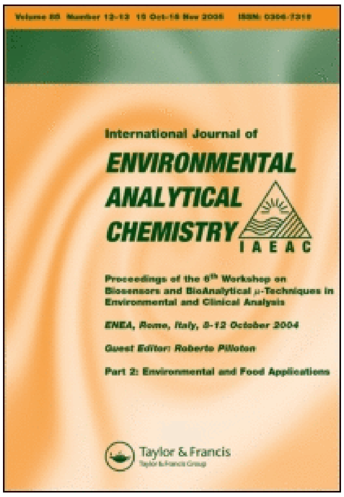

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Souza, Juliana M. O. and Tarley, César R. T.(2009) 'Sorbent separation and enrichment method for cobalt ions determination by graphite furnace atomic absorption spectrometry in water and urine samples using multiwall carbon nanotubes', International Journal of Environmental Analytical Chemistry, 89: 7, 489 — 502

To link to this Article: DOI: 10.1080/03067310802617602

URL: http://dx.doi.org/10.1080/03067310802617602

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 7, 15 June 2009, 489–502

Sorbent separation and enrichment method for cobalt ions determination by graphite furnace atomic absorption spectrometry in water and urine samples using multiwall carbon nanotubes

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(*Received 15 August 2008; final version received 11 November 2008*)

A new cobalt ions pre-concentration method, optimised by fractional factorial design, using multiwall carbon nanotubes (MWCNTs) with further Graphite Furnace Atomic Absorption Spectrometry (GFAAS) quantification is described. The method explores the high chemical and physical stability of MWCNTs for improving the detectability of GFAAS. It is based on off-line pre-concentration of 20.0 mL of sample previously buffered (pH 8.82) on MWCNTs at a flow rate of 10.0 mL min^{-1}. After the pre-concentration procedure, the elution step was carried out with 500 μL of 0.524 mol L^{-1} HNO_3 solution at a flow rate of 2.0 mL min^{-1}. Fractional factorial designs and response surface methodology were employed for optimisation of all chemical parameters involved in the pre-concentration procedure, including pre-concentration flow rate, buffer and eluent concentration, sample pH and elution volume. The method provides a linear calibration range from 0.03 up to 7.00 μg L^{-1} with linear correlation coefficient higher than 0.9994 and limits of detection and quantification of 0.01 and 0.03 μg L^{-1}, respectively. Repeatability of the six measurements was found to be 2.38 and 1.84% for 0.3 and 4.5 μg L^{-1} cobalt concentration, respectively. By pre-concentrating 20.0 mL of sample, a pre-concentration factor (PF) of 19.10-fold and a consumption index of 1.05 mL were obtained. The pre-concentration efficiency (PE) was found to be 9.55 min^{-1}. The proposed method was successfully applied for the pre-concentration and determination of cobalt in water and urine samples with satisfactory recovery values.

Keywords: cobalt; multiwall carbon nanotubes; pre-concentration; biological and water samples

1. Introduction

The development of analytical methods based on pre-concentration/extraction has been widely investigated for toxic metals determination in water samples and biological samples. The increasing interest in this field of the analytical science is due to the necessity of establishing contaminant levels of toxic metals in a great variety of samples when environmental or nutritional aspects are emphasised [1]. As example, the cobalt determination in environmental samples is necessary since this element is used in many industrial processes, such as production of catalysts, pigments and metallic alloys and can be released in aquatic bodies with consequent contamination of the aquatic organisms,

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802617602
http://www.informaworld.com

mainly by bioaccumulation of the element in fish [2]. In this way, environmental organisations often establish requirements for the surveillance or monitoring of a particular area or ecosystem. From the nutritional point of view, although cobalt is considered an essential trace element for the human body, being a component of cyanocobalamin or vitamin B_{12}, which is responsible for red blood cells synthesis, it can be toxic at higher concentrations [3]. Cobalt poisoning has been demonstrated to significantly affect human life span, development, reproduction, behaviour, behavioural plasticity and induces cytotoxicity of human keratinocytes [4]. Hence, cobalt monitoring, especially in individuals exposed to cobalt powder, has been of great interest. Cobalt is mainly excreted in urine and the amount found in these samples is an important parameter to evaluate symptoms related to contamination. This biological fluid has been widely used as biomonitoring material in clinical chemistry as well as for occupational, toxicological and environmental studies due to its simple mode of collection and storage [5–7]. In general, cobalt concentration in urine is considered to be near $0.5\,\mu g\,L^{-1}$ in healthy population [8].

Obviously, considering the high complexity of matrix and low concentration, pre-concentration/extraction methods are commonly required for a reliable analysis. Liquid–liquid extraction, ion exchange, co-precipitation, cloud point extraction and solid phase extraction are the most used pre-concentration/extraction methods for these purposes. The advantages of these methods are attributed to their ability in removing matrix interference as well as in improving the sensibility of the analytical technique and lead to a higher confidence level and easy determination of the trace elements. Solid phase extraction still presents advantages over those liquid–liquid extractions, including high enrichment factor, ease regeneration of solid phase and absence or low consumption of hazardous organic solvents. Literature survey has shown several publications involving the use of solid phase extractor, such as chelating resins [9], polyurethane foam [10], ion-imprinted polymers [11], polymers loaded with chelating reagents [12], fullerenes [13], modified silica [14] and natural adsorbents [15]. However, the development of new solid-phase pre-concentration systems has still been growing and continues to be the target of analytical research [16].

Some properties must be considered in the establishment of a sorbent candidate including large specific surface area, chemical resistance, adsorptive capacity, life-time, selectivity and high clean-up capacity. Undoubtedly, these properties are in general found in both single wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs). Studies have demonstrated the excellent performance of these materials as an analytical adsorbent for metal ions, pesticides and phenolic compounds [17–19]. Though carbon nanotubes provide attractive features as solid sorbents, many studies have been devoted to the understanding of physical chemical sorption processes, including kinetic process and adsorption isotherm, while few analytical solid-phase pre-concentration methods have been developed. In this sense, at the best of our knowledge, cobalt adsorption on carbon nanotubes was recently demonstrated using FAAS as detector, but no analytical data and figures of merits were reported [20]. In another work, the authors use carbon nanotubes as solid extractor for cobalt ions as ammonium pyrrolidine dithiocarbamate (APDC) chelates [21]. In this work, high sampling volume (500 mL), use of organic solvent as eluent, high limit of detection and use of chelating agent were observed.

Thus, in the present work a simple and reliable method for cobalt determination at $ng\,L^{-1}$ levels based on metal pre-concentration on MWCNTs with further determination by GFAAS is presented. The method was successfully applied for cobalt determination in water samples and urine samples without sample treatment, thus attesting the excellent cleanup capacity of carbon nanotubes for complex matrices, unlike some solid-phase extraction and cloud point extraction methods that require urine mineralisation previous to sample analysis [22,23]. Finally, in order to improve the performance of the analytical method and reduce sample/reagents consumption and analysis time, the whole optimisation procedure was accomplished by using fractional factorial design and Doehlert design, which are more effective and allow more than one variable to be optimised simultaneously.

2. Experimental

2.1 *Instrumentation*

A Graphite Furnace Atomic Absorption Spectrometer (Zeiss AA55, Germany) equipped with deuterium lamp for background correction and a hollow cathode lamp as radiation source for cobalt was used. The hollow cathode lamp was operated at 5 mA and the wavelength was set at 240.7 nm. The spectral slit width of 0.2 nm was selected. Aliquots of 20 µL of every sample and calibration solution using MPE 5 autosampler were injected directly into the pyrolysate coated graphite tube without L'vov platform with transversal heating. Argon 99.996% (White Martins, Brazil) was used as purge gas. The software was used to obtain and process spectral data, represented by peak area. The pH values of samples were measured using a pH-meter (Metrohm). In order to carry out the off-line cobalt pre-concentration a peristaltic pump (Ismatec®), tygon tubes to propel samples and reagents solutions and a Teflon® injector commutator were employed. Deionised water (18.2 M Ω cm), obtained from Milli-Q Academic purification system was used to prepare all the solutions. The mini-column (6.0 × 1.0 cm i.d.), employed for packing MWCNTs was made of polyethylene containing glass wool placed at both ends of the mini-column aiming at preventing sorbent losses during the system operation. The mini-column was not filled completely with MWCNTs in order to avoid overpressure.

2.2 *Reagents*

All chemicals used were of analytical-reagent grade. In order to prevent metal contamination from laboratory glassware it was kept 24 h in a 10% (v/v) HNO_3 solution. Nitric Acid used for preparing eluent solution and for sample decomposition was obtained from Merck (Germany). Cobalt standard solutions were prepared by appropriate dilution from a 1000 mg L^{-1} cobalt solution. Acetate, borate, Tris-HCl and phosphate buffer solutions were prepared from their respective salts purchased from Merck. The pH of the buffer was adjusted with sodium hydroxide and nitric acid solutions. MWCNTs (95% of purity) were kindly provided from CNT Co., Ltd (Korean). Prior to use, this material was oxidised with concentrated HNO_3 in order to create binding sites onto MWCNTs surface [24]. The treatment was carried out by dispersion in 30 mL of concentrated HNO_3 of 500 mg of MWCNTs being further refluxed for 1 h at 120°C. Afterwards, the material was washed with ultra pure water until the acid excess (neutral pH of solution) was removed, dried at 100°C and stored until use. All solutions of the foreign ions (Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Sb^{3+}, Cr^{3+}, Al^{3+}, Mn^{2+} and Fe^{3+}) used in the interference study were prepared by dilution from a Merck standard solution at 1000 mg L^{-1}.

2.3 *Pre-concentration procedure*

The off-line pre-concentration procedure was accomplished by percolating aliquots of 20 mL of samples previously buffered (pH 8.82 with 0.005 moL L^{-1} phosphate buffer) at a flow rate of 10.0 mL min^{-1} onto 30 mg of MWCNTs. After the pre-concentration procedure, the elution was carried out with 500 µL of 0.524 mol L^{-1} nitric acid solution at a flow rate of 2.0 mL min^{-1}, by switching the injector commutator to the elution position. The eluate was collected into an autosampler cup and an aliquot of 20 µL was introduced into the graphite furnace by the autosampler. The measurements were evaluated by peak area of the absorbance signals.

2.4 *Batch adsorption experiments*

In order to achieve the adsorption capacity, adsorption experiments were performed in batch procedure at room temperature. MWCNTs samples of 50.0 mg were taken and stirred in closed polyethylene flasks with 50 mL of Co^{2+} solutions with increasing concentration ranging from 0.2 up to 6.0 mg L^{-1}. The sample pH (8.82) adopted in these experiments was that previously optimised from column pre-concentration procedure, while the shaking time was 20 min. The adjustment of the pH was carried out with sodium hydroxide solutions. The content of Co^{2+} ions adsorbed by MWCNTs expressed as adsorption capacity (q) in mg g^{-1} was determined by applying the following equation:

$$q = \frac{(C_o - C_f)V}{m}$$

where C_o and C_f are the initial and final concentrations of Co^{2+} ion in the aqueous solution, respectively, V is the volume of metal ion solution and m is the mass MWCNTs.

2.5 *Multivariate optimisation*

In the optimisation stage, the absorption spectrometric measurements were taken by pre-concentrating 20 mL of 10.0 µg L^{-1} cobalt solution onto MWCNTs. The effect of five factors i.e. pre-concentration flow rate, eluent and phosphate buffer concentration, pH of samples and elution volume on the pre-concentration performance were investigated from a 2^{5-1} fractional factorial design. The levels investigated for these factors are shown in Table 1. After establishing those important factors, a more adequate chemometric tool known as Response Surface Methodology using Doehlert matrix as experimental design was employed for optimisation of these three factors. For this task, the pre-concentration

Table 1. Factors and levels used in 2^{5-1} fractional factorial design used for the optimisation pre-concentration procedure of cobalt on MWCNTs.

Factors	Minimum level (−)	Maximum level (+)
Pre-concentration flow rate (PFR) (mL min^{-1})	5.0	10.0
Sample pH	4.0	8.0
Phosphate buffer concentration (BC) (mol L^{-1})	0.01	0.1
Eluent concentration (HNO_3) (EC) (mol L^{-1})	0.5	1.0
Elution volume (EV) (µL)	500	1000

assays were carried out by pre-concentrating 20 mL of 5.0 μg L^{-1} cobalt solution. The analyses of the experimental assays were processed using the STATISTICA software package (StatSoft, Tulsa, USA).

2.6 *Samples preparation*

Stream and river water samples were collected, respectively, near Alfenas city, Minas Gerais – Brazil and Furnas, Minas Gerais – Brazil. These samples were collected in polypropylene bottles followed by adding three drops of concentrated HNO_3 for each 100 mL of stream and river water samples respectively, in order to avoid growth of microorganisms. Afterwards, the samples were filtered under vacuum using 0.45 μm cellulose acetate membranes and the pH value was adjusted to 8.82 with 5.0×10^{-3} mol L^{-1} phosphate buffer. Mineral water samples were acquired from a local supermarket and analysed in a similar way, except for the filtering procedure. Tap water was analysed by the same procedure as the other water samples. Finally, samples were spiked with a known amount of cobalt and determined by the proposed method. Urine samples were collected from healthy volunteers and then the pH was adjusted to 8.82 with phosphate buffer and analysed without further treatment.

3. Results and discussion

3.1 *Multivariate optimisation*

The setting up of a sorbent solid-phase pre-concentration method of analysis requires consideration of a great number of factors. Thus, the choice of the chemical and flow factors that play important role was made in accordance to tests obtained by our research group in the development of sorbent solid-phase pre-concentration methods. The first screening of the effect of factors was accomplished by 2^{5-1} fractional factorial design containing 16 assays (Table 2). The influence of changing the level of one factor on the result (peak area) was evaluated from the Pareto chart, which is a usual way to use analysis of variance (ANOVA) in graphical form. When horizontal bars are higher than the vertical line established at a confidence interval of 95%, the factors are statistically significant [24] (Figure 1).

As one can see from Pareto chart, the buffer concentration has great influence on analytical response with negative effect (−18.74), thus indicating that the use of minimum level (0.01 mol L^{-1}) increases the analytical signal. This result was expected since it is known that high buffer concentration affects the metal ions adsorption on MWCNTs in a wide pH range [24]. The strongly dependent adsorption of Co^{2+} to MWCNTs on buffer concentration (or ionic strength) indicates that the adsorption mechanism of Co^{2+} occurs by electrostatic ion exchange with the functional groups at the MWCNTs surface, while the mechanism based on chemicomplexation is weak. It seems that Co^{2+} ions form electrical double layer with MWCNTs surface, which naturally favour the adsorption when the concentration of the buffer concentration is decreased. Another possible explanation is associated to the influence of buffer concentration on the activity coefficient of Co^{2+}. In this case, the transfer of Co^{2+} ions towards the MWCNTs surface is seriously decreased. As regards the effect of elution volume, a negative effect was also obtained (−11.37) and obviously, high elution volume can significantly decrease the analytical signal owing to the dilution of eluate. Thus, 500 μL were chosen as best value taking into

Table 2. 2^{5-1} Fractional factorial design and its results for pre-concentration of cobalt on MWCNTs with quantification by GFAAS.

Assays	pH	PFR	BC	EC	EV	Absorbance (peak area)
1	−	−	−	−	+	1.603/1.668
2	+	−	−	−	−	2.182/2.076
3	−	+	−	−	−	2.057/2.064
4	+	+	−	−	+	1.609/1.559
5	−	−	+	−	−	1.267/1.470
6	+	−	+	−	+	1.578/1.370
7	−	+	+	−	+	0.915/0.948
8	+	+	+	−	−	1.449/1.490
9	−	−	−	+	−	2.072/1.917
10	+	−	−	+	+	1.364/1.390
11	−	+	−	+	+	1.661/1.661
12	+	+	−	+	−	1.859/1.900
13	−	−	+	+	+	0.923/1.090
14	+	−	+	+	−	1.390/1.376
15	−	+	+	+	−	1.302/1.080
16	+	+	+	+	+	1.170/1.208

Note: PFR: pre-concentration flow rate; BC: buffer concentration; EC: eluent concentration; EV: elution volume.

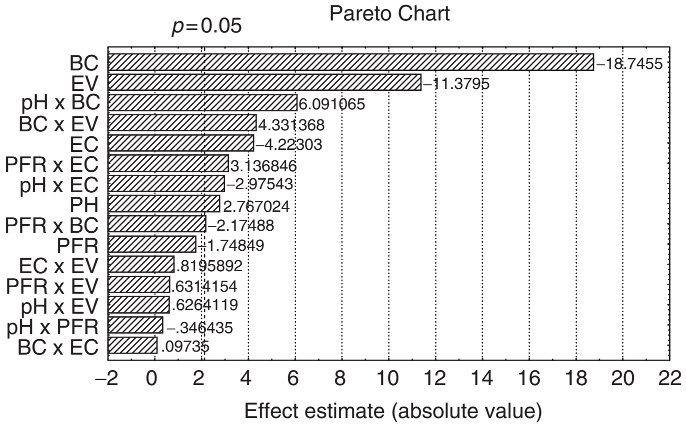

Figure 1. Pareto chart built from data displayed in Table 2.

account the high analytical signal observed and due to the absence of memory effect during pre-concentration/elution steps.

High nitric acid concentration as eluent is not indicated in the sorbent solid-phase pre-concentration method, based on negative effect (−4.22). This result corroborates with that effect of the buffer concentration. A lower buffer concentration must be used and, as a consequence, it would not be able to maintain the sample buffered when high nitric acid solution is employed as eluent. The positive effect of sample pH (2.76) ensures better adsorption of cobalt ions on the surface of MWCNTs. Thus, pre-concentration efficiency increases from pH 4.0 to 8.0. Pre-concentration flow rate ranging from 5.0 up to 10 mL min^{-1}, on the other hand, does not alter adsorption capacity of cobalt ions towards

Table 3. Doehlert design used in the final optimisation of chemical factors.

Assays	EC (mol L^{-1})	BC (mol L^{-1})	pH	Absorbance (peak area)
1	0.46 (0)	0.0275 (0)	8 (0)	0.880
2	0.46 (0)	0.0275 (0)	8 (0)	0.877
3	0.46 (0)	0.0275 (0)	8 (0)	0.829
4	0.46 (0)	0.0275 (0)	8 (0)	0.996
5	0.90 (1)	0.0275 (0)	8 (0)	0.797
6	0.68 (0.5)	0.0500 (0.866)	8 (0)	0.702
7	0.68 (0.5)	0.0350 (0.289)	10 (0.817)	0.251
8	0.02 (−1)	0.0275 (0)	8 (0)	0.128
9	0.24 (−0.5)	0.0050 (−0.866)	8 (0)	0.876
10	0.24 (−0.5)	0.0200 (−0.289)	6 (−0.817)	0.673
11	0.68 (0.5)	0.0050 (−0.866)	8 (0)	0.919
12	0.68 (0.5)	0.0200 (−0.289)	6 (−0.817)	0.813
13	0.24 (−0.5)	0.0500 (−0.866)	8 (0)	0.633
14	0.46 (0)	0.0425 (0.577)	6 (−0.817)	0.170
15	0.24 (−0.5)	0.0350 (0.289)	10 (0.817)	0.422
16	0.46 (0)	0.0125 (−0.577)	10 (0.817)	0.320

Note: BC: buffer concentration (phosphate buffer); EC: eluent concentration.

MWCNTs, showing a fast kinetic process of adsorption. So, 10 mL $\min^{-1}$ was used in order to enhance the sample throughput of the method.

As mentioned, the more important factors, in accordance with 2^{5-1} fractional factorial design, were eluent concentration, buffer concentration and pH of sample. The other factors, such as pre-concentration flow rate and elution volume were fixed at 10 mL $\min^{-1}$ and 500 µL, respectively. Previous to the final optimisation by Doehlert design, different kinds of buffers were evaluated (borate, phosphate, Tris-HCl and acetate). The influence of these different kinds of buffers on Co^{2+} adsorption on MWCNTs was evaluated from univariate method using those levels employed in fractional factorial design (pH 4.0 and 8.0). So, the effect of acetate buffer (pH buffering range 3.75–5.75) was investigated only in pH 4.0, phosphate buffer was investigated in pH 4.0 and 8.0 due to its wide buffering range and both borate (pH buffering range 8.0–10.0) and Tris-HCl (pH buffering range 7.0–9.0) were investigated in pH 8.0. Phosphate buffer presented (data not shown) the best results and it was chosen in the following experiments using response surface.

Design factors in the coded and original units are listed in Table 3. In order to quantitatively elucidate the effects of these three factors, the absorbance was subjected to regression analysis. From Doehlert design a full quadratic polynomial was achieved, which enables to establish the relationship between the three factors and the analytical response

$$\begin{aligned}\mathrm{Abs} = {} & -3.9219 + 3.8779\mathrm{EC} - 2.2361\mathrm{EC}^2 - 78.2901\mathrm{BC} - 8.9481\mathrm{BC}^2 \\ & + 1.3063\mathrm{pH} - 0.0952\mathrm{pH}^2 + 1.3091\mathrm{EC.BC} - 0.1817\mathrm{EC.pH} \\ & + 8.9080\mathrm{BC.pH}\end{aligned}$$

from this equation three response surfaces were obtained and are illustrated in Figure 2 in order to verify the adjustment of the quadratic model with those experimental data,

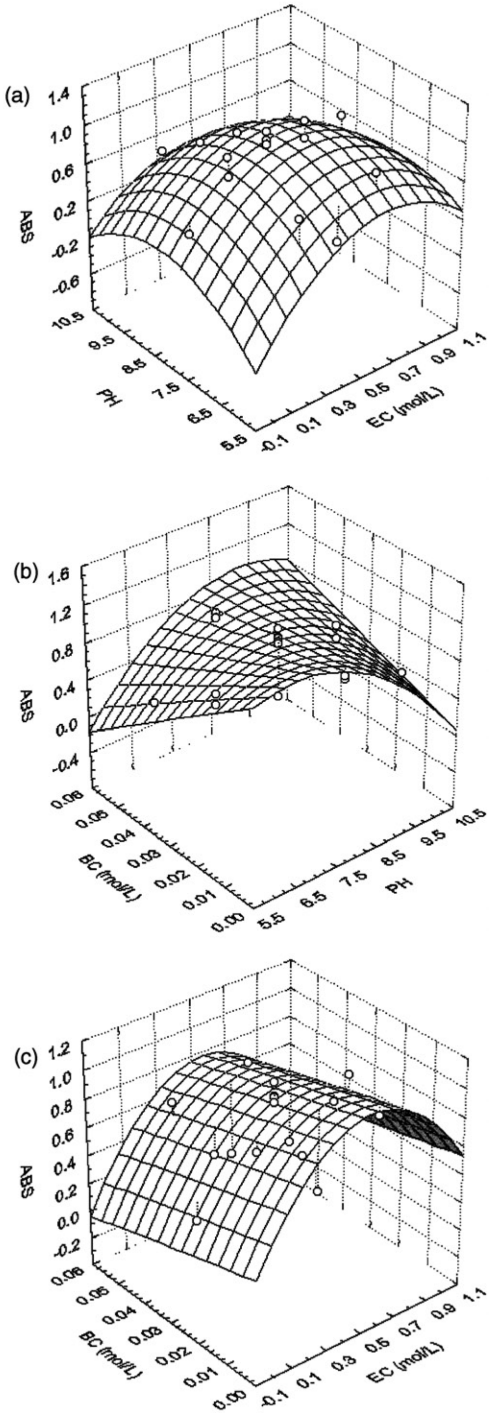

Figure 2. Surface responses obtained from the Doehlert design for three factors shown in Table 3.

Table 4. Analysis of variance obtained from the Doehlert design shown in Table 3.

Effects	SS	df	MS	*F*	*p*
EC	0.125972	1	0.125972	25.14757	0.015269
EC^2	0.249870	1	0.249870	49.88118	0.005835
BC	0.129146	1	0.129146	25.78122	0.014756
BC^2	0.000049	1	0.000049	0.00971	0.927718
pH	0.073034	1	0.073034	14.57969	0.031609
pH^2	0.489203	1	0.489203	97.65889	0.002204
EC.BC	0.000168	1	0.000168	0.03353	0.866387
EC.pH	0.023005	1	0.023005	4.59255	0.121506
BC.pH	0.192826	1	0.192826	38.49369	0.008437
Lack of fit (lof)	0.128287	3	0.042762	8.53657	0.055796
Pure error (pe)	0.015028	3	0.005009		
Total SS	1.252742	15			

Note: $R^2 = 0.8865$ and R^2 adjusted = 0.714.

ANOVA was employed (Table 4). Thus, Fisher distribution (*F*-test) was used in comparing two variation sources (lack of fit and pure error). When the MS_{lof}/MS_{pe} ratio is higher than tabled *F*, it is possible to affirm that the quadratic model presents lack of fit. MS_{lof} (0.042762) is the sum of squares of lack of fit (0.128287) divided by the degree of freedom (3). In a similar way, MS_{pe} is the sum of squares of pure error (0.015028) divided by 3 degrees of freedom. Thus, by comparing the experimental value of $F = MS_{lof}/MS_{pe}$ (8.53657) with that tabled $F_{3,3}$ value (9.28) at 95% confidence level, we can confirm that the quadratic model does not present lack of fit. Hence, the response surface showed maximum values of absorbance, at $5.0 \times 10^{-3}\,mol\,L^{-1}$ phosphate buffer, pH 8.82 and $0.524\,mol\,L^{-1}$ nitric acid eluent.

3.2 *Batch adsorption experiments*

The maximum adsorption capacity (MAC) of MWCNTs towards Co^{2+} depends on sample pH and shaking time. Thus, as previously optimised, the optimum sample pH of Co^{2+} adsorption on MWCNTs was 8.82, while the dependence of shaking time on the adsorption profile is shown in Figure 3. From the results obtained, 20 min of shaking time were sufficient for attaining the equilibrium time of Co^{2+} between both the solid and liquid phases. Therefore, this value was chosen for assessing the influence of the initial concentration of Co^{2+} on the maximum adsorption capacity. Figure 4 shows the adsorption profile of Co^{2+} at their initial concentration range of $0.2–6.0\,mg\,L^{-1}$. It was observed that the amount of adsorbed Co^{2+} increased significantly with increasing metal concentration. After initial concentration of $4.0\,mg\,L^{-1}$, a saturation condition of those binding sites of MWCNTs was observed. Thus, the MAC was found to be $4.0\,mg\,g^{-1}$.

3.3 *Interference study*

The effects of 10 foreign ions (Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Sb^{3+}, Cr^{3+}, Al^{3+}, Mn^{2+} and Fe^{3+}) on the determination of $4.0\,\mu g\,L^{-1}$ of cobalt were studied with the optimised

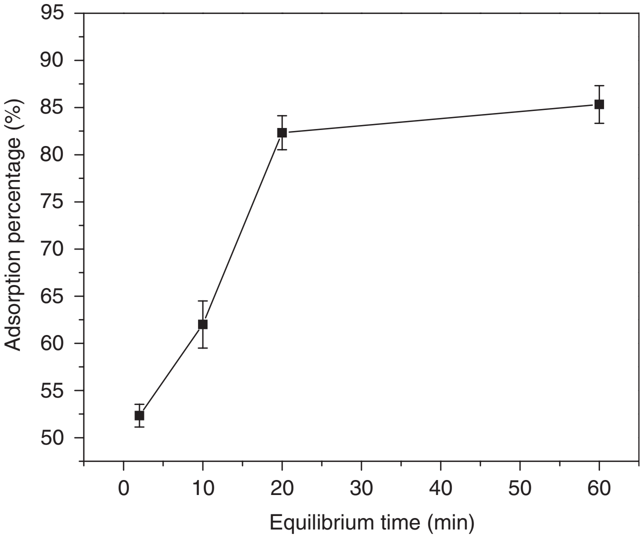

Figure 3. Co^{2+} ions adsorption profile on MWCNTs at different shaking times. Cobalt concentration was 3.0 mg L^{-1}.

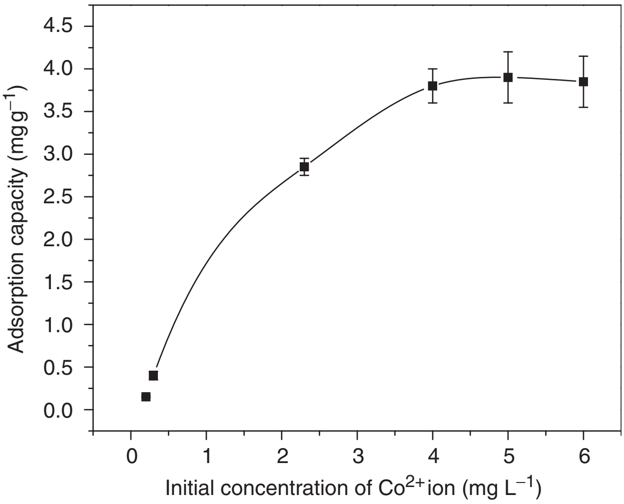

Figure 4. Effect of the initial concentration of Co^{2+} ions on the equilibrium adsorption capacity at pH 8.82.

conditions described above. These metals were investigated owing to their possible competition for those MWCNTs sites present on the surface. The ratios analyte: interferent were 1 : 1, 1 : 10 and 1 : 100 (Table 5). The criterion for interference was an absorbance value varying by more than 10% from the expected value for cobalt alone. According to Table 5, all ions studied did not interfere. These results are of paramount importance and show that the method presents reliable selectivity and, as will be demonstrated later, it will allow the pre-concentration and quantification of cobalt ion in real samples.

Table 5. Influence of coexisting ions in the cobalt pre-concentration on MWCNTs.

Ion	Ratio analyte : foreign ion	Recovery (%)
Cu^{2+}	1 : 1	98.5
	1 : 10	102.7
	1 : 100	96.8
Sb^{3+}	1 : 1	93.6
	1 : 10	96.1
	1 : 100	96.7
Ni^{2+}	1 :1	97.8
	1 : 10	98.2
	1 : 100	99.4
Pb^{2+}	1 : 1	99.7
	1 : 10	100.2
	1 : 100	98.6
Zn^{2+}	1 : 1	100.1
	1 : 10	96.9
	1 : 100	97.2
Cd^{2+}	1 : 1	99.9
	1 : 10	104.4
	1 : 100	98.4
Cr^{3+}	1 : 1	108.9
	1 : 10	100.1
	1 : 100	99.4
Al^{3+}	1 : 1	96.4
	1 : 10	99.4
	1 : 100	98.9
Fe^{3+}	1 : 1	108.4
	1 : 10	102.1
	1 : 100	100.8
Mn^{2+}	1 : 1	91.7
	1 : 10	98.5
	1 : 100	93.8

3.4 *Analytical characteristics*

Under the optimum conditions achieved by factorial design analysis and by pre-concentrating 20 mL of aqueous standard solutions, the calibration curve was obtained in the range of 0.03 (limit of quantification) up to 7.00 $\mu g\,L^{-1}$ with a correlation coefficient (r) higher than 0.9994. The calibration curve obtained was $Abs = 0.2884[Co^{2+} (\mu g\,L^{-1})] + 0.0462$. A limit of detection ($LOD = 3SD/m$, where SD is the standard deviation for 10 replicates determination of the blank signal and m is the slope of the calibration curve) [25] of 0.01 $\mu g\,L^{-1}$ for cobalt was obtained, while the limit of quantification (LOQ = 10SD/m) was found to be 0.03 $\mu g\,L^{-1}$. The relative standard deviations for six replicates measurements of 0.3 and 4.5 $\mu g\,L^{-1}$ were 2.38 and 1.84%, respectively. By pre-concentrating 20 mL of sample, a pre-concentration factor (PF) of 19.10-fold was obtained. It was calculated as the ratio between the slopes of analytical curves with and without the pre-concentration procedure. A consumptive index of 1.05 mL (CI = sample volume/PF) was achieved. The pre-concentration efficiency (PE) provides a better evaluation of procedure performance. The value of PE establishes the sensitivity

Table 6. Comparison among different pre-concentration methods for cobalt determination by GFAAS.

Pre-concentration modality	LD* (μg L^{-1})	Reagent	Linear range (μg L^{-1})	Sample volume (mL)	Samples	Ref.
Cloud point extraction	0.38	PAN	1.0–120	10	Urine	[23]
Cloud point extraction	0.01	–	–	5	Drinking water	[26]
Flotation separation	0.0012	HMDC	–	1000	Fresh water	[27]
Coprecipitation	0.03	Disulfide	0–20	200	Water samples	[28]
Solid-phase extraction with activated carbon	0.03	–	0.05–0.35	10	Drinking waters	[29]
Solid-phase extraction with MWCNTs	0.01	–	0.03–7.0	20	Water samples and urine	This work

Note: PAN = 1-(2-Pyridylazo)-2-(naphtol), HMDC = Hexamethylenedithiocarbamate.

enhancement using a pre-concentration time of 1 min. Thus, the PE was found to be 9.55 min^{-1}.

Comparative analytical figures of merit for different pre-concentration methods for the determination of cobalt by GFAAS have been presented in other works (Table 6). By using those results, it can be shown that the proposed method is comparable to the previously reported ones, with such advantages as a much better sensitivity, low sample consumption and absence of chelating agent.

3.5 *Real sample application*

Considering the free-interference cobalt determination in accordance to interference studies an external calibration curve was employed for analysis and cobalt determination in water and urine samples. For water and urine analysis, samples were submitted to sample preparation described in experimental section of this article. After that, addition and recovery tests were carried out in order to check the accuracy of the method. The data obtained (Table 7) for samples spiked with cobalt showed good recoveries, thus attesting that the sorbent solid-phase pre-concentration associated to GFAAS determination is suitable for monitoring cobalt ions in water and urine samples without exhaustive time consuming sample treatment. The cobalt amount obtained in human urine samples ranging from 0.175 up to 0.75 μg L^{-1} is within the level commonly found in healthy people.

4. Conclusion

The analytical method described here demonstrates a new application of MWCNTs for improving the detectability of GFAAS for cobalt determination in different kinds of water samples, including environmental samples such as river water. In addition, the method presents excellent cleanup capacity for urine analysis and can be successfully applied for management of non-occupational exposure of people to the element. The great advantages of the present method, in comparison to previously published ones using pre-concentration procedures, include simplicity, good selectivity, high sensibility, absence of hazardous organic solvents and chelating agents. Moreover, life-time of MWCNTs

Table 7. Recovery percentage for cobalt ions determination in tap, mineral, stream, river water samples and urine samples.

Samples	Added amount ($\mu g\,L^{-1}$)	Determined amount* ($\mu g\,L^{-1}$)	Recovery (%)
Tap water	–	ND	–
	3.0	2.9 ± 0.2	95.0
Mineral water	–	ND	–
	3.0	2.99 ± 0.05	99.7
	6.0	5.60 ± 0.03	93.3
Stream water	–	0.11 ± 0.03	–
	3.0	3.17 ± 0.30	101.9
River water	–	ND	–
	3.0	2.83 ± 0.08	94.3
Urine sample (A)[a]	–	0.15 ± 0.01	–
	0.15	0.30 ± 0.07	100.0
Urine sample (B)[b]	–	0.07 ± 0.01	–
	0.07	0.13 ± 0.01	92.9
Urine sample (C)[b]	–	0.10 ± 0.01	–
	0.15	0.23 ± 0.02	92.0

Notes: Confidence interval 95%. *The results are expressed as mean value ± SD based on three replicate ($n = 3$) determinations. [a]Urine sample diluted 5 times, [b]Urine sample diluted 2.5 times.

minicolumn is longer than other synthetic or natural adsorbents, in which more than 600 pre-concentration/elution steps were carried out without losses of adsorption capacity.

Acknowledgements

The authors would like to thank the CNPq, CAPES and FAPEMIG for the financial support and fellowships. The authors also would like to thank Prof. Maria Antonieta Alvarenga for language assistance.

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