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New Concepts of Sampling

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Based on previous papers and a recent book published by the author, we propose the term "sampling" to characterize all steps that relate the sample to the process of analysis. The analyst has to understand that no analysis is better than the sample itself, and is thus obliged to give more importance to the sampling process. The paper discusses the correlation "Method–Sample–Instrument," the relationship of the history of the sample to the development of the analytical process, and the influence of the sampling process on the reliability of the analytical information. We conclude that sampling must include all the separation techniques. The main field of chemical analysis in the future, the hyphenated techniques, and the connection between sampling and pattern recognition are also discussed.

INTRODUCTION

Though numerous reviews concerning the analytical process have been published, only very few have examined the sampling process.

One of the most important of these was published by Smith and James (*1*) in 1981, but this deals only with the sampling of bulk materials.

On the occasion of an IUPAC meeting concerning collaborative interlaboratory studies in chemical analysis, the present author presented a lecture concerning sampling which mentioned that "the reliability of any analysis depends, in the first place, on the accuracy with which the sample (i.e. portion of the whole) subjected to actual examination is truly representative of the whole body which it is supposed to characterise" (*2*). Later, it was pointed out that, for correct sampling, it is necessary to consider the history of the sample, its homogeneity, and the influence of the process of sample preparation on the operational parameters of the analytical process (*3*). Based on these considerations, in 1991, Baiulescu and co-workers published a book entitled "Sampling" (*4*), in which they proposed the inclusion in the sampling process of all steps connected with the sample up to measurement. In such a way, we can include all the separation processes in sampling.

It is to be concluded that:

(1) In planning an analytical experiment, strategy is a necessary and sufficient condition, which is related to some causal correlations. Only by making strategic decisions can the analyst guide the experiment toward a well-defined goal, which in this case is to ensure satisfactory quality control.

(2) To act strategically in analytical chemistry and in chemical analysis means to know the history of the sample, to ensure its homogeneity, to plan its chemical analysis, and to be aware of, and take into account, the influence of the sample upon the analytical process.

(3) The ultimate purpose of the strategy in an analytical process is to ensure the acquisition of the maximum possible amount of information from the sample in the shortest possible time and with the highest possible reliability (*4*).

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METHOD–SAMPLE–INSTRUMENT CORRELATION

On the occasion of a meeting of the Chemical Society in 1980, the author presented a plenary lecture concerning "Moral Ageing of Analytical Methods" (*5*). This paper discussed three types of correlations: (a) the method–instrument correlation; (b) the man–instrument correlation; and (c) the method–man–instrument correlation.

We consider that the sample acts as a glue between method and instrument. To obtain reliable analytical information, it is very important to know the history of the sample. In this way, we can divide analytical methods into nondestructive and destructive methods.

For acquiring knowledge of a sample, the analyst has to learn basic chemistry as well as mathematics, physics, and automation (or, at least, to know how to pose realistic problems for specialists in these scientific fields).

Only knowing the correlation method–sample–instrument, "chemical analysis—the applicative side of analytical chemistry—has now became a constituent, integral part of the production process; it contributes to the optimisation of the process of controlling the quality of the industrial products" (*5*).

It is concluded that the history of the sample has the main role in the development of the analytical process.

THE THREE STEPS OF THE ANALYTICAL PROCESS

In a book published in 1982 (*6*), the analytical process is divided into three steps:

$$\text{input} \Rightarrow \text{black box} \Rightarrow \text{output.}$$

These represent the three main chapters of the book. This book, dedicated to education and teaching in analytical chemistry, was well received by analytical chemists and was translated in Chinese in 1993.

Based on the above considerations, we can evaluate the ratio of importance of these three steps of the analytical process to be 40% for input, 20% for black box, and 40% for output. The high percentage accorded to input, i.e., sampling is due to the inclusion of separation methods. In this way, we can conclude that the sampling process is more and more complicated as a function of the history (nature) of the sample. For analysis of complex samples, as in environmental analysis, food analysis, and clinical analysis (domains valuable also in the future), the sampling process has a very important role. We must be very attentive, especially for trace analysis, to problems connected with the contamination of the sample during sample preparation.

Inclusion of solvent extraction and especially chromatographic methods in the sampling process ensures good reliability of the final analytical information.

This opinion not widely accepted by analysts, considering the difference between sampling and sample preparation. But we consider that our proposal will be accepted in the future, as all steps of the sampling process are automated. In this way, the process of sampling will become a main step in chemical analysis.

INFLUENCE OF THE SAMPLING PROCESS ON RELIABILITY OF THE ANALYTICAL INFORMATION

The shortest definition of reliability is as follows: Reliability is maintaining quality over time. In this way, the concept can be applied in various fields of science and technology, as well as in chemical analysis.

Due to the complexity of the analytical process, the reliability of the analytical information is a complex function,

$$R_{AI} = f(R_S, R_M, R_I, R_{DP}),$$

in which the terms in parentheses are related with to Sample, Method, Instrument, and Data Processing.

Reliability of the sampling process represents the “art” of the analyst. It belongs in the education of the analyst in various fields of chemistry as well as in connected disciplines. The problems imposed by the obtaining of correct sample reliability are more complex that those concerning the other steps of the analytical process. Sampling represents, in our opinion, the main source of errors related to the final analytical information.

It is quite enough to mention the oldest method of gold analysis, so-called “fire assay,” in which sampling has practically the main importance. This fact is due to the special properties of gold ores, where gold is distributed nonhomogeneously.

A similar situation can be observed with much more complex systems for sample preparation, as in biological and clinical analysis.

HYPHENATED TECHNIQUES: SAMPLING + ANALYSIS

Hyphenated techniques are very important techniques for analytical control due to the need to characterize complex samples to the maximum extent and in the minimum imposed time.

A representative example is so-called “stripping analysis,” initiated by Kemula and widely utilized now for trace analysis. The sensitivity of this technique is due to the fact that it consists in two steps. The first step represents the sampling process (preconcentration on mercury drops), and the second represents the pure analytical step, consisting in registration of the redissolution wave.

Currently, due to the complexity of the samples, we commonly use more complex hyphenated techniques with high efficiency and flexibility. These techniques are used especially to characterize news kind of samples, which require less quantity and higher sensitivity and selectivity during analysis.

We can mention the connection of CGC with high efficiency detectors such as FTIR (nondestructive) and/or MS (destructive). It is also convenient to use MS/MS detection, to improve the reliability of the analytical information.

Hyphenated techniques are presently generally used for sample characterization. It is enough to mention the couplings TA/CGC, CGC/AEDMIP, HPLC/MS, HPLC/FTIR, HPLC/DAD.

Using CGC/FTIR/MS for example, we can obtain much more information and a higher degree of certainty about the analyzed sample, especially when dealing with natural products. Such is the case of pheromone characterization, which opens the way to new kinds of synthetic products with ecological action.

We consider that the future of hyphenated techniques will be ensured by the three main fields in which chemical analysis is involved, concerning complex samples and routine sample analysis: environmental analysis, food analysis, and clinical analysis.

In our opinion, in the next future, the quality and the performance of hyphenated techniques will be improved due to automation. In this way, we will obtain much more reliable analytical information.

Concerning the correlation method–man–instrument, influenced by the nature of the sample, automation can eliminate subjective errors due to the analyst.

The analyst of the future can be called a system analyst, because he need only program and supervise the experiments of the analytical process.

To conclude, we must follow the planning of analytical experiments must have a lawful character (*4*):

(1) The lawful character of the planning of an analytical experiment is imposed by the sample to be analyzed.

(2) The lawful character implies the need to observe the legality of the experiment, that is, to use standard methods of analysis at some stage.

(3) The lawful character has some direct repercussions on the implementation of chemical-analytical control by in-line production processes.

The future of chemical analysis will be ensured by a co-operation between the analyst's intelligence and the computer's intelligence and skill.

SAMPLING AND PATTERN RECOGNITION

There is a strong connection between sampling and pattern recognition, but to obtain reliable analytical information by this technique, it is necessary that the sample should be characterized from qualitative and quantitative points of view.

In pattern recognition, it is necessary to utilize, if possible, high purity samples to be sure on the nature and compound's structure.

For this reason, it is necessary to use much more sophisticated separation techniques such as hyphenated techniques in advance of the pattern recognition step.

REFERENCES

1. Smith, R.; James, G. V. *The Sampling of Bulk Materials.* R. Soc. of Chemistry, London, 1981.

2. Baiulescu, G. E. Sampling. In *Collaborative Interlaboratory Studies in Chemical Analysis* (H. Egan and T. S. West, Eds.), pp. 153–154. Pergamon, Oxford, 1982.

3. Baiulescu, G. E.; Mircea, D.; Zugravescu, P. Gh. *Rev. Chim.*(*Bucharest*),1984, **35,** 1023–1026.

4. Baiulescu, G. E.; Dumitrescu, P.; Zugravescu, P. Gh. *Sampling*, pp. 169–171. Ellis Horwood, Chichester, 1991.

5. Baiulescu, G. E. *Pure Appl. Chem.*, 1980, **52,** 2525–2539.

6. Baiulescu, G. E.; Patroescu, C.; Chalmers, R. A. *Education and Teaching in Analytical Chemistry.* Ellis Horwood, Chichester, 1982.