Determination of trace amount of cadmium using dispersive liquid-liquid microextraction-slotted quartz tube-flame atomic absorption spectrometry

Merve Fırat, Sezgin Bakırdere, Maral Selin Fındıkoğlu, Emine Betül Kafa, Elif Yazıcı, Melda Yolcu, Çağdaş Büyükpınar, Dotse Selali Chormey, Sabriye Sel, Fatma Turak *

Yıldız Technical University, Department of Chemistry, 34349 Istanbul, TURKEY

A B S T R A C T

This study was performed to develop a sensitive analytical method for the determination of cadmium by slotted quartz tube-flame atomic absorption spectrometry (SQT-FAAS) after dispersive liquid-liquid microextraction (DLLME). The parameters affecting the cadmium complex formation and its extraction output were optimized to obtain high extraction efficiency. These included the pH and amount of the buffer solution, and the concentration of the ligand. The DLLME method was comprehensively optimized based on the type and amount of extraction solvent, dispersive solvent and salt. The type and period of mixing needed for a more effective extraction was also investigated. In order to further improve the sensitivity for the determination of cadmium, the flame atomic absorption spectrometry was fitted with a slotted quartz tube to increase the residence time of cadmium atoms in the pathway of incident light from a hollow cathode lamp. The limits of detection and quantitation (LOD and LOQ) for the FAAS were found to be 42 and 140 $\mu g \, L^{-1}$, respectively. Under the optimum conditions, LOD and LOQ of the FAAS after DLLME were calculated as 1.3 and 4.4 $\mu g \, L^{-1}$, respectively. Combining both optimized parameters of the DLLME and SQT-FAAS gave 0.5 and 1.5 $\mu g \, L^{-1}$ as LOD and LOQ, respectively. Accuracy of the method was also checked using a wastewater certified reference material (EU-L-2), and the result was in good agreement with the certified value.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The toxicity of heavy metals has led to many legislations imposing limits on the amount that can be consumed, and recommended methods to be used for sampling and analysis of food stuffs [1–3]. Cadmium, a typical heavy metal is classified as one of the ten chemicals that are of great public concern [4]. Though many benefits have been derived from the numerous applications of cadmium, it persists in the environment and can reach humans by accumulating in the food chain [5]. In the human body, cadmium tends to accumulate in organs such as the kidney, heart, lungs, and causes bone softness [6]. Cadmium has been classified as Group 1 carcinogen by the International Agency for Research on Cancer [7,8]. The World Health Organization (WHO) and the Environmental Protection Agency (EPA) have limited the level of cadmium in drinking water to 3.0 $\mu g \, L^{-1}$ and 5.0 $\mu g \, L^{-1}$, respectively [9,10]. These low limits therefore require very sensitive analytical techniques for accurate and precise determinations. Flame atomic absorption spectrometry is a commonly used analytical technique for the

determination of heavy metals. One major disadvantage of this technique is its low sensitivity for most metals due to the low nebulization efficiency of the system [11]. Other techniques such as graphite furnace atomic absorption spectrometry (GFAAS), hydride generation atomic absorption spectrometry (HG-AAS), inductively coupled plasma-mass spectrometry (ICP-MS) and anodic stripping voltammetry (ASV) have been used to reach lower detection limits due to their relatively higher sensitivities [12–16].

Studies to improve the LOD/LOQ of the FAAS for metals have been reported in literature and these involve modification of the system and using extraction methods prior to analyte determination. Modification of the FAAS includes the use of slotted quartz tubes to increase the residence time of atoms in the flame, which consequently leads to increased absorbance as analytes interact more with the hollow cathode lamp light [17,18].

In addition, trapping studies using SQTs have been performed to get lower detection limits [19–23]. This is achieved by coating the inner walls of the tube with metals having higher melting points than the analytes under study [24]. Atoms of the analyte adsorb to the walls of the coated tubes under fuel-lean flame conditions in accordance with the inverse relation between adsorption and temperature. Atoms

---

* Corresponding author.
E-mail address: fturak2005@yahoo.com.tr (F. Turak).

adsorb more at lower temperatures and become concentrated at the coated surface. The trapped atoms are then released by changing to a fuel-rich flame or using a small volume of organic solvents such as methyl isobutyl ketone that give off high temperatures upon burning [25].

Extraction methods have been used to improve the LOD/LOQ of the FAAS for metals by forming metal complexes with a variety of ligands [26]. These include solid phase extraction (SPE), solidified floating organic drop microextraction (SFODME) and cloud point extraction (CPE) [27–29]. Other extraction methods employed for metals without the use of ligands have been reported in literature [30–32]. Dispersive liquid-liquid microextraction (DLLME) is a rapid, cheap and sensitive extraction method, which has been successfully applied for the determination of cadmium in water, food, forensics and environmental samples. The limits of detection reported in some literature using this method are 20 ng g^{-1}, 0.004 μg L^{-1}, 0.3 ng mL^{-1}, 0.4 μg L^{-1} and 0.6 ng L^{-1} [33–38].

The aim of this study was to create a new method (DLLME-SQT-FAAS) for the determination of cadmium at trace levels. Conditions of DLLME and parameters of SQT-FAAS were optimized to get lower detection limit for cadmium.

2. Materials and methods

2.1. Apparatus

A slotted quartz tube attached to a flame atomic absorption spectrophotometer (Analytik Jena NovAA 300) was used for the determination of cadmium. An air/acetylene mixture was used to generate the flame. A hollow quartz tube was custom cut to fit the AAS burner with the following dimensions; 16 mm internal diameter, 18 mm outer diameter, 13 cm length, 5.5 cm entrance slot and 3.0 cm exit slot. The SQT was aligned over the flame ensuring that light from the hollow cathode lamp passed through to reach the detector. The cadmium hollow cathode lamp was operated at 2.0 mA and a 0.50 nm spectral bandpass. Absorption measurements were performed using the 228.8 nm analytical line and a deuterium (D_2) lamp was used as background correction system.

2.2. Chemicals

All reagents used in this study were of analytical grade. A 1000 mg L^{-1} Cd standard stock solution was used to prepare working standards by diluting appropriate aliquots with deionized water obtained from a Milli-Q® Reference Ultrapure Water Purification System. pH 7.0 and 8.0 buffer solutions were prepared using potassium dihydrogen phosphate and sodium hydroxide, pH 9.0 using di-sodium tetraborate decahydrate and hydrochloric acid, pH 10 using di-sodium tetraborate decahydrate and sodium hydroxide, and pH 11 using sodium bicarbonate and sodium hydroxide. Diphenylcarbazone (Riedel-de Haen) stock solution was prepared in methanol and used to form cadmium complexes. Methanol, ethanol, isopropyl alcohol, chloroform, carbon tetrachloride, dichloromethane, sodium chloride, potassium chloride and potassium nitrate, all obtained from Merck (Germany) were used in the DLLME optimization process. A wastewater certified reference material (EU-L-2) was used for accuracy check.

2.3. Dispersive liquid-liquid microextraction process

1.0 mL of ligand solution was added to a 15 mL centrifuge tube containing 8.0 mL aqueous standard/sample and 0.50 mL buffer solution. The resulting orange-red colored solution was shaken slightly and injected with the ethanol/chloroform (3.0 mL/0.35 mL) mixture, which was prepared in a separate tube. It was then centrifuged for 2.0 min at 3461 g, and the bottom chloroform phase containing extracted cadmium complex was transferred into a clean tube and totally evaporated. 0.15 mL concentrated nitric acid was used to dissolve the

cadmium complex residue and placed in a water bath (40 °C) to speed up the dissolution. Vapor that arose from the heating process were condensed in a fridge and then centrifuged to ensure all droplets returned to the bottom of the tube. This was then analyzed by the FAAS instrument.

2.4. Samples

Tap water samples were taken from Davutpaşa, Kavacık and Maltepe districts of Istanbul, Turkey. Municipal wastewater was obtained from Paşaköy Advanced Biological Wastewater Treatment Plant, a submerged type membrane bioreactor, and was stored at −4 °C. The wastewater sample was filtered through a 125 mm filter paper and an RC 0.45 μm syringe filter prior to analysis.

3. Results and discussions

The optimization process was carried out with 50 ng mL^{-1} Cd standard solutions in a stepwise manner (keeping other parameters constant while optimizing one). The optimization of complex formation and DLLME was achieved with the FAAS, and these optimum parameters were in turn used to optimize the SQT system. All extractions were done in duplicates and optimum parameters were selected based on the highest average absorbance.

3.1. Complex formation optimization

Factors affecting the formation of the cadmium diphenylcarbazone complex were optimized to obtain a high complex output. These included amount and pH of the buffer solution, concentration of ligand and mixing period. The pH of an aqueous solution determines the state in which an analyte will exist; ionic or molecular. The pH of the buffer solution was varied between 7.0 and 11. A linear increase in absorbance was recorded up to pH 9.0, after which a plateau was observed as shown in Fig. 1. pH 10 was selected from the plateau region because it had a relatively lower standard deviation. The optimum amount of buffer solution was also studied by adding 0.50, 1.0 and 2.0 mL borax hydroxide to standard solutions. A fourth amount study was done by diluting an aliquot of the cadmium standard solely with the buffer solution. There was no significant difference between the absorbances recorded at different buffer solution amounts and as such, 0.50 mL was selected for further studies. The optimum concentration of the ligand was then studied using 0.02, 0.05, 0.10 and 0.20% (w/v). The absorbances recorded were not very different from each other but 0.05% w/v was selected because it was marginally higher than the other concentrations (Fig. 2) and produced a shaper peak. The absorbance signal of optimum ligand concentration is shown in Fig. S1 (Appendix). The effect of mixing period on the cadmium complex formation was studied for
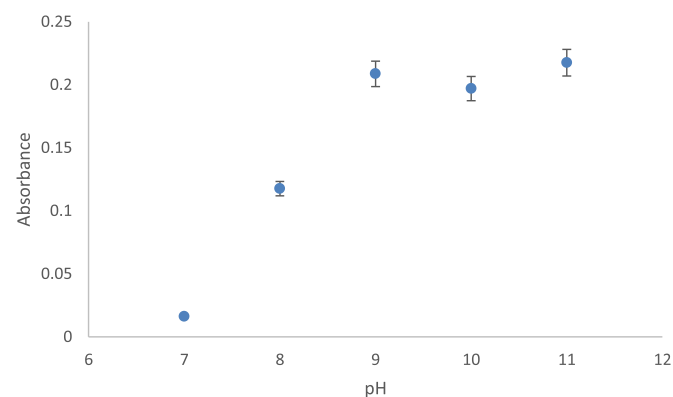

Fig. 1. A plot of buffer solution pH values against absorbance (error bars are standard deviations for $n = 2$).