



Slurry analysis of cadmium and copper collected on 11-mercaptopundecanoic acid modified TiO₂ core-Au shell nanoparticles by flame atomic absorption spectrometry

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ABSTRACT

Separation/preconcentration of copper and cadmium using TiO₂ core-Au shell nanoparticles modified with 11-mercaptopundecanoic acid and their slurry analysis by flame atomic absorption spectrometry were described. For this purpose, at first, titanium dioxide nanoparticles were coated with gold shell by reducing the chloroauric acid with sodium borohydride and then modified with 11-mercaptopundecanoic acid. The characterization of modified nanoparticles was performed using ultra-violet spectroscopy and dynamic light scattering. Copper and cadmium were then collected on the prepared sorbent by batch method. The solid phase loaded with the analytes was separated by centrifugation and the supernatant was removed. Finally, the precipitate was slurried and directly aspirated into the flame for the determination of analytes. Thus, elution step and its all drawbacks were eliminated. The effects of pH, amount of sorbent, slurry volume, sample volume and diverse ions on the recovery were investigated. After optimization of experimental parameters, the analytes in different certified reference materials and spiked water samples were quantitatively recovered with 5% RSD. The analytes were enriched up to 20-fold. Limits of detection ($N = 10, 3\sigma$) for copper and cadmium were 0.28 and 0.15 ng mL⁻¹, respectively.

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1. Introduction

Copper makes up about 0.007% of Earth's crust so that it is the 25th most abundant element. About 40% of the annual production of Cu is used for the manufacture of alloys. Because of their fungicidal properties, Cu salts have been used since ancient times for crop production and wood preservatives [1]. Copper is an essential trace element for human body and higher mammals and also for numerous plants. It is a powerful antioxidant, which acts on the body to remove free radicals and to prevent cell structure damage. However, it is toxic above excessive intakes causing irritation of nose and throat, nausea, vomiting, and diarrhea and damage to liver and kidneys. People with Wilson's disease are at greater risk from overexposure to copper. The maximum contaminant level goals for copper is 1.3 mg L⁻¹. EPA has set this level of protection to prevent potential health problems [2]. Recommended daily intake for copper is 2 mg and it has toxic effects above 10 mg. The literature is full of information on the source of copper, its positive and negative health effects

Cadmium makes up about 5×10^{-5} % of the Earth's crust (0.06–1.1 mg kg⁻¹). It is found nearly in all zinc ores and provided as a side product during zinc refinement. The distribution of Cd on land is a consequence of emissions from industrial plants, especially zinc smelters and iron and steel works and from waste incineration plants and Brown-coal fired power stations [3]. Cadmium is used in alloys, alkali batteries, plastics (as stabilizer or pigments) and metal plating. In drinking water, the maximum permissible concentrations in England and in USA are 0.05 and 0.01 mg kg⁻¹, respectively. According to nutrition habits, daily average intake of cadmium quantity from foods is 1–10 μg [3]. There are numerous reports on the industrial uses of cadmium, its emissions, levels in the environment and effects on human health [4,5].

Cadmium is a neurotoxic and nephrotoxic heavy metal, even at trace levels. The main sources of cadmium in the air are the burning of fossil fuels such as coal or oil and the incineration of municipal waste. The acute (short-term) effects of cadmium in humans through inhalation exposure consist mainly of effects on the lung, such as pulmonary irritation. Chronic (long-term) inhalation or oral exposure leads to a build-up of cadmium in the kidneys. Experimental and epidemiological studies have provided substantial evidence that low levels of long-term exposure to cadmium can attribute to an increased risk of cancer [6,7].

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Flame atomic absorption spectrometry (FAAS) is an important tool for the determination of trace elements. However, when the concentration of the analyte is too low to be determined directly and/or interferences due to matrix cannot be eliminated, the use of a separation/preconcentration technique is necessary. For this purpose, the most commonly and practically applied method is the solid phase extraction method in which the analyte is collected on a sorbent by ion-exchange or complex formation using different materials such as polymeric resins, silica, activated carbon with or without chelating groups and subsequently eluted by means of a convenient reagent [8–11]. Co-precipitation is another common separation/enrichment method which is based on coprecipitation of the analyte(s) with a carrier precipitate and subsequent elution of analyte or dissolution of the precipitate. In all of these separation methods, an elution step is necessarily applied in order to transfer the analyte into solution phase for its measurement. However, elution step may have some potential disadvantages, namely it is quite time consuming; there is a potential risk of uncontrollable contamination from lab wares and eluents which causes high and/or irreproducible blank values; incomplete and irreproducible elution causes poor recoveries and precisions; the reagents for elution are expensive and mostly hazardous for human-health and contribute to environmental pollution. Therefore, the quality of analytical parameters of a preconcentration/separation method with regard to accuracy, precision, limit of detection, enrichment factor is closely related to the elution step. However, the numbers of studies to eliminate the elution step in coprecipitation and sorption methods are limited. In general, the analyte elements were collected on a sorbent or co-precipitated as usual. In next step, no elution was applied. Instead, the sorbent or analyte carrying precipitate was dissolved and directly introduced in to FAAS or ETAAS. Alternatively, the analyte was determined by slurry sampling or solid sampling analysis of the sorbent or precipitate. For this purpose, analyte was bound to a water-soluble polymer which was precipitated in the excess of acetone. The precipitate was separated from the supernatant, dissolved in small volume of water and introduced in AAS [12–15].

In other applications, the various solid sorbents loaded with the analytes were separated from the solution and directly determined by solid sampling AAS or slurry sampling. However, most of the studies were carried out by ETAAS because it is more appropriate to solid or slurry sampling techniques. The drawbacks of elution step and the advantages of its elimination were discussed in a similar manner as stated in this paper [16–20]. In a paper described by Qian et al, ultra-trace arsenic was collected on nano sized TiO_2 colloids and determined by atomic fluorescence spectrophotometer with slurry sampling [21]. However, modified nanoparticles have not been used as sorbents for direct slurry sampling.

Slurry method has many advantages compared to solution technique, e.g. there is no loss of time for sample dissolution or leaching; the risk of contamination as well as analyte loss during sample preparation is at minimum level and there is hardly is almost no risk of environmental pollution and instrument corrosion from acidic solutions. However, slurry sampling is not free of drawbacks. The main problem with slurry technique is the preparation of a slurry staying homogeneous at least during the whole analysis which requires careful optimization of some experimental parameters such as particle size, slurry volume, effective mixing, the addition of dispersants, the ratio of solid matter to total slurry volume, etc. [22–30].

In this study, copper and cadmium were collected on 11-mercaptoundecanoic acid modified TiO_2 core-Au shell nanoparticles ($\text{TiO}_2@Au\text{-MUA}$) by batch technique. The sorbent loaded with the analyte elements was then precipitated; slurried and aspirated directly into the flame. The most important advantage as well as the novelty of this method is that the nanoparticles loaded with

the analytes could be directly aspirated to the FAAS and thereby the elution step and its drawbacks were eliminated. Owing to the ultra-fine particle size of nanoparticles, there was no problem with respect to homogeneity and stability of the slurry. However, the complete precipitation of sorbent especially from high volume of samples was the most critical step of this procedure. Both the outstanding benefits and drawbacks of the method were discussed.

2. Experimental

2.1. Apparatus and reagents

A Varian 280 FS Flame Atomic Absorption Spectrophotometer equipped with a 5 cm air/acetylene burner was used for the determination of analyte element. The wavelengths were set to 324.8 and 228.8 nm for copper and cadmium, respectively. The slit widths for copper and cadmium were 0.5 nm. The pH of the samples was adjusted by $0.1 \text{ mol L}^{-1} \text{ NH}_4\text{OH}$ or $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ and controlled using WTW pH 340-A/SET2 pH meter. Vortex-2-Genie was used for homogenous mixing.

All chemicals were of analytical reagent grade (Merck, Germany). Stock solutions (1000 mg L^{-1}) of analyte element were prepared from Titrisol concentrates (Merck) and further diluted with distilled-deionized water daily. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was purchased from Fluka, sodium borohydride was purchased from Merck, 11-mercaptoundecanoic acid was purchased from Sigma-Aldrich, and TiO_2 anatase was purchased from Alfa Aesar. Distilled-deionized water was used in all dilutions.

11-Mercaptoundecanoic acid (MUA) modified TiO_2 core-Au shell ($\text{TiO}_2@Au$) nanoparticles, i.e., $\text{TiO}_2@Au\text{-MUA}$ were synthesized in the laboratory as described elsewhere [31]. The size distribution measurements of colloidal TiO_2 and $\text{TiO}_2@Au$ nanoparticles were performed with a Malvern Zetasizer Nano ZS instrument. The absorption spectra of colloidal TiO_2 and $\text{TiO}_2@Au$ nanoparticles were measured by Perkin Elmer Lambda 25 UV/Visible absorption spectrophotometer.

Waste-water (CRM-WW) and sea-water (NAAS-5-SW) certified reference materials were bought from High-Purity Standards (USA) and National Research Council Canada, respectively. The CRM sample solutions, which were sold as 10.0 mL of concentrates, were further diluted appropriately. Results were given as the averages of at least three independent replicate analyses.

2.2. Preparation of 11-mercaptoundecanoic acid modified $Au@TiO_2$ particles

$\text{TiO}_2@Au$ nanoparticles were prepared according to the method described by Kamat et al. with some modifications [31]. For this purpose, at first, 1 g of colloidal TiO_2 was suspended in 100 mL of water and 0.2 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was added into this suspension to obtain 5 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in the suspension. The solution was stirred for 15 min to allow the complete adsorption of $[\text{AuCl}_4]^-$ ions onto the TiO_2 surface. Reduction of the $[\text{AuCl}_4]^-$ was achieved by the dropwise addition of sodium borohydride (1%, w/v) until a color change was observed. The $\text{TiO}_2@Au$ nanoparticles were washed three times with water. In order to modify $\text{TiO}_2@Au$ nanoparticles with 11-mercaptoundecanoic acid (MUA), 5 ml of MUA (0.3 mmol) was added into this suspension and stirred for 2 h for the attachment of the molecules on the Au surfaces through the thiol bond (Au-S).

2.3. Procedure for slurry sampling

In order to collect the analyte element by batch technique, 1 mL of sorbent ($\text{TiO}_2@Au\text{-MUA}$) was mixed with 40 mL of sample solution. The pH of the solution was adjusted to 7.5 and vortexed

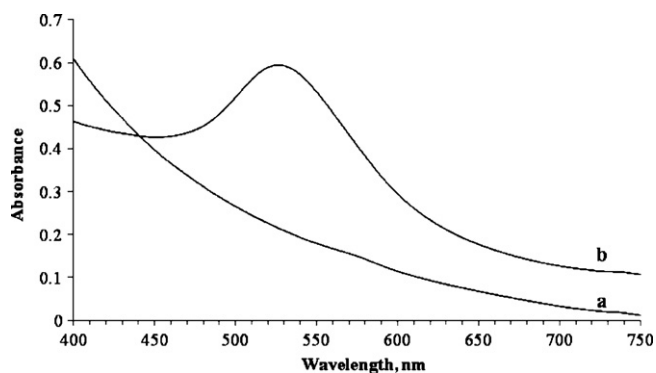


Fig. 1. UV/Vis absorption spectra of (a) bare TiO₂ and (b) TiO₂@Au nanoparticles.

for about 1 min. The solid part carrying the analytes was precipitated by centrifugation for 10 min at 7000 rpm. The supernatant was drawn using a micropipette. The last drops of liquid phase were removed by vaporization in water bath in a few minutes. The slurry of the sorbent was then prepared in 1% HNO₃ and homogenized by vortex for 1 min. For the preconcentration of analytes, the slurry volume was not lower than 2 mL. The slurry was then aspirated into the flame. In order to eliminate any possible sensitivity differences between the analytes in the slurry and in matrix free aqueous calibration solution due to e.g. different aspiration rates and/or atomization yields, TiO₂@Au-MUA was added to the calibration solutions. The analytes in the slurry of the sorbent were determined against the TiO₂@Au-MUA added calibrant. Thereby, the analytes in calibration solutions and in the slurry of the sorbent were aspirated and atomized under the same conditions. In addition, the results for the optimization of experimental parameters were confirmed from the analyte concentration remaining in the supernatant after sorption. To provide the same physical conditions, in all quantifications, blanks, standards and samples were subjected to the same experimental procedure.

3. Results and discussion

3.1. Characterization of MUA modified TiO₂@Au nanoparticles

Fig. 1 shows the absorption spectra of colloidal TiO₂ and TiO₂@Au nanoparticles. There is no absorption maximum for TiO₂ nanoparticles. However, when the TiO₂ nanoparticles were coated with the Au shell, a maxima was observed at 530 nm. The color of the TiO₂ turns into dark purple from pale yellow as the core-shell nanoparticles are formed which also indicates the formation of the TiO₂@Au nanoparticles. Dynamic light scattering was used to obtain information about the particle size distribution in a colloidal suspension. Fig. 2 shows the size distribution of the TiO₂ and TiO₂@Au nanoparticles. As expected, the average size of the TiO₂@Au (350 nm) nanoparticles is larger than the bare TiO₂

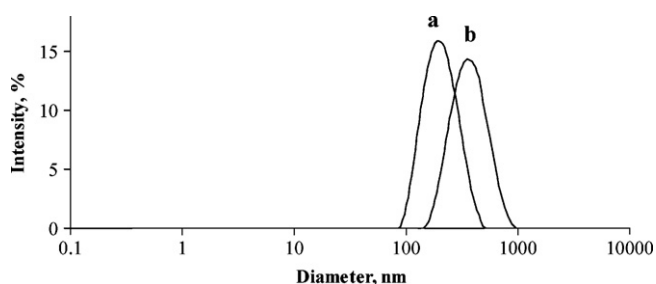


Fig. 2. Size distribution profile of (a) TiO₂ and (b) TiO₂@Au nanoparticles.

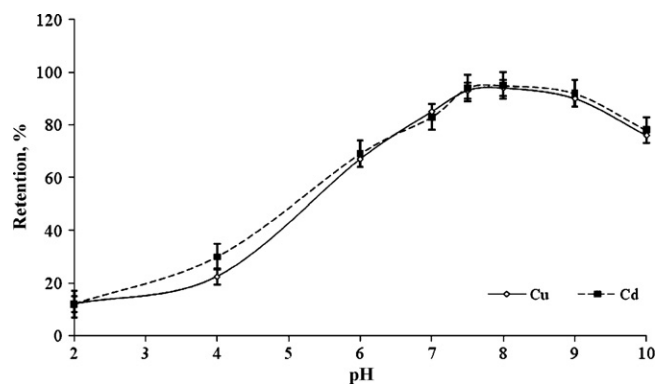


Fig. 3. The effect of pH on the retention of 1 mg L⁻¹ of Cu (♦) and Cd (■).

(200 nm) nanoparticles. This also indicates that the TiO₂ nanoparticles were successfully coated with Au shell. It is naturally expected that thiolated molecules can be chemically bound on gold surfaces. Therefore, the prepared TiO₂@Au nanoparticles were modified with 11-mercaptoundecanoic acid through the thiol bond as mentioned in Section 2. The free carboxylic acid functional group was used to bind analytes.

3.2. Optimization of experimental parameters

3.2.1. Effect of pH and chelating agent

The sorption capability of the chelating agent, i.e., MUA depends on the pH of the sample. As can be seen from Fig. 3, when the pH of solution was adjusted to pH ≥ 7.5, both copper and cadmium could be quantitatively retained on the TiO₂@Au-MUA. The better retention of analytes at alkaline pH values should be due to deprotonation of the carboxyl group of the 11-mercaptoundecanoic acid which is the general case for all acidic functional groups. Therefore, the pH of all solutions was adjusted 7.5 throughout this study.

3.2.2. Effect of shaking time on retention

Copper and cadmium were completely sorbed on TiO₂@Au-MUA immediately because after the sample and sorbent were mixed only for 1 min and then the solid phase was precipitated, no analyte was remained in the supernatant solution. Therefore, the duration of shaking time could not be investigated as an experimental parameter.

3.2.3. Effect of amount of sorbent

The optimization of the amount of TiO₂@Au-MUA is important to be sufficient for the retention of all the analytes completely as well as not to consume the sorbent excessively. It was found that to retain the both analytes 1–2 mL of sorbent was enough (Fig. 4). At higher amounts of sorbent, the decrease in the recovery of analytes may be attributed to non-efficient aspiration rate of concentrated solid phase particles of slurry to the flame. At low sorbent amounts, the analyte may not be quantitatively bound at given conditions. Therefore, 1 mL of sorbent was used with maximum 40 mL of sample for quantitative recovery and satisfactory precision.

3.2.4. Effect of sample volume

From a series of experiments, it was found that the copper and cadmium in 40 mL of sample solution were quantitatively (>90%) sorbed on 1 mL of TiO₂@Au-MUA. For sample volumes higher than 40 mL, the retention of analytes was not quantitative any more. The most likely explanation is that the nanoparticles in high volumes could not be precipitate completely at even prolonged centrifugation time. Actually, the volume of Falcon tubes used in the centrifugation of sorbent is 50 mL. Therefore, the maximum sam-

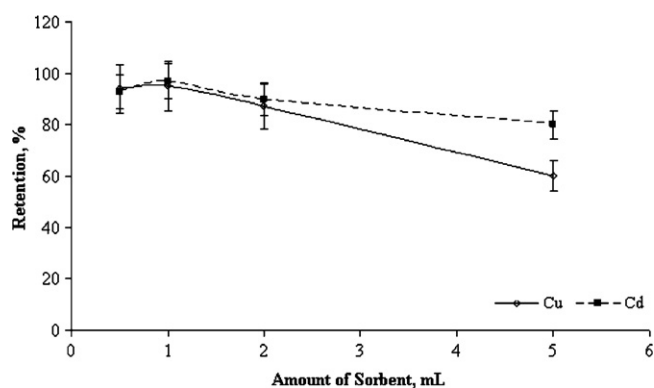


Fig. 4. The effect of amount of sorbent on the retention of 1 mg L^{-1} of Cu (♦) and Cd (■).

ple volume together with sorbent and pH adjustment reagent to be added was limited as 50 mL. When the copper and cadmium in 40 mL of sample were retained on 1 mL of sorbent and a 2 mL of slurry was prepared, a 20-fold enrichment was obtained which was mostly enough to detect the analytes in all samples studied. Consequently, in all experiments, sample volume did not exceed 40 mL.

3.2.5. Effect of foreign ions

The effects of various foreign ions on the sorption of analyte elements were investigated. For this purpose, eight different chemical species were added to the test solution containing Cu and Cd and the retentions of analyte elements were investigated. The results are shown in Table 1. The tolerance limits of foreign ion concentrations were selected for the analytes to be determined with maximum $\pm 10\%$ accuracy.

Obviously, $\text{TiO}_2\text{@Au-MUA}$ could be successfully used for the determination of Cu and Cd in the presence of foreign ions at their concentrations given in the table. The tolerance concentrations of foreign ions are above of those in most commonly studied samples having very heavy matrices e.g. sea-water, serum etc.

3.2.6. Effects of total slurry volume on homogeneity of slurry

The effects of total slurry volume on the recovery of copper and cadmium were investigated and the results are given Fig. 5. Owing to the ultra-fine particle size of nanoparticles, the slurry prepared simply by means of a vortex was homogeneous and remained stable during the whole analysis even in the absence of any dispersant. Therefore, throughout this study, no any dispersant was used to maintain the homogeneity. At elevated slurry volumes, the recovery was reduced. The likely explanation is that the sorbent particles were not homogeneously distributed in the slurry. Moreover, at excessive slurry volumes, the concentration of the particles, i.e., enrichment factors may be too small to detect the ultra-trace analyte concentrations. On the other hand, the low precisions ($>10\%$ RSD) were obtained for ≤ 1 mL of total slurry volumes which may

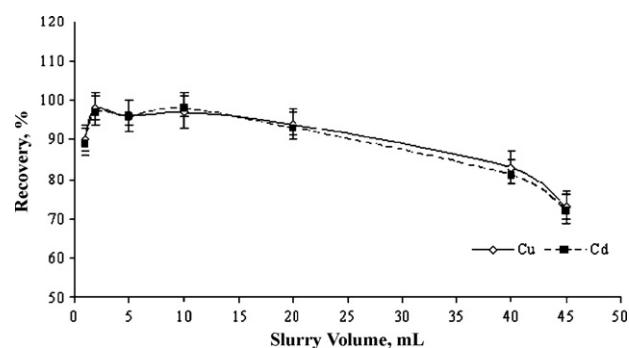


Fig. 5. The effect of slurry volume on the recovery of 1 mg L^{-1} of Cu (♦) and Cd (■).

be attributed to the fact that the slurry density (the amount of solid material per total slurry volume) was too much to be completely, repeatedly and precisely introduced into the flame. In addition, the volume of slurry below 1 mL was not enough to repeat the measurements of the two analytes a few times. Therefore, to aspirate the sample solution three times for each analyte at least 2 mL of slurry was used. As a result, when the sample volume was below 40 mL and final slurry volume was 2 mL, recoveries were quantitative (90–98%) with satisfying precision ($<10\%$ RSD) as well as the enrichment was enough to detect the analytes in studied samples.

3.2.7. Stability and homogeneity of slurry

Owing to the extremely small size of sorbent particles, there was no need to add any dispersant to prepare homogeneous slurry and to stabilize it. In addition, particle size was small enough not to clog the burner head and nebulizer capillary during aspiration. Therefore, it was not necessary to investigate the effects of larger particle size of the sorbent on the results. When the total slurry volume was 2 mL, both the recovery was quantitative and the lowest standard deviation was obtained which reveals that the sorbent was effectively precipitated, homogeneously dispersed and stayed stable during three successive aspirations (short-term stability). After their preparation, the measurement procedure of all slurry samples in AAS did not exceed 1 h. To be sure of the homogeneity of the slurried samples during whole analysis period (long-term stability), the measurements were repeated by aspirating samples after 1 h of slurry preparation and the results were reproducible (long-term stability).

These results obviously showed that at optimum conditions the slurry prepared was homogeneous and stayed stable (in short-term and a 1 h of long-term) without needing any dispersant until the end of the analysis. This is the advantage of nanoparticles with respect to slurry homogenization/stabilization.

3.3. Validation of the method

To validate the method in different matrices, the copper and cadmium were determined in sea-water (NAAS-5-SW) and waste water (CRM-WW) certified reference materials after suitable enrichment. The sorbent ($\text{TiO}_2\text{@Au-MUA}$) was added to both blanks and standards to provide the same conditions as the sample especially to maintain the same aspiration rate and atomization yield.

As can be seen from Table 2, there were no significant differences between mean concentrations of the analytes found as the average of three replicate determination and their certified values at 95% confidence level. This obviously shows that after optimization of experimental conditions, the analyte elements in different heavy matrices were quantitatively sorbed on $\text{TiO}_2\text{@Au-MUA}$ and the sorbent collecting the analytes was successfully analyzed by slurry analysis. Therefore, the standard addition method was not applied.

Table 1

Effect of foreign ions on the sorption of Cu and Cd (analyte concentration: 1.00 mg L^{-1} ; $N=3$).

Species	Added as	Concentration of the diverse ion (mg L^{-1})	Recovery (%)	
			Cu	Cd
Na^+	Na_2SO_4	6600	106	92
K^+	KCl	300	98	90
Mg^{2+}	MgCl_2	380	106	92
Cl^-	NaCl	7400	98	90
NO_3^-	NaNO_3	1100	98	90
SO_4^{2-}	Na_2SO_4	1400	106	92

Table 2

Analytical results for the determination of Cu and Cd in spiked and unspiked sea-water and waste-water certified reference materials.

Analyte	Waste water (high purity standard-WW)			Sea water (NAAS-5-SW)		
	Certified	Found ^a	Recovery (%)	Certified	Found ^a	Recovery (%)
Cu ($\mu\text{g/L}$)	25.0 \pm 0.1	27.0 \pm 3.0	108	0.297 \pm 0.046	0.332 \pm 0.038	112
Cd ($\mu\text{g/L}$)	25.0 \pm 0.1	24.0 \pm 2.1	96	0.023 \pm 0.003	0.024 \pm 0.002	104

^a Mean \pm 95% confidence limits.**Table 3**

Analytical results for the determination of Cu in various spiked/unspiked water samples.

Sample	Cu ($\mu\text{g L}^{-1}$)		
	Added	Found ^a	Recovery (%)
Drinking water ^b	–	20.0 \pm 1.0	96
	10.0	28.8 \pm 2.2	
Mineral water ^b	–	13.0 \pm 0.4	97
	10.0	22.3 \pm 0.9	
Tap water ^c	–	15.0 \pm 0.3	96
	10.0	24.0 \pm 1.2	
Sea-water ^d	–	10.0 \pm 0.8	95
	10.0	19.0 \pm 1.3	

^a Mean \pm 95% confidence limits.^b Drinking water and mineral water samples were provided in markets in Istanbul, Turkey.^c From tap water system of lab, Istanbul, Turkey.^d From Marmara Sea, Istanbul, Turkey.

Preconcentration factor up to 20 could be obtained. The limit of detection (LOD) of the method for copper and cadmium was 0.28 and 0.15 $\mu\text{g L}^{-1}$ which were calculated according to 3σ of a blank solution ($N = 10$) subjected to the presented procedure. The values of certified reference material NAAS-5-SW for copper and cadmium (0.297 and 0.023 ng mL^{-1}) appear to be below the limits of detection (0.28 and 0.15 ng mL^{-1}). However, it should be noted that since the samples were enriched, the concentrations measured after enrichment were well above LOD and LOQ. Actually, the reason for the preconcentration is to increase the analyte concentration above its LOD value.

Finally, the spiked and unspiked copper and cadmium contents of various water samples (tap water, sea-water, mineral water, and processed bottled drinking water) were determined using the proposed method and the results were given in Tables 3 and 4.

The concentrations of analytes added to the water samples were successfully recovered in 95% confidence interval. The copper and cadmium concentrations found in drinking water were well below the maximum level goals stated by EPA which were 1.3 and 0.005 mg L^{-1} , respectively [2].

Table 4

Analytical results for the determination of Cd in various spiked/unspiked water samples.

Sample	Cd ($\mu\text{g L}^{-1}$)		
	Added	Found ^a	Recovery (%)
Drinking water ^b	–	2.2 \pm 0.2	110
	10.0	13.4 \pm 2.0	
Mineral water ^b	–	5.1 \pm 0.3	106
	10.0	16.0 \pm 1.0	
Tap water ^c	–	10.0 \pm 0.4	100
	10.0	21.0 \pm 3.0	
Sea-water ^d	–	6.3 \pm 0.5	94
	10.0	15.3 \pm 1.4	

^a Mean \pm 95% confidence limits.^b Drinking water and mineral water samples were provided in markets in Istanbul, Turkey.^c From tap water system of lab, Istanbul, Turkey.^d From Marmara Sea, Istanbul, Turkey.

4. Conclusion

The presented method is based on the sorption of copper and cadmium on $\text{TiO}_2/\text{Au-MUA}$ and subsequently their determination by slurry technique in FAAS. The proposed technique is simple and fast. The elimination of elution step reduces the time required for analysis. The risk of contamination from eluents and apparatus is lower. Finally, appropriate preconcentration factors can be achieved by adjusting the volume of the suspension, appropriately. Although the elimination of elution step and introduction of sorbent as its slurry has some advantages, the sorption of analytes quantitatively as well as the preparation of homogeneous and stable slurry necessitates the optimization and control of many parameters carefully. In these respects, $\text{TiO}_2/\text{Au-MUA}$ is a convenient material. The analytes could be collected fast and quantitatively as well as homogeneous slurry remaining stable during the whole analysis could be obtained without needing any surfactant and complicated mixing apparatus.

It can be concluded that the proposed technique can be effectively and practically used for the preconcentration and separation of copper and cadmium prior to their determination by FAAS. Moreover, there is no reason this technique cannot be applied for the determination of other heavy metals. Other chelating agents may be bound to nanoparticles for the slurry analysis of sorbent without applying elution not only for FAAS but ETAAS as well.

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