

Separation and extraction of Cd (II) ion by solid phase extraction on sodium dodecyl sulfate (SDS)-coated alumina as their Traces Using a New Ligand 3,3',3'',3'''-tetraindolyl (terephthaloyl) dimethane (TTDM), before Their Flame Atomic Absorption Spectrometric Determinations in Colored Hair and Dryer Agents of Paint

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Abstract

A sensitive and selective solid phase extraction procedure for the determination of traces of Cd(II) ion has been developed. An alumina-sodium dodecyl sulfate (SDS) coated on with 3,3',3'',3'''-tetraindolyl (terephthaloyl) dimethane (TTDM). The influences of the analytical parameters including pH and sample volume were investigated. Common coexisting ions did not interfere on the separation and determination of analytes under study. The adsorbed analytes were desorbed by using 6mL of 4 mol L⁻¹ nitric acid. The responses are linear 0.01–0.90 for Cd²⁺ ion and detection limit for Cd²⁺ ion were found to be 1.1 (ng mL⁻¹), respectively. The relative standard deviation of the method was found to be less than 3.0%. The presented procedure was successfully applied for determination of analytes in Colored Hair and Dryer Agents of Paint.

Keywords: Cd(II); Surfactant coated on alumina; Solid phase extraction; Determination; Atomic absorptionspectrometry.

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1. Introduction

The toxicity and the influence of trace amount of metal ions emerged from their essential feature are very important in the context of pollution and nutritional view. Modern and even sensitive reasonable cost instruments such as flame atomic absorption spectroscopy (FAAS) fail to directly determine trace amount of metal ions in various environmental and biological complicated matrix samples due to their inadequate detection limits and interference from various species^[1,2]. These difficulties and limitations can be overcome with doing a preliminary separation and/or preconcentration step and subsequent measurement by FAAS to decrease the matrix interference (by its simplification) or improve in the detection limit^[3-6]. Solid phase extraction (SPE) composed of two distinct stages; a) selective and reversible binding of analytes to a solid support (modified); and b) their subsequent elution with a small volume of solvent that make possible simultaneous simplified matrices and enhance in sensitivity. Among various sorbents, silica gel chemically bonded with various organic compounds has received great attention due to its good mechanical and thermal stability, less susceptibility to swelling and shrinking^[7-11]. Our environment contains countless sources of cadmium and in the modern world this element is ubiquitous in food, water and air. The greatest human cadmium exposure comes from tobacco smoke and food consumption, most of which arises from the uptake of cadmium by plants from fertilizers, sewage sludge, manure and atmospheric deposition^[12]. Cadmium is not only regarded as essential to human life, but is now known to be extremely toxic^[13] and accumulates in humans mainly in the kidneys^[14]. Prolonged intake, even of tiny amounts, leads to severe dysfunction of the kidneys. Cadmium is widely found in society, either in useful products or in controlled wastes. The sensitivity of analytical techniques is often insufficient for its determination. Several methods have been developed to separate and determine Cd²⁺ ion. Traditionally, organic solvents^[15-17]. The SPE can easily be adapted for FAAS to improve the detection limit and selectivity of determinations. In our laboratory using various types of sorbents including activated carbon^[18], SDS-coated alumina^[19], modified chromosorb^[20], and modified polyvinyl chloride^[21], separation and/or preconcentration of metal ions has been gaining

popularity because of its high concentrating ability and simple operation. Among the various solid phases, those obtained by immobilization of chelating agent on support viz. alumina and silica gel have gained much attention with high repeatability and large lifetime. The design of a stable and selective solid phase sorbents for separation and preconcentration of a target metal ion depends on different factors such as the nature of solid support, its surface area and activity^[22]. Among these adsorbents, alumina is an important place in the solid phase extraction studies of heavy metal ions^[23]. A new modification mode for the alumina to use in solid phase extraction works was introduced by Hiraide et al^[24]. The organic reagent is incorporated in the cores of admicelles of sodium dodecyl sulfate attached to alumina surfaces. New organic reagents are immobilized on surfactant coated on alumina for separation and enrichment of different metal ions^[25,26], and recently polyaromatic hydrocarbon as well^[27]. The purpose of this work is to investigate the feasibility of absorption of these ions including Cd(II) ion on SDS coated on alumina modified with TTDM ^[28]. The parameters including pH of sample, amount of ligand and solid phase, type of eluting agent and flow rate were optimized.

2. Experimental

2.1. Instruments

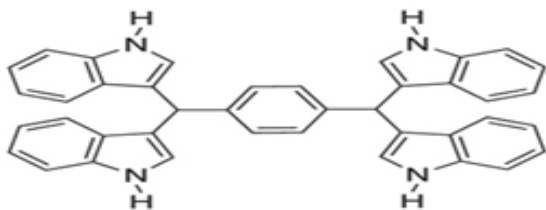
All the determinations of the analytes were carried out using a Sens AA GBC double beam atomic absorption spectrometer (AAS) equipped with deuterium background corrector. Hollow cathode lamps were used as radiation sources and the operational conditions of the equipment were established according to the manufacturer's recommendations for each element. An adjustable capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomizations. The UV/Vis spectra were obtained from a Perkin-Elmer, model Lambda 2 spectrophotometer. A Genway model 3510 pH/Ion meter with a combined glass electrode was used for pH measurements. Laboratory glassware was kept overnight in 10% nitric acid solution. Before use, the glassware was rinsed with distilled deionized water and dried in a laminar flux cabinet.

2.2. Reagents

Doubly distilled deionized water was used throughout the experimental work. Stock solutions of all under study elements were prepared by dissolving appropriate amount of ultrapure salt obtained from Merck (Darmstadt, Germany) in $4 \text{ mol L}^{-1} \text{ HNO}_3$. Working standard solutions were obtained by appropriate dilution of the stock standard solution. The pH was adjusted by addition of 0.1 mol L^{-1} nitric acid or 0.1 mol L^{-1} potassium hydroxide. The Al_2O_3 and sodium dodecyl sulfate (SDS) were purchased from Merck. The SDS solution was prepared by dissolving 1.0 g of surfactant in 100 mL volumetric flask while stirring. The ligand 3,3',3'',3'''-tetraindolyl (terephthaloyl) dimethane (TTDM) was synthesized according to literature.

2.3. Synthesis of 3,3',3'',3'''-tetraindolyl (terephthaloyl) dimethane (TTDM)

To synthesize TTDM (Figure 1), a mixture of indole (4 mmol, 0.468 g), terephthalaldehyde (1 mmol, 0.134 g), and $\text{Al}(\text{HSO}_4)_3$ (2 mmol, 0.636 g) in dimethyl sulfoxide (5 mL) was heated in an oil bath at 120°C . The reaction mixture was filtered after 1 h. The residue was washed with ethanol ($2 \times 4 \text{ mL}$). water (40 mL) was then added to the filtrate, and the precipitate filtered. The product was purified by column chromatography on silica gel, using eluent: ethyl acetate/*n*-hexane (10:90) to give pure tetra(indolyl)methane 0.492 g, 87% yield. Purification and characterization was achieved according to our previous report^[28].



Scheme 1. The structure of ligand 3,3',3'',3'''-tetraindolyl (terephthaloyl) dimethane (TTDM).

2.4. Preparation of solid phase

A 15 mL of sodium dodecyl sulfate (SDS – TTDM solution) was added to 30 mL of water solution containing 1 g of the Al_2O_3 particles. While shaking the suspension with a stirrer, the pH was adjusted to 2 with 2 mol L^{-1} hydrochloric acid to form TTDM impregnated ad micelles on alumina particles. After mixing for 15 min, the supernatant

solution was discarded and the remaining was used as modified solid phase. The solid phase was purified by passing 6mL of 4 mol L⁻¹ HNO₃ and neutralized with 0.1mol L⁻¹ KOH. The sorbent in refrigerator is stable for at least one month. The SDS concentration was fixed below the CMC of SDS (8×10⁻³ mol L⁻¹) to avoid formation of micelles in the aqueous solution.

2.5. Application to real samples

Two kinds of naphthenates, cadmium naphthenate, were selected among the various types of dryer agents. These kinds of paint additives are some resistant soap prepared from naphthenic acid, a sort of acid which is found naturally in raw oil, and they widely are used in the paint technology as the catalysts in drying process of the paint film^[29]. Analysis of the both samples was performed as the following: A sample of the dryer containing 5 mg of the metal was piped into a 100 mL beaker and 2 mL concentrated nitric acid was added. The mixture was boiled for about 3 minutes on a hot plate with rapid stirring. When the hydrolysis was completed, the naphthenic acids along with the solvent present separated as a clear light yellow layer. The contents of the beaker were cooled and transferred to a separating funnel and 10 mL of ethyl acetate was added to it. The lower aqueous layer containing the metal was drawn off into a 250 mL beaker. The organic layer was then washed twice with 10 mL DDW and the washing was added to the beaker each time^[30]. The determination of cadmium in colored hair samples of human was performed as the following: prior to analysis, each individual hair sample was cut into a size less than 1cm and mixed to make a representative hair sample. After washing, the sample was dried in an oven at 50 °C for 5 minutes. 100 mg of the sample was heated in the presence of 10 mL concentrated nitric acid on a hot plate for about 20 minutes. After a clear solution was formed, 1 mL of H₂O₂ 30% was added and again heated to one-fourth volume^[31].

3. Results and discussion

The adsorption of SDS on alumina is highly dependent on the solution pH. Negatively charged SDS was more effectively and nearly quantitatively retained (about 99% even in 4 mol L^{-1} nitric acid) on the positively charged alumina surfaces at pH 1–4. Therefore, retention of organic compounds on SDS-coated alumina³²⁻³⁴ occurs. This phenomenon greatly increases by decreasing the pH due to the higher charge density on the mineral oxide surface^[32,33]. The anionic surfactant SDS is effectively retained on positively charged alumina surfaces via formation of self-aggregates^[34] over a wide pH range (2–12), whereas very little amount of SDS could be retained on inert surface of alumina. Therefore, alumina is essential for the preparation of surfactant-coated sorbents. It was also confirmed that, while solid phase of alumina or alumina coated with SDS show low tendency for retention of Cd^{2+} ion, the solid phase of immobilized Schiff base on surfactant-coated alumina was capable of retaining these metal ions from the sample solution quantitatively. Therefore, it was chosen as the sorbent for subsequent work.

3.1. Spectrophotometric titration

Standard stock solutions of ligand ($3.5 \times 10^{-6} \text{ mol L}^{-1}$) and metal ions ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) were prepared by dissolving appropriate and exactly weighed pure solid compounds in pre-calibrated 25.0 mL volumetric flasks and diluted to the mark with aceto nitrile or methanol. Working solutions were prepared by appropriate dilution of the stock solutions. Titration of the ligand solution ($1.0 \times 10^{-6} \text{ mol L}^{-1}$, 3.5 mL) was carried out by the addition of micro liter amounts of a concentrated standard solution of the metal ion in aceto nitrile or methanol (0.05 mol L^{-1}) using a precalibrated micro syringe^[35]. The spectra of TTDM with the addition of Cd^{2+} ion, corresponding mole ratio plot and curve fitting at wavelengths of 498 or 495 nm, are depicted in Figure 2, respectively. complexation occurs through binding of Cd^{2+} ion to nitrogen atoms, leading to the ML, or ML, ML_2 models. Formation constants and stoichiometries of complexes were calculated using the Kinfite program^[36] and results are shown in Table 1.

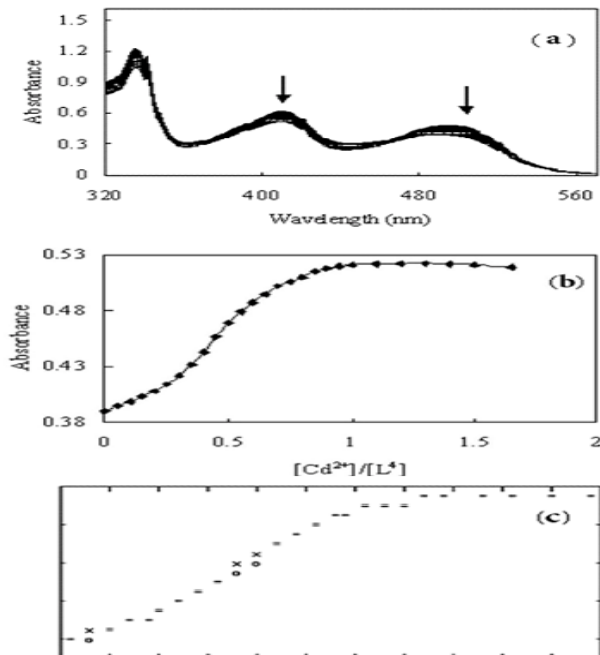


Figure 2. U.V- Visible spectra for titration of TTDM (3.5×10^{-6} mol/L) with Cd^{2+} (5.0×10^{-5} mol/L) in MeOH ($T = 25^{\circ}C$) and $I = 0.05$ M) (a) molar ratio plot at 495 nm (b) and corresponding curve fitting (c).

Table 1. Stepwise stability constants of complexation between metal ions and TTDM in MeOH.

Metal ion	Log K_1	Log K_2	M/L
Cd^{2+}	$5.7 + 0.23$	$1.2 + 0.3$	1:1 , 1:2

3.2. Effect of pH on metal ion recovery

pH is one of the important factors which affect the efficiency of retention/elution metal ions by solid phase extraction^[37-39]. The effect of pH was studied by varying pH in the range of 5–12. It can be seen from Fig. 3. that the adsorption amounts of mixed hemimicelles systems decreased obviously with the increasing of pH. Especially, when pH was above the potential of zero charge (PZC) of alumina (about 10.0), the

adsorption amount of SDS-coated alumina had a sharp decrease. With increasing the pH, the positive charge of alumina surface reduced gradually and became negative charged when the pH was above its PZC. As a result, the SDS molecules desorbed from alumina surface gradually and begin to decrease. On the other hand the progressive decrease in the retention of these metal ions at a low pH is due to the competition of the hydrogen ion with the metal ions for complexation and binding to Schiff base. The decrease in absorption at $\text{pH} > 9.5$ is probably due to the precipitation of Cd^{2+} ion as insoluble $\text{M}(\text{OH})_2$ or $\text{M}(\text{OH})^+$. To achieve high efficiency and good selectivity, a pH of 9.5 was selected for subsequent work.

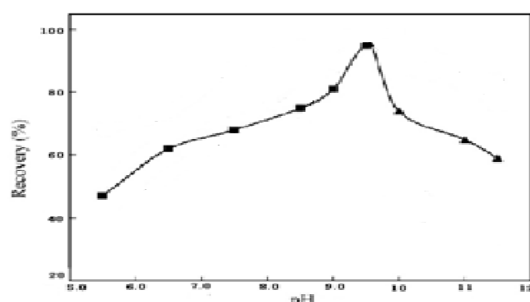


Fig. 3. Effect of pH on recovery of metal ions (N= 3), Conditions: 250mL of sample at various pH, eluent, 6mL of $4.0 \text{ mol L}^{-1} \text{ HNO}_3$, solid phase, 1.0 g Al_2O_3 , 60mg SDS and 10mg ligand.

3.3. Effect of amount of ligand on metal ion recovery

In order to investigate the optimum amount of ligand for the quantitative extraction of the metal ions by the SDS-coated alumina, the extraction was conducted by varying the amount of ligand from 0 to 50mg. Therefore, solid phase comprises of various amount of ligand coated on constant amount of alumina were prepared and enrichment experiment was carried out, results are shown in Fig. 4. As can be seen, with increasing amount of ligand up to 10mg an increase in recoveries can be achieved and further increase does not enhance the efficiency. The various amount of solid phase has been used for the preconcentration of understudy Cd^{2+} ion and results display that up to 1.0 g of solid phase, the extractions efficiency was increase and further addition has not significant effect on recoveries.

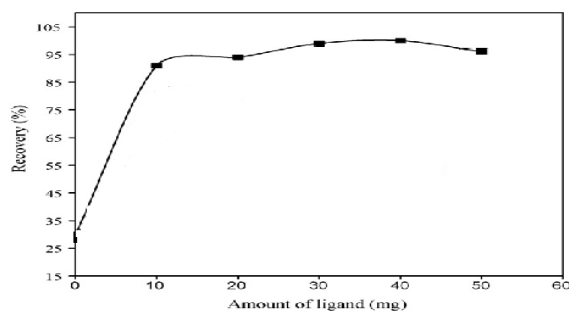


Fig. 4. Effect of amount of TTDM on recovery of metal ions ($N= 3$), Conditions: 250mL of sample at pH 9.5, eluent, 6mL of 4.0 mol L⁻¹ HNO₃, solid phase, 1.0 g Al₂O₃, 60mg SDS and different amount of ligand.

3.4. Amount of SDS

The influence of SDS amount on the percentage of complexed ions ad-solubilized was investigated by shaking 250mL of a solution containing 50µg of each Cd²⁺ ion with solid phase containing various amounts of SDS, 1 g γ- Al₂O₃ and 10 mg TTDM at pH 9.5 for 90min with stirring rate 300 rpm. In the absence of SDS, metal ions retained on TTDM alumina with 60% lower efficiency for all ions. The retention of metal ions on hemi-micelles, which have a hydrophobic surface, was clearly dependent on analyte complex polarity. Therefore, addition of SDS is necessary. The formation of minute amounts of ad-micelles was essential to achieve complete ad-solubilization of chelates of these ions. At surfactant concentrations higher than about 60 mg/g alumina, a decrease in the retention percentage of ions was observed, as a result of the formation of micelles (Fig. 5). The adsorption amount began to decrease when the SDS added exceeded 60mg for 1.0 g of alumina. It can be explained by the fact that with more SDS added, its molecules began to form micelles in the bulk aqueous solution; moreover, the micelles make the TTDM distribute into the bulk solution again. In this region the slope of alumina adsorption curve is flat, which indicated that the interactions between TTDM and SDS-coated alumina were strong. As a result, it was more difficult for SDS-coated alumina to desorb TTDM into aqueous solution.

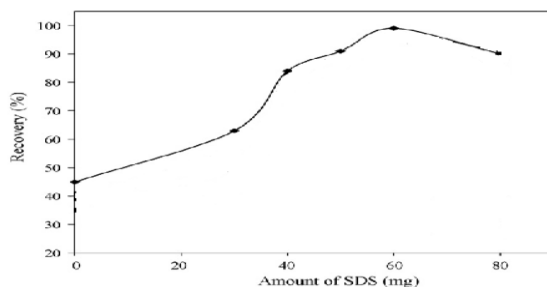


Fig. 5. Effect of amount of SDS on recovery of metal ions ($N= 3$), Conditions: 250mL of sample at pH 9.5, eluent, 6mL of 4.0 mol L⁻¹ HNO₃, solid phase, 1.0 g Al₂O₃, various amount of SDS and 10mg ligand.

3.5. Eluent types and eluent volume

In order to choose the most effective eluent for desorbing the Cd²⁺ ion from the sorbent surface, a series of eluents (different acids) were used in order to find a selective eluent for desorbing enriched ions from sorbent surfaces. A total of 6ml of 4.0 M of the above-mentioned eluents were used for desorbing the adsorbed ions. The results (Table 2) showed that the recovery is best when nitric acid solution was used as the eluent. The influence of the concentration of nitric acid on the desorption of these ions was studied. For desorbing 40 µg of ions, already adsorbed on 1.0 g of adsorbent, different concentrations of the eluent (nitric acid) have been used. At concentrations more than 4 M the extraction efficiency reached maximum.

3.6. Effect of time and rate of shaking

The efficiencies of the analyte deposition depend on the contact time and stirring rate of sample with the solid phase. It is necessary to require the preconcentrate of metal ions in short time. In this regard, a replicate six set of analyte and adsorbents were prepared and stirring at different time intervals (20–120 min) with stirring rate of 100–400 rpm. It was observed that 90 min mixing at 300rpm stirring rate to optimum recoveries of Cd²⁺ ion. On the other hand, a set of similar solid phase

Table 2: Effect of type and concentration of eluting agent on recovery of the analytes.

Eluent	Recovery (%)
	Cd
8mL 4mol L ⁻¹ H ₃ PO ₄	28.7
8mL 4mol L ⁻¹ H ₂ SO ₄	12.4
8mL 4mol L ⁻¹ HCL	58.6
8mL 4mol L ⁻¹ CH ₃ COOH	29.6
8mL 2mol L ⁻¹ HNO ₃	64.5
8mL 3mol L ⁻¹ HNO ₃	73.2
8mL 4mol L ⁻¹ HNO ₃	98.5
8mL 5mol L ⁻¹ HNO ₃	84.0
4mL 4mol L ⁻¹ HNO ₃	90.0
6mL 4mol L ⁻¹ HNO ₃	98.5
9mL 4mol L ⁻¹ HNO ₃	98.5
10mL 4mol L ⁻¹ HNO ₃	98.5

extraction were carried out at 300rpm while keeping the temperature at 25–60°C for 90min. Later on, the residual concentration was determined where the metal ion uptake was estimated. The TTDM adsorption amounts of SDS-coated alumina systems decreased with increasing temperature. The decreased adsorption amounts suggested that the two-adsorption systems were exothermic. With the increasing of temperature the adsorbate–adsorbent bonds were weakened and TTDM had desorption trend from the solid phase to solution phase. It can also be proved by the changes of SDS

adsorption amounts. With the temperature increasing, the bond between alumina and SDS became weak and partial SDS molecules began to desorb from alumina surface.

3.7. Investigation of method performances

Added 250mL of solution of metal ions in the range of 0.01–1.00 gmL^{-1} with coated adsorbents at the optimum conditions, to obtain the calibration curves, repeatability and reproducibility. The responses are linear 0.01–0.90 for Cd^{2+} ion. The sensitivity of developed method was reproduced by detecting the limit of detection (LOD), defined as the lowest concentration of Cd^{2+} ion below which quantitative sorption of the metal ion by basic alumina is not perceptibly seen. The limit of detection (LOD) of the present work were calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions (without samples or standards). The limit of detections based on three times the standard deviations of the blank ($N= 5$, $\text{LOD} = \bar{X}_b + 3s$, where LOD is the limits of detection and \bar{X}_b is the blank value) for Cd^{2+} ion were found to be 1.1 (ng mL^{-1}), respectively. It was found that the recovery for Cd^{2+} ion was 98.7 and with RSD of 1.7.(Table 3). It was also observed that recovery for repeated recovery on the same solid phase not varies more than 3%. Therefore, understudy solid phase can be repeatedly use without considerable loss of uptake capacity^[40].

Table 3: Specification of Method at Optimum Conditions for Each element According.

parameters	Value for each ion
	Cd
Linear Range ($\mu\text{g mL}^{-1}$)	0.01-0.90
Detection Limit (ng mL^{-1})	1.1
RSD %	1.7
Recovery %	98.7

3.8. Effect of foreign ions

To assess the possible applications of the procedure, the effect of foreign ions or/and often accompany analyte ions in various real samples, which are interfere with the determination of Cd^{2+} ion, was examined at optimized conditions. The results are given

in Table 4. A fixed amount of understudy analytes were taken with different amounts of foreign ions and proposed procedure was followed. The recoveries of analytes were higher than 98%. Tolerable limit was defined as the highest amount of foreign ions that produced an error which is not exceeding 3%, in the determination of investigated analyte ions by the combination of the SDS-coated alumina solid phase extraction procedure followed by the flame atomic absorption spectrometry. It was observed that, most of the ion tested, have no significant effect on the recoveries of analyte ion. Cd²⁺ ion were quantitatively recovered in the presence of optimum mount of alkaline, earth alkaline, transition and Cd²⁺ ion as well as some anions.

Table 4: Effects of the matrix ions on the recoveries of the examined metal ions (N=3).

Analyte	Ions	Interference/ analyte ratio($\mu\text{g L}^{-1}$)	Recovery (%)
Cd ²⁺	Li ⁺ , K ⁺ , Na ⁺ , NO ₃ ⁻ , Cl ⁻	1000	101.2
	Ca ²⁺ , Mg ²⁺ , Ba ²⁺	1000	100.3
	Zn ²⁺ , Cu ²⁺ , Mn ²⁺	250	99.1
	Fe ³⁺ , Al ³⁺	500	99.3
	Cr ³⁺	300	98.9
	Ni ²⁺ , Pb ²⁺ , CO ²⁺	800	100.2
	SO ₄ ²⁻ , CLO ₄ ⁻	1000	99.8

3.9. Real samples – evaluation of method

The proposed procedure was applied to dryer agents and colored human hair samples for the cadmium determination. Two usual kinds of dryers, cadmium naphthenates containing known amounts of cadmium ion, were treated by the solid phase extraction after the digestion procedure. The accuracy of the method is confirmed by making a comparison between the certified and found data given in (Table 5, 6). On the other hand, due to the lack of a certified reference material to evaluate the recoveries of the analyte, the method of standard addition (simple spiking/ recovery tests) was used for the analysis of the hair sample and the results are presented in (Table 5, 6). The relative standard deviations for five replicate measurements of the sample in each investigation, all below 2%, revealed that the precision and the reproducibility of the technique are acceptable.

3.10. Comparison with literature

A comparison of the proposed system with other preconcentration procedures using several sorbents is given in Table 7^[41-44]. As Table 7 shows, the proposed method shows comparable capacity level, lower detection limit, and wider linear range and is a convenient, safe, simple, rapid and inexpensive method for the determination of trace quantities of these cations in dryer agents and colored human hair samples with satisfactory results. The proposed preconcentration system shows good preconcentration factors with reasonable preconcentration time over other preconcentration methods^[45-47]. As seen from Table 6, the detection limit for the proposed method was comparable to those given by the many methods.

Table5. Determinations of cadmium in certified dryer agent samples submitted to the solid phase extraction procedure. (N=5)

Sample	Analyte	Found ($\mu\text{g/g}$) ^a	Certified ($\mu\text{g/g}$)
Cadmium naphthenate	Cd	0.232 \pm 0.003	0.236

Table 6. Determinations of cadmium in female human colored hair submitted to the solid phase extraction procedure. (N=5)

Analyte	Added($\mu\text{g/g}$)	Found($\mu\text{g/g}$)	RSD %	Recovery %
Cd	0	0.87	1.4	---
	75	11.10	1.0	102.3
	150	21.23	0.8	101.8

Table7.Comparativedatafrom recent papers on preconcentration studies.

Analytes	Methodand apparatus	EF	DL ($\mu\text{g/L}$)	R.S.D. (%)	Ref.
Cd(II), Co(II), Pb(II)	SPE/FAAS	50.0	1.2-3.1	1.0-3.2	[41]
Cd(II), Pb(II)	SPE/FAAS	288.0	0.07–0.09	1.2 – 2.1	[42]
Cd(II)	SPE/FAAS	75.0	0.6	<3.7	[43]
Cd(II), Zn(II), Ni(II)	SPE/FAAS	80.0	2.1–2.3	1.23–1.31	[44]
Cd(II)	SPE/FAAS	80.0	1.1	<1.7	Present work

^aEF: enrichment factor, DL: detection limit, R.S.D.: relative standard deviation; SPE: solid phase extraction.

4. Conclusion

The TTDM loaded on SDS-coated alumina is sensitive and accurate adsorbent for determination of trace amounts of Cd²⁺ ion. The results presented in this paper have confirmed the applicability of the separation and preconcentration of metals. This method is simple and there is no necessity for elaborating a cleanup procedure, but the retained metals were simply eluted with 6mL of 4 mol L⁻¹ HNO₃ and were analyzed by FAAS. Each solid phase can be used for at least 10 successive analyses without considerable change in Cd²⁺ ion recovery. As a result it can be concluded that the proposed procedure can be satisfactorily considered as an alternative application for preconcentration and separation of traces of Cd²⁺ ion from aqueous solute. The performance characteristics of the proposed method and other selected SPE/FAAS systems for comparative purposes in the literature are given in Table 5. The proposed procedure shows good detection limits and precision with reasonable eluent volume, flow rate and preconcentration factor over other SPE off-line preconcentration methods^[48-53]. The method is simple, accurate can be applied for the determination of Cd²⁺ ion dryer agents and colored human hair samples^[54].

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