

There is growing interest in the field of microextraction, as demonstrated by a steady increase in the publication of scientific articles that describe research in this area. A decade ago, there were only a few publications per year covering this topic, compared to 2005, when the number of publications approached 600. A majority of the papers is dedicated to development and application of nonexhaustive extraction techniques, which possess additional advantages other than micro-scale format.

Despite this apparent scientific success, some resistance remains within regulatory agencies to support the development and acceptance of methods based on microextraction procedures. Their main concern is based on the ability of nonexhaustive microextraction methods to deliver accurate and reproducible data, since the published recoveries are far from 100%, and therefore, calibration based on volume is not possible. In most cases, the calibration is performed based on partitioning equilibria or extraction rates. Reliance on physicochemical constants, such as the distribution constant or the diffusion coefficient for successful quantitation, might seem unconventional or even uncomfortable to some researchers who have been using traditional exhaustive extraction techniques for calibration. As theory indicates, however, these constants define the extraction process, and there is an opportunity to take advantage of this fact to develop unique approaches and provide additional information about the investigated system.

Physicochemical constants can be frequently estimated from simple experiments or calculated by considering the molecular structures of the analytes, extraction phase, and matrix; this strengthens the merit of this approach. For equilibrium microextraction techniques, the extraction phase/sample matrix distribution constant is used to quantitate the concentration of analytes in the sample matrix. For extraction approaches controlled by mass transfer, calibration can be based on the diffusion coefficient in the sample matrix for constant extraction time under well-defined convection conditions. When the derivatization reaction kinetics control the rate of extraction, the rate constant can provide a means of calibration. Occasionally, in membrane microextractions, a combination of constants defines the rate of extraction and can also be used for the calibration.

One of the major arguments against the use of microextraction is that physicochemical constants are affected by a number of experimental conditions, including temperature and sample matrix properties. However, the influence of temperature change can be eliminated by fixing the extraction temperature in the laboratory. Alternatively, the effect can be adjusted for by monitoring the temperature and applying a correction factor for on-site analyses. In addition, unique extraction configurations can be developed based on the temperature dependence, in which the sample matrix is heated and the fiber coating is cooled. This facilitates a faster mass transport of the analytes to the extraction phase while enhancing the distribution constant, which results in improved method sensitivity. The distribution constants that describe partitioning between the extraction phase and water or air facilitate direct calibration of simple matrices. For more complex matrices, internal standards or standard addition calibrations, routinely applied in exhaustive techniques to monitor recoveries, can be used to compensate for matrix variations. More recently, calibrations that involve introduced standards via the extraction phase allow for convenient on-site calibration.

One can draw several parallels between developments and applications of extraction techniques with electrochemical methods. For instance, the coulometric technique corresponds to total or exhaustive extraction methods. Although this method has excellent accuracy and precision, it is not used frequently because of the length of time that is required for completion. Equilibrium potentiometric techniques are more frequently used (pH electrode), particularly when the sample is a simple mixture and/or the selectivity of the membrane in an ion-selective electrode is sufficient to quantitate the target analyte in complex matrices. The equilibrium microextraction approach has further advantages in selectivity because the extraction is coupled with separation and/or specific detection (e.g., mass spectrometry), which enables the

simultaneous identification and quantitation of many components. The advantage of electrochemical methods is a short response time because of the low capacities of the electrodes. The design of micro-systems with a cylindrical geometry facilitates rapid extraction, as in microelectrodes. Both approaches facilitate the integration of sampling with the sample preparation step, eliminating need for the separate step of sampling. Some electrochemical methods, such as amperometry, are based on mass transport through the boundary layer, as in pre-equilibrium extraction techniques. Analogously, extraction calibration based on diffusion coefficients can be accomplished as long as the agitation conditions are constant, the extraction times are short, and the coating exhibits a high affinity for the analytes.

Microextraction techniques have been developed not only to address the need for a reduction in the size of the extraction instrumentation and solvent use, but also to explore the capability of this approach to facilitate rapid and convenient sample preparation both in the laboratory and for on-site applications. There are many advantages of microextraction, which can be realized, to a greater or lesser degree, depending on the geometric configuration of the instrument. Some designs better address issues associated with agitation and others address the ease of implementing on-site analyses or sample introduction to the analytical instrument. For example, full automation of standard delivery, extraction, and introduction is possible for gas chromatography using a coated fiber format and for liquid chromatography when an internally coated capillary is utilized. Conversely, the use of either coated fibers (solid-phase microextraction) or hollow fibers that contain small amounts of solvent (liquid-phase microextraction) arranged in a 96-fiber configuration facilitate application with a multiwell format for high-throughput sample processing. The thin-film microextraction format, characterized by high surface area contact between the extraction phase and sample matrix, results in high extraction rates and, therefore, high sensitivities at short extraction times. Small extraction devices facilitate on-site applications, including in vivo analyses, and allow for coupling to a variety of analytical micro-instrumentation, including capillary and microfluidics systems.

The nonexhaustive microextraction techniques possess unique advantages because, typically, only a small portion of the target analyte is removed from the matrix. This feature allows for the monitoring of chemical changes, partitioning equilibria, and speciation in the investigated system because sampling causes a minimum perturbation to the system. Therefore, the use of microextraction-based strategies results in better characterization and more accurate information about the investigated system or process, compared to exhaustive techniques. Nonexhaustive microextraction techniques provide signal magnitudes that are proportional to the free concentration of target analyte, defining the fraction of the analyte that is bioavailable. This unique feature of the nonexhaustive techniques allows for the measurement of binding constants in complex matrices, providing additional information about the investigated system. It also indicates, as mentioned previously, the need for careful calibration and optimization. Therefore, the development of robust quantitative analytical methods based on microextraction requires more time, but when the procedures are optimized they are more convenient and cost effective compared to conventional exhaustive extraction approaches.

This special issue contains articles that elaborate on the above topics and demonstrate the practical application of microextraction approaches. There are numerous untapped opportunities available for exploration, especially considering the unique features of microextractions that have been emphasized here, making this research direction vital and scientifically rewarding.



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