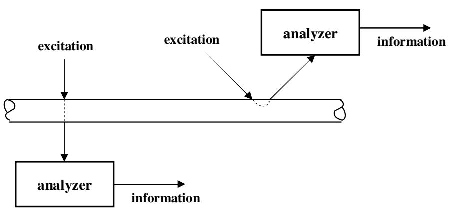


Figure 2e. Non-invasive measurement

The analytical determination is influenced by many factors. Some of them can be controlled and some of them are uncontrollable. The stochastic variations in the signal or the result are basically affected by stochastic variations in the process itself and by the uncertainty in the analytical procedure. Uncertainty in sampling, sample preparation and calibration together with reproducibility of the analytical method will contribute to the uncertainty in the result of the analysis. How these different factors do affect the measured signal or result of the analysis is schematically shown in Figure 3.

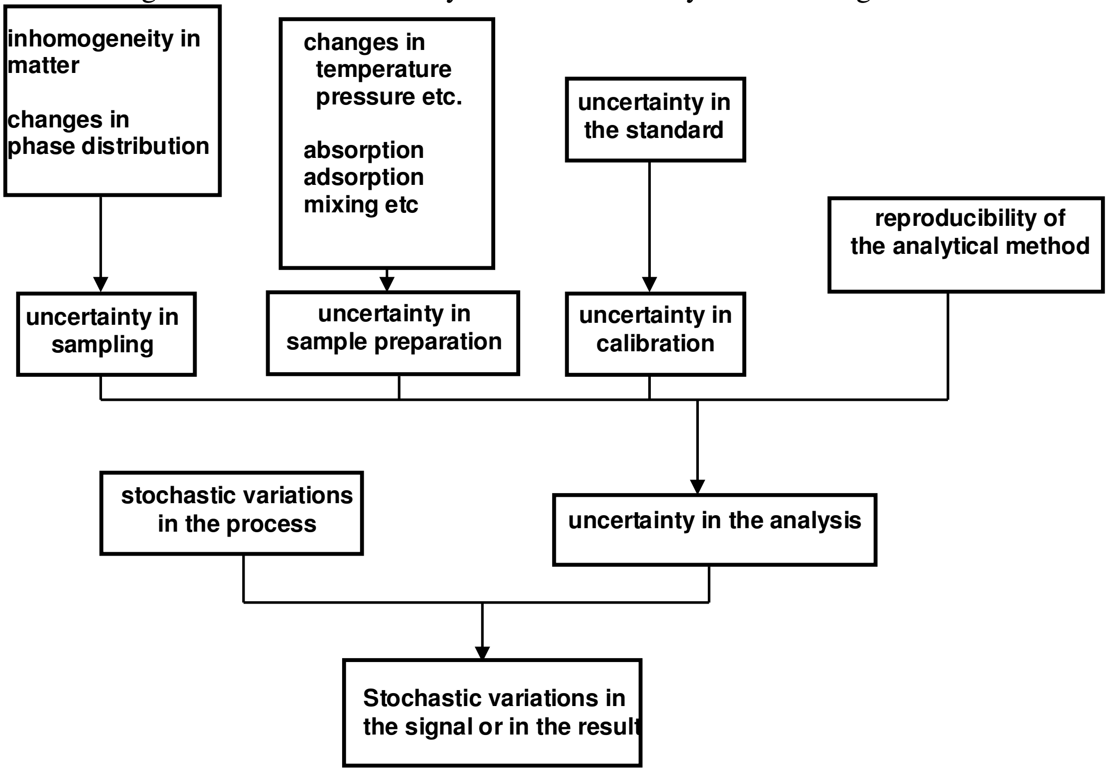


Figure 3. Factors influencing the result of measurement

Process analytical determinations as integrated part of a production plant are shown in Fig. 4. On-line and in-line measurements are shown as examples of process analytical methods and flow injection analysis is used as the example of the on-line method. In both methods specific determination of the analyte is done by using a chemical sensor as example of detection. The sensor surface senses only a specific compound and gives a response, e.g. electrical, photometric, change in mass or temperature, that depends on concentration of the species to be determined. The measured signal has then to be transferred to information that describes the state of the process. This information is used to control the process. Similar feed-back structure is used in many different systems, e.g. to decide what kind clothing would be required when going out or what kind of medication a patient needs.

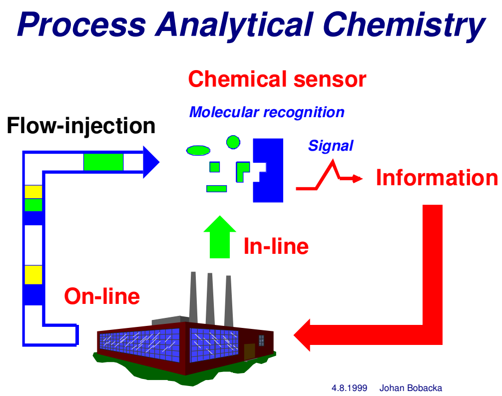


Figure 4. Process analysis in a production plant: from measurement to information

Process control and chemical sensors

The bottleneck in implementation of in-line methods is the lack of reliable chemical sensors. It can be expected that the same technology that revolutionized electronics will have a major importance in development of chemical sensors. There are a big number of sensors working in laboratory experiments but the number of commercially available sensors is less. The number of publications describing practical applications of sensors is less than publications describing interferences in the sensor response. An important field of research in the sensor technology is development of new materials having sensor functions. Such materials are e.g. conducting polymers and different carbon materials, fullerenes, carbon nanotubes and graphene. Study on nano-structures in chemical sensors is an intensive field of research at the moment. Implementation of these materials in sensor applications requires thorough knowledge of their chemical and physical properties as well. In developing new sensor materials the analytical chemist has to work together with scientists in the field of material technology.

The use of in-line working sensors gives several advantages to process control. The time constant of a sensor is in the order of few seconds whereas the time constant of a chemical process is typically several minutes or even hours. This means that a great number of measurements can be performed, i.e. information from several sensors can be acquired during the time corresponding to the time constant of the process. A network of sensors implemented in a process facilitates considerably the optimal and flexible control of the process. This results in increase in the efficiency of the process, better quality of the end product and makes it also easy to change production parameters. More analytical information can be received by using an array of sensors where the sensors respond differently to different compounds. In such an array even a less selective sensor may be used to measure the concentration of a particular component in the sample. Under normal production conditions of a chemical process the variations of the concentrations of the components involved in the process are rather small. The interfering substances and their concentrations are normally well known as well as their effects on the response of the sensors used. This gives the possibility to use less selective and sensitive sensors because the necessary corrections for the interferences in the response can be done in advance. An example of this kind of correction is the use of gas filters in IR-measurement of process gases. When measuring simultaneously concentrations of the interfering substances and knowing the selectivity of the sensors relevant analytical information can be found. These concepts are used in neural networks consisting of several sensors. Chemometrical methods are of importance in extracting relevant information from measured data.

The use of less selective and sensitive sensors, however, creates also some risks. There are cases where the process parameters like temperature, pressure are changed dramatically or there are big variations in the quality of raw material. It may then happen that less sensitive sensors fail to give reliable information of the conditions in the process resulting in wrong correction actions of the controlling system and control personnel. Severe accidents have happened due to mall-function of the analytical instrumentation used in process control.

The electrical response of a sensor can with advantage be transformed to an optical signal. Use of fiber optics makes it then easy to transport the signal to the control unit of the plant. Optical signals are also less sensitive to different kind of electromagnetic interferences than the electrical signals.

Concluding remarks

In process analytical chemistry continuous analytical measurements are used. It should be emphasized that the use of sound engineering, instrumentation and thorough understanding of the chemical background of the problem are the necessary increments in planning and implementation of a successful process analytical system. The roots of process analytical chemistry are deep in the traditional analytical chemistry. Finally, it should be emphasized that even in process analytical measurements, as in any analytical work, **an analytical method is useful only when know its limitations and the result of an analysis is correct only when we know its error.**

Figure 1

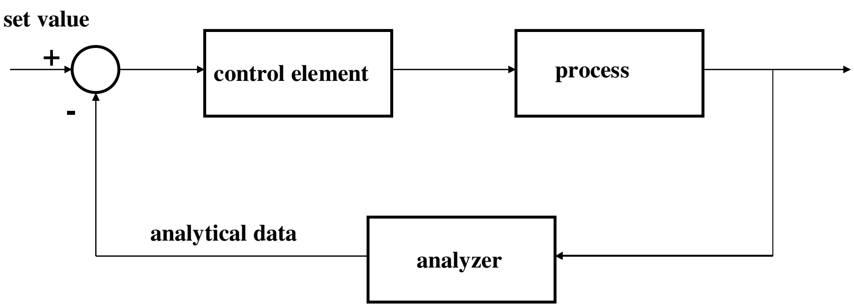

set value
+
-
control element
process
analytical data
analyzer

Figure 2a

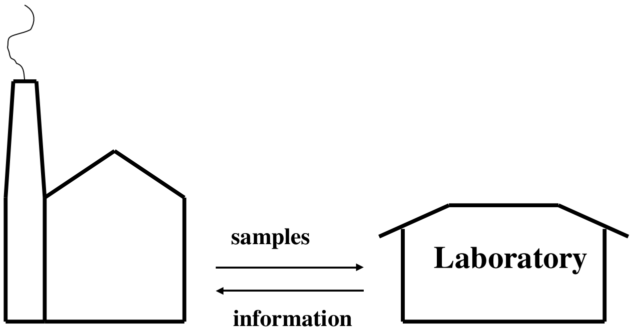


Figure 2b

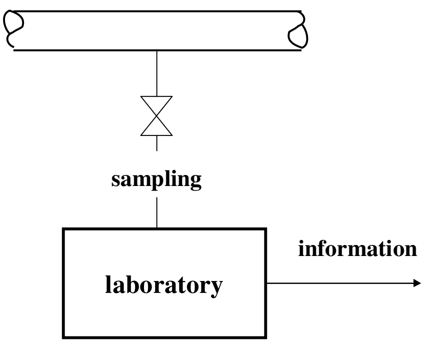


Figure 2c

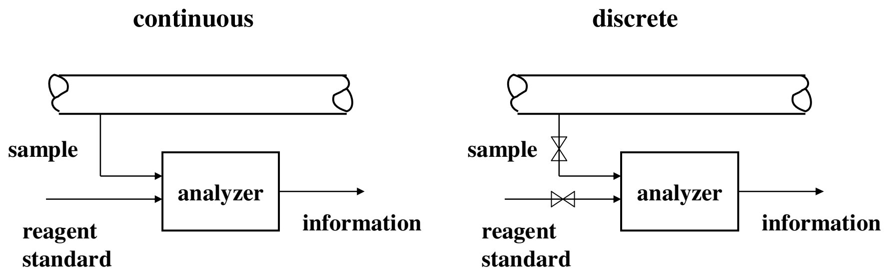


Figure 2d

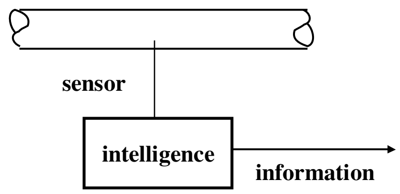


Figure 2e

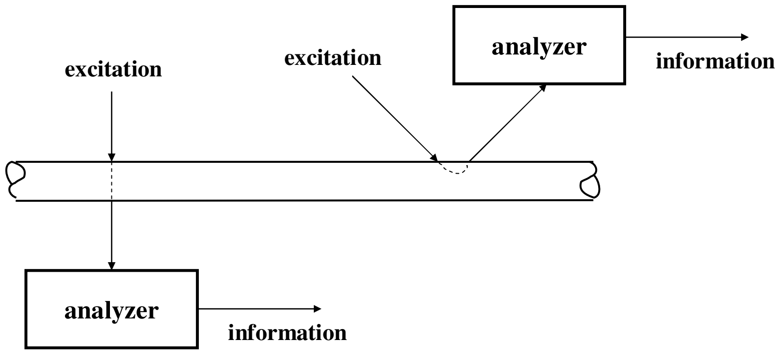


Figure 3

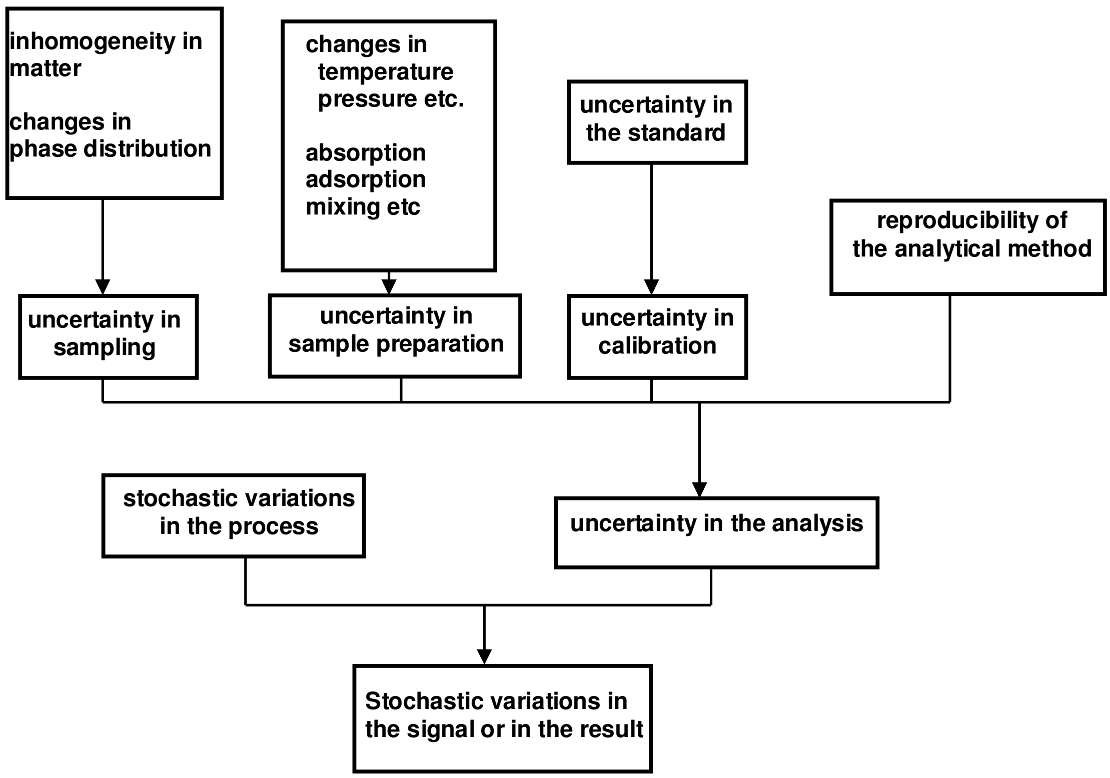
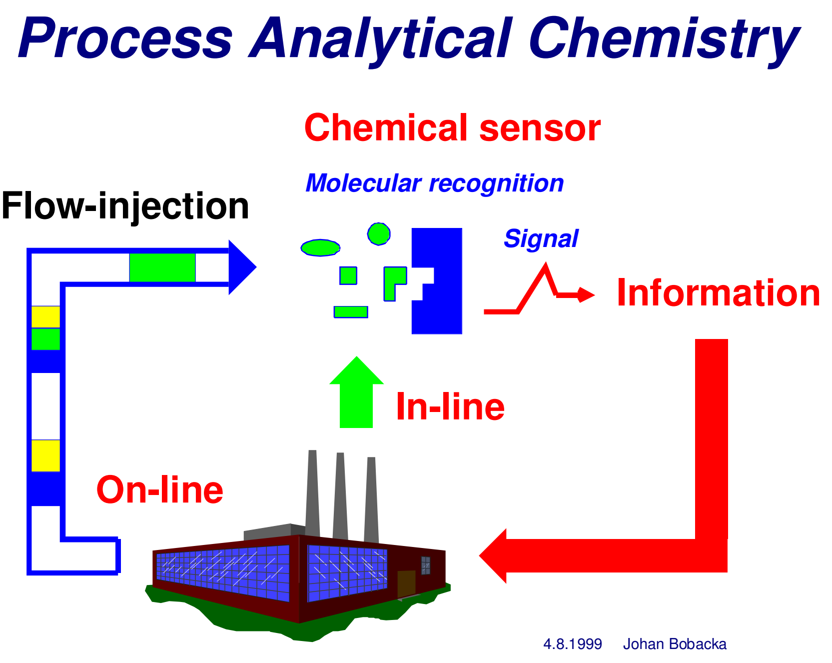


Figure 4



Process Analytical Chemistry
Chemical sensor
Molecular recognition
Flow-injection
Signal
Information
In-line
On-line
4.8.1999 Johan Bobacka