

Determination of trace amounts of chromium ions in water and food samples using ligand-less solid phase extraction-based on modification of boehmite nanoparticles

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Abstract

Chromium is one of the hazardous pollutants in industrial effluents. In this study, a new nano-boehmite modified with sodium dodecyl sulphate is developed for preconcentration trace amounts of chromium ions as a prior step to its determination by flame atomic absorption spectrometry. We investigated the effect of various parameters on the recovery of the analyte ions, including pH of sample solution, amount of sorbent, sample volume on extraction efficiency of the chromium ions. Under the best experimental conditions, the calibration curve was linear in the range of 1.0 -700.0 ng.mL⁻¹ of chromium with R² = 0.997. Detection limit was 0.6 ng.mL⁻¹ in the original solution (3Sb/m) and the relative standard deviation for seven replicate determination of 0.5 µg.mL⁻¹ chromium was ±2.4%. The developed method was successfully applied to the extraction and determination of chromium in water and food samples with satisfactory results.

Keywords: Solid phase extraction; preconcentration; nano boehmite; chromium; flame atomic absorption spectrometry.

Introduction

Toxic metal ions are main sources of contamination in environmental and water resources. Chromium is ubiquitous in nature, occurring in various chemically, physically and morphologically different forms. The metal ions may also enter tap water supply systems from the corrosion inhibitors used in water pipes and containers. Chromium is one of the most abundant elements with the potential to contaminate groundwater, and so can be a most important source of drinking water contamination [1]. Due to that, trace and ultra-trace

determinations of chromium in environmental and biological samples have become of increasing interest [2,3]. The direct determination of extremely low concentrations of the required trace metals by modern spectroscopic methods is still difficult due to insufficient sensitivity of the techniques and matrix interferences [4]. The determination of low concentrations of Cr in water samples requires powerful analytical techniques and only few of them have satisfactory sensitivity. Flame atomic absorption spectrometry (FAAS) is widely used by the technique for quantification of metal

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species. The determination of metals in food is usually associated with a step of preconcentration of the analyte before detection, due to low concentrations of the element present in the matrices [5,6]. A variety of procedures for preconcentration of metals, such as liquid-liquid extraction (LLE), coprecipitation, cloud point extraction (CPE) and solid phase extraction (SPE), have been developed [7-13]. SPE is an attractive method that reduces consumption and exposure to solvent, disposal costs and extraction time [14-17]. Nowadays, investigation for finding new materials as solid phase extractor is an important issue to preconcentrate transition metals traces levels. Recently, nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties [18-20]. Fulfilling the aim of this study, we developed a nano boehmite based solid phase extraction method for preconcentration and determination of trace amounts of chromium from water and food samples. Chromium formed stable complexes with sodium dodecyl sulphate coated nano boehmite in a column extraction procedure. Afterward, the extracted chromium ions were eluted from the surface of the adsorbent and determined using flame atomic absorption spectroscopy. To the best of our knowledge, sodium dodecyl sulphate coated nano boehmite has not been employed previously for the extraction and determination of chromium ions from aqueous samples.

Experimental

Instrumentation

A novAA 400p atomic absorption spectrometer (Anaalyticaljena-Germany) equipped with chromium hollow cathode lamp was used for absorbance measurements at

wavelength of 357.9 nm. An acetylene-Nitroxide flame was used for the determination of chromium ions and their flow rates were 10.0 L min⁻¹ and 0.8 L min⁻¹, respectively. Also, this device was equipped with a 50 mm burner head and deuterium background correction. A Metrohm 692 pH meter (Herisau, Switzerland) and Scanning Electron Microscope (Cam Scan MV2300) were used for pH measurements and nanoparticles size, respectively. Funnels-tipped glass tube (5*100 mm) equipped with stopcock was used as column for the preconcentration purposes.

Chemicals, materials, and standards

All the reagents were of the analytical grades obtained from Merck (Darmstadt, Germany). The laboratory glassware was kept overnight in a 1.4 mol.L⁻¹ HNO₃ solution. Before using, the glassware was washed with double distilled water and dried. Standard solution of Cr(III) ions at a concentration of 1000.0 µgmL⁻¹ was prepared by dissolving appropriate amounts of Cr(NO₃)₃•4H₂O (Merck, Germany) in deionized water containing 1 mL concentrated nitric acid (Merck, Germany). The working reference solutions were obtained daily by stepwise dilution from stock solution with double distilled water. A buffer solution with pH = 7.0 was prepared from 0.1mol/L disodium hydrogen phosphate. The solution of alkali metal salts (1% w/v) and various metal salts (0.1% w/v) were used to study the interference of ions. Al(NO₃)₃•9H₂O and CH₄N₂O was supplied by Merck.

Column preparation

A small amount of glass wool was placed in the end of column (100 mm length and 5mm i.d.) equipped to

stopcock, to prevent loss of the sorbent during sample loading. Then, the column was packed with 40.0 mg of the sorbent. The bed height of the sorbent in the column was approximately 4.0 mm. It was preconditioned by passing buffer solution prior to use.

Synthesis of boehmite nanoparticles

18.75 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 6 g of urea, $\text{CH}_4\text{N}_2\text{O}$ were dissolved in 100 and 30 mL of distilled water, respectively, at room temperature in beakers and magnetically stirred to achieve homogeneous solutions. Then, urea solution was added to $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution and stirred at room temperature for 20 min before the mixed solution was transferred into a 200 mL Teflon-lined stainless autoclave and heated at 200 °C for several hours under autogenously pressure. After reaching room temperature, the precipitate was filtered, washed four times with distilled water, and finally dried in an oven at 60 °C for 24 h under air to afford a dried sample of nano boehmite [21]. The microstructure of the nano boehmite was observed by Scanning Electron Microscope (SEM) (Cam Scan MV2300) and is shown in Figure 1. The scanning electron micrograph was recorded without sample coating. This figure shows that the adsorbent had a regular surface, indicating relatively high surface areas.



Figure 1. SEM of nano boehmite

Modification of boehmite nanoparticles

50 mg of sodium dodecyl sulfate (SDS) was added to 50 mL of water solution containing 1 g boehmite nanoparticles. SDS was attached on boehmite nanoparticles while shaking the suspension with a stirrer. After mixing for 3 h, the supernatant solution was discarded and the remaining was stored for later use. Positively charged boehmite nanoparticles surfaces effectively sorbed negatively charged SDS, then positive Cr(III) sorbed negatively charged SDS. The modified structure of the nano boehmite with SDS was shown in Figure 2.

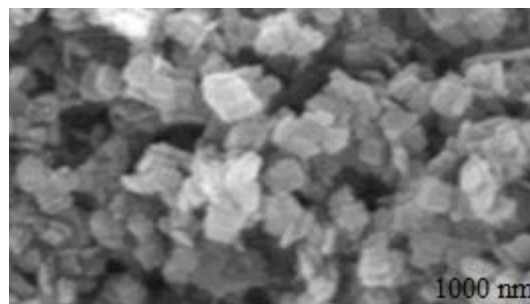


Figure 2. SEM of modified nano boehmite

FTIR spectra

The resulting interaction between SDS with boehmite nanoparticles was characterized by FTIR spectroscopy. The FTIR spectra of boehmite nanoparticles and SDS were recorded using KBr pellet method. In Figure 3, typical FTIR spectral patterns were shown for unmodified boehmite nanoparticles and SDS/ boehmite nanoparticles. The characteristic bands of SDS/ boehmite nanoparticles can be observed in spectrum of boehmite nanoparticles modified with SDS (brown curve). The results confirm the formation of a connection between the surface of the boehmite nanoparticles and SDS.

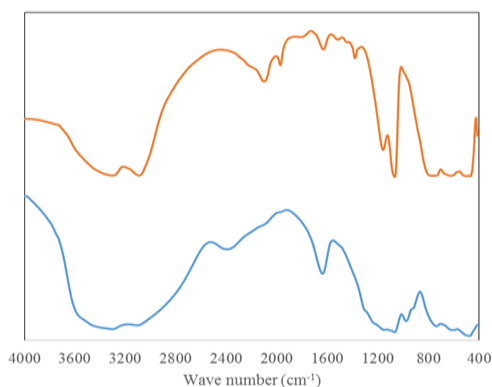


Figure 3. FT IR spectra (blue curve unmodified sorbent and brown curve is modified adsorbent)

Procedure

Column method was applied for the preconcentration process. Twenty five milliliters of a solution containing 0.2 mg.L^{-1} chromium and 2.0 mL of phosphate buffer (pH 7.0) were passed through the column at a flow rate of 3 mL.min^{-1} . The retained chromium ion was eluted from the sorbent by 3.0 mL of 1 mol.L^{-1} of HNO_3 in ethanol solution and was aspirated into an air-acetylene flame for the determination of chromium by FAAS.

Preparation of samples

Water samples (tap, well, river, and snow) were collected in acid leached polyethylene bottles. Tap water sample was collected from Kermanshah (Kermanshah, Iran). The well water sample was collected from our university (Kermanshah, Iran). The River water sample was collected from Rijab River (Kermanshah, Iran). The only pretreatment was acidification to pH 2.0 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. The samples were filtered before analyses through a cellulose membrane of $0.45 \text{ }\mu\text{m}$ pore size (Millipore).

Results and discussion

In this study, the optimum sorption and desorption properties of modified nanoboehmite for chromium ions were found by using the column technique. Quantitative recovery was obtained for chromium without using a chelating agent. The effect of some analytical parameters such as pH, amount of adsorbent, type and volume of eluent solution, flow rate of sample solution, and volume of sample solution on the recovery of the chromium ions have been investigated.

Effect of the pH

The pH is an important factor affecting the removal of metal ions from aqueous solutions. Dependence of metal sorption on pH is related to both the metal chemistry in the solution and the ionization state of functional groups of the adsorbent which affects the availability of binding sites [22]. The pH of sample solutions containing $12.5 \text{ }\mu\text{g}$ of Cr(III) ions was studied over the range of 3.0–10.0. The pH of sample solutions was adjusted by 0.1 mol.L^{-1} NaOH or HNO_3 solutions. The results are given in Figure 4 and showed that with the increase of pH, the adsorption efficiency of the analytes improved dramatically and reached maximum at pH 7.0. The same results were obtained using buffer. Accordingly, further studies were done at pH 7.0 using a 0.1 mol.L^{-1} phosphate buffer solution. The volume of buffer was also studied. The results showed that addition of 1.0–4.0 mL of buffer did not have any effect on the extraction of the analyte ions. Therefore, 2.0 mL phosphate buffer solution was used in all subsequent experiments.

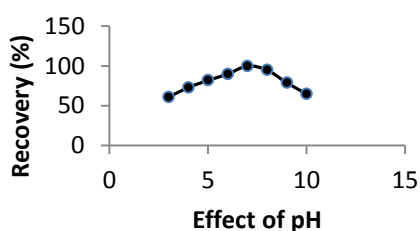


Figure 4. Effect of pH

Effect of amount of the sorbent

The amount of sorbent is another important parameter that affects the recovery. A quantitative retention is not obtained when the amount of sorbent is less. For this purpose, different amounts of the sorbent (10.0–100.0 mg) were examined. The results showed that when the sorbent quantity was greater than 40.0 mg, quantitative recoveries of the metal ions were obtained. With respect to these results, 50.0 mg of sorbent was chosen for further experiments.

Selection of the best eluent and optimization of its concentration and volume

In order to choose the most effective eluent, various acidic solutions on the pre-concentration yield of the chromium

ion were studied under the optimum conditions. The results showed that the acids with ethanol provided higher recovery efficiency compared to the acids in aqueous solutions (Table 1). Quantitative recoveries for chromium ions were obtained with HNO₃ in ethanol. Therefore, HNO₃ in ethanol was selected as eluent for further applications. After the above findings, the experiments were carried out for selecting the concentration of HNO₃ solution in ethanol. For this purpose, HNO₃ solution in ethanol was studied at the concentrations between 0.50–2.0 mol.L⁻¹. The results showed that the recovery values increased with adding HNO₃ to ethanol. After 1.0 mol.L⁻¹ HNO₃, the analyte was quantitatively recovered. The optimum HNO₃ concentration was determined as 1.0 mol.L⁻¹ HNO₃ in ethanol. The influence of the volume of 1 mol.L⁻¹ HNO₃ in ethanol between 0.5 and 5.0 mL was also examined. The results showed that 3.0 mL of 1.0 mol.L⁻¹ HNO₃ in ethanol was sufficient for complete desorption of the chromium ion from surface of sorbent.

Table 1. Types of eluent on the recovery of chromium ions at concentrations of 5.0 µg

Type of eluent	Recovery ^a (%)
	Cr(III)
HCl in methanol	91.26
HCl in ethanol	92.25
HCl in water	89.37
HNO ₃ in methanol	95.66
HNO ₃ in ethanol	98.26
HNO ₃ in water	83.17
CH ₃ COOH in methanol	63.26
CH ₃ COOH in ethanol	66.98
CH ₃ COOH in water	54.75

Effect of flow rate of sample and eluent solution

The retention of an element on the sorbent also depends on the flow rate of the sample solution. Thus, the effect of flow rate of the sample and elution solution on the retention and recovery of chromium ions were investigated. For this purpose, the solutions containing Cr(III) ions were passed through the column with the flow rates adjusted in a range 0.1–5.0 mL.min⁻¹. It was observed that at flow rates greater than 4 mL.min⁻¹, the recovery of chromium ion was decreased. The reason for this decrease is probably insufficient contact of the chromium ions and the sorbent to reach equilibrium. Therefore, a flow rate of 3 mL.min⁻¹ was selected for subsequent experiments. For desorption of chromium ions, flow rate was varied between 0.5 and 4.0 mL.min⁻¹. It was observed that at flow rates greater than 2.0 mL.min⁻¹, there was a decrease in the recovery of chromium. Therefore, a flow rate of 1.0 mL.min⁻¹ was adequate for desorption of the analyte ion.

Effect of sample volume (Breakthrough volume)

Breakthrough volume is another parameter that influences the preconcentration factor. It is very important to get satisfactory recoveries for the analytes ions from a large volume of the sample solutions. Breakthrough volume depends on the type and nature of the sorbent and also the type and concentration of sample constituents. Therefore, the effect of sample volume on the retention of chromium ions from the sample solution was investigated. For this purpose, 25.0-1000.0 mL of aqueous solution, containing 1.0 µg of chromium ions, were processed according to the analytical procedure. It

was observed that quantitative extraction of Cr(III) ions (>95%) were obtained up to 600.0 mL. Above 600.0 mL, the recovery of Cr(III) ion was decreased. As the sample volume increases, analyte (Cr³⁺) concentration comes down. Also, increasing the distance between the analyte ions, the amount of sorbent is fixed so effective that collision is reduced between analyte and sorbent. As a result, the percent recovery is reduced above 600 mL of sample volume. Therefore, preconcentration factor of 200.0 was obtained for chromium ion. However, for convenience, all the experiments were carried out with 25.0 mL of the aqueous phase.

Sorption capacity of the sorbent

The sorption capacity of sorbent for chromium ions was also evaluated. In this case, a column containing 100.0 mg of sorbent was used and different volumes of 10.0 µg.mL⁻¹ chromium ions were passed through the column. The outlet solution was collected and the presence of the analyte ions was tested by FAAS. When chromium ions were detected in the outlet solution, the test was stopped and the sorption capacity was calculated. The sorption capacity of sorbent for chromium was found to be 30.26 mg g⁻¹.

Effect of foreign ions

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference may be attributed to the separation step. To perform this study, interference ions in different interference-to-analyte ratios were added to a solution containing 5.0 µg of Cr(III) ions and were subjected to the analytical procedure. The tolerance limits of the interference ions (error ±5%) were showed in Table 2 and demonstrated that the presence of large

amounts of species commonly present in water samples have no significant effect on the SPE of chromium ions.

Table 2. Tolerance limits of foreign ions

Foreign ions	Added as	Interference Cr(III) ratio
PO_4^{3-}	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	2500
H_2PO_4^-	$\text{K}_2\text{HPO}_4 \cdot 6\text{H}_2\text{O}$	2500
HPO_4^{2-}	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	2500
Na^+	NaNO_3	2000
K^+	KCl	2000
Zn^{2+}	ZnCl_2	1500
Ni^{2+}	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	900
Mn^{2+}	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	600
Cu^{2+}	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	550
Rh^{3+}	$\text{Rh}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	500
Fe^{2+}	FeCl_2	120
Fe^{3+}	FeCl_3	100
Bi^{3+}	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	100
Ag^+	AgNO_3	100

Calibration, precision and detection limit

Under the optimized conditions, calibration curve was constructed for the determination of Cr(III) according to the SPE procedure. The calibration graph was linear in the range of 1.0–700.0 ng mL^{-1} for Cr(III). The line equation for Cr(III) was $A = 1.431C + 0.027$ ($R^2 = 0.997$). In this equation, *A* is the absorbance value, *C* is the concentration of analyte ion ($\mu\text{g mL}^{-1}$) and *R* is the correlation coefficient. The

limit of detection based on $3S_b/m$ for Cr(III) ion was 0.6 ng mL^{-1} . Eight replicates determination of $0.5 \mu\text{g mL}^{-1}$ Cr(III) gave a mean absorbance of 0.023 with relative standard deviation of 2.4%.

Analysis of water samples

The analytical procedure has been applied to the determination of chromium ions in different water samples after standard addition. The results are given in Table 3. The

recovery of chromium ions from water samples spiked with chromium ions was also studied. According to this Table, the added chromium ions can be quantitatively recovered from the water

samples by the analytical procedure. These results demonstrate the applicability of the analytical procedure for chromium ions determination in water samples.

Table 3. Determination of chromium ions (n=3) in various water samples

Sample	Added($\mu\text{g.mL}^{-1}$)	Found ($\mu\text{g.mL}^{-1}$)	Recovery%
Tap water	0.0	0.12 \pm 0.01	-
	10.0	10.1 \pm 0.03	99.80
Well water	0.0	ND	-
	10.0	10.1 \pm 0.03	101.00
River Water Rijab, Kermanshah)	0.0	0.61 \pm 0.02	-
	10.0	10.61 \pm 0.01	100.00

ND: Not detect

Analysis of chromium ions in the rice, oak and black tea samples

The applicability of the proposed method was evaluated in the food samples. A 1.0 g of the dry rice, oak and black tea samples were taken in beaker (100 mL) and dissolved in concentrated nitric acid and perchloric acid (3:1) by heating on a heater, individually. The solution was cooled, diluted and filtered in calibration flasks, individually. A 25.0 mL of the pretreated sample solution was taken

individually and chromium ion was determined by the proposed procedure. The recovery of chromium ions from food samples spiked with chromium ions was also studied. The related results are presented in Table 4. According to this Table, the added chromium ions can be quantitatively recovered from the plant samples by the analytical procedure. These results demonstrate the applicability of the analytical procedure for chromium ions determination in plant samples.

Table 4. Determination of chromium in food sample (n=3)

Sample	Added($\mu\text{g/g}$)	Found ^a ($\mu\text{g/g}$)	Recovery%
Rice	0.0	ND	-
	10.0	9.98 \pm 0.03	99.80
Oak (near in the cement factory-Sarableh-Ilam)	0.0	3.1 \pm 0.04	-
	10.0	13.1 \pm 0.02	100.00
Black tea	0.0	0.2 \pm 0.01	-
	10.0	10.1 \pm 0.03	99.01

^aAverage \pm standard deviation (n=3)

ND: not detected.

Comparison with other methods

A comparison of the extraction procedure with the other reported preconcentration methods [23-26] for chromium ions are given in Table 5. Some parameters obtained were comparable to the ones presented by

other methods described in the literature. The obtained detection limit by the extraction procedure is comparable to most of those reported in the literature.

Table 5. Comparison of the proposed procedure with the other reported procedures for preconcentration of chromium

Method	Linear rang (ng/mL)	PF ^a (mL)	LOD ^b (ng/mL)	RSD (%)	Ref.
SPE-FAAS	1.0-100	100	0.51	2.5	[23]
SPE-FAAS	0-250	75	7.7	-	[24]
SPE-FAAS	-	31	1.94	<10	[25]
SPE-FAAS	-	80	0.6	<6	[26]
SPE-FAAS	1.0-700	200	0.6	2.4	This work

^aPreconcentration Factor

^bLimit of Detection

Conclusion

This paper proposes a new method for the preconcentration and determination of trace amounts of chromium by SPE

combined with FAAS. This new nanoparticle metal extractor has high capacity, good stability and fast adsorption and desorption kinetics. High preconcentration factor was

obtained easily by this method. This method is characterized with simplicity, rapidity, reliability, safety and low cost which are suitable parameters for the determination of trace amounts of chromium ion in water and food samples.

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