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Surfactant-mediated microextraction approach using switchable hydrophilicity solvent: HPLC-UV determination of Sudan dyes in solid food samples

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ABSTRACT

An easy performed surfactant-mediated microextraction approach using switchable hydrophilicity solvent was proposed for the sample pretreatment of solid food samples. The procedure included mixing of solid food sample and aqueous solution of sodium hexanoate provided a micellar solution formation. By this sample pretreatment step, the hydrophobic analytes were extracted into the micellar solution. The injection of sulfuric acid solution into the sample suspension decreased the pH value of the aqueous phase and as a result promoted the hexanoic acid phase formation and final phase separation from the sample suspension. The performance of the suggested approach was demonstrated by the HPLC-UV determination of Sudan dyes (Sudan I, Sudan II and Sudan III) in spiked salted salmon and spices powder samples. This analytical task was used as a proof-of-concept example. The LOD values, calculated from the blank tests based on 3σ, were 0.15 μmol L^{-1} (0.19 mg kg^{-1}), 0.02 μmol L^{-1} (0.028 mg kg^{-1}) and 0.10 μmol L^{-1} (0.18 mg kg^{-1}) for Sudan I, Sudan II and Sudan III, respectively. The sample pretreatment time was 25 min. The proposed method has advantages in comparison with previous developed methods for Sudan dyes determination due to the low consumption of extraction solvent and simplicity of sample pretreatment steps. The developed method can be applied for hydrophobic analytes microextraction from various solid samples (pharmaceutical, food, soil samples, etc.).

1. Introduction

The determination of the residues and contaminants in the complex samples matrices usually requires combination of several steps of sample pretreatment [1]. Sample pretreatment plays a crucial role in chemical analysis due to its great influence to the reliability and accuracy of the results.

Nowadays, microextraction techniques are much more preferable for sample pretreatment instead of the conventional methodologies such as liquid-liquid extraction and solid-phase extraction. The reason is that the microextraction techniques correspond to Green analytical chemistry and require minimum volumes of the organic solvents for extraction, resulting in low waste generation and less toxicity. In liquid-liquid microextraction methods, the latter requirement is ensured by using only a small amount (up to around 100 μL) of the organic solvent, while the volume of the aqueous phase is of the order of several mL [2]. Moreover, the microextraction procedures generally have better efficiency, shorter extraction time, lower cost and are easily automated based on flow systems [3,4].

Homogeneous liquid-liquid microextraction (HLLME) is one of the effective sample preparation techniques. The HLLME assumes the phase separation and extraction of the target analytes from homogeneous sample solution. The benefit of the HLLME is its infinitely large interaction surface between organic and aqueous phases [5].

Recently, so called switchable hydrophilicity solvents (SHSs) have been suggested as extractants for the HLLME. In this case the HLLME procedure is based on the reversible switching between hydrophobic water-insoluble and hydrophilic water-soluble forms of SHS [6]. Such reversible switching simplifies the phase separation and provides excellent field for the development of SHS based microextraction procedures for different target analytes. It was found that medium chain fatty acids provide switchable behavior [7]. In this case phase separation and microextraction are achieved by simple changing of the solution pH. Various approaches for the sample pretreatment of aqueous samples using the medium chain fatty acids as the SHSs have been presented in literature: fatty-acid-based in-tube dispersive liquid-liquid microextraction [7], automated effervescence-assisted switchable solvent-based HLLME

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[8], SHS microextraction with solidification of floating organic droplet [9], effervescence tablet-assisted switchable solvent-based microextraction [10] and automated continuous homogeneous microextraction [11].

It is known, that medium chain fatty acid salts can have behavior of anionic surfactants and can form micelles solution [8]. This approach can be used for extraction of hydrophobic analytes from solid samples into micelles solution. Moreover, switchable behavior of the medium chain fatty acids can be used for additional preconcentration of the hydrophobic analytes from micelles solution and analytes separation from sample suspension. To the best of our knowledge, the sample pretreatment of solid samples based on two phenomena described has not been presented in literature.

In this work, a surfactant-mediated microextraction approach for the pretreatment of solid food samples based on micellar solution formation and switchable behavior of the medium chain fatty acid has been presented for the first time. The hexanoic acid was investigated as the SHS for the pretreatment of solid food samples. It was established that sodium salt of hexanoic acid acted as anionic surfactant and formed micellar solution results in efficient extraction of hydrophobic analytes from solid food samples. When mineral acid was added to the sample suspension, the sodium hexanoate was switched to hexanoic acid. The organic phase containing target analytes was then separated from the aqueous sample suspension.

To demonstrate the efficiency of the suggested approach, the proposed procedure was applied to determine Sudan dyes (Sudan I, Sudan II and Sudan III (ESM Fig. 1)) as proof-of-concept analytes in solid food samples using HPLC-UV. In recent years, the determination of Sudan dyes in food has become an important task of food quality control. Despite the fact that Sudan dyes provide genotoxic carcinogenic effect to the humans, they are still utilized illegally in some daily foodstuffs because of its colorfastness and low cost [12].

2. Experimental

2.1. Reagents and solutions

All chemicals and reagents were of analytical grade. Ultra pure water from Millipore Milli-Q RG (Millipore, California, USA) was used. Sudan I (1 (phenylazo) 2 naphthol), Sudan II (1 [(2,4 dimethylphenyl) azo] 2 naphthol) and Sudan III (1 (4 phenylazophenylazo) 2 naphthol) (dyes content ≥95%) were purchased from Vecton (St. Petersburg, Russia). Sudan dyes stock solutions (1 g L^{-1}) were prepared by dissolving of corresponding amount of the reagents in acetonitrile. The solutions were stored in a dark place at 5 °C and used within 1 month. Working solutions of Sudan dyes were prepared immediately before the experiments by dilution of the stock solutions by water. Solution of sodium hexanoate (2.5 mol L^{-1}) was prepared by mixing 2.9 g of hexanoic acid (Sigma, Germany) and 5 mL of 5 mol L^{-1} NaOH and then diluting to 10 mL with deionized water.

2.2. Samples

Salted salmon and spices powder from different brands produced by domestic companies were purchased from local supermarkets (St. Petersburg, Russia). The salted salmon samples were homogenized using a mixer and stored at 8 °C at a refrigerator before analysis.

Spiked samples were prepared by addition of calculated volumes of solutions of Sudan dyes in acetonitrile to homogenized salted salmon and spices powder samples. Then, the acetonitrile was evaporated at 80 °C using a RV 8 V rotary evaporator (IKA, Germany). Afterwards, prepared spiked samples were stored at 8 °C at a refrigerator for 1 month and then analyzed by the developed and reference procedures.

2.3. Microextraction procedure

At the first stage (Fig. 1) 200 ± 10 mg of sample was placed into a polypropylene vial and 1 mL of sodium hexanoate solution (2.5 mol L^{-1}) was added. The mixture obtained was mixed and placed into an ultrasonic thermostating bath (Sapphire, Russia, 130 W, 35 kHz) and thermostated (salted salmon samples at 60 °C for 20 min, spices powder samples at 70 °C for 10 min). After cooling 200 μL of 6 mol L^{-1} H_2SO_4 were added and the hexanoic acid phase containing analytes was separated. After that, to precipitate solid sample particles the mixture was centrifuged at 3000 G for 10 min and the upper homogeneous organic layer was aspirated for analysis and injected into a HPLC-UV system. After centrifugation the solid sample particles were remained in the bottom aqueous phase.

2.4. HPLC-UV procedure

Chromatographic separation was carried out using a LC-20 Prominence HPLC-UV system (Shimadzu, Japan) with Luna C18 (150 mm × 3 mm, 100 Å; Phenomenex, USA) at 30 °C. UV–vis spectrophotometer set at 506 nm was used as the detector, and the volume of the injected sample was 20 μL. The gradient elution program was used as follows:

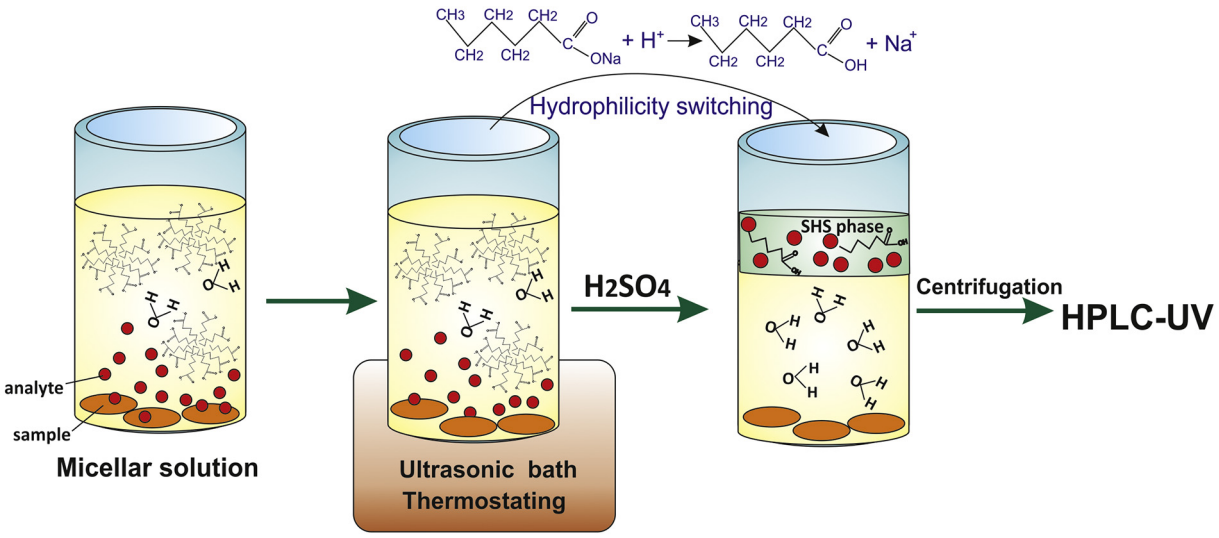

Fig. 1. The procedure for surfactant-mediated microextraction of Sudan dyes from solid food samples using switchable hydrophilicity solvent.