



# [PMIM]Br@TiO<sub>2</sub> nanocomposite reinforced hollow fiber solid/liquid phase microextraction: An effective extraction technique for measurement of benzodiazepines in hair, urine and wastewater samples combined with high-performance liquid chromatography



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## ABSTRACT

A new design of hollow fiber solid-liquid phase microextraction (HF-SLPME) was developed for the determination of benzodiazepines (BZPs) in hair, urine and wastewater. The membrane extraction with 1-pentyl-3-methylimidazolium bromide coated titanium dioxide ([PMIM]Br@TiO<sub>2</sub>) sorbent used in this research is a two-phase supported membrane extraction consisting of an aqueous (donor phase), and n-octanol/nano [PMIM]Br@TiO<sub>2</sub> (acceptor phase) system operated in direct immersion sampling mode. The 1-pentyl-3-methylimidazolium bromide (ionic liquid) coated nano TiO<sub>2</sub> dispersed in the organic solvent (n-octanol) is held into a porous membrane supported by capillary forces and sonification. It is in contact with the feed phase, which is the aqueous sample. The experimental setup is very simple and highly affordable. The hollow fiber is disposable, so single use of the fiber reduces the risk of cross-contamination and carry-over problems. The proposed method allows the very effective and enriched recuperation of BZPs into one single extract. In order to obtain high extraction efficiency of the analytes using this novel sorbent, the main parameters were optimized. Under the optimized extraction conditions, the method showed good linearity (0.05–6000 ng mL<sup>-1</sup>), low limits of detection (0.08–0.5 ng mL<sup>-1</sup>) and good enrichment (533–1190).

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## 1. Introduction

Benzodiazepines (BZPs) as introduced in 1960 for the first time are an important class of drugs having various properties such as anxiolytic, anticonvulsant, sedative, muscle relaxant, and hypnotic [1,2]. These compounds may also be used in the treatment of alcohol withdrawal and to induce amnesia in surgical procedures [3,4].

The usefulness of BZPs varies considerably because there are large differences in selectivity among these drugs [5]. Due to their half-lives, BZPs are classified into various types including ultra-short and short acting, intermediate acting, and long acting. Short and intermediate acting BZPs are used for the treatment of insomnia, while long acting BZPs are preferred for the treatment of anxiety [6,7].

However, these drugs are also associated with abuse and have serious problems in many countries such as driving under the influence of drugs, behavioral disinhibiting, generating hostility, suicide or drug-facilitated crimes, especially sexual assaults [8,9]. Consequently, according to the forensic and clinical toxicology importance of BZPs, reliable, sensitive and fast analytical methods are required for the simultaneous determination of BZPs in complicated matrices.

Over more than 20 years hair has been identified as a good analytical specimen and probative evidence for chronic drug use [10]. Analysis of the hair specimen provides sufficient evidence of previous drug usage as well as information on the duration for which the drug was used, and thus can serve as key evidence in legal decisions. Hair specimens in compared to blood and urine samples, are less invasive and easier to collect, store and dispatch [11].

Several methods have been described in the literature for the simultaneous determination of BZPs including gas chromatography-mass spectrometry (GC-MS) [12–16], liquid

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