Extraction Methods in Organic Analysis

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Edited by

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Extraction Methods in Organic Analysis

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Preface

Sample extraction plays an ever increasing role in modern analytical methodology. Similar to sampling, it provides one of the key steps prior to the final analytical determination, and, if carried out effectively, it assures the validity of the measurement. The explosion of interest in extraction and sample preparation methodologies in recent years has seen the introduction of many new techniques, fuelled by scientific and industrial demand for faster and simpler analysis. Much has been published on the topic in journals, and a considerable database of applications has evolved. However, there have been few books dedicated to extraction methods in organic analysis, especially the newer methods. The aim of this book is therefore to provide a complete, up-to-date and practical reference work for scientists and technologists involved in both sample preparation and analysis, whether in academic or industrial laboratories and irrespective of scientific discipline.

I have attempted to include all of the most important new developments in the area. Following a short introduction, chapter 2 sets the scene by describing the more classical methods used in liquid/liquid and liquid/solid extractions. Chapters 3 and 4 consider the applications and developments of Solid Phase Extraction (SPE), Solid Phase Micro Extraction (SPME), and Membrane Extraction with Sorbent Interface (MESI). Chapters 5, 6 and 7 describe the key alternative technologies for solid/liquid extraction: Supercritical Fluid Extraction (SFE), Pressurised Fluid Extraction (PFE) or Accelerated Solvent Extraction (ASE) and Microwave-Assisted Solvent Extraction (MAE). Each of these chapters is designed to provide an insight into the basic principles, the theory, the equipment, the strategies for method development, the applications and the future developments and directions. The final three chapters revisit the application areas in greater depth, examining the main areas for extraction technology: Biological and Pharmaceutical Analysis, Analysis in the fields of Polymers and Polymer Additives, and Environmental Monitoring.

To cover such a wide remit, authors have been sought from both the academic and industrial sectors, to bring the necessary expertise and balance to the volume. This, I feel, has helped to produce an informed and comprehensive review of the current status of organic extraction technology.

I would like to thank the authors for the time, energy and effort that went into the writing of each chapter, and for their excellent manuscripts, which required little or no editing.

A.J. Handley

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1 Introduction

Alan J. Handley

Organic analysis plays an important role in the development of current science as it underpins many of the key areas of technology, such as pharmaceutical and biological science, polymer technology, food technology and agrochemicals, and it can provide the means of monitoring and regulating such industries. The dictionary describes organic analysis as the resolution of a chemical compound into its proximate or ultimate parts, and the determination of its elements or the foreign components it may contain. This process can be designed to provide qualitative data, but it can also lead to the need for quantitative measurement.

Analysis is comprised of three key processes: sample preparation, sample analysis and data handling and interpretation—often described as the 'Analysis Cycle' (Figure 1.1).

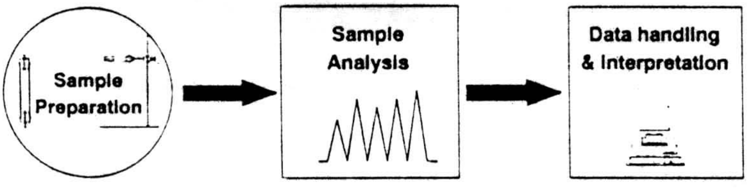

Figure 1.1 The Analysis Cycle.

Although some samples are inherently ready for analysis, most require some form of pretreatment before they can be presented to the analytical technique of choice. The pretreatment will depend on the physical requirements of the instrument (liquid, solid or gaseous sample), the scope of the measurement (ppb, ppm, percentage levels of the determinants), and the complexity of the sample. Sample pretreatment in its simplest form can involve dilution, filtration, evaporation or centrifugation. However, with the continuing trend to examine more complex samples and samples with constituent components at lower and lower levels, sample extraction is becoming increasingly important as a preparation step. This is evident if we examine the main areas from which we obtain or generate samples for organic analysis.

Product development—the pharmaceutical industry has seen an explosion of newer products requiring development and testing, with analytical assays having to be closely regulated and determinations made in very complex matrices.

Product formulation—the pharmaceutical, food and agrochemical industries are required to control and monitor lower and lower levels of by-products in their formulations which, in themselves, are becoming more complex in nature.

Product production—increasing pressures to control plant effluents, together with the ability of newer analytical technologies to measure lower and lower compound levels, has resulted in increased regulatory restrictions on compounds previously considered to be nondetectable.

All these factors result in the need for more sample pretreatment/extraction prior to analysis, to enable accredited analytical data to be obtained. This may involve either sample clean-up, sample concentration, or changing the physical form of the sample to make it more amenable to the analytical technique of choice (Figure 1.2).

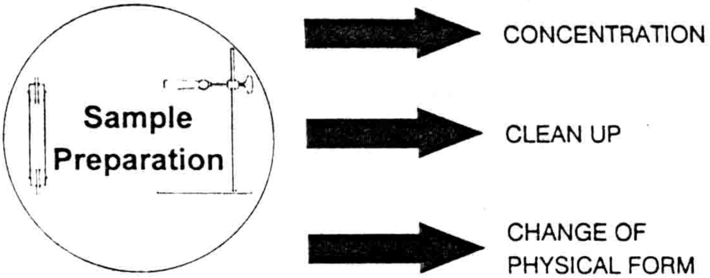

Figure 1.2 The role of extraction in sample preparation.

Sample extraction encompasses all those steps necessary to prepare the original sample for determination by the chosen method. Strategically, the extraction method chosen can influence the entire process, and will depend on: the chemistry of the analyte(s); the nature of the matrix; the objectives of the analysis; and the limit of determination. The relative importance of these factors will vary depending on the measurement requirement.

Many extraction practices, however, are based on classical methodologies of liquid/liquid or liquid/solid extraction, using practices (separating funnels and Soxhlet extractors) which have not changed appreciably for the past one hundred years. The most commonly used technique has been liquid extraction, based on the observation that organic compounds can usually be removed from a matrix by extraction with a water-immiscible solvent. This method relies largely on the relative solubility, diffusion, partitioning, viscosity or surface tension of the component(s) of interest and the solvent. At first sight, this may appear simple and straightforward but, to achieve high recoveries, it is often necessary to repeat the extraction process several times and then to bulk the fractions together prior to analysis. This is also true of solid/liquid extraction, where samples have to be continually extracted—in some cases for days—to obtain the desired efficiency of extraction. So, while classical extraction procedures can be very effective, they can also be extremely labour-intensive and time-consuming, and can require large amounts of solvent.

Two principal factors have been responsible for speeding up developments in the area of extraction:

(i) The need for faster, high throughput analysis. If we look back at the Analysis Cycle, there have been tremendous advances in the automation capabilities of the equipment for both analytical measurement and data-handling, to the extent that, for a complete qualitative and quantitative analysis, the analysis times have decreased from hours or sometimes days. Thus, in many cases, sample preparation or extraction is now the major rate-determining step in the analysis.

(ii) The concerns about the hazardous nature of many of the commonly used solvents, the problems and cost of disposal, and the associated question of solvent emissions during the concentration of large volumes of sample extracts.

Recent years have seen considerable efforts to develop alternative and improved methods of extraction, and to make them commercially available. This has resulted in a number of systems being developed commercially for both liquid/liquid and solid/liquid extraction (Table 1.1).

Table 1.1 Extraction technologies

Classical	Primary sample matrix	Primary extraction phase	New technologies
Solvent extraction Membrane extraction	Liquid	Liquid	Solid phase extraction Solid phase micro-extraction
Soxhlet	Solid	Liquid	Accelerated or pressurised fluid extraction, Microwave-assisted solvent extraction, Supercritical fluid extraction

Some, such as Supercritical Fluid, Accelerated or Pressurised, and Microwave-assisted Extraction, use different driving conditions to speed up the process, while others use alternative technologies, such as Solid Phase and Solid Phase Micro-extraction, to reduce solvent volumes. Other approaches have involved the evolution of classical methodology, with the launch of the automated Soxhlet and countercurrent extraction systems.

Such developments have resulted in systems now capable of providing: faster extractions and systems which are easier to automate; completeness of extraction, with recoveries equal to or exceeding those of older methods; analyte selectivity; robust and reproducible methodology, equal to or exceeding that of older methods; elimination of the use of some of the more hazardous solvents, by the selection of different modes of extraction (pressure, temperature and density); reduction of solvent volumes and, hence, reduction in the cost of operation (solvent use and disposal); and ease of coupling to other analytical instrumentation.

The chapters that follow describe the various technologies in full, together with the processes, the equipment, the protocols for method development, and the many applications.