ELLIS HORWOOD SERIES IN ANALYTICAL CHEMISTRY

SAMPLING

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Table of contents

1 Introduction 7

2 History of the sample 12
  2.1 Basic chemistry 12
  2.2 Geochemistry 20
  2.3 Physiology 28
  2.4 The environment 37

3 Homegeneity of the sample 45
  3.1 Samples for destructive analyses 46
  3.2 Samples for non-destructive analyses 61

4 Chemical analysis of the sample 80
  4.1 Methods of analysis 84
  4.2 Instruments for analysis 96
  4.3 Automation and robotics 112

5 Influence of sampling on the analytical process 130
  5.1 The operational parameters of the analytical process 134
  5.2 The reliability of the analytical information 144
  5.3 No analysis is better than the sample itself 159

Appendix 172

References 173

Index 181

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  4.2 Instruments for analysis 96
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5 Influence of sampling on the analytical process 130
  5.1 The operational parameters of the analytical process 134
  5.2 The reliability of the analytical information 144
  5.3 No analysis is better than the sample itself 159

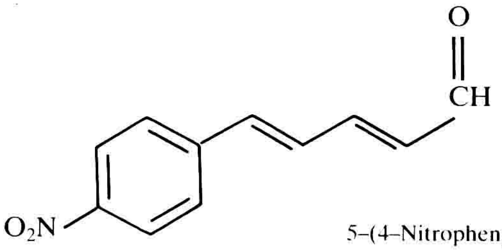
Appendix 172

References 173

Index 181

1

Introduction



NPPD

5-(4-Nitrophenyl)-2,4-pentadiene-1-al

> "The sample acts as a 'Spy Dust,' it is the role of the analyst to detect it."
>
> G.E.B.

Writing a book on 'Sampling' is perhaps as difficult as producing a best-seller. Such a claim might be vindicated by the fact that the problem of sampling involves a vast amount of knowledge in various fields — chemistry, geochemistry, physiology, the environment, and many other disciplines. Probably for this reason, the sampling problem, though very important, has often been overlooked by analytical chemists, who tended to regard it as a self-evident problem and treated it as a secondary topic; for them the primary interest has always been chemical analysis. This fact has had unfavourable repercussions on the analytical process in general and on the chemico-analytical control process in particular.

Whereas many books devoted to various techniques of analysis and of data processing have been published, the sampling process has been dealt with in only a limited number of survey articles and and books, an example being the book by Smith and James [1], and the section "Sampling for Chemical Analysis" in the *Analytical Chemistry Fundamental Reviews* [2].

If we consider the time spent on the three steps of the general analytical process [3], the literature data and our own experience, as well as chemometric and scientometric evaluations, show that the proportions are:

SAMPLING	MEASUREMENT	DATA PROCESSING
40%	20%	40%

At first sight, these figures may seem exaggerated, particularly as far as the sampling process is concerned. However, if we take into account on the one hand that the measurement process is nowadays largely automated and hence implicitly fast, and on the other that the sampling process consists of many preliminary steps before measurement — including separation — then the proportion given above for the sampling step, 40%, appears fully plausible.

In the future, as methods of analysis are further improved, the time taken for the analysis proper, i.e. measurement, will certainly be further reduced. The time assigned to sampling, on the other hand, can only be reduced by changing analytical science itself, by setting up methods that are as sensitive and selective as possible, and thus eliminating preconcentration steps and the separation of the components of a sample of complex composition. Improving the sampling process therefore means perfecting the total analytical process.

The sampling process is extremely intricate, and inadequate understanding of it can adversely and directly affect the analytical result and the reliability of the analytical information. In principle, knowledge of the sampling process means knowledge of the general analytical process and its application to solution of analytical problems. It might become a necessary requirement in the future that analytical chemistry teaching in higher-education institutions should begin with a study of the sampling process.

Unlike other languages, English, though very rich in terms, uses a single word, *sampling*, for describing several steps of the analytical process — picking out, storing, homogenizing and processing the sample for subsequent analysis. It is our opinion, based on many years' experience in teaching and laboratory work in analytical chemistry and chemical analysis, that the sampling process should also include the separation methods. These methods form a preliminary step in the measuring process, that is of analysis. In this way, the field of the sampling process would be considerably expanded and we could better argue for giving sampling more earnest attention. Many 'routine' analytical chemists of today still think that picking out the sample and processing it is the job of the auxiliary laboratory personnel, of the technicians. We do not contest such a view, but would stress that the personnel concerned should be carefully advised of the importance of the sample for the analytical process, on contamination hazards, and on possible degradation of the sample during processing. Starting with picking out the sample, and ending with the measurement and analysis of its individual components, we should always pay proper attention to knowledge of the sample's history and be sure of its homogeneity.

For these reasons, in this work we shall give correspondingly large weight to the problems of the history and homogeneity of samples of different origin. The analytical chemist must realize that lack of data concerning the history of the sample may affect the results of the analysis, and the analytical information in general, to a larger extent than does the measurement itself, as experienced chemists are doubtless aware. Ignorance of the sample's history may lead, for instance, to an incorrect selection of the analysis method and of the instruments used. Hence, it could prevent the adaptation of the operational parameters of the analysis method to the functional parameters of the measuring instrument. It follows that the sample analysed acts as the link for matching the method and instrument.

This work therefore proposes to discuss the problem of sampling from the general point of view of the analytical process, but also as a philosophical aspect of analytical chemistry and of chemical analysis. It is only on these lines that this book could contribute, in our opinion, to the education of future chemists in general and of analytical chemists in particular.

If we examine the general relation which characterizes any analytical measurement process,

$$P=f(C)$$

i.e. the relation which links a physical property (P) to the concentration of the component determined (C), we see that it is necessary to choose the physical property which gives the optimum sensitivity and precision in relation to the concentration of that component.

For these reasons, the methods of analysis, whether destructive or not, will be very diverse, but in any case a correct sampling procedure has to be applied to ensure the success of the determination.

Although many chemists believe that non-destructive methods lead to smaller errors from sample contamination, since they do not need dissolution or decomposition steps, the risk of contamination still exists. Because of the very high sensitivity of these methods, any surface modification, or lack of homogeneity of the surface and its contamination may lead to large errors in the analytical results. Hence utmost attention should be paid to the sample preparation process, regardless of the proposed analysis method. In destructive analyses it is necessary to use adequate reagents, with impurity levels below the level of the trace components to be determined. Reagents of very high purity are available today and these can be safely used in trace analysis, so destructive analysis can be carried out with very small errors caused by contamination. Even more important perhaps than contamination is the risk of loss of analyte during the preliminary steps, which should be avoidable, but can arise from lack of basic knowledge of chemical properties [4].

The most difficult problem, however, is how to ensure the best possible correlation between the two fundamental parameters of the analytical process — sensitivity and selectivity. Since it has been noticed that acting upon one of these parameters disturbs the other, an interdependence must exist between them. This can be most easily seen in the design of organic reagents. The desire to obtain organic reagents which give reactions that are as sensitive as possible has led to the synthesis of some reagents with remarkable performances from the point of view of sensitivity, e.g. dithizone or Arsenazo III, but unfortunately lacking in selectivity. To increase their selectivity can also be regarded as a sampling problem, since it is a problem of acting upon the sample to be analysed.

Analysis of some materials of great technological importance — in the nuclear or semiconductor industries for instance — or of some biological materials, often involves either a preconcentration or separation of the components of a complex mixture. This has led to the investigation, development and perfecting of new separation techniques. As already said, since the separation process precedes the measurement, it too must be included in the sampling process; it is only in this way that the place and role deserved by separation in the framework of the general analytical process may be recognized. The sample to be analysed, or rather its complexity, has necessitated the improvement of some separation techniques such as solvent extraction or the chromatographic methods, to mention only the most important of them.

Today we have at our disposal lanthanides of an advanced degree of purity, which are used in some frontier technologies. It is enough to mention here only the field of colour television, which has benefited most from the lanthanide compounds. Only 50 years ago, to obtain high-purity lanthanides seemed an unrealistic dream, especially in the case of neighbouring lanthanides with extremely close properties, such as the neodymium–praseodymium pair (which at one time were mistakenly thought to be a single element, called didydium).

The same problem may appear in the case of elements with very close ionic radii such as zirconium and hafnium or niobium and tantalum. Without separation techniques such as solvent extraction or the various chromatographic methods, getting such metals in the degree of purity needed both in laboratory work and by modern technologies would not have been possible. It is perhaps enough to mention here that the production of hafnium-free zirconium constitutes today a milestone of nuclear technology.

The study and even the discovery of natural radioactive materials, particularly the separation of the radioactive isotopes, have benefited tangibly from the separation techniques, starting with separation by fractional precipitation and continuing with distillation, volatilization and extraction, and with the chromatographic techniques. For laboratory use and, as a follow-up for engineering purposes, ‘tandem’ separation techniques have been used. In this way, techniques such as chromatographic extraction (used mainly for separating radionuclides) and ion-exchange chromatography have arisen. Both techniques have benefited from the introduction of liquid ion-exchangers.

From such facts, the importance of the separation processes is evident, but it apparently contradicts our introductory remarks concerning the lack of surveys of the sampling process. Including separation methods in the sampling process would mean that we already have enough books and survey articles in this field. However, few of the analytical chemists who work in the field of separation methods or teach analytical chemistry have had this idea of including the separation methods in the sampling process, and for this reason, in many chemistry and allied courses the separation methods are still taught after, and not before, the analysis methods, which contradicts the logic of the analytical process.

The purpose of this book — or, if you wish, its originality — is vested in the priority given to the separation process and its inclusion in the general process of sampling. We think that in this way we might contribute to the logical understanding of analytical chemistry as a science and of chemical analysis as an art [5] by chemistry students and chemical analysts.

To substantiate this claim, let us take two extremely complex analysis systems — analysis of petroleum fractions and analysis of the volatile components of coffee. In both cases, direct analysis cannot be carried out and high-performance separation techniques have to be called upon, for example capillary-column gas chromatography. The great efficiency of this technique permits separation of over a hundred components from such a complex mixture. The separation technique, and hence the sampling process, has also imposed the choice of a suitable detector, the mass spectrometer. This example shows that the improvement of the separation techniques has implicitly led to their coupling with suitable detectors, which is why such 'tandem' techniques as GC–MS, GC–FTIR, etc. have arisen.

To close these introductory remarks on the sampling process, let us point out the interdependence between two high-efficiency separation methods, gas chromatography (GC) and high-performance liquid chromatography (HPLC). These techniques are extensively applied for analysing various samples — inorganic, organic or biological. Although they are comparable in performance, they are also complementary. Whereas GC is mostly adequate for analysing volatile components which do not decompose at the relatively high temperature of the column, HPLC, which uses pressure as the main working parameter, covers a wider range of compounds and is applied with good results to thermally degradable compounds (such as dyes, active biological products, etc.). These techniques have already evolved beyond laboratory work and have produced either process chromatographs (GC) or industrial preparative chromatographs (HPLC, fitted with large-diameter columns, for obtaining high-purity solvents or pharmaceutical products).

It is evident then that the 40% allotted above to sampling time is not in the least exaggerated. The sampling process is the beginning of every analysis and at the same time it becomes a component of the engineering processes, especially of present day technologies such as the nuclear and semiconductor industries or biotechnology.

In what follows we shall try to scan, within four short chapters, the sampling process in the framework of the whole analytical process, with a view to clarify and establish the role, place and importance of the sampling process for basic and applied research in chemistry in general and in analytical chemistry in particular.

2

History of the sample

> "Today's trends are yesterday's dreams and tomorrow's accomplishments."

To ensure that analytical information is both reliable and accurate, the analytical chemist must be aware of, and if necessary take into account, the history of the sample to be analysed. This requires the analytical chemist to have a working knowledge of scientific disciplines in addition to chemistry, or to be prepared to acquire the knowledge necessary, after considering the nature of the sample.

We have stated elsewhere [6,7] that "the history of the sample influences indirectly, the precision and accuracy of the analytical results". Thus an awareness of the history of the sample will influence the analytical process in general and the chemico-analytical control process in particular.

An understanding of the importance of the history of the sample should be acquired at an early stage during the education of an analytical chemist. Unfortunately, the rather narrow approach often adopted during the education and training of chemists in general and analytical chemists in particular, does not allow for an in-depth study of other important scientific disciplines such as geochemistry, physiology, environmental science, etc. However, the varied nature of the sample to be analysed often requires knowledge of these other disciplines, in order that a correct approach can be made both to taking the sample and analysing for the components of interest. A good analogy is medical practice, where the doctor always takes a thorough case history before attempting a diagnosis.

Figure 2.1 illustrates the most significant connections of the history of the sample; we shall examine them in detail in this chapter.

2.1 BASIC CHEMISTRY

The first necessity for an analytical chemist is to have a sound knowledge of basic chemistry. This involves knowledge of the properties of both inorganic and organic substances, as well as a thorough understanding of physical chemistry.

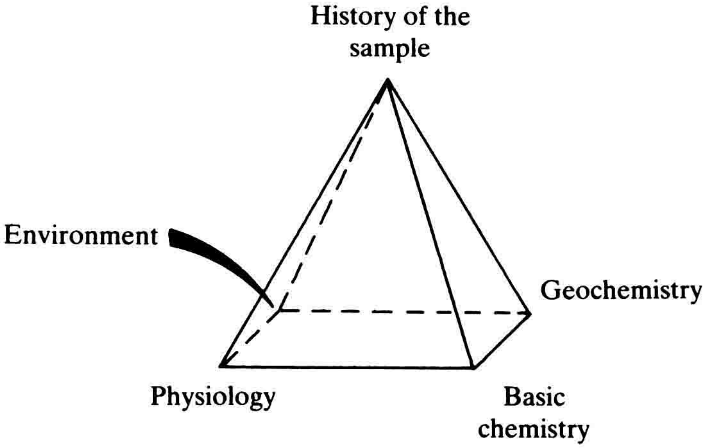


Fig. 2.1 — Connections of the history of the sample [5,7].

The rapid development of theoretical chemistry has caused many chemists, and unfortunately many analytical chemists, to neglect their knowledge of descriptive chemistry, so much so, that the need for this very knowledge of descriptive chemistry often causes chemical analysis to be regarded as an 'art'. Only by knowledge of the properties of the elements and their compounds, can correct analytical decisions be made. Unfortunately, there are few short textbooks available which are able to cover all the basic principles of chemistry and therefore it is often necessary to refer to specialist texts in inorganic, organic, physical and biological chemistry, etc. in order to find the necessary information about a sample.

Because of the increasing specialization in the various fields of fundamental chemistry, there is a growing lack of general knowledge in the field. Education in chemistry in general, and especially in analytical chemistry, should try to ensure that the student acquires adequate background knowledge not only of the various fields of chemistry, but of allied scientific disciplines as well. We argued this point more completely in a book entitled "Education and Teaching in Analytical Chemistry" [8].

Let us consider a number of examples derived from laboratory practice, which support the argument that a sound knowledge of basic chemistry is often required for the sampling process. The analytical chemist, like an 'artist', will have to learn first the 'musical notes', in order to produce a 'symphony' that is to characterize a sample of a material.

There are three fundamental interdependent concepts of analytical chemistry — quality, quantity and structure. To characterize any kind of material — any type of sample, we have to establish first the nature of the components constituting it, that is its quality; then we have to find the ratios between these various components, i.e. to analyse the sample quantitatively; finally, and most importantly, we must elucidate the component structure(s) by means of the various methods of structural analysis. It is a great mistake, unfortunately still made today in many institutions of higher