Solvent Microextraction

Theory and Practice

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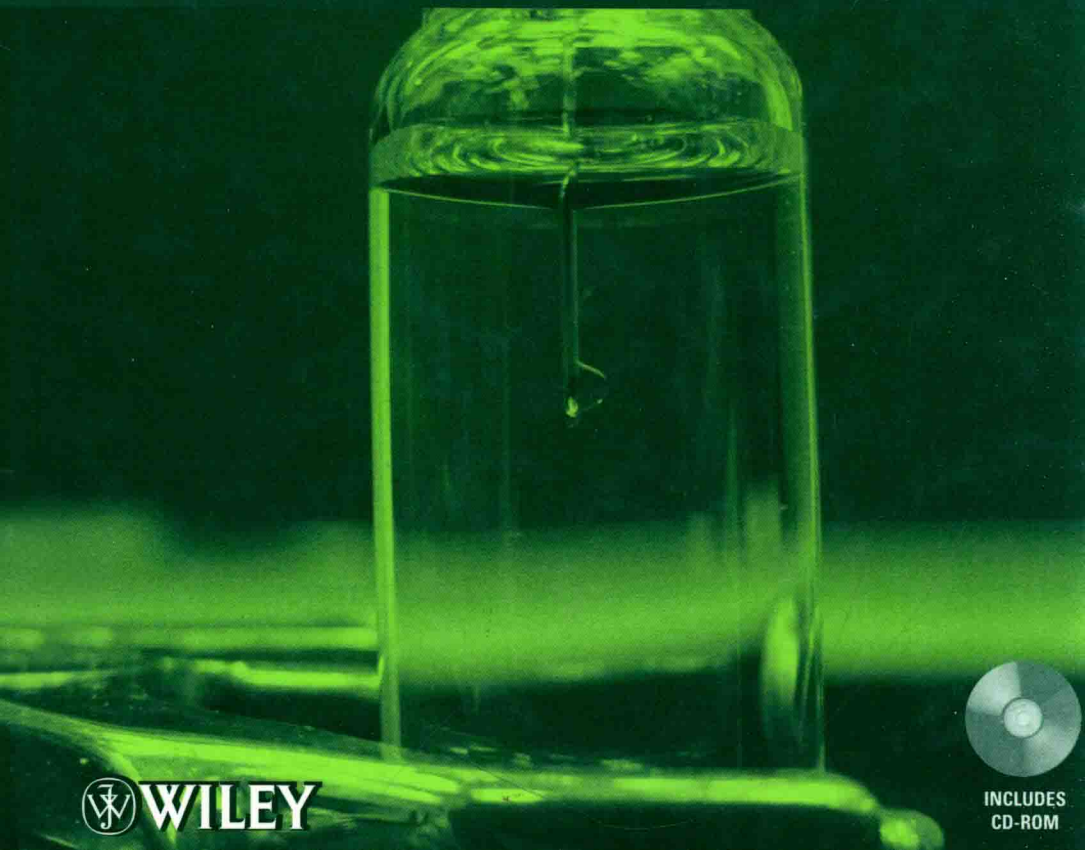

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Theory and Practice

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SOLVENT MICROEXTRACTION

We dedicate this book to our parents, wives, and children, and thank them for their love, patience, and understanding:

to Cora, Michael, and Sarah

to Anna, Marcin, and Katarzyna

and to Lori, Erin, and Ben

PREFACE

From its inception as a curious and possibly useful academic research technique, solvent microextraction (SME) has, in the last dozen or so years, blossomed and matured into an important tool not only for research, but also for practicing industrial, forensic, clinical, and environmental analysts. SME has been used in the analysis of metabolic products in biological fluids, in contaminants in drinking and wastewater, in soils, in foods, in plastics, and in pharmaceuticals. It is a unique methodology, requiring little more than a manual microsyringe and a few microliters of solvent, in its simplest forms, for the extraction and concentration of ultratrace to percent levels of volatile, semivolatile, polar, or ionized organic and inorganic analytes from liquids and solids. The number of application papers in the field has grown to well over 600, an indication of its usefulness. However, SME has also suffered from two major deficiencies: the inability to automate the procedure and a single source the analyst could use to find a useful compilation of reference material, a guide to proper experimental procedures, and a better understanding of how and why the technique works. Recently, the ability to completely automate the single-drop microextraction mode of SME has been made available, which allows the unattended sampling and instrumental analysis of samples. Removing the second deficiency, making SME a truly practical analysis tool, is the purpose of this book, which we hope will find its place on the shelf with other useful manuals available to the practicing analyst.

Acknowledgments

We wish to acknowledge the following individuals and organizations whose help was invaluable in completing this work. Students who have worked with us over the years to develop the SME technique include Aaron Theis, Philip Tourand, Susan Hansen, Jenna Bungert, Adam Waldack, Jenna Schwartz, and Charlene Schnobrich

from St. Cloud State University, and Joel Austin, Andrew Essenmacher, Ryan Jones, Casey Essary, Donald Harris, Rashad Simmons, Sydney Forrester, and Nicole Booms from Kettering University. In addition, we wish to thank Bruce Deitz from the Kettering University library for his help in obtaining and compiling references, Ingo Christ and Chromsys LLC for the research collaboration and the single magnet mixer used in this work, and finally, CTC Analytics AG for making available the PAL autosampler instrumentation used in developing the experimental procedures described in this book.

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CHAPTER 1

SOLVENT MICROEXTRACTION: COMPARISON WITH OTHER POPULAR SAMPLE PREPARATION METHODS

1.1 INTRODUCTION

One of the most important steps in any analytical procedure is sample preparation. Most analyses are carried out on samples containing complex mixtures of very small amounts of the chemicals that need to be identified and/or quantified. At the same time, most sample matrices, such as soils or wastewater, are also very complex. Thus, a successful sample preparation method typically has three major objectives: (1) sample matrix simplification and/or replacement, (2) analyte enrichment, and (3) sample cleanup.

Many useful sample preparation methods have been developed over the years to address specific needs for analyzing waste and drinking water, foods, medicinals, soil, and air. As an example, many of the most important methods were codified for the analysis of waste and drinking water samples, as exemplified by the U.S. Environmental Protection Agency's (EPA's) 500 and 600 methods. However, these sample preparation and analysis methodologies, which originally involved traditional laboratory liquid–liquid, liquid–solid, and gaseous extractions, suffered from a number of limitations, including the requirement for significant time-consuming manual labor or in some cases, the use of large quantities of hazardous extracting solvents. As a result, there has been a continual search for improved sample preparation procedures with the following goals: (1) reduction in the number of steps

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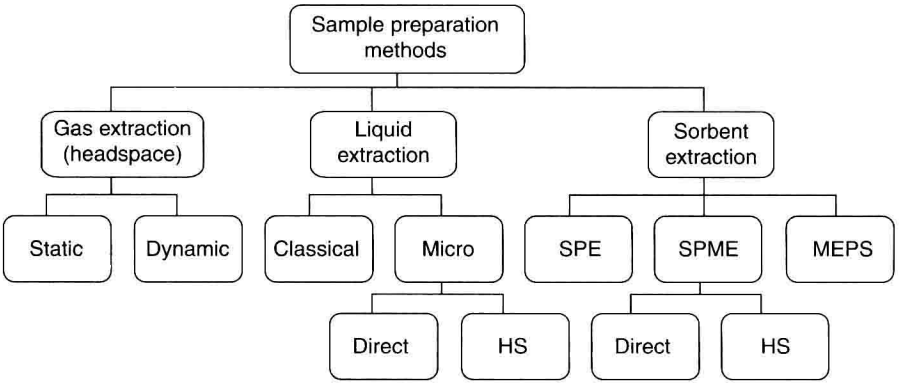

FIGURE 1.1. Sample preparation methods for aqueous and solid samples.

required for the procedure, (2) reduction or total elimination of solvents required for extraction, (3) adaptability to field sampling, and (4) automation.

The more commonly used sample preparation methods for water and solid matrix samples are represented schematically in Figure 1.1. *Solvent microextraction* (SME) is a fairly recent development in sample preparation that has the potential for meeting all four goals cited above. SME, which, in its most commonly used modifications, has also been referred to as *liquid-phase microextraction* (LPME), *single-drop microextraction* (SDME), or *dispersive liquid–liquid microextraction* (DLLME), can integrate sampling, analyte extraction and concentration, and sample introduction into a single step. Because it is the most comprehensive descriptive term available, we have decided to use the term SME originally coined by Jeannot and Cantwell[1] to cover all of the variations of this method. SME is compatible and has been used successfully with most common analytical instrumentation, including gas chromatography (GC), high-performance liquid chromatography (HPLC), capillary electrophoresis (CE), and atomic absorption spectroscopy (AAS). In its simplest and earliest practical variation, SME consists of a single drop of extracting solvent suspended from a GC syringe needle that is immersed in an aqueous sample solution. The same GC syringe is then used to introduce the solvent drop with extracted analytes into the GC (see Figure 1.2).

SME has its origins in traditional sample preparation methodologies, including liquid–liquid extraction, and in this chapter we not only give a brief history of the method, but also provide a general comparison with other commonly used sample preparation techniques. We include the advantages and disadvantages of each method, allowing the reader to gauge whether SME would be an appropriate method for their sample preparation needs.

1.2 COMPARISON OF SAMPLE PREPARATION METHODS

As indicated above, many of the most useful sample preparation methods have been rigorously detailed and codified into methods adopted by the U.S. EPA and other

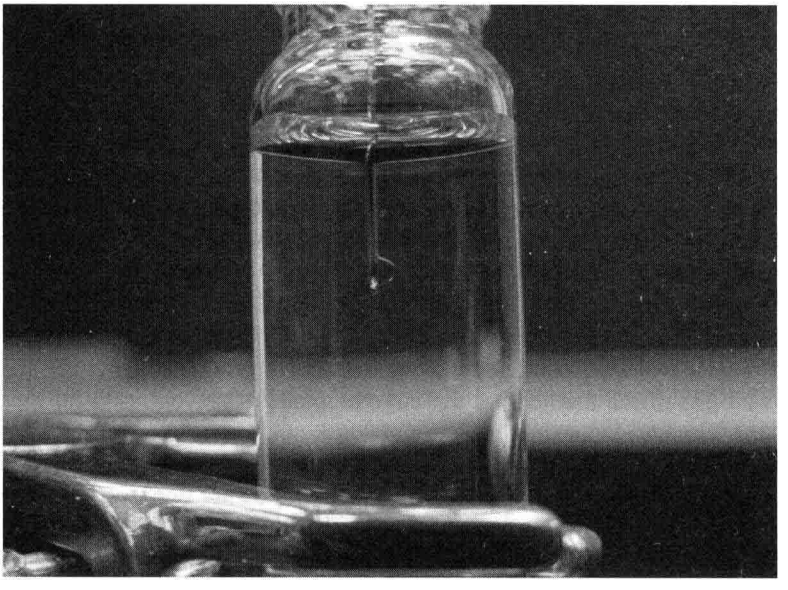

FIGURE 1.2. A 1-μL drop of octane suspended in aqueous solution on the tip of a Hamilton 701 GC syringe needle.

national and state agencies. The most commonly used procedures include variants of liquid–liquid extraction, sorbent extraction [solid-phase extraction (SPE)] and headspace extraction [including purge-and-trap (PT)], all based on classical chemical laboratory analysis techniques. More recently, solid-phase microextraction (SPME) has been developed and used for many environmental, forensic, and food analysis applications.[2,3] SME, in its most commonly implemented format, is very similar to SPME, using 1 to 2 μL of solvent at the end of a syringe needle to extract a sample rather than a liquid or porous polymer coating on a fused silica or metal fiber. Each of these techniques has advantages and disadvantages, and no one technique can be or should be used for all analyses. A number of other techniques, such as supercritical fluid extraction, cryogenic trapping, microextraction in packed syringe, and stir bar sorptive extraction are important in their own right, but are not discussed here. In addition, although SME and other techniques discussed here may be used for atmospheric sampling, we limit our discussion to extraction from liquid and solid matrices.

1.2.1 Liquid–Liquid Extraction

Traditional liquid–liquid extraction methodology was taken directly from standard techniques used for the purification of chemicals prepared in the laboratory. Thus, a solvent such as dichloromethane, pentane, or ether is used to extract analytes from water using a separatory funnel or continuous extractor, and from solids such as soil or plant material using a Soxhlet extractor. Specific examples include EPA method 625 for municipal wastewater, method 525.2 for drinking water, and method 551.1 for chlorination disinfection by-products in drinking water.

1.2.1.1 EPA Method 625: Liquid–Liquid Extraction EPA method 625 is used for the analysis of 54 specific chemicals, including industrial by-products and pesticides, and seven chemical mixtures [chlordane, toxaphene, and the polychlorinated biphenyls (PCBs)] commonly found in municipal and industrial wastewater.[4] The method involves extracting a liter of sample with 450 mL or more of dichloromethane, which is then evaporated to a volume of 1 mL. Next, a 1-μL aliquot of the concentrate is analyzed by GC or GC-mass spectrometry (MS). A continuous extractor using 500 mL of solvent can also be used for the extraction, to limit emulsion formation.

The major advantages of this method are simplicity and the ability to extract many analytes at once into a solvent compatible for analysis by GC-MS, which in turn is capable of separating, identifying, and quantifying each analyte. The major disadvantages of the method are the large amounts of solvent used for the extraction, the manual labor involved, emulsions sometimes formed when using a separatory funnel, the time required for the extraction (up to 24 h for a continuous extractor), and the fact that the method actually does not concentrate the analytes significantly. True, 1 L of water is concentrated into 1 mL of dichloromethane, a 1000-fold enrichment, but only 1 μL is analyzed, 1/1000 of the extract. Thus, if an analyte is present at a concentration of 1 μg/L, only 1 ng is actually analyzed. A consequence of the need to evaporate the solvent is that this method is not applicable to volatile chemicals. Another major disadvantage is the relatively large amount of water sample, 1 L, that is required, making this method difficult to automate. Finally, the method will require two preparations and analyses per sample if both basic and neutral/acidic components are present, effectively doubling the analysis time. However, despite these difficulties, method 625 does yield method detection limits (MDLs) of 1 to 5 μg/L (1 to 5 ng/mL) for each analyte, and fairly good precision and accuracy.

1.2.1.2 EPA Method 551.1: Micro Liquid–Liquid Extraction Several new methods have been developed to address the disadvantages of solvent use, manual labor, and time required for sample preparation methods such as 625. One method includes EPA method 551.1, which is a micro extraction method for analysis of the chlorination disinfection by-products, including the trihalomethanes, and several chlorinated industrial solvents and pesticides.[5] The method involves extracting 50 mL of drinking water saturated with salt with either 3 mL of methyl *tert*-butyl ether or 5 mL of pentane (compared to 500 mL of solvent for method 625, thus the term *micro*), followed by analysis of 1 to 2 μL of the extractant by GC with an electron capture detector (ECD). If pentane is the solvent of choice and 2 μL of the concentrate is injected, the analytes have been concentrated tenfold, but only 1/2500 of the analytes are then analyzed. For example, if the original sample contained 1 μg/L of an analyte, only 20 pg would be analyzed. However, because the ECD is very sensitive and selective for halogenated compounds, the effective method detection limit is approximately 0.1 μg/L (0.1 ng/mL) or less. This method does require significantly less solvent and water sample than method 625, and no solvent concentration is needed, enabling analysis of volatile as well as nonvolatile