



Combined hollow fiber-based liquid–liquid–liquid microextraction and in-situ differential pulse voltammetry to improve selectivity, sensitivity, and interference elimination in electrochemical analysis

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ABSTRACT

In this paper, a combined hollow fiber-based liquid three-phase microextraction and voltammetric method are applied for the first time as a highly selective and sensitive method of electrochemical analysis. Desipramine, used as a model compound was extracted from 8 mL aqueous solution (donor phase, 0.10 mol L⁻¹ NaOH) through a thin phase of propyl benzoate inside the pores of a polypropylene hollow fiber and finally into a 10 μ L acidic acceptor solution inside the hollow fiber. Three microelectrodes designed and constructed for the purposes of this study were placed into the two ends of the hollow fiber inside the acceptor solution, and voltammetric analysis was performed in-situ during the extraction. After 15 min, the final stable signal was used for analytical applications. Under the optimized conditions, an enrichment factor of 301 was achieved and the relative standard deviation (R.S.D.) of the method was 6.2% ($n = 5$). The calibration curve was obtained in the range of 5–5000 nmol L⁻¹ with a reasonable linearity ($R^2 > 0.988$) and the limit of detection (LOD) was found to be 0.8 nmol L⁻¹. Finally, the applicability of the proposed method was evaluated by extraction and determination of desipramine in plasma and urine samples without any dilutions.

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1. Introduction

An essential limitation of electroanalytical techniques in analyzing complex real samples is their lack of selectivity. In fact, it often happens that different species undergo redox reactions at potential values that are very close to each other. In the case of differential pulse voltammetry, serious overlapping occurs when the difference in peak potentials is less than 0.10V divided by the number of electrons involved in the electrode charge transfer. Prevalent experimental manipulations, such as changing the supporting electrolyte pH or using modified electrodes and chemometric methods, offer efficient options to overcome the problem of overlapping signals [1]. Moreover, the application of pretreatment techniques could be an alternative for the elimination of the interferences encountered in the electrochemical analysis of complex matrices such as urine and plasma.

Hollow fiber-based liquid–liquid–liquid microextraction (HF-LLLME) is a sample preparation technique. Originally introduced by Pedersen-Bjergaard and Rasmussen [2] in 1999 with its basic principles clearly described elsewhere [3–6], it is based on the use

of disposable and porous hollow fibers made of polypropylene. HF-LLLME combines extraction, preconcentration and sample clean-up in one step. In the three-phase mode, analyte extraction occurs through three liquid phases, including: (1) the sample solution (donor phase), where pH is adjusted to keep compounds neutrally charged; (2) the organic extracting phase, which is immobilized in fiber pores; and (3) the receiving aqueous phase (acceptor phase), with a pH that is adjusted to ionize the analytes. Compounds in their non-ionized form are extracted into the organic solvent and subsequently back extracted into the acceptor phase, which can be directly analyzed via high performance liquid chromatography (HPLC) [7–9]. Additional advantages of HF-LLLME are its tolerance to a wide pH range and applications in assays that are not suitable for SPE or SPME. Sample carryover can be avoided because the hollow fiber used in HF-LLLME is cheap, making it affordable to dispose after a single use [10].

The aim of the present study is to combine the hollow fiber-based liquid–liquid–liquid microextraction (HF-LLLME) technique with differential pulse voltammetry in order to improve selectivity and sensitivity in electrochemical analysis. To the best of our knowledge, this is the first time the combined HF-LLLME and differential pulse voltammetry employed for in-situ analysis is reported. Desipramine hydrochloride, used as a model compound, is a tricyclic antidepressant prescribed to elevate mood and to promote recovery of a normal range of emotions in patients with depressive

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