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Fabric phase sorptive extraction for the fast isolation of sulfonamides residues from raw milk followed by high performance liquid chromatography with ultraviolet detection

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ABSTRACT

Fabric phase sorptive extraction (FPSE) is a novel sample preparation technique which utilizes advanced material properties of sol–gel derived microextraction sorbents and the hydrophilic property of the cellulose fabric substrate, resulting in a highly sensitive and fast microextraction device, capable of extracting target analyte(s) from any complex aqueous sample matrices. Due to the low organic solvent consumption, FPSE meets all green analytical chemistry (GAC) criteria. This technique was applied, for the first time, for the determination of sulfonamides residues in milk using a highly polar sol–gel poly (ethylene glycol) (sol–gel PEG) coated FPSE media. The developed HPLC method was validated according to the European Union Decision 2002/657/EC. Decision limit (CC_α) values were 116.5 μg kg^{-1} for sulfamethazine, 114.4 μg kg^{-1} for sulfisoxazole and 94.7 μg kg^{-1} for sulfadimethoxine, whereas the corresponding results for detection capability (CC_β) were 120.4 μg kg^{-1} for sulfamethazine, 118.5 μg kg^{-1} for sulfisoxazole and 104.1 μg kg^{-1} for sulfadimethoxine.

1. Introduction

The sulfonamides or sulfa drugs, derivatives of sulfanilamide, competitively inhibit folic acid synthesis in microorganisms and were formerly used as bacteriostatic against a wide variety of bacteria and some protozoa. All sulfonamides are characterized by the same chemical nucleus as shown in Table 1S (Supplementary material). They are effective in treating infections caused by many gram-negative and gram-positive microorganisms. In veterinary medicine practice, they are widely used in farm animal feedstuff and fish cultures for prophylactic and therapeutic purposes (Mosby, 2009).

Milk is one of the most universally consumed foods with great significance in human growth and well-being. As the sample matrix, milk is very complex in nature consisting of water, lactose, protein, fat, minerals, and vitamins (Samanidou & Nisyriou, 2008). The food quality of milk is frequently impaired due to the prevalent use of antibiotics in veterinary medicine (Samanidou, Kabir, Galanopoulos, & Furton, 2015). Improper use of drugs and an insufficient withdrawal period can result in noncompliant residues. Every drug has a certain withdrawal period before the residue levels in the animal body decline below the tolerance level. If this withdrawal period is not maintained in milk producing cows, it may results in the presence of their residues in milk. Monitoring of such residues in products designated for human consumption is vital for the maintenance of the consumer's health (Tolika, Samanidou, & Papadoyannis, 2011).

The European Union has adopted maximum residue level (MRL) for sulfonamides in foodstuffs of animal origin, which in the case of milk is 100 μg kg^{-1} (European Commission, 37/2010). Performance criteria of analytical methods and the interpretation of results in the official control of residues in products of animal origin is regulated by the European Decision (2002/657/EC).

Routine monitoring of the presence of sulfonamides' residues in milk is generally carried out using a number of approaches, most of which use high performance liquid chromatography coupled with

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a variety of detectors. However, no matter how sophisticated analytical instrument is used, sample preparation is still an indispensable and determinative step in milk analysis.

For the isolation of sulfonamides in milk, various sample pre-treatment techniques have been proposed including solid phase extraction (SPE) (Hou et al., 2014; Koesukwiwat, Jayanta, & Leepipatpiboon, 2007a, 2007b; Samanidou, Tolika, & Papadoyannis, 2008), stir bar sorptive extraction (SBSE) based on polymer monolith material (Huang, Qiu, & Yuan, 2009), molecularly imprinted polymer (RA-MIP) with restricted access and selectivity for sulfonamides (Xu et al., 2010), a miniaturized graphene-based pipette tip extraction (M-G-PTE) (Yan, Sun, Liu, Ho, & Song, 2014) and liquid–liquid extraction (Nebot, Regal, Miranda, Fente, & Cepeda, 2013; Tolika et al., 2011).

Sulfonamides are highly polar and consequently very hydrophilic. Efficient extraction of polar analytes from aqueous solution still remains a daunting challenge to separation scientists (Quintana & Rodriguez, 2006). Commercially available polyacrylate (PA) and Carbowax-divinyl benzene polar sorbents in solid phase microextraction (SPME) and recently introduced polyacrylate (PA) and ethylene glycol/silicone (EG/Silicone) polar sorbents in stir bar sorptive extraction (SBSE) have shown poor extraction efficiency for highly polar analytes (Gilart, Marcé, Borrull, & Fontanals, 2014; Quintana & Rodriguez, 2006). For example, Gilart et al. (2014) reported a maximum 3% absolute recovery of highly polar analytes with $\log K_{ow}$ values between 0.6 and 1.9 in SBSE when the most polar PA and EG/Silicone phases were employed. Furthermore, these techniques are recommended for direct immersion extraction from only clean sample matrices. For environmental or biological samples containing excessive particulates, tissues, biomasses, headspace extraction is the preferred mode. However, due to the strong hydrophilic property of polar analytes and relatively low volatility, their availability in the headspace is limited. As a result, both SPME and SBSE have shown limited success in handling polar analytes. As such, there is a legitimate demand for a robust solvent-less/solvent-minimized microextraction technique that can effectively address this burgeoning analytical problem pertaining to polar analytes.

Current trend in analytical sample preparation favors miniaturized extraction techniques with minimized solvent consumption, however the majority of the analytical methods developed so far for sulfonamides are still based on conventional extraction techniques consuming high volume of organic solvents and often require protein precipitation as a pre-sample preparation treatment. These approaches are laborious, time consuming and often lead towards significant loss of analytes and poor reproducibility.

Although equilibrium driven sorbent based sorptive microextraction techniques e.g., solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), in-tube SPME, thin film microextraction (TFME) significantly reduce toxic and hazardous organic solvent consumption compared to liquid–liquid extraction, the pristine organic polymers used as the sorbent in these techniques have some major limitations that include low thermal and chemical stability; swelling if exposed to organic solvents; slow analyte diffusion due to the viscous nature of the polymers; difficulty in immobilizing the polymer onto the substrate surface, especially if the organic polymer is polar (Blomberg, 1990; Rotzsche, 1991). These sorbent related limitations have impaired the expected growth of these green techniques to a great extent, leaving no choice for the analysts but using solid phase extraction as a compromise which still employs relatively high volume of organic solvents. In addition, SPE is a multi-step, laborious, expensive and often require solvent evaporation and sample reconstitution following the analyte extraction and elution process.

The limited selectivity imparted by the organic polymers and slow analyte diffusion due to their high viscosity have been eloquently addressed by introducing sol–gel coating technology (Chong, Wang, Hayes, Wilhite, & Malik, 1997) that offers a convenient pathway to integrate organic polymers into inorganic polymeric network at a molecular level homogeneity, resulting in a robust sponge-like highly porous hybrid organic–inorganic material system with extremely high thermal, solvent, and chemical stability. The hybrid organic–inorganic sorbent material subsequently becomes chemically incorporated into the substrate surface *via* strong covalent bond if the substrate surface possesses sol–gel active moieties. The simplicity in the synthesis process and the advanced material properties of sol–gel sorbents have played a phenomenal role in creating numerous unique microextraction sorbents, particularly polar ones. Among them, sol–gel polyethylene glycol (sol–gel PEG) and its different modifications have demonstrated remarkable performance in extracting polar analytes (Kulkarni, Shearrow, & Malik, 2007; Racamonde et al., 2015). Following the success of sol–gel technology, Kabir and Furton (2014) developed a novel sorptive microextraction technique, fabric phase sorptive extraction (FPSE) that integrates the advantages of sol–gel technology as well as the rich surface chemistry of cellulose cotton fabric substrates, resulting in a flexible, robust microextraction device possessing high sample capacity, fast extraction equilibrium, and very high solvent and chemical stability. The operational simplicity, inherent advantages as microextraction device, ability to extract target analyte(s) directly from raw sample matrix containing particulates, biomasses, debris without any sample pre-treatment and cost-effectiveness of FPSE have been manifested in a number of recent articles dealing with a wide variety of analytes in environmental and biological samples (Kabir & Furton, 2014; Kumar et al., 2014; Racamonde et al., 2015; Rodríguez-Gómez et al., 2014; Samanidou et al., 2015). One major advantage of FPSE is its ability to immobilize highly polar polymers in a sol–gel hybrid organic–inorganic network, chemically bonded to the fabric substrate, resulting in a microextraction device that can efficiently extract both polar and non-polar analytes directly from aqueous sample matrix.

The main objective of the current study described herein was the application of fabric phase sorptive extraction for the fast isolation of sulfonamides residues from raw milk without any prior pre-treatment of the milk sample. To the best of our knowledge, this article represents the first report on FPSE of sulfonamides residues directly from raw milk. The total elimination of protein precipitation from the sample preparation regimen is a significant step forward towards the simplification of sample preparation practice which is still considered to be the most laborious and time consuming and hence the rate determining step in the analytical process. The developed method was validated according to European Union Decision 2002/657/EC.

2. Experimental

2.1. Materials and reagents

Substrates for fabric phase sorptive extraction (FPSE) media, sew essentials unbleached 100% cotton Muslin, were purchased from Jo-Ann Fabric (Miami, FL, USA). Short-chain poly(ethylene glycol) (average molecular weight, 300 Da), acetone, dichloromethane, methyltrimethoxysilane (MTMS), trifluoroacetic acid (TFA) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Sodium hydroxide and hydrochloric acid were purchased from Thermo Fisher Scientific (Milwaukee, WI, USA).

Sulfamethazine (SMTH), Sulfisoxazole (SIX) and Sulfadimethoxine (SDMX) were purchased from Sigma–Aldrich (St. Louis, MO, USA). HPLC grade methanol and acetonitrile were obtained from Fisher Scientific (Steinheim, UK), acetic acid was purchased from Merck (Darmstadt, Germany), whereas formic acid was purchased from Chem-Lab NV, Zedelgem, Belgium).