Simultaneous determination of opioid drugs in urine with high-performance liquid chromatography–ultraviolet after supramolecular based magnetic NP solid-phase extraction

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Published in Micro & Nano Letters; Received on 17th September 2016; Accepted on 25th October 2016

A simple and rapid extraction/preconcentration procedure using supramolecular based magnetic nanoparticle (MNP) solid-phase extraction method by sodium dodecyl sulphate (SDS)-coated MNPs has been developed for both removal and preconcentration of three important opioid drugs named morphine, codeine and methadone before their high-performance liquid chromatography–ultraviolet determination. To get insight configuration of SDS molecules on the surface of the MNPs, zeta potential measurements were performed in different SDS (mg)/mg of MNPs ratios. Parameters affecting the extraction and preconcentration efficiency of the opioids were optimised as recovery by one variable at-a-time methodology and the obtained recoveries were 91, 94 and 98% for morphine, codeine and methadone, respectively. Under optimum conditions (such as pH = 3.5; adsorbent amount = 60 mg; eluent solvent volume = 2 ml of acetonitrile, sample volume = 200 ml etc.), the method was linear in the range of 1–200 ng ml\(^{-1}\) with enrichment factors (EFs) of 91, 94 and 98 for morphine, codeine and methadone, respectively, and the limits of detection were <0.27 ng ml\(^{-1}\). Finally, the proposed method was successfully applied for both removal and trace determination of the targeted drugs in urine samples.

1. Introduction: The opium group of narcotic drugs is among the most powerfully acting and clinically useful drugs producing depression of the central nervous system [1]. They are either derived from or related to active compounds extract of the exudates derived from seedpods of the opium poppy. Three most consumed drugs of this group are morphine, codeine and methadone. These drugs are principally analgesics, but they possess numerous other useful properties such as induce sleep in the presence of pain, check diarrhoea, suppress coughs, ease dyspnoea, facilitate anaesthesia, sedation and detoxification or temporary maintenance in narcotic addiction [2].

Routine urine monitoring of patients receiving opioid drugs treatment is often performed through gas chromatography–mass spectrometry (GC–MS) along with some derivatisation or immunoassay analysis. Although immunoassays are rapid and amenable to automation, they are often expensive and tend to suffer from cross-reactivity with opiate drugs. For GC–MS analysis, the structure of some opiate drugs such as methadone can change at the high temperatures of injector port and some may have poor reproducibility by undergoing chemical rearrangement during the derivatisation procedure [3]. Using simple high-performance liquid chromatography–ultraviolet (HPLC–UV), not only eliminates the necessity of derivatisation, but the achieved chromatographic separation and sensitivity also allows for the successful quantification of the free and conjugated species.

Laboratory drugs of abuse testing have traditionally been based on urine, due to its concentrations of metabolites and/or parent drugs being usually higher than in another biological matrix such as hair, blood, or oral fluid, as well as being higher in the volume collected (about 20 ml). Depending on the half-life of the drug, the excretion pattern and the sensitivity of the analytical test, many drugs maybe detected in urine for a few days to a week following the last use of the drug. According to this, urine is the selected biological matrix if a recent past use of a drug has to be proven, for example, in pre-employment, random, return-to-duty, follow-up, sport drugs of abuse testing, or in drug-facilitated sexual assault cases wherein low drug levels have to be detected.

On the other hand, the reliability of forensic, toxicological, or drugs of abuse analyses depends heavily on appropriate preparation of the samples. So, in order to extract opiates from the urine matrix for quantitative studies, an approach that can be taken is solid-phase extraction (SPE). There have been major recent developments in extraction methodology including improved SPE methods such as magnetic nanoparticles (MNP)-based SPE due to simplicity and faster operation, better EF, reduced organic solvent consumption, quick phase separation and lower cost. MNP-based SPE methods have many advantages arising from the inherent characteristic of magnetic particles. In this technique, analytes adsorb on the surface of magnetic beads which can be isolated from sample solution by applying a strong external magnetic field. Then, the absorbed analytes can desorb in a small fraction of an appropriate eluent and get ready for further determination [4]. Owing to these interstice characteristics along with large surface area and good diffusion [5], MNP-based adsorbent has been widely used for separation, removal and preconcentration of many chemicals such as dyes [6, 7], metals [8, 9] and drugs [10].

In this Letter, a supramolecular mixed hemimicelles magnetic solid phase extraction (MSPE) procedure was proposed for simultaneous extraction and preconcentration of morphine, codeine and methadone in human urine samples prior to be determined by HPLC–UV detection. The method combines the advantages of supramolecular based extraction and MSPE which avoids many time-consuming column-passing process of loading large volume samples by rapid separation of magnetic adsorbents.

2. Experimental results
2.1. Chemicals and reagents: All chemicals and reagents were of analytical grade and used without further purifications. Ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), sodium dodecyl sulphate (SDS), sodium chloride, methanol, acetone, acetic acid and hydrochloric acid were prepared from Merck (Darmstadt, Germany). The opiate drugs including morphine, codeine and methadone were supplied by Sigma (Bornem, Belgium) and deionised water was used through the experiment.

Micro & Nano Letters, pp. 1–5
doi:10.1049/mnl.2016.0603
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