



Ultrasound-assisted single-drop microextraction for the determination of cadmium in vegetable oils using high-resolution continuum source electrothermal atomic absorption spectrometry[☆]

Jorge S. Almeida^a, Taiana A. Anunciação^a, Geovani C. Brandão^{a,c}, Alailson F. Dantas^a, Valfredo A. Lemos^b, Leonardo S.G. Teixeira^{a,c,*}

^a Departamento de Química Analítica, Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Salvador, Bahia 40170-280, Brazil

^b Laboratório de Química Analítica (LQA), Universidade Estadual do Sudoeste da Bahia, Campus de Jequié, Jequié, Bahia 45506-191, Brazil

^c INCT de Energia e Ambiente, Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Salvador, Bahia 40170-280, Brazil

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ABSTRACT

This work presents an ultrasound-assisted single-drop microextraction procedure for the determination of cadmium in vegetable oils using high-resolution continuum source electrothermal atomic absorption spectrometry. Some initial tests showed that the best extraction efficiency was obtained when using ultrasound instead of mechanical agitation, indicating that acoustic cavitation improved the extraction process. Nitric, hydrochloric and acetic acids were evaluated for use in the extraction process, and HNO₃ gave the best results. A two-level full-factorial design was applied to investigate the best conditions for the extraction of Cd from the oil samples. The influences of the sonication amplitude, time and temperature of the extraction were evaluated. The results of the design revealed that all of the variables had a significant effect on the experimental results. Afterward, a Box–Behnken design was applied to determine the optimum conditions for the determination of cadmium in vegetable oil samples. According to a multivariate study, the optimum conditions were as follows: sonication amplitude of 60%, extraction time of 15 min, extraction temperature of 46 °C and 0.1 mol L⁻¹ HNO₃ as the extractor solution. Under optimized conditions, the developed method allows for the determination of Cd in oil samples with a limit of quantification of 7.0 ng kg⁻¹. Addition and recovery experiments were performed in vegetable oil samples to evaluate the accuracy of the method, and the recoveries obtained varied from 90% to 115%. The samples were also analyzed after the acid digestion procedure, and the paired *t*-test (95% confidence level) did not show significant differences from the proposed method.

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1. Introduction

Vegetable oils are extracted from seeds of cereals, legumes and some fruits to give palm and olive oils. In general, oil extraction is based on the crushing of raw materials for oil extraction and is a common procedure. Oils are consumed by humans and have application in the food, pharmaceutical, cosmetic and chemical industries and as a feedstock for biodiesel production [1,2].

The metal content in foods is an important parameter for their quality control. The nutritional value and stability of oil can be compromised by the presence of some metals [3]. In addition, monitoring the concentrations of toxic metals, such as cadmium, in vegetable oils is

important due to the toxic nature of some of these species and their deleterious effects on oxidative stability, even at low concentrations [4].

The metals in vegetable oils may have different sources, such as from treatment processes (bleaching, refining and deodorizing), the corrosion of processing and milling equipment, storage procedures, residues of fungicides used in agriculture, soil contamination or metals emitted by vehicles and industries near the site of cultivation [5–7]. For the determination of metals in vegetable oils, the Environmental Protection Agency (EPA), in methods 3031 and 3051, recommends sample digestion with inorganic acids and the subsequent determination of metals by flame atomic absorption spectrometry (F AAS), graphite furnace atomic absorption spectrometry (GF AAS) or inductively coupled plasma optical emission spectrometry (ICP OES) [8,9].

Among these analytical techniques, the atomic spectrometric techniques are most commonly used for the determination of metals in vegetable oils [3,10]. Despite high sensitivity and selectivity, the analysis of samples by spectrometry techniques requires pretreatment to remove the organic matrix before the determination of the analytes. Different analytical strategies have been developed to eliminate the organic

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* Corresponding author at: Departamento de Química Analítica, Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Salvador, Bahia 40170-280, Brazil. Tel.: + 55 71 3283 6830; fax: + 55 71 3235 5166.

E-mail address: lsgt@ufba.br (L.S.G. Teixeira).

Table 1

Temperature program for the determination of cadmium in vegetable oil samples by HR-CS ET-AAS after an ultrasound-assisted acid microextraction procedure.

| Stage | Temperature, °C | Ramp, °C min ⁻¹ | Hold time, min | Ar flow rate, L min ⁻¹ |
|-------------|-----------------|----------------------------|----------------|-----------------------------------|
| Drying | 90 | 10 | 20 | 2.0 |
| Drying | 110 | 10 | 20 | 2.0 |
| Pyrolysis | 350 | 10 | 10 | 2.0 |
| Pyrolysis | 800 | 50 | 20 | 2.0 |
| Atomization | 1900 | 2500 | 5 | Stop |
| Clean | 2450 | 500 | 4 | 2.0 |

matrix, to separate the metal from the matrix or to prepare the sample for detection. These strategies include extraction with acids [10], solid phase extraction [11], ashing [12], dilution with organic solvents [13], acid digestion [7] and the formation of emulsions or microemulsions [3]. However, most of these procedures have the disadvantages of increasing the limit of detection due to the dilution of the sample, the employment of large volumes of toxic reagents or the application of time-consuming procedures.

Liquid–liquid extraction has the advantages of easy implementation and a preconcentration step that usually occurs prior to the extraction phase. However, the large volume of reagent that is required can be a disadvantage. Based on this disadvantage, the extraction procedure is miniaturized to increase the analytical sensitivity by reducing the amount of reagent [14]. Single-drop microextraction (SDME) is a strategy that, in combination with different techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) [15,16], UV–vis spectrophotometry [17], and electrothermal atomic absorption spectrometry (ET-AAS) [18,19] has been used for the determination of cadmium in biological, rice and water samples. In addition, the use of ultrasound has received acceptance for analyte extraction and separation from the organic phase [20]. The use of ultrasound energy and microextraction has been exploited for metal extraction from different samples, such as biological samples [21], natural waters [22], soil [23], fruit [24] and vegetable oils [4,25].

In this work, a procedure for the determination of cadmium in vegetable oils was developed using ultrasound-assisted single-drop microextraction (UA-SDME) and detection using high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS ET-AAS) with direct drop sampling. The microextraction process was assisted by ultrasound to increase the extraction efficiency, and the drops were directly introduced into the graphite furnace.

2. Experimental

2.1. Instrumentation

All determinations of cadmium were performed using a high-resolution continuum source electrothermal atomic absorption spectrometer model ContraA 700 (Analytik Jena AG, Jena, Germany)

equipped with a xenon short-arc lamp as a continuum radiation source, a charge-coupled device (CCD) array detector and a double-echelle monochromator. Pyrolytically coated graphite tubes and platforms were transversely heated. An autosampler (SSA 600) for the introduction of solid samples was repurposed for the direct introduction of the drops into the graphite furnace. All measurements were performed using the main spectral line of cadmium at 228.8018 nm. The absorbance signal was obtained from an integrated peak area using three pixels. Table 1 shows the graphite furnace temperature program utilized for the determination of cadmium. Argon gas (White Martins, São Paulo, Brazil) with a purity of 99.999% was used as the purge gas and protective gas during all heating stages, except for the atomization stage.

An ultrasonic bath model 75D (VWR InternationalTM, Cortland, New York, USA) with a controlled and adjustable temperature, 60 kHz power and 2-L internal capacity was employed for the cadmium extraction procedure in the vegetable oil samples. A chromatography glass syringe (Hamilton, Nevada, USA) with an internal volume of 20 μL and a stainless steel tip and plunger was used as the support for the extracting solution. After all experiments, the syringe was washed with detergent in an ultrasonic bath and then rinsed with deionized water. No corrosion was observed on the tip of the syringes after at least 200 experiments.

2.2. Reagents, solutions and samples

All aqueous solutions were prepared with analytical grade reagents and ultrapure water with a resistivity of 18 $\text{M}\Omega\text{ cm}^{-1}$ obtained from a Milli-Q® (Millipore, Bedford, USA) water purification system. The glassware and flasks to prepare the solutions were first decontaminated in a 10% (v/v) HNO_3 bath for 24 h. Afterward, the glassware was rinsed with water before use.

The organic analytical curve was established by diluting a multi-element organic standard containing 900 $\mu\text{g g}^{-1}$ of cadmium in base oil (AccuStandard Inc., New Haven, USA). The organic standards were subjected to the same extraction process as the samples. Base oil (AccuStandard) was used as the analytical blank and subjected to the same extraction process. The analytical curve was established over the concentration range from 0.01 to 1.0 $\mu\text{g kg}^{-1}$. The extracting solution (0.1%, v/v) was prepared from concentrated nitric acid (Merck) by diluting with water.

The vegetable oil samples (soybean, corn, sunflower, cotton and canola) were acquired from supermarkets in Salvador, Bahia, Brazil. The samples were stored in the dark at room temperature before the analysis.

2.3. Optimization of the ultrasound-assisted acid extraction procedure

A multivariate method was applied to investigate the best conditions for the extraction of cadmium from vegetable oil using a diluted acid solution. Initially, a full two-level factorial design was applied to evaluate the statistical significance of the effects and interactions of the following factors: amplitude of sonication, extraction time and temperature. Afterward, a Box–Behnken design was applied to determine the

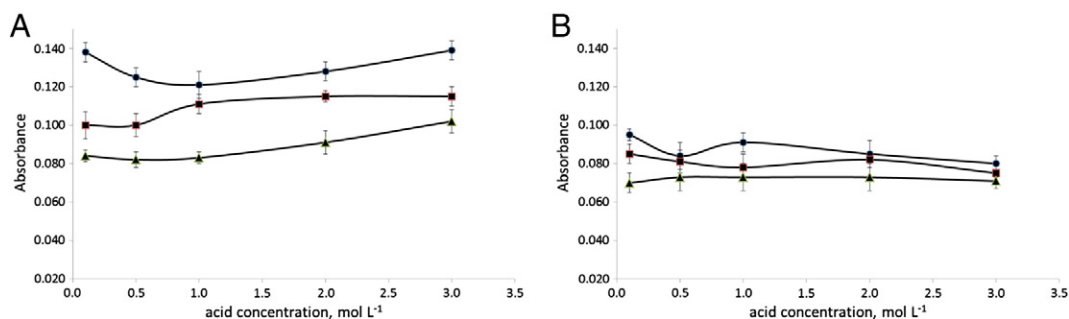


Fig. 1. Evaluation of the acids as the extracting solvent by (A) ultrasound and (B) mechanical stirring: (●) nitric acid, (■) hydrochloric acid and (▲) acetic acid. Experimental conditions: extraction time, 10 min; Cd concentration, 1.0 $\mu\text{g kg}^{-1}$; extracting solution volume, 5 μL ; and extraction temperature, 28 °C. Error bars correspond to the standard deviation of three replicates.

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