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Review

Electrochemically assisted solid based extraction techniques: A review

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ABSTRACT

The complexity of the matrices of the analytes from a biological sample or environmental origin can disturb the separation and data analysis steps. Thus, the major incentive of recent research trends in environmental and bioanalysis research is to achieve faster, simpler, inexpensive, and more environmental-friendly sample preparation techniques. Application of auxiliary energies is one of the efficient strategies to reach the aforementioned purposes. Among these, application of electrical driving force in different extraction techniques has found remarkable consideration in recent years attributed to its ability in control of different properties of an extraction system such as selectivity, clean-up, rate, and efficiency by imposition of a variable potential difference. This review attempts to explain the principles of electrically assisted solid based extraction techniques as well as different roles of electrical field in these methods in more details. Also, advantages, disadvantages, and limitations of these techniques are discussed providing coherent information and useful insights for future researches.

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Abbreviations: CE-MS, Capillary electrophoresis–mass spectrometry; CV, cyclic voltammetric; EA-SPME, electrically assisted solid phase microextraction; EC-SPE, electrochemical solid-phase extraction; EC-SPME, electrically controlled SPME; EMLC, electrochemically modulated liquid chromatography; EM-SPME, electro-membrane surrounded solid phase microextraction; ES-SPME, electrosorption SPME; EQCM, electrochemical quartz crystal microbalance; ESI, electrospray ionization; FIA, flow injection analysis; ICP-MS, inductively coupled plasma mass spectrometry; LLE, liquid–liquid extraction; MIP, molecular imprinted polymer; PGC, porous graphitic carbon; PPy, polypyrrole; QRE, silver quasireference electrode; SCE, saturated calomel electrode; SEM, scanning electron microscopy; SPE, solid phase extraction; SPME, solid phase microextraction

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1. Introduction

Sample preparation is of vital importance in analysis of trace amounts of target analytes or their analysis in complicated matrices. Some sample cleanup, analyte isolation from the interferences, and their preconcentration to a suitable level may be required before instrumental analysis. Sample preparation could be explained as the experimental steps required making a sample ready for analysis. A good sample preparation method should be as fast as possible, reproducible, involve minimum number of steps, has relatively low cost, be environmental friendly, and offer high recoveries, and also have the potential to become automated [1].

Solid phase based extraction techniques are well-known sample preparation methods, which have been associated with many advances in the past few years. Liquid–solid extraction or solid phase extraction (SPE) was first introduced as a replacement for liquid–liquid extraction (LLE). The technique utilizes a solid support to isolate and preconcentrate the analyte of interest [2–4]. A typical SPE has four processing steps; including conditioning, sample application, washing impurities, and elution of target analytes. Pawliszyn et al. have presented for the first time the miniaturized format of SPE; named solid-phase microextraction (SPME), in which sampling, isolation, and enrichment of analytes and its introduction into the analysis instrument can be done in one step [5]. SPME requires a small amount of extraction phase coated on a solid support. Selectivity of this technique is determined by composition of the extraction phase.

Electrical field induced extraction technique is a topic that is less investigated. A significant growing trend can be observed in the annual number of publications related to the electrically assisted extraction techniques as well as the number of citations to these works in the literature. Thus, it can be concluded that these methods are gradually becoming a quite common place in the analysis of various environmental and biological samples.

In this review, the focus is centered on the electrically assisted solid based extraction techniques to present a general vision of the effect of electric fields on carrying out sample treatment and also to evaluate the real potential of these methods. Advantages, disadvantages, and limitations of these techniques are discussed. These points can be helpful in future scientific researches to overcome current problems and improve electrical induced solid based extraction methods.

For this purpose, a comprehensive survey of past and present novelties and applications of the electrically assisted solid based extraction techniques will be provided. Also, a conceptual clustering method was applied for investigation of different aspects of various electrically assisted techniques and a powerful and innovative way was employed to keep information in the mind for a long period of time.

2. Solid based extraction techniques

Electrochemical techniques have found remarkable applications in SPE and SPME techniques including synthesis of sorbents and enhancement of extraction [6–9]. In the case of synthesis of sorbents, the electrochemical method provides tailoring of key characteristics including thickness, conductivity, degree of oxidation, color, and morphology [10]. This fact has propelled various research groups toward synthesis of new coatings [11–14]. Among the newest, there has been growing interest in conducting polymers due to their multifunctional properties [11].

The idea of application of electrical field in solid-phase extraction originates from a technique termed electrochemically modulated liquid chromatography (EMLC) [15]. EMLC was first reported by Fujinaga et al. in 1963 [16]; then by Blaedel and Strohl [17] and independently by Roe in 1964 [18]. Generally, an electrical field has two effects in the solid based extraction techniques; it directly affects the surface of solid sorbents and provides manipulation possibility of extraction [7–9,19–21], or has an indirect effect so that only provides an electrokinetic migration of charged analytes toward solid sorbent [22] or facilitates elution of the analytes [6]. Electrically assisted solid-phase extraction/microextraction and electrokinetic trapping are the instances for direct and indirect effects of electrical field in solid based extraction techniques, respectively.

According to the literature, the substantial increasing trend in application of the electrical field in solid based extraction techniques

can be attributed to several reasons;

1. Properties of the conducting polymer can be modified by varying the conditions during the electropolymerization step to enable extraction of analytes with different sizes and charges.
2. Compared to conventional solid based extraction techniques, in which a material with a fixed number of exchange sites is employed, electrically assisted one offers higher flexibility. This is because the properties of the material and thus the number of exchange sites can be externally controlled by electrochemically controlling the charge of the material [23,24].
3. The use of polymer based fiber films in solid based extraction techniques can be extended to the analysis of neutral, electroinactive analytes by taking the advantage of electrochemically controlled hydrophobic/hydrophilic 'switching' [25].
4. Electrically assisted solid based extraction techniques can be used to extract ions and analytes that normally need to be derivatized prior to traditional solid based extractions [26,27].
5. In electrically assisted solid based extraction techniques, the extraction and desorption steps are performed merely by altering the potential of the conducting polymer coated electrode. In this approach, there is thus no need for changes of the solvent in order to enable desorption of the compounds [28].
6. By altering the electrochemical potential of the polymer, desorption of electrostatically held analytes may also be faster compared to the desorption techniques normally used in traditional solid based extractions [29]. This makes the technique particularly interesting for use in conjunction with miniaturized analytical systems.

2.1. Electrokinetic trapping

Electrokinetic trapping is a technique, in which charged species migrate in opposite direction of their net charge under electrical field and are trapped by different strategies such as solid sorbent [30], ion selective membrane [31], hydrogel plug [32], and microporous polymer network material (monolith) [33]. The retained charged species are released from the trap by a pressure driven flow in the absence of the electric field. This technique has drawn much attention due to its potential application in biological sciences; especially for preconcentration of proteins and DNA [30–33].

Singh et al. used silica sorbents as trapping materials for preconcentration and determination of chicken egg albumin so that preconcentration values greater than 1000-fold were achievable by this way [30]. Schematic presentations of the setup used are shown in Fig. 1A and B. About 10 cm of a 30-cm fused silica capillary column was packed with porous silica particles as the stationary phase. The capillary column was conditioned at a pH of about 8.3 using 50 mM tris(hydroxymethyl)aminomethane (TRIS) buffer. A sample containing 100 mg L⁻¹ of chicken egg albumin as well as caffeine in 50 mM TRIS was electrokinetically injected onto the stationary phase by applying a voltage of about 50 kV through the stationary phase by means of power supply and electrodes.

It should be noted that albumin species were labeled with fluorescein to permit detection possibility by laser induced dispersed fluorescence. Albumin has a negative charge at pH 8.3, whereas caffeine is a neutral compound in this pH and therefore, can be used as an evidence for electrokinetic trapping of albumin. The electrodes are disposed on either side of the stationary phase and preferably in inlet and outlet reservoirs. The voltage was applied for about 10 min, during which the uncharged caffeine was eluted from the column.

Under the influence of the applied electric field, only neutral caffeine was eluted in about 8 min from the packed column (Fig. 1C) and no evidence was observed for elution of negatively charged albumin species during different investigated times

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