Talanta 147 (2016) 561–568

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Iron oxide functionalized graphene oxide as an efficient sorbent for dispersive micro-solid phase extraction of sulfadiazine followed by spectrophotometric and mode-mismatched thermal lens spectrometric determination

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ARTICLE INFO

Article history:
Received 30 August 2015
Received in revised form
10 October 2015
Accepted 12 October 2015
Available online 23 October 2015

Keywords:
Dispersive micro-solid-phase extraction
Iron oxide functionalized graphene oxide
Mode-mismatched thermal lens spectrometry
Diazotization
Sulfadiazine

ABSTRACT

A simple and rapid dispersive micro-solid phase extraction (DMSPE) combined with mode-mismatched thermal lens spectrometry as well as fiber optic linear array spectrophotometry was developed for the separation, extraction and determination of sulfadiazine. Graphene oxide was synthesized using the modified Hummers method and functionalized with iron oxide nanoparticles by means of a simple one step chemical coprecipitation method. The synthesized iron oxide functionalized graphene oxide was utilized as an efficient sorbent in DMSPE of sulfadiazine. The retained analyte was eluted by using 180 μL of a 6:4 mixture of methanol/acetic acid solution and was spectrophotometrically determined based on the formation of an azo dye through coupling with thenoyltrifluoroacetone. Under the optimized conditions, with the application of spectrophotometry technique and with a sample volume of 100 mL, the method exhibited a linear dynamic range of 3–80 $\mu g\,L^{-1}$ with a detection limit of 0.82 $\mu g\,L^{-1}$, an enrichment factor of 200 as well as the relative standard deviations of 2.6% and 4.3% ($n=6$) at 150 $\mu g\,L^{-1}$ level of sulfadiazine for intra- and inter-day analyses, respectively. Whereas, through the application of the thermal lens spectrometry and a sample volume of 10 mL, the method exhibited a linear dynamic range of 1–800 $\mu g\,L^{-1}$ with a detection limit of 0.34 $\mu g\,L^{-1}$ and the relative standard deviations of 3.1% and 5.4% ($n=6$) at 150 $\mu g\,L^{-1}$ level of sulfadiazine for intra- and inter-day analyses, respectively. The method was successfully applied to the determination of sulfadiazine in milk, honey and water samples.

1. Introduction

Sulfadiazine belongs to sulfonamides group as the most employed antibacterial agents in veterinary medicine for the treatment of infectious diseases or as the growth promoters [1]. However, inadequate use of these antibiotics or long exposure to their trace residues may lead to the emergence of antibiotic resistance in both human and veterinary populations [2]. Furthermore, it is well established that sulfonamides have relatively long half-lives and potential carcinogenic effects [3,4]. Thus, their widespread application is associated with the risk of contamination of foodstuffs with their residual or metabolites endangering the consumers' health. Accordingly, the development of a reliable analytical method for rapid, accurate and sensitive determination of sulfadiazine as one of the most utilized sulfonamides seems an urgent necessity.

Various analytical techniques including capillary zone electrophoresis [5,6], different chromatographic methods (HPLC, LC/MS, GC, and TLC) [7–10], enzyme-linked immunosorbent assay (ELISA) [11], different modes of electrochemical techniques [12–14] and chemiluminesance [15,16] have been applied for the determination of residual sulfadiazine in different matrices. Although these methods have their own advantages of selectivity and high sensitivity, they often need time-consuming sample preparation steps, high-cost operations and suffer from complex and expensive instrumentation. Spectrophotometric techniques are the most commonly utilized methods due to merits such as wide availability of the instrument, inherent simplicity, low cost, adequate precision and accuracy. These merits make the spectrophotometric techniques especially convenient for the routine analysis of

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http://dx.doi.org/10.1016/j.talanta.2015.10.033
0039-9140/

different analytes. In this regard, several spectrophotometric methods have been developed for the determination of sulfadiazine in different matrices. The majority of the developed spectrophotometric techniques for determination of sulfadiazine are based on the formation of a detectable azo dye by the diazotization of sulfadiazine followed by its coupling with different reagents including 8-hydroxyquinoline [17], iminodibenzyl [18], phloroglucinol [19] and α-naphthylamine [20].

Thermal lens spectrometry (TLS) is an extremely sensitive indirect spectrophotometric method which relies on the measurement of the thermal gradient produced by the absorption of a laser beam. Several experimental configurations including single-beam and dual-beam laser thermal lens spectrometry have been developed. In dual-beam set up, the sample is excited by a pump laser with a radial Gaussian intensity profile. The non-radiative relaxation of the excited states will lead to the local heating as well as the formation of the transverse refractive index gradient which behave like a diverging lens. The thermal lens signal (TLS) is measured using a probe beam which is focused at some distance from the sample. Mode-mismatched TLS is a configuration of dual beam laser TLS in which the pump beam waist is located on the sample and the probe beam waist at the specified distance relative to the sample. Thus, with this configuration, the sensitivity of thermal lens spectroscopy is enhanced [21]. As the thermal lens spectroscopy is based on the direct measurement of the absorbed optical energy, its sensitivity is higher than the conventional absorption techniques and can be used for measurements of analytes with very low absorption coefficient. The other advantages of the thermal lens technique are the possibility of obtaining very low detection limits, capability of analysis of small-volume of sample, wide dynamic range in comparison with spectrophotometry and the dependency on thermo-optical properties of solvents [22]. Thermal lens spectrometry has been successfully applied to the determination of trace amounts of different analytes [23,24] but there are no reports on its application in the determination of sulfadiazine.

Furthermore, the determination of trace amounts of sulfadiazine in complex matrix required an efficient separation step. Several sample preparation methods including cloud point extraction [25], solid phase extraction [8,26], and liquid phase extraction [27,28] have been reported for sulfadiazine. Solid phase extraction (SPE) is a well-accepted procedure for the sample clean-up and preconcentration of different analytes. However, in the conventional mode of SPE, considerable time is required for the extraction of the analyte into the sorbent due to the limited interface between the sorbent and the sample solution [29]. To overcome this limitation, the research activities have been focused on the development of time-saving and high efficient micro-extraction techniques. In this regard, a new mode of solid phase extraction known as dispersive micro-solid phase extraction (DMSPE) has been recently developed. This method is based on the dispersion of the sorbent in the sample solution containing target analytes which allows complete interaction of the sorbent with analyte in a short period of time followed by a remarkable decrease in the required extraction time. DMSPE has been increasingly applied for the separation and preconcentration of some analytes [30–34]. In designing the DMSPE procedure, selection of the appropriate sorbent is one of the most important factors. In this regard, different sorbent materials including carbon nanotubes [34], modified magnetic particles [30,31], modified silica [32], magnetic molecularly imprinted microspheres [33] and graphene oxide [35] have been used. Among these sorbents, graphene oxide as one of the most important derivatives of graphene has attracted great attention for the application in sample clean-up procedures. The abundance of oxygenous functional groups (epoxide, hydroxyl, and carboxylic groups), large specific surface area, and high water solubility has made graphene oxide an ideal sorbent [36]. However, high water solubility of graphene oxide and consequently, the difficulty in its separation from the aqueous phase, poses restrictions to its application as the sorbent [37]. The introduction of magnetic properties into graphene oxide can efficiently eliminate this limitation through the combination of the superb properties of graphene oxide with the separation convenience of magnetic materials. According to our literature survey, graphene oxide and magnetic graphene oxide have not so far been used for the dispersive micro-solid phase extraction of simultaneous or individual sulfonamide compounds.

In our previous study, a modified simple one-step co-precipitation method for the preparation of functionalized graphene oxide with iron oxide nanoparticle sorbents was utilized for dispersive micro-solid phase extraction of gold ions [38]. The unique advantages of this method as well as the fact that there is no other report about the utilization of magnetic graphene oxide in dispersive micro-solid phase extraction motivated us to investigate its capability for the extraction and separation of sulfadiazine. The extracted sulfadiazine was then converted to an azo dye upon reaction with thenoyltrifluoroacetone as a novel coupling agent and was quantified with fiber optic linear array spectrophotometry and mode-mismatched thermal lens spectrometry. The conditions regarding the extraction, preconcentration and determination were optimized and the method was successfully applied to the determination of sulfadiazine in different matrices.

2. Experimental

2.1. Reagents and materials

Sulfadiazine was purchased from the Alfa Aesar (Karlsruhe, Germany) and thenoyltrifluoroacetone was supplied by Sigma-Aldrich (USA). The other chemicals used in this study were purchased from the Merck Company (Darmstadt, Germany). All the sample solutions were prepared using double distilled water. A stock standard solution of sulfadiazine (1000.0 mg L^{-1}) was prepared through dissolving an appropriate amount of the bulk drug in a dilute alkaline solution. Working solutions were prepared daily via serial dilution of the stock solution. Thenoyltrifluoroacetone solution (1.0%) was prepared by dissolving an appropriate amount of the reagent in ethanol.

2.2. Instrumentation

An optimized angled mode-mismatched thermal lens spectrometer (OAMTLS) was designed in our laboratory (Fig. 1). In this configuration, we used a Nd-YAG laser (532 nm, 100 mW, TEM00) as a pump source and a He–Ne laser (632.8 nm, 10 mW, TEM00) as a probe source. A 8.5 cm focal length converging lens was used to focus the pump beam which encounters the cell surface after 0.5 Hz modulation by the mechanical chopper. Modulation of the pump beam decreases the effect of spherical aberration of the thermal lens and enhances the signal-to-noise ratio of the measured data [39]. Furthermore, pump beam modulation reduces the amount of deposited heat inside the sample and therefore the possibility of the sample degradation at the focusing point is significantly reduced. A 1.2 cm × 1.2 cm × 0.1 cm quartz cell with 0.1 cm optical path was utilized for holding the samples during the experiments. The probe beam was reflected from the mirror in a way to make an angle of ~11° with the direction of the pumping radiation and converged by a lens (f=22 cm) to produce a waist location before the sample cell. A mismatched parameter was achieved by the optimization of distance (5 cm) between the probe beam waist location and the sample. Then, the probe beam