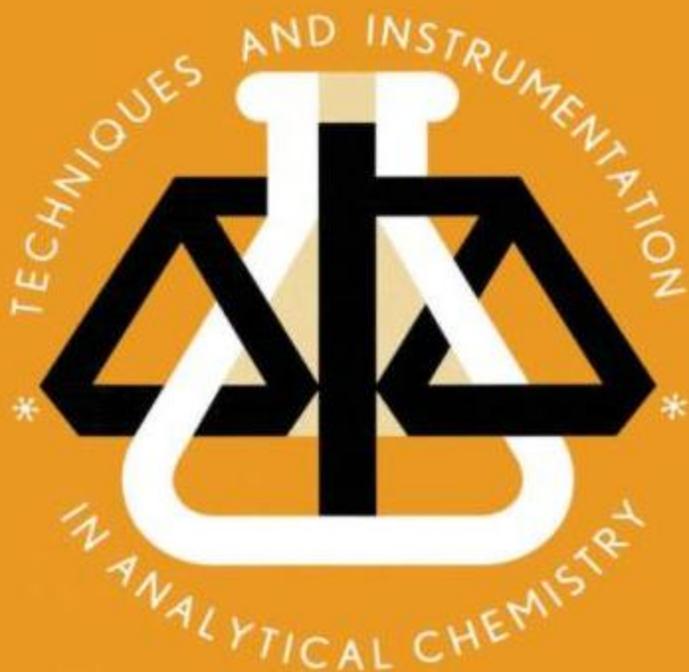


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ACCELERATION AND AUTOMATION OF SOLID SAMPLE TREATMENT

M.D. LUQUE DE CASTRO
and
J.L. LUQUE GARCÍA

ELSEVIER SCIENCE B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

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Contents

Foreword by Freddy Adams	xiii
Preface	xv
CHAPTER 1. INTRODUCTION TO SOLID SAMPLE PRETREATMENT	
1.1 Conventional procedures for sample pretreatment and their standardization	1
1.2 The state of the art in sample preparation	2
1.3 Problems encountered in automating sample preparation	4
1.4 Batch versus serial approaches to automated sample preparation	5
1.5 Definitions and restrictions of term meanings	7
1.5.1 Sample preparation and sample pretreatment	7
1.5.2 Solid sampling	7
1.5.3 Digestion versus leaching	8
1.5.4 Use of a leaching step versus a digestion step	8
1.5.5 Leaching versus extraction	8
1.6 Some notes on the book contents	9
References	10
CHAPTER 2. ANALYTICAL FREEZE-DRYING	
2.1 Introduction	11
2.2 Steps of the freeze-drying process	12
2.2.1 The freezing step	12
2.2.2 The sublimation step	13
2.2.3 The desorption step	16
2.3 Variables influencing the freeze-drying process	17
2.4 Freeze-drying methods	19
2.4.1 The manifold method	19
2.4.2 The batch method	21
2.4.3 The bulk method	21
2.5 Computer-assisted analytical freeze-drying	21
2.5.1 Computer-assisted freezing	21
2.5.2 Computer-assisted sublimation	22

2.5.3	Computer-assisted desorption	23
2.6	Laboratory-scale freeze-dryers	23
2.6.1	Basic components of a laboratory freeze-dryer	23
2.6.2	Evolution of laboratory freeze-dryers	24
2.6.3	Laboratory-designed freeze-dryers	26
2.6.4	Commercially available freeze-drying equipment	27
2.7	General aims of analytical freeze-drying	30
2.7.1	Increasing long-term storage stability	30
2.7.2	Preparing tissues for microscopic examination	31
2.7.3	Preparing samples as an intermediate step in (bio)chemical analytical procedures	31
2.7.4	Recovering products from a reaction mixture	32
2.8	Analytical uses of freeze-drying	32
2.8.1	Reagents	33
2.8.2	Standards	33
2.8.3	Samples	35
References	39

CHAPTER 3. ANALYTICAL USES OF ULTRASOUNDS

3.1	Introduction	43
3.2	General aspects of the cavitation phenomenon	44
3.3	Types of ultrasonic devices	46
3.4	Ultrasound-assisted leaching	48
3.4.1	Batch systems	49
3.4.2	Continuous systems	54
3.4.3	Ultrasound-assisted leaching versus other leaching techniques	60
3.5	Ultrasound-assisted sampling	61
3.5.1	Ultrasonic nebulizers	62
3.5.2	Ultrasonic slurry sampling	66
3.5.3	Acoustically levitated droplets	69
3.6	Ultrasound-assisted electroanalysis	71
3.7	Other analytical uses of ultrasounds	75
3.7.1	Ultrasonic degassing	75
3.7.2	Ultrasonic filtration	77
References	79

CHAPTER 4. SOLID SAMPLE TREATMENTS INVOLVING THE REMOVAL OF VOLATILE SPECIES

4.1	Introduction	83
4.2	Hydride and cold mercury vapour generation	84
4.2.1	Introduction	84
4.2.2	Samples, analytes and reagents	84
4.2.3	The separator and its associated equipment	86
4.2.4	Variables influencing vapour generation	89

4.2.5	Features of methods based on hydride or cold mercury vapour generation	90
4.2.6	Applications	91
4.3	Headspace sampling	93
4.3.1	Introduction	93
4.3.2	Equipment and procedures	93
4.3.3	Theoretical background	103
4.3.4	Variables affecting performance	113
4.3.5	Calibration and analytical features	121
4.3.6	Applications	125
4.4	Analytical pervaporation	128
4.4.1	Introduction	128
4.4.2	Principles of pervaporation	128
4.4.3	The analytical pervaporator and auxiliary units	130
4.4.4	Pervaporation efficiency	134
4.4.5	Variables influencing analytical pervaporation	135
4.4.6	The physics of analytical pervaporation: kinetics of the mass transfer process	139
4.4.7	Analytical features of pervaporation methods	141
4.4.8	Scope of application of analytical pervaporation	143
4.4.9	Prospects for analytical pervaporation	154
4.5	Solid-phase microextraction (SPME)	154
4.5.1	Introduction	154
4.5.2	Principles, devices and theoretical aspects of SPME	155
4.5.3	Variables affecting SPME	161
4.5.4	Analytical features of SPME	169
4.5.5	Advantages and shortcomings of SPME	170
4.5.6	Applications of SPME	171
References	173

CHAPTER 5. MICROWAVE-ASSISTED SOLID SAMPLE TREATMENT

5.1	Introduction	179
5.2	Fundamentals of microwave energy and its interaction with matter	180
5.2.1	Dissipation factor	181
5.2.2	Transformation of microwave energy into heat	181
5.2.3	Microwave heating	182
5.3	Microwave equipment	183
5.3.1	Main components of a microwave device	184
5.3.2	Closed-vessel microwave systems	186
5.3.3	Open-vessel microwave systems	192
5.3.4	Closed versus open microwave systems	205
5.4	Variables governing microwave-assisted processes	207
5.4.1	Microwave power and exposure time	207

5.4.2	Temperature and pressure	208
5.4.3	Type of solvent	208
5.4.4	Influence of sample viscosity and sample size on microwave heating	211
5.5	Applications of microwaves to solid sample treatment	212
5.5.1	Microwave-assisted digestion	212
5.5.2	Microwave-assisted extraction	218
5.5.3	Microwave-assisted sample drying	222
5.5.4	Microwave-assisted distillation	223
5.5.5	Microwave-assisted protein hydrolysis	223
5.6	Safety considerations on the use of microwave energy	224
	References	225

CHAPTER 6. HIGH-PRESSURE, HIGH-TEMPERATURE SOLVENT EXTRACTION

6.1	Introduction	233
6.2	Variables affecting the extraction process	235
6.2.1	Temperature	236
6.2.2	Pressure	237
6.2.3	Solvent type	238
6.2.4	Solvent volume	239
6.2.5	Solvent flow-rate	240
6.2.6	Matrix composition	240
6.2.7	Sample size	241
6.2.8	Extraction time	242
6.3	Accelerated solvent extraction (ASE)	242
6.3.1	Steps involved in the ASE process	243
6.3.2	ASE devices	245
6.3.3	Combination of ASE with other operations of the analytical process	247
6.3.4	Applications of ASE	249
6.3.5	Comparison of ASE with other solid-liquid extraction (leaching) techniques	253
6.4	Dynamic pressurized hot solvent extraction (DPHSE)	259
6.4.1	DPHSE devices	260
6.4.2	Steps of the DPHSE process	263
6.4.3	Water as a leaching agent	265
6.4.4	Automation and improvement of steps subsequent to DPHSE	266
6.4.5	Applications of DPHSE	269
6.4.6	Comparison of DPHSE with other leaching techniques	273
	References	274

CHAPTER 7. ANALYTICAL SUPERCRITICAL FLUID EXTRACTION

7.1	Introduction	281
7.2	Properties of supercritical fluids	281
	7.2.1 Properties of the supercritical region	283
	7.2.2 The solubility parameter	285
7.3	Laboratory-built and commercial supercritical fluid extractors	286
	7.3.1 Basic components of a supercritical fluid extractor	286
	7.3.2 Operational modes	290
	7.3.3 Commercial supercritical fluid extractors	290
7.4	Variables influencing supercritical fluid extraction (SFE)	292
	7.4.1 Properties of the supercritical fluid	294
	7.4.2 Properties of the analyte	300
	7.4.3 Properties of the sample	301
	7.4.4 Dynamic and geometric variables	303
	7.4.5 Analyte collection modes	306
7.5	Approaches to improving SFE performance	307
	7.5.1 Using an alternative supercritical fluid	309
	7.5.2 Ion-pairing	311
	7.5.3 Esterification and related reactions	312
	7.5.4 Formation of organometals	312
	7.5.5 Chelation	313
	7.5.6 Micellization	314
7.6	Hyphenated techniques	315
	7.6.1 Supercritical fluid extraction–chromatography	316
	7.6.2 Miscellaneous combinations	321
	7.6.3 Types of detectors used in combination with supercritical fluid extractors	325
7.7	Applications of supercritical fluid extraction	328
	7.7.1 Selectivity in supercritical fluid extraction	329
	7.7.2 Scope of application	329
	7.7.3 Comparison with other analyte removal techniques	331
7.8	Present and future of supercritical fluid extraction	340
	References	341

CHAPTER 8. DEVICES FOR SOLID SAMPLE TREATMENT PRIOR TO INTRODUCTION INTO ATOMIC SPECTROMETERS: ELECTROTHERMAL DEVICES AND GLOW-DISCHARGE SOURCES

8.1	Introduction	347
8.2	Electrothermal atomizers and vaporizers	348
	8.2.1 Fundamentals of electrothermal vaporizers and atomizers	348
	8.2.2 Solid sampling modes in electrothermal vaporizers and atomizers	355

8.2.3	Variables of solid sampling with electrothermal vaporizers and atomizers	358
8.2.4	Steps of an electrothermal solid sampling process	364
8.2.5	Instrument parameters affecting solid sampling with electrothermal atomizers and vaporizers	366
8.2.6	Use of modifiers in electrothermal solid sampling	366
8.2.7	Shortcomings of electrothermal sampling	373
8.2.8	Calibration in methods involving electrothermal sampling of solid samples and slurries	374
8.2.9	Applications of electrothermal solid sampling prior to introduction into an AAS, ICP-AES, AFS or ICP-MS instrument	377
8.3	Glow-discharge sampling	385
8.3.1	Introduction	385
8.3.2	Principles of the glow-discharge	386
8.3.3	Glow-discharge sources: geometry and improvements	393
8.3.4	Nature of the sample for glow-discharge sampling	399
8.3.5	Sample state and preparation for glow-discharge sampling	399
8.3.6	Variables affecting glow-discharge sampling	400
8.3.7	Glow-discharge sampling as coupled to spectrometric detection ...	404
8.3.8	Advantages and restrictions of glow-discharge sampling	413
8.3.9	Models and calibration in methods involving glow-discharge sampling	413
8.3.10	Applications of glow-discharge sampling in combination with spectrometries	416
8.3.11	Trends in glow-discharge sampling	424
8.4	Other solid sampling approaches	425
8.4.1	Arc nebulization	425
8.4.2	Direct sampling insertion devices	427
References	427

CHAPTER 9. LASER-ASSISTED SOLID SAMPLING

9.1	Introduction	435
9.2	Laser ablation	437
9.2.1	Features of ablation lasers	437
9.2.2	Steps and thresholds in laser ablation	440
9.2.3	Craters and amount of ablated material	441
9.2.4	Sample preparation for laser ablation	442
9.2.5	Ablation cells	443
9.2.6	Transport of ablated material	445
9.2.7	Mixed gas sample introduction	445
9.2.8	Equipment	446
9.2.9	Calibration techniques for laser ablation-atomization-ionization-excitation-detection	446

9.2.10	Shortcomings of laser ablation	448
9.2.11	Selected applications of laser ablation sampling prior to atomization–ionization–excitation–detection	449
9.2.12	Comparison of laser-assisted sampling with other sampling techniques	456
9.3	Laser-induced plasma spectroscopy	461
9.3.1	Introduction	461
9.3.2	Features of LIBS	461
9.3.3	Steps and thresholds in LIBS	462
9.3.4	Experimental set-up for LIBS	464
9.3.5	Basic aspects of LIBS	464
9.3.6	Variables affecting LIBS performance	466
9.3.7	Shortcomings of LIBS	473
9.3.8	Data collection: detector delay	477
9.3.9	Data analysis	479
9.3.10	Applications of LIBS	480
9.3.11	Comparison of LIBS with alternative techniques	489
9.3.12	Laser-induced breakdown–mass spectrometry	492
References	495

CHAPTER 10. ROBOTIC SOLID SAMPLE PRETREATMENT

10.1	Introduction	501
10.2	Workstations, robots, modules and peripherals	503
10.2.1	Workstations	503
10.2.2	Robots	506
10.2.3	Modules and peripherals	508
10.2.4	Detectors	510
10.2.5	Miscellaneous considerations on workstations and robotic stations	511
10.3	The role of robots in the analytical process	512
10.3.1	Single-task robots and simple uses of robotics	512
10.3.2	Sample preparation	513
10.3.3	Robotic development of the whole analytical process	515
10.3.4	Combining robotic and continuous systems for more reliable development of the whole analytical process	516
10.4	Analytical scope of application of robotics	521
10.5	Present and future of robotics	524
References	526
Index	529

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 helped 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.

Freddy Adams
University of Antwerp, Belgium

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

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.