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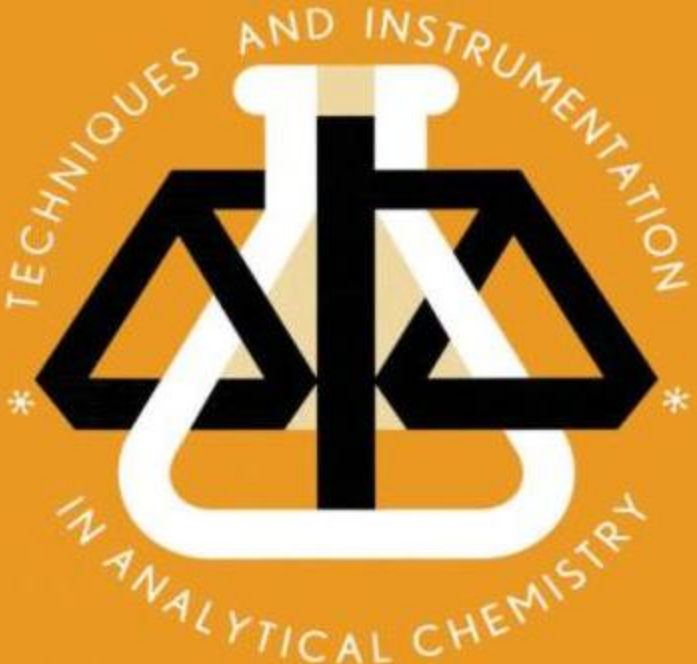

ACCELERATION AND AUTOMATION OF SOLID SAMPLE TREATMENT

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Foreword

Writing a book is always an audacious act, but writing a book such as this one on sampling and sample pretreatment is even more than that: it is a real challenge. The book encompasses the entire field of analytical chemistry and oozes a profound knowledge of the concepts involved.

The role of the analytical chemist has changed profoundly over the past few decades. The levels of analytes that can be determined routinely have decreased by several orders of magnitude and the sample sizes that need to be handled have dropped significantly in recent years. In parallel, the overall number of determinations that need to be performed has grown enormously. Also, the advent of intelligent instruments and laboratory automation has help analytical chemistry become a real information science. This significant, steady progress in analytical science, however, has been brought about as much by gradual advances in the preliminary steps of the analytical process (e.g. sample handling) as by a number of leaps in technological progress.

Often, in discussing analytical science, chemical measurements are reduced to fundamental processes such as detection, identification or quantitation. Although analytical and data processing techniques are dealt with in many books, sampling and sample pretreatment have so far been the subject matters of only a few books and review articles. This sustained lack of attention is surprising if one considers the overall time spent on these preparatory stages leading to the final analytical act and when one realizes how intricately the quality of the results depends on the initial, preparatory steps of an analysis. The development of clean sampling and handling techniques, which involves substantial investments of time and resources, has always been a mandatory step towards obtaining accurate, reliable final analytical data.

Scientific journals are rarely considered to be appropriate forums for discussing the guiding principles behind sampling and sample pretreatment. A book like this, which brings together all relevant wisdom and knowledge on this particular field, is therefore a more than welcome addition to the analytical chemist's library.

This particular book is designed to provide the analytical chemist with the background required to understand the concepts inherent in automated solid sample pretreatment. Its chapters provide a logical, systematic introduction to all aspects involved in the different methods of sample pretreatment and their automation. Topics such as freeze-drying, ultrasounds, microwave treatment, high pressure, high temperature solvent extraction, superfluid extraction, laser ablation and laser-induced plasma spectroscopy, the use of electrothermal devices and glow-discharge processes, are dealt with in sequence in all their relevant aspects. One chapter is devoted to specific sample pretreatment methods

involving the removal of volatile species and provides a comprehensive discussion of hydride generation, headspace sampling, pervaporation and solid-phase micro-extraction. Automated and computer-controlled methods are given proper emphasis throughout, and the role of workstations and robots in the analytical process is discussed in a separate chapter.

Many of the ideas presented in this book have matured through the years from the wide experience gathered by the authors in the pursuit of their research on analytical chemistry and practical analysis at the University of Córdoba, where Professor Luque de Castro leads a research group specializing in "Innovations in Continuous and Discrete (Robotic) Systems for the Automation of Analytical Methods" at the Department of Analytical Chemistry. Her research interests include the combined use of discrete (robotic) and continuous (flow injection and completely continuous flow) systems for the development of fully automated methods; the design of flow-through (bio)chemical sensors; immunoassays; chromatographic and non-chromatographic continuous separation techniques; solid-sample pretreatment by subcritical and supercritical fluid extraction; focused and multimode microwaves and ultrasounds; laser-induced processes; applications to environmental, clinical and food analysis; and on-line process monitoring. She has co-authored several books on subjects such as Flow Injection Analysis, Automatic Methods of Analysis, Non-Chromatographic Continuous Separation Techniques, Analytical Supercritical Fluid Extraction and Flow-Through (Bio)chemical Sensors.

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Preface

Analytical Chemistry has traditionally been largely ignored by society and even by the scientific community, which, at most, has used it in the service of the other sciences. At present, Chemistry itself appears to have been reduced to a similar status. For example, the cover story of the August 20, 2001 issue of Time magazine was entitled "America's Best Science and Medicine" and, in it, the editors focused on the most exciting fields of research and then looked for the men and women who were doing the most cutting-edge research in such fields. The eighteen individuals honoured by the magazine — none of whom was a chemist — were conducting work in fields such as cell biology, the human origin, child psychology, pediatrics, genomics, cardiology, oncology, climatology, ecology, AIDS research, astrophysics, paleontology, biomedical engineering, neurobiology, cell death, spinal cord repair and molecular mechanics. In this issue, Time reflected present social perceptions in positing the following two destructive equations: science = biology and cutting edge = medical progress. Clearly, however, all these sciences rely on Chemistry and, ultimately, on Analytical Chemistry — which, invariably, provided the data that led to the achievements distinguished by Time.

We analytical chemists have always been aware of such unfair ignorance and yet have continued to work in pursuance of our goals. This book is a modest contribution intended to help those aiming to meet one of the most pressing needs of Analytical Chemistry: automation. A need that has arisen from the increasing demand for analyses in various fields of social interest including industry, health and the environment. Because sample pretreatment is the single step of the analytical process in greatest need of automation, this book compiles the wide range of tools available for this purpose with a view to assisting current and future users in choosing the best tool for each problem. Also, because full automation is almost always impossible, the primary goal — and also the main achievement in some cases — is to expedite this analytical step. Hence the book's title.

Rather than a comprehensive discussion of available choices for expediting or automating sample pretreatment, this book provides a description of the most widely favoured choices at present and those with a high potential which, however, remains largely unexplored. Its ten chapters revolve around this criterion.

The first chapter introduces both general aspects of sample preparation and the main problems encountered in automating sample treatments. The second provides a brief discussion of the underexploited potential of freeze-drying for delivering samples in forms that facilitate their subsequent analysis. Chapter 3 is devoted to a kind of energy that has also received inadequate attention from analysts: ultrasounds.

Those analytes that are either volatile or easily converted into volatile products are good candidates for separation from solid matrices by use of classical techniques such as hydride generation and dynamic or static headspace sampling, or more recent alternatives such as solid-phase microextraction and analytical pervaporation — with which virtually the whole research group headed by the authors is acquainted; all are dealt with in Chapter 4. The growing use of microwaves in both batch and continuous systems is the subject matter of Chapter 5, where the authors have strived — whether successfully or not readers will tell — to avoid overemphasizing their own work. The controversial, sparse applications of high-pressure, high-temperature solvent extraction, a widely used technique of a high potential, are systematically discussed in Chapter 6.

Chapter 7 describes the rapid expansion of supercritical fluid extraction but also how its scope has been restricted by differences in the behaviour of analytes naturally occurring in samples and those added to them for the purpose of analysis. Chapters 8 and 9 deal with various atomic techniques in which the authors are no experts, so any omissions or overpraising are totally unintentional. Chapter 8 is concerned with the use of electrothermal vaporizers and atomizers, and glow-discharge sources, with solid samples; it also provides a brief description of alternative techniques with a weaker impact that include arc nebulization and direct solid sample insertion. Chapter 9 describes the most salient laser-based techniques for solid sampling, namely: laser ablation and laser-induced breakdown spectroscopy; this chapter and the previous one examine the advantages and disadvantages of coupling the respective devices to analytical instruments.

Finally, Chapter 10 focuses on robotic treatment, the only currently available choice for completely automated solid sampling by virtue of its ability to have samples weighed without human intervention. Because of their high cost, robotic stations and, especially, workstations, are inaccessible to many users, so their capabilities are only outlined in the book. Would-be users should thus seek more comprehensive information — which continues to grow and change day by day, particularly as regards workstations — before they embark on the costly venture of setting up a robotic configuration.

The authors wish to express their gratitude to Antonio Losada, MSc, for his linguistic revision of the manuscript, Francisco Doctor for drawing the artwork and José Manuel Membrives for producing the tables.

The authors
Córdoba, December 2001

Chapter 1

Introduction to solid sample pretreatment

1.1. CONVENTIONAL PROCEDURES FOR SAMPLE PRETREATMENT AND THEIR STANDARDIZATION

Analytical processes typically consist of several discrete steps. While some steps such as measurement and transduction of the instrumental signal, and data collection and processing, are common to all analytical processes, those preceding the insertion of the treated sample into the instrument for measurement (viz. sampling, dissolution, clean-up, preconcentration, individual separation, derivatization), which are critical with a view to ensuring the obtainment of accurate, reproducible results, vary markedly from process to process. Virtually all analytical methods include a sample preparation step. Despite the dramatic advances in analytical equipment and microcomputer technology, many sample preparation practices continue to rely on 19th-century technologies. For example, the ubiquitous *Soxhlet extraction* was developed more than one hundred years ago; also, many of the sample preparation techniques currently in use have been around for decades with little or no improvement over the years.

The most common methods for analyte removal or sample dissolution are as follows:

(a) *Leaching*, which involves a solid–liquid extraction with an appropriate solvent (water for ionic compounds or a more or less polar solvent for non-ionic substances).
(b) *Sample digestion*, which is usually done with pure or mixed concentrated acids.
(c) *Fusion*, in which the sample is mixed with an appropriate flux material and heated until melting, after which the mixture is allowed to cool and the fusion cake dissolved in a suitable solvent.
(d) *Dry ashing*, which is especially common as a preliminary step in the analysis of organic samples for metallic and non-metallic elements. The sample is heated at 400–500°C in a muffle furnace for several hours and the target elements are either converted into gaseous species and collected into an appropriate absorber for determination or kept as a residue and dissolved into a suitable acid for analysis.

One of the main constraints on conventional procedures for sample preparation is their lack of uniformity. In fact, many users introduce specific modifications in the general procedures that eventually result in enormous differences in the way they are implemented. Such a lack of uniformity precludes comparison of results obtained using what was seemingly the same procedure and validation of the ensuing methods. Comparability of the results can thus only be achieved by using actually identical procedures; this justifies the efforts currently in progress at standardizing sample preparation procedures.