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Determination of Cadmium by Flame-Atomic Absorption Spectrometry After Preconcentration on Silica Gel Modified with Cupferron

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Este trabalho descreve um método para a pré-concentração de cádmio com sílica gel modificada com cupferron e sua determinação por espectrometria de absorção atômica com chama. O efeito do pH, a quantidade do material adsorvente, a concentração de eluente, volume da amostra e quantidade do analito adsorvido foram otimizados. O efeito de interferentes foi avaliado para diversos íons mostrando que a extração de cádmio somente é afetada por Zn(II) e Cu(II), dependendo da concentração dos mesmos, mas pode ser minimizada pela adição de 0,05 mmol de KI. Foi obtido um fator de enriquecimento de até 30 vezes. Os limites de detecção e de quantificação foram de 0,5 μg L^{-1} (3σ) e 2,0 μg L^{-1} (10σ), respectivamente, com rsd de 1,1% (n=10). A exatidão foi avaliada com material de referência certificado e o resultado obtido (3,93 ± 0,01 μg g^{-1}) concordou com o valor certificado (4,15 ± 0,38 μg g^{-1}). O teor de cádmio em esmalte de unhas foi determinado, obtendo-se recuperações quantitativas para as amostras enriquecidas com o analito. O método proposto caracteriza-se pela simplicidade, eficiência e baixo custo.

A method for the determination of cadmium by flame atomic absorption spectrometry (FAAS) after its preconcentration onto a column containing silica gel modified with cupferron was developed. The pH, amount of adsorbent material, concentration of eluent, volume of sample and amount of Cd were optimized. The effect of several foreign ions was also investigated and showed that the retention of cadmium depended on the amounts of Zn(II) and Cu(II) present and that these interferences could be overcome by using a 0.05 mmol KI. An enrichment factor of up to 30 was obtained , the LOD was 0.5 μg L^{-1} (3σ) and the LOQ was 2.0 μg L^{-1} (10σ) with rsd of 1.1% (n = 10). The accuracy of the proposed method was ascertained by using certified reference material and the obtained result (3.93 ± 0.01 μg g^{-1}) agrees with the certified value (4.15 ± 0.38 μg g^{-1}). The determination of Cd in nail polish showed quantitative recoveries for the spiked samples. The proposed method is characterized by simplicity, efficiency and low cost.

Keywords: cadmium, solid-liquid extraction, cupferron, FAAS

Introduction

Cadmium is considered a non-essential and highly toxic element, with a serious cumulative effect.[1] Its toxicity is comparable to that of arsenic and mercury but its letal potential is higher than that of any other metallic element.

Interest in the potential link between Cd and carcinogenicity has draw attention to the Cd concentration in body fluids, tissues and foods. Although reports of weak carcinogenic activity are inconclusive, measurement of cadmium in body fluids is still used for exposure monitoring because of its very toxic effects. Besides this, the analyses of different kinds of samples are also very important in order to know other sources of contamination.[2]

Nowadays there are many known sources of contamination by cadmium, owing to the large number of its inorganic salts, which are used in catalytic and synthetic reactions, in Ni-Cd battery manufacturing and as stabilizers for plastics and pigments,[3,4] but we need also to consider that there are still many unknown sources .

The FAO-WHO Joint Expert Commitee on Food Additives recommended a provisional maximum tolerable daily intake for Cd from all sources of 1-1.2 μg kg^{-1} body mass. Considering the problems caused by the presence of cadmium in the human organism and in the environment, years of effort have been devoted to the development of more effective, fast, precise and accurate approaches to the determination of this element in biological and environmental materials, using numerous analytical methods.[2]

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Regarding the concentration of Cd in different matrices there is a need to develop sensitive analytical methods to determine this analyte at low concentrations. Flame atomic absorption spectrometry (FAAS) is largely used for the determination of metals, showing good selectivity but low detectability, which may be improved by a preconcentration step.[4] Several methods for the separation and preconcentration of metals have been developed, enhancing the detectability and the versatility of the instrumental analytical techniques. Solid-liquid extraction with organic reagents immobilized onto solid sorbents has been widely used. [2,5-8]

Among the characteristics of these solid sorbents are their great selectivity and facility of manipulation. Cadmium may be coprecipitated as its hydroxide and it reacts with several organic reagents containing the R-OH group, such as 8-hydroxyquinoline and cupferron, [9] which are widely used for metal separation.[10]

Thus, in 1997, Kubová *et al.*[7] determined lead and cadmium in human hair by AAS after preconcentration by the solid phase extraction using chelating ion-exchange with bound 8-hydroxyquinoline. Yaman,[2] in 1998, determined cadmium and lead in human urine by STAT-FAAS after preconcentration on activated carbon using cupferron as chelant. In 2000, Xu *et al.*[5] used a mini column packed with silica C_{18} to preconcentrate Cd with ammomium pyrrolidinedithiocarbamate as the organic reagent.

In the present work a methodology for the determination of cadmium after its preconcentration using silica gel modified with cupferron is described. The metal ion is eluted with an HCl solution and its concentration is determined by flame atomic absorption spectrometry. The optimized methodology was applied to samples of nail polish.

Experimental

Apparatus

The absorption measurements were made with a Perkin-Elmer model 5100 atomic absorption spectrometer, equipped with a hollow cathode lamp for cadmium as well as a deuterium lamp for background correction, under the following conditions: wavelength: 228.8 nm; slit width: 0.7 nm; lamp current: 8 mA; flame: air/acetylene. The pH-measurements were made by a Hanna Instruments pH-meter equipped with a combined electrode.

The preconcentration system consisted of glass columns (4 mm internal diameter and 25 cm long) equipped with a Teflon® tap. The solution containing the analyte passed through the column, where the modified silica gel was maintained between two portions of glass wool in order to avoid movement of the solid material.

For sample treatment, a microwave-assisted furnace, Provecto Analitica DGT 100 Plus, and a hot plate from Quimis were used.

Reagents

All the reagents were of analytical reagent grade. Deionized water (Milli-Q Water Purification System - Millipore, Bedford, USA) was used throughout.

The Cd standard solution was prepared from a standard solution (Cadmium Standard per Assorbimento Atomico, Carlo Erba, 1000 mg L^{-1}). Appropriate dilutions were made from this solution, whenever necessary, with deionized water.

Preparation of silica gel modified with cupferron

Silica gel (Merck, 35-70 mesh ASTM) was modified by mixing of 0.30 g of cupferron, dissolved in 50 mL of p.a. ethanol, and 10 g of previously activated silica (120 °C for 24 h). The complete evaporation of the ethanol allows deposition of cupferron on the surface of the silica, which can then be used for the preconcentration of cadmium.

General procedure

The columns were packed with 0.5 g of silica-cupferron and conditioned with a buffer solution (sodium acetate-acetic acid) at pH 5.5. An aliquot of the sample solution containing cadmium was taken in a 150 mL beaker and the pH was adjusted to 5.5. It was then passed through the column at a flow-rate of 3 mL min^{-1}. Later, the metal complex formed on the modified silica was eluted with adequate volumes (5.0 to 25.0 mL) of 0.5 mol L^{-1} HCl.

The final solution was aspirated into an air-acetylene flame and the absorbance was measured against a similarly prepared reagent blank. In order to verify the mass balance of the system the solution which passed through the column and was not retained by the adsorbent material was also analyzed by FAAS after treating with nitric acid and heating.

Determination of cadmium in certified standard material

To carry out the digestion of the certified biological standard material (NBS1566a) in the microwave oven, 500 mg of the sample was weighed directly into a Teflon flask and 12 mL of concentrated nitric acid were added. The

microwave program used was: first step, 15 min at 200 W; second step, 5 min at 500 W; third step, 10 min a 0 W. The digested material was transferred to a beaker, the pH was adjusted to 5.5 and 0.05 mmol of KI was added, as masking reagent. The final volume was adjusted to 100 mL with deionized water. The concentration of cadmium was determined by FAAS after the preconcentration step through the column using the conditions described in the general procedure.

Determination of cadmium in nail polish samples

The cadmium content was determined in samples of nail polish according to two experimental procedures, with and without spiking with the analyte before the preconcentration step. For the spiked procedure, to 250 mg of sample were added 5 μg of Cd. The samples were dissolved in 10 mL of acetone and treated with 10 mL concentrated HNO_3 and 5 mL of H_2O_2 in a hot plate. The volume was completed to 100 mL after the adjustment of pH to 5.5. After the preconcentration step the recovery of cadmium was evaluated and the concentration of cadmium in the nail polish was determined by FAAS.

Results and Discussion

Effect of pH

The pH of the aqueous phase is an important factor in solute distribution with accentuated acid-base properties. As a result, the reaction between Cd and cupferron can be influenced by changes of pH. In order to optimize this experimental variable, the effect of the pH on the solid-liquid extraction during complex formation was investigated over the pH range 1-10. Figure 1 shows the effect of pH on cadmium extraction using the Silica-
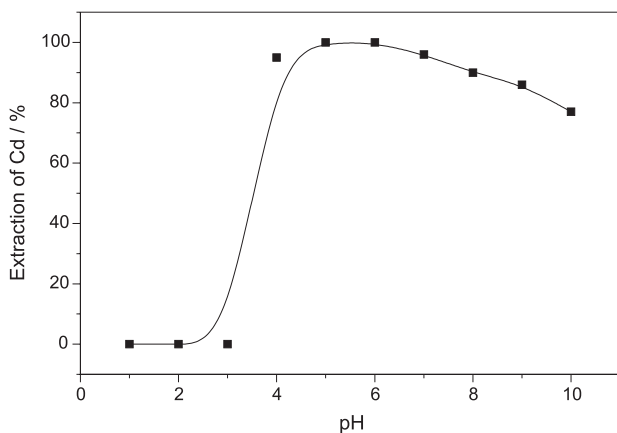
Figure 1. Effect of pH on the extraction of the Cd-cupferron complex.

Cupferron system; the results agree with those obtained by Yaman and Güçer.[10] The adsorption of cadmium was quantitative in the range pH 4.0 to 6.0 and pH 5.5 was then chosen for the remaining studies.

Study of the amount of cupferron for silica gel modification

The amount of chelating reagent required for the modification of the surface of silica gel was investigated between 1 and 4% (m/m) and it was determined that the recovery of up to 200 mg cadmium was quantitative using 500 mg of 3% (m/m) modified silica gel.

Study of the eluent for Cd-cupferron complex

According to the literature[9] an adequate solvent for complete elution of Cd ion from the Cd-cupferron complex is a solution of hydrochloric acid. Concentrations of HCl varying from 0.2 to 1.0 mol L^{-1} were studied in order to optimize this parameter. It was observed that the recovery of the metal does not depend on the HCl concentration. Thus 0.5 mol L^{-1} HCl was chosen as the eluent for this system.

Study of column capacity

The column capacity can be evaluated in two different ways: the sample volume that passes through the column and the amount of analyte that is retained in this process.

Considering the sample and the concentration of the analyte, sometimes it will be necessary to have a large volume of sample in order to reach the detection limit of the technique. With this system it was possible to utilize volumes up to 150 mL of samples containing 40 μg of cadmium without affecting the complete retention of the element.

To determine the amount of analyte retained on the column, increasing quantities of Cd were introduced into the column. It was possible to obtain quantitative recovery by using 0.5 g of modified silica and up to 200 μg of Cd, that means that the column capacity was 0.4 mg per gram of modified silica.

Characteristics of the system Cd-silica-cupferron

It is possible to carry out the determination of cadmium after its preconcentration with 0.5 g of silica-cupferron within the range from 1 to 200 μg, using sample volumes of up to 150 mL. Considering that the cadmium complex is quantitatively eluted with 5.0 ml of 0.5 mol L^{-1} HCl it

was possible to obtain an enrichment factor of 30. The precision of the method was evaluated as the relative standard deviation of ten replicates of a cadmium solution and a value of 1.1% was found.

Effect of foreign ions

As cupferron can react with different metals it was necessary to investigate the effect of other ions on the system studied. Samples containing 40 μg of cadmium and 40 to 200 μg of other metal ions were prepared and the determination of Cd(II) was carried out by the procedure described. Figure 2 shows the effect of Al(III), Fe(III), Co(II), Ni(II), Zn(II) and Cu(II). As can be seen, the recovery of cadmium was affected by all of these ions, but only zinc and copper showed interferences at concentrations less than 3 times that of cadmium. To minimize this effect, some reagents, such as sodium thiosulfate, sodium cyanide or potassium iodide, were studied as masking agents for the system. The use of 0.05 mmol of KI was adequate to provide the complete recovery of cadmium even in the presence of a 4-fold excess of Cu (II) or Zn(II) and also for a solution containing 5-fold excess of all the foreign ions studied. The presence of anions such as chloride, nitrate, sulfate and phosphate did not affect the recovery of cadmium even in an 1000-fold related to the Cd concentration.
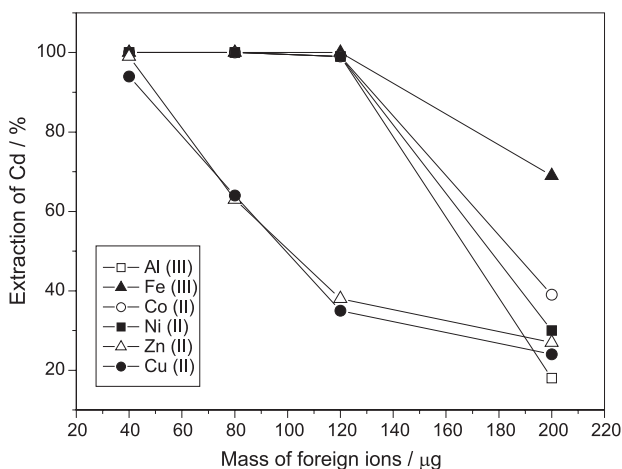
Figure 2. Effect of several foreign ions on the determination of 40 μg of cadmium.

Figures of merit

Considering that it is possible to retain 200 μg of cadmium from 150 mL of solution passing through a column (250 x 4 mm) filled with 0.5 g of modified silica, the elution of the resulting complex with 5.0 mL of 0.5 mol L^{-1} HCl, at a flow rate of 3 mL min^{-1}, gives a limit

of determination of 2.0 μg L^{-1} and an enrichment factor of 30. The precision, expressed as a relative standard deviation (RSD, n=10) is 1.1%. The limit of detection, calculated as three times the blank standard deviation was 0.5 μg L^{-1}, obtained from the calibration curve (Y = 0.00182 + 1.54118 X; R = 0.99977).

The proposed method was applied for the determination of cadmium in oyster tissue certified material, that contains 4.15 ± 0.38 μg g^{-1}. The result obtained (3.93 ± 0.01 μg g^{-1} for n=3) in the presence of the masking reagent was in reasonable agreement with the certified value, showing that it is possible to use the proposed system for the determination of cadmium, even in complex samples.

The results obtained in this work allows the determination of cadmium in low levels of concentration in different samples and may be compare with other works described in the literature. Spinola Costa *et al.*[11] described a preconcentration factor of 13 and limit of detection of 30 μg L^{-1} for the determination of cadmium in brine samples by ICP OES, while de Melo Gomes *et al.*[12] obtained a preconcentration factor of 20, for the analysis of fuel ethanol. Pereira and Arruda[13] described a preconcentration factor of 100 using vermicompost as adsorbed material for the determination of 5 μg L^{-1} level of cadmium. Using Slotted Tube Atom Trap (STAT)-FAAS Yaman[14] obtained good enrichment factor (about 150) for the determination of cadmium in water after the preconcentration with cupferron.

Determination of cadmium

Brazilian Agency for Health and Safety[15] does not allows the presence of Cd and its compounds in cosmetic products, although concentrations of up to 100 mg L^{-1} of heavy metals may be present as organic dyes, with the exception of lead. Considering this information and the work described by Rastogi,[16] which analyzed samples of finger paints and make-up paints, it was expected to find low levels of Cd in nail polish samples. Table 1 shows the amounts of Cd found in unspiked and spiked (5 mg of the metal) samples of nail polish. As can be seen, there is a

Table 1. Cadmium content in nail polish (n=3)

Sample	Added Cd (μg)	Found values (μg g^{-1})	Recovery (%)
Brown nail polish	-	23.26 ± 0.10	
	5.0	45.10 ± 0.10	110
Red nail polish	-	29.92 ± 1.15	
	5.0	49.61 ± 1.15	96
Orange nail polish	-	44.92 ± 1.15	
	5.0	66.93 ± 1.15	110

considerable amount of cadmium in the nail polish analyzed. The performance of the proposed method was adequate, regarding the recovery values determined with the spiked samples.

Conclusions

The proposed method for solid-liquid extraction is convenient, simple, sensitive and of low cost. The preparation of the solid adsorbent is very simple. The preconcentration of cadmium is effective and Cd elution is quantitative in a small volume of 0.5 mol L^{-1} HCl solution.

A preconcentration factor of 30 was obtained, considering the relation between final volume and initial volume of sample. The precision of the method was good with a rsd of 1.1% for concentrations of cadmium around 0.4 mg L^{-1} corresponding to 40 μg of the element .

Considering the preconcentration factor used, the detection limit and quantification limit calculated were 0.5 and 2.0 μg L^{-1} of Cd respectively, showing the potentiality of the method. The accuracy of the proposed method, evaluated by analysing a certified reference material, was adequate for analytical purpose and the results of nail polish analyses showed the presence of high amounts of this metal in these samples. Considering the wide use of nail polish by women, care must be taken with this probable source of cadmium.

Acknowledgements

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