separations

MDPI

Editorial

Trends in Microextraction Techniques for Sample Preparation

Victoria F. Samanidou

Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece; samanidu@chem.auth.gr; Tel.: +30-23-1099-7698

Received: 23 October 2017; Accepted: 18 December 2017; Published: 21 December 2017

Although analytical scientists equivocally agree that "no sample preparation" would be the best approach, the fact is that all samples that are handled in any analytical laboratory need to undergo treatment to some extent prior to their introduction to the analytical instrument. This step has been widely recognized as the major step in the chemical analysis workflow. Therefore, the next best strategy is to find the most adequate methodology that would comply with all of the current trends in sample preparation, such as speed, automation, operator safety, and less solvent consumption, but with no compromise regarding analytical performance.

Classical methodologies based on solid phase extraction (SPE) and liquid-liquid extraction (LLE) tend to have many drawbacks as they include complicated, time-consuming steps that require large sample sizes and large amounts of organic solvent. As a result, they are being progressively replaced by miniaturized, environment-friendly techniques, such as microextraction by packed sorbent (MEPS), fabric phase sorptive extraction (FPSE), and dispersive liquid–liquid microextraction (DLLME). Additionally, due to the evolution of technology and nanotechnology, novel extraction sorbents have been synthesized with improved properties, enhanced selectivity, easiness in handling, etc. This combination has opened up new potentials to extract target analytes from sample matrices with a high impact of endogenous interferences.

The so-called microextraction techniques have sparked the excitement of the scientific community, and already gained interest among analytical chemists, as they conform to green analytical chemistry demands and ensure environmental protection and public safety. Savings in cost and time are considered valuable benefits to using novel microextraction approaches in sample handling. Selectivity, sensitivity, and lower detection limits are also included among the performance characteristics required to meet the legislation criteria.

The target of this Special Issue is to present the state of art microextraction sample preparation techniques. Modern, simple, and efficient methods for preconcentration and separation methods are described for different analytes isolated from various matrices.

Thirteen outstanding contributions are included and briefly presented below.

Abuzar Kabir, Marcello Locatelli, and Halil Ibrahim Ulusoy critically audit the progress of microextraction techniques in recent years in their very comprehensive review, "Recent Trends in Microextraction Techniques Employed in Analytical and Bioanalytical Sample Preparation". Microextraction techniques have indisputably transformed analytical chemistry practices, from biological and therapeutic drugs monitoring to the environmental field, food samples, and phyto-pharmaceutical applications [1].

Soledad Cárdenas and Rafael Lucena present a remarkable review on the recent advances in extraction and stirring integrated techniques. Since microextraction techniques are usually non-exhaustive processes that work under the kinetic range, the improvement of the extraction kinetics necessarily improves the performance. The extraction yield and efficiency is related to how fast the analytes diffuse in samples, therefore, stirring the sample during extraction is crucial. The stirring

can be done with an external element, or it can be integrated, with the extraction element in the same device. This article emphasizes the potential of promising approaches rather than their applications [2].

Theodoros Chatzimitakos and Constantine Stalikas provide a snapshot of the most important features and applications of different carbon-based nanomaterials in their excellent review, "Carbon-Based Nanomaterials Functionalized with Ionic Liquids for Microextraction in Sample Preparation". These features include fullerenes, carbon nanotubes, nanofibers, nanohorns, and graphene, all functionalized with ionic liquids for sample preparation. Emphasis is given to the description of the different works that have provided interesting results for the use of graphene and carbon nanotubes in this analytical field [3].

Viktoria Kazantzi and Aristidis Anthemidis focus on the background and sol-gel chemistry for the preparation of new fabric sorbents, as well as applications of fabric phase sorptive extraction (FPSE) for extracting target analytes in their review of fabric sol-gel phase sorptive extraction technique. Some of the new fabric sorbents include various organic and inorganic analytes in different types of environmental and biological samples in high throughput analytical, environmental, and toxicological laboratories [4].

Fabric phase sorptive extraction (FPSE) is a quite recent sample preparation technique that combines the advanced material properties of sol-gel derived microextraction sorbents, and the flexibility and permeability of fabric, to produce a robust, simple, and green device for extracting target analytes directly from various sample matrices. New modes of FPSE, including stir FPSE, stir-bar FPSE, dynamic FPSE, and automated on-line FPSE, are also highlighted and commented upon in detail. Abuzar Kabir, Rodolfo Mesa, Jessica Jurmain, and Kenneth G. Furton in their work "Fabric Phase Sorptive Extraction Explained" present the theory and working principle of fabric phase sorptive extraction (FPSE). As a representative sorbent, sol-gel poly(ethylene glycol) coating was generated on cellulose substrates. Five (cm^2) segments of these coated fabrics were used as the FPSE devices for sample preparation using direct immersion mode. An important class of environmental pollutants—substituted phenols—was used as model compounds to evaluate the extraction performance of FPSE. The high primary contact surface area (PCSA) of the FPSE device and porous structure of the sol-gel coatings resulted in very high sample capacities and incredible extraction sensitivities in a relatively short period of time. Different extraction parameters were evaluated and optimized. The new extraction devices demonstrated part per trillion level-detection limits for substitute phenols, a wide range of detection linearity, and good performance reproducibility [5].

Shivender Singh Saini, Abuzar Kabir, Avasarala Lakshmi Jagannadha Rao, Ashok Kumar Malik, and Kenneth G. Furton present, "A Novel Protocol to Monitor Trace Levels of Selected Polycyclic Aromatic Hydrocarbons in Environmental Water Using Fabric Phase Sorptive Extraction Followed by High Performance Liquid Chromatography-Fluorescence Detection". FPSE was applied for the first time, to the trace level determination of selected polycyclic aromatic hydrocarbons (PAHs) in environmental water samples using a non-polar sol-gel C_{18} coated FPSE media. Several extraction parameters were optimized to improve the extraction efficiency and to achieve high detection sensitivity. The developed and validated FPSE-HPLC-FLD protocol is simple, green, fast, and economical, with adequate sensitivity for trace levels of four selected PAHs, and seems to be promising for the routine monitoring of water quality and safety, as proved by application to the analysis of environmental water samples [6].

Natalia Manousi, Georg Raber, and Ioannis Papadoyannis in their work, "Recent Advances in Micro-extraction Techniques of Antipsychotics in Biological Fluids Prior to Liquid Chromatography Analysis", present an overview of microextraction techniques that are used prior to liquid chromatography analyses both for forensic toxicology in different biological matrices as well as therapeutic drug monitoring. Antipsychotic drugs are a class of psychiatric medication worldwide that is used to treat psychotic symptoms, principally bipolar disorder, schizophrenia, and other psycho-organic disorders, and therefore the necessity for sensitive analytical methods for their determination is of utmost importance [7].

Victoria Samanidou, Dimitrios Bitas, Stamatia Charitonos, and Ioannis Papadoyannis, in their review, "On the Extraction of Antibiotics from Shrimps Prior to Chromatographic Analysis", describe the need for sensitive and selective methods of monitoring residue levels in aquaculture species for routine regulatory analysis. It is well known that the widespread use of antibiotics in veterinary practice and aquaculture has led to the increase of antimicrobial resistance in foodborne pathogens that may be transferred to humans [8].

Global concern is reflected in the regulations from different agencies that have set maximum permitted residue limits on antibiotics in different food matrices of animal origin. Since sample preparation is the most important step, several extraction methods have been developed. The review summarizes the extraction trends for several antibiotics classes from shrimps, and compares the performance characteristics of the different approaches. In their work, "Trends in Microextraction-Based Methods for the Determination of Sulfonamides in Milk", Maria Kechagia and Victoria Samanidou describe the state of the art sulfa drugs that are used in the dairy farming industry in several countries to prevent infection. This increases the possibility that residual drugs could pass through milk consumption, even at low levels. These traces of sulfonamides will be detected and quantified in milk. Therefore, microextraction techniques must be developed to quantify antibiotic residues, taking the requirements of green analytical chemistry into consideration as well [9].

Ana Isabel Argente-García, Yolanda Moliner-Martínez, Esther López-García, Pilar Campíns-Falcó, and Rosa Herráez-Hernández, in their research article, "the Application of Carbon Nanotubes Modified Coatings for the Determination of Amphetamines by In-Tube Solid-Phase Microextraction and Capillary Liquid Chromatography", present a study in which polydimethylsiloxane (PDMS)-coated capillary columns (TRB-5 and TRB-35), both unmodified and functionalized with single-wall carbon nanotubes (SWCNTs) or multi-wall carbon nanotubes (MWCNTs), have been tested and compared for the extraction of amphetamine, methamphetamine, and ephedrine by in-tube solid-phase microextraction (IT-SPME). Prior to their extraction, the analytes were derivatized with the fluorogenic reagent 9-fluorenylmethyl chloroformate. The method was applied to the determination of the tested amphetamines in an oral fluid using a TRB-35 capillary column functionalized with MWCNTs [10].

In their work, "Design of a Molecularly Imprinted Stir-Bar for Isolation of Patulin in Apple and LC-MS/MS Detection", Patricia Regal, Mónica Díaz-Bao, Rocío Barreiro, Cristina Fente, and Alberto Cepeda present a rapid and selective method based on magnetic molecularly imprinted stir-bar (MMISB) extraction developed for the isolation of patulin, using 2-oxindole as a dummy template. Patulin is produced by a mold species that is normally related to vegetable-based products and fruit, mainly apple. Its ingestion may result in agitation, convulsions, edema, intestinal ulceration, inflammation, vomiting, and even immune, neurological, or gastrointestinal disorders. For this reason, the European Commission Regulation (EC) 1881/2006 established a maximum content for patulin of 10 ppb in infant fruit juice, 50 ppb for fruit juice for adults, and 25 ppb in fruit-derived products. The successful MMISB approach has been combined with high performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) to determine patulin [11].

Evangelos D. Trikas, Rigini M. Papi, Dimitrios A. Kyriakidis and George A. Zachariadis developed their research paper, "Sensitive LC-MS Method for Anthocyanins and Comparison of Byproducts and Equivalent Wine Content", for the detection and identification of these compounds in the solid wastes of the wine-making industry (red grape skins and pomace), using liquid–liquid extraction prior to the liquid chromatography–mass spectrometry technique (LC-MS). The complete process was investigated and optimized, starting from the extraction conditions (extraction solution selection, dried matter-to-solvent volume ratio, water bath extraction duration, and necessary consecutive extraction rounds), and continuing to the mobile phase selection [12].

Last but not least, Lingshuang Cai, Somchai Rice, Jacek A. Koziel and Murlidhar Dharmadhikari present "an Automated Method for Selected Aromas of Red Wines from Cold-Hardy Grapes Using Solid-Phase Microextraction and Gas Chromatography-Mass Spectrometry-Olfactometry". The effects of SPME coating selection, extraction time, extraction temperature, incubation time, sample volume,

desorption time, and salt addition were studied. The developed method was used to determine the aroma profiles of seven selected red wines originating from four different cold-hardy grape cultivars. The presented method can be useful for grape growers and winemakers for the screening of aroma compounds in a wide variety of wines, and can be used to balance desired wine aroma characteristics. The aroma profile of red wine is complex, and research focusing on aroma compounds and their links to viticultural and enological practices is always of high importance [13].

As the Guest Editor of this Special Issue, I would like to thank all of the authors for their contributions, and reassure the readers that this field is expanding, so many other microextraction approaches are yet to evolve.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Kabir, A.; Locatelli, M.; Ulusoy, H.I. Recent Trends in Microextraction Techniques Employed in Analytical and Bioanalytical Sample Preparation. *Separations* **2017**, *4*, 36. [CrossRef]
2. Cárdenas, S.; Lucena, R. Recent Advances in Extraction and Stirring Integrated Techniques. *Separations* **2017**, *4*, 6. [CrossRef]
3. Chatzimitakos, T.; Stalikas, C. Carbon-Based Nanomaterials Functionalized with Ionic Liquids for Microextraction in Sample Preparation. *Separations* **2017**, *4*, 14. [CrossRef]
4. Kazantzi, V.; Anthemidis, A. Fabric Sol-gel Phase Sorptive Extraction Technique: A Review. *Separations* **2017**, *4*, 20. [CrossRef]
5. Kabir, A.; Mesa, R.; Jurmain, J.; Furton, K.G. Fabric Phase Sorptive Extraction Explained. *Separations* **2017**, *4*, 21. [CrossRef]
6. Saini, S.S.; Kabir, A.; Jagannadha Rao, A.L.; Malik, A.K.; Furton, K.G. A Novel Protocol to Monitor Trace Levels of Selected Polycyclic Aromatic Hydrocarbons in Environmental Water Using Fabric Phase Sorptive Extraction Followed by High Performance Liquid Chromatography-Fluorescence Detection. *Separations* **2017**, *4*, 22. [CrossRef]
7. Manousi, N.; Raber, G.; Papadoyannis, I. Recent Advances in Microextraction Techniques of Antipsychotics in Biological Fluids Prior to Liquid Chromatography Analysis. *Separations* **2017**, *4*, 18. [CrossRef]
8. Samanidou, V.; Bitas, D.; Charitonos, S.; Papadoyannis, I. On the Extraction of Antibiotics from Shrimps Prior to Chromatographic Analysis. *Separations* **2016**, *3*, 8. [CrossRef]
9. Kechagia, M.; Samanidou, V. Trends in Microextraction-Based Methods for the Determination of Sulfonamides in Milk. *Separations* **2017**, *4*, 23. [CrossRef]
10. Argente-García, A.I.; Moliner-Martínez, Y.; López-García, E.; Campíns-Falcó, P.; Herráez-Hernández, R. Application of Carbon Nanotubes Modified Coatings for the Determination of Amphetamines by In-Tube Solid-Phase Microextraction and Capillary Liquid Chromatography. *Separations* **2016**, *3*, 7. [CrossRef]
11. Regal, P.; Díaz-Bao, M.; Barreiro, R.; Fente, C.; Cepeda, A. Design of a Molecularly Imprinted Stir-Bar for Isolation of Patulin in Apple and LC-MS/MS Detection. *Separations* **2017**, *4*, 11. [CrossRef]
12. Trikas, E.D.; Papi, R.M.; Kyriakidis, D.A.; Zachariadis, G.A. A Sensitive LC-MS Method for Anthocyanins and Comparison of Byproducts and Equivalent Wine Content. *Separations* **2016**, *3*, 18. [CrossRef]
13. Cai, L.; Rice, S.; Koziel, J.A.; Dharmadhikari, M. Development of an Automated Method for Selected Aromas of Red Wines from Cold-Hardy Grapes Using Solid-Phase Microextraction and Gas Chromatography-Mass Spectrometry-Olfactometry. *Separations* **2017**, *4*, 24. [CrossRef]