Analytica Chimica Acta 932 (2016) 22–28

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Simultaneous extraction and determination of albendazole and triclabendazole by a novel syringe to syringe dispersive liquid phase microextraction-solidified floating organic drop combined with high performance liquid chromatography

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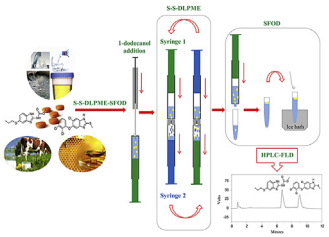
HIGHLIGHTS

- A novel dispersive liquid phase microextraction was developed for ALB and TCB.
- The analytes are extracted in a closed system using of two connected syringes.
- The dispersion is done by injection & back injection of mixture of solvent/sample.
- The dispersion is done without the use of dispersing agent, ultrasonic bath or vortex mixer.
- The combination of method with HPLC-FLD allows trace determination of ALB and TCB.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 March 2016
Received in revised form
7 May 2016
Accepted 9 May 2016
Available online 20 May 2016

Keywords:
Syringe to syringe dispersive liquid phase microextraction-solidified floating organic drop
High performance liquid chromatography
Albendazole
Triclabendazole

ABSTRACT

A syringe to syringe dispersive liquid phase microextraction-solidified floating organic drop was introduced and used for the simultaneous extraction of trace amounts of albendazole and triclabendazole from different matrices. The extracted analytes were determined by high performance liquid chromatography along with fluorescence detection. The analytical parameters affecting the microextraction efficiency including the nature and volume of the extraction solvent, sample volume, sample pH, ionic strength and the cycles of extraction were optimized. The calibration curves were linear in the range of 0.1–30.0 μg L^{-1} and 0.2–30.0 μg L^{-1} with determination coefficients of 0.9999 and 0.9998 for albendazole and triclabendazole respectively. The detection limits defined as three folds of the signal to noise ratio were found to be 0.02 μg L^{-1} for albendazole and 0.06 μg L^{-1} for triclabendazole. The inter-day and intra-day precision (RSD%) for both analytes at three concentration levels (0.5, 2.0 and 10.0 μg L^{-1}) were in the range of 6.3–10.1% and 5.0–7.5% respectively. The developed method was successfully applied to determine albendazole and triclabendazole in water, cow milk, honey, and urine samples.

1. Introduction

Albendazole (ALB) and triclabendazole (TCB) are two kinds of benzimidazole anthelmintic drugs (BADs). These drugs are widely

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http://dx.doi.org/10.1016/j.aca.2016.05.014
0003-2670/

used for the control and treatment of parasitic infections in animals and agriculture. However, long-term use of BADs can cause several toxic effects including congenic malformations, diarrhea, polyploidy, necrotic lymphoadenopathy, and pulmonary edemas [1]. The widespread and improper use of BADs can also result in contamination of dairy products and water by their residue, which is a potential threat to human consumers [2]. So, the government and corresponding organizations have set a maximum concentration level (MCL) or maximum residue limits (MRLs) to control the amount of BADs in drinking water and food samples. For example, Codex [3] and the Australian Government has recommended an MRL of <100 μg kg^{-1} for benzimidazole anthelmintics in milk [4], the European Water Framework Directive has set an MCL of 0.1 mg L^{-1} for most benzimidazole compounds in natural waters [5], and the European Community legislation has set an MRL of 10 and 100 μg kg^{-1} for TCB and ALB in milk respectively [6]. Therefore, development of accurate analytical techniques to monitor and determine these drugs in food and environmental samples is a challenging task [7].

Various analytical techniques such as spectrophotometry [8], spectrofluorimetry [9], capillary zone electrophoresis (CZE) [10], and high performance liquid chromatography (HPLC) [11] have been used to determine these drugs. Among the mentioned techniques, high performance liquid chromatography combined with mass-spectrometry [12], ultraviolet [13], or fluorescence detection system [14] is widely applied to determine ABDs in different real samples. However, due to the low concentration of the drugs in real samples and the complexity of sample matrices, direct drug determination by HPLC is difficult or impossible. Thus, a separation and preconcentration step is required prior to drug analysis by HPLC. In this regard, several sample preparation methods including liquid-liquid extraction (LLE) [15], solid-phase extraction (SPE) [16], solid phase microextraction (SPME) [11] and liquid phase microextraction (LPME) [17] have been used. However, traditional sample pretreatment methods (i.e. LLE and SPE) are time-consuming as well as labor-intensive, and LLE needs large volumes of highly pure and toxic organic solvents. To overcome these limitations, sample pretreatment has moved toward miniaturization of traditional extraction methods, which has resulted in development of SPME and LPME.

Liquid phase microextraction (LPME) is a miniaturized mode of LLE that greatly reduces the consumption of organic phases [18]. LPME has the advantages of low cost, simple operation, low toxicity and a high enrichment factor. Different modes of LPME that have been developed include single drop microextraction (SDME) [19], hollow fiber liquid phase microextraction (HF-LPME) [20], dispersive liquid phase microextraction (DLPME) [21,22], and solidified floating organic drop microextraction (SFODME) [23,24]. Among these modes, DLPME has been widely used for the extraction of different analytes from various matrices [25]. In this mode of LPME, the extraction solvent with a density higher or lower than that of water is mixed with a polar solvent such as methanol or acetonitrile (as a dispersive solvent) and is rapidly injected into the aqueous sample containing the analyte. In this state, a cloudy solution containing fine droplets of the extraction solvent is formed in the aqueous phase which results in rapid extraction of the target analyte. DLPME has the advantages of rapidity, simplicity, low cost, use of low amounts of organic solvents, possibility of obtaining a high enrichment factor as well as no need for a large sample volume and a specific extraction vessel. However, this method is a ternary component solvent system, and the dispersive solvent may cause an increase in the solubility of the extraction solvent in the aqueous phase as well as a decrease in the partition coefficients of analytes between the aqueous phase and the extraction solvent. Furthermore, separation and recovery of the extraction solvent is difficult. To resolve these drawbacks, ultrasonic-assisted emulsification microextraction (UAEME) [26], vortex assisted emulsification microextraction (VAEME) [27,28], and DLPME based on solidified floating organic drop (DLPME-SFOD) [29,30] have been developed. In VAEME and UAEME, the dispersive solvent is eliminated and the extraction solvent is dispersed in the aqueous sample by the use of vortex energy and ultrasound radiation respectively. However, these methods require longer extraction time than the traditional DLPME as the dispersion of the solvent takes longer time, and the ultrasonic energy may cause the degradation of analytes and complexes. In DLPME-SFOD mode, a low-toxin and low-density organic solvent, such as 1-dodecanol, with a melting point near the room temperature is used as the extraction solvent. This simplifies the solvent recovery at the end of extraction as the solvent solidifies and floats on the top of the sample solution. However, the method is still a three-phase system and does not alleviate the need for a dispersive solvent.

In this research, a new mode of DLPME called 'syringe to syringe dispersive liquid phase microextraction-solidified floating organic drop (SS-DLPME-SFOD) is designed. In this method, two disposal syringes are connected to each other through one needle and used as an extraction flask. The sample solution along with the extraction solvent is put in syringe 1, and then syringe 2 is connected to it. The solvent is simply dispersed in the aqueous phase through the injection and back injection of the mixture of the sample and the extraction solvent into the extraction vessel. Finally, the mixture is transferred to a centrifuge tube, and the phases are separated and easily recovered by centrifugation and solidification of the extraction solvent in an ice bath. This technique does not require a dispersive solvent, vortex mixer or ultrasound bath. In addition, as the extraction is performed in a closed system, it prevents the loss of the extraction solvent through evaporation and alleviates the harmful effects of hazardous analytes and toxic organic solvents on the operator and the environment. The designed method is applied for simultaneous separation and preconcentration of trace amounts of ALB and TCB from various samples before their determination by high performance liquid chromatography.

2. Experimental

2.1. Chemicals and reagents

Albendazole and triclabendazole of analytical reagent grades were supplied from Sigma Aldrich (St. Louis, MO, USA). HPLC grade water and methanol, dipotassium hydrogen phosphate, hydrochloric acid, sodium chloride, 1-dodecanol, 1-decanol, and 2-undecanol (of analytical grade) were provided from Merck (Darmstadt, Germany). The stock standard solutions of ALB and TCB were prepared at the concentration of 100 mg L^{-1} by dissolving an appropriate amount of each drug in methanol. The solutions were then kept in a refrigerator at −4 °C. Working standard solutions were prepared on a daily basis by diluting the stock standard solution adequately with high purity water (HPLC grade). All the prepared standard and solutions were kept in clean polypropylene bottles (Nalgene, Lima, OH, USA).

A phosphate buffer solution (2.0 mol L^{-1}, pH = 8.0) was prepared by dissolving 358 g of dipotassium hydrogen phosphate in 900 mL of deionized water, adjusting its pH to 8.0 with hydrochloric acid and diluting the solution to 1000 mL with deionized water.

2.2. Instrumentation

A Knauer HPLC system (Berlin, Germany) composed of LC-pump 1000, 20 μL sample loop and a fluorescence detector RF-10A_{XL} (Shimadzu, Japan) was used for chromatographic analysis. The