Talanta 94 (2012) 201–208

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A nano-structured material for reliable speciation of chromium and manganese in drinking waters, surface waters and industrial wastewater effluents

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ARTICLE INFO

Article history:
Received 29 November 2011
Received in revised form 8 February 2012
Accepted 13 March 2012
Available online 18 March 2012

Keywords:
Speciation
Chromium and manganese
Solid phase extraction
Nano-structured layered double hydroxides
Flame atomic absorption spectrometry

ABSTRACT

A simple solid phase extraction system based on the applying the nickel–aluminum layered double hydroxide (Ni–Al LDH) as a nano-sorbent was developed for the speciation analysis of chromium and manganese by flame atomic absorption spectrometry (FAAS). The method is based on the fact that Cr(VI) and Mn(VII) oxyanions could be adsorbed on the Ni–Al(NO_3^-) LDH and/or exchanged with LDH interlayer NO_3^- ions at pH 6.0, whereas Cr(III) and Mn(II) cations pass through the LDH-packed column without retention. The determinations of total Cr and Mn, and hence indirectly Cr(III) and Mn(II), involve the pre-oxidations of Cr(III) and Mn(II) to Cr(VI) and Mn(VII) with H_2O_2 and acidic solution of KIO_4, respectively. Several important factors affecting the retention efficiency were investigated and optimized. In the optimum experimental conditions, the limits of detection ($3S_b/m$) for Cr(VI) and Mn(VII) were 0.51 and 0.47 ng mL^{-1}, and the relative standard deviations were 2.5 and 3.2% ($C = 30.0$ ng mL^{-1}, $n = 6$), respectively. The presented method was validated by the analysis of a certified reference material, and applied to the speciation of Cr and Mn in drinking waters, surface waters and industrial wastewater effluents.

1. Introduction

It is well known that the toxicological and biological properties of most elements depend on their chemical forms. Information about the oxidation state of trace elements is as important to know as its chemical structure. It has been reported that the same metal ion may possess different toxicity in its different oxidation states, which are responsible for their different physico-chemical and biological activities [1]. Speciation analysis of toxic heavy metals has special importance due to its impact on environmental chemistry, ecotoxicology, clinical toxicology and food industry.

Chromium is one of the most abundant elements on earth and is found naturally in rocks, soil, plants, animals, volcanic dust and gases. In aqueous solution, it is mainly present as Cr(III) and Cr(VI) oxidation states, which have different toxicities, motilities and bio-availabilities [2]. Cr(III) appears to be essential for the living organisms especially human beings. It has an important role in glucose, lipid and protein metabolism and exhibits much less toxicity, whereas Cr(VI) is highly toxic and potentially responsible for carcinogenic effects in humans [3]. World Health Organization (WHO) recommends a guideline value of 0.05 mg L^{-1} for Cr in drinking water [4].

Manganese is also an essential element for humans and animals. It is naturally occurring in many surface water and groundwater sources, and this is the most important source for drinking water [5,6]. The greatest exposure to manganese is usually from food. Adverse effects can result from both deficiency and overexposure. Deficiency signs include poor reproductive performance, growth retardation, congenital malformations in offspring, abnormal function of bone and cartilage and impaired glucose tolerance [7]. On the other hand, high doses of manganese cause DNA mutations, neurological disorders like manganism, over flow of liver, hallucinations, depression and excessive sleeping [8]. The world health organization has proposed a guideline value of 0.4 mg L^{-1} for the maximum permissible concentration of Mn in drinking water [9]. The most prevalent oxidation states of manganese are Mn(II) and Mn(VII). Mn(II) is toxic to mitochondria in cells [10], whereas Mn(VII) is widely used as an oxidizing agent in synthetic as well as in analytical chemistry and also as a disinfectant. Therefore, in order to obtain correct information on toxicity and biotransformation of chromium and manganese, there is a need to develop analytical methods not only to determine the total chromium and manganese in the different environmental samples but also to determine their species separately with sufficient precision and sensitivity.

Direct determination of low levels of these two heavy metal species in real samples appears to be a difficult task by the instrumental techniques like atomic absorption spectrometry, inductively coupled plasma-optical emission spectrometry, inductively

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doi:10.1016/j.talanta.2012.03.022

coupled plasma-mass spectrometry, etc. In general, previous treatment of samples involving separation and pre-concentration schemes is required in order to improve the selectivity and sensitivity of the techniques by both removal of interferences and increasing the concentration of the analyte [11–13]. For this purpose, various separation and pre-concentration methods, such as co-precipitation [14,15], ion-exchange [16,17] liquid–liquid extraction (LLE) [18,19], liquid phase micro-extraction (LPME) [20,21] cloud point extraction (CPE) [22–24] solid phase extraction (SPE) [25–28], ion chromatography [29,30] and capillary electrophoresis (CE) [31] have been developed.

Among these procedures, SPE is found very important place in the speciation studies of metal ions due to its simplicity, selectivity, flexibility, environment-friendly, ease of automation, high enrichment factor, rapid phase separation and the sorbent easy to recover. In SPE procedures, the choice of the sorbent is a key point because it can control the analytical parameters such as selectivity, affinity and capacity. Up to now, many sorbents such as functionalized resin, naphthalene, silica, TiO_2, alumina, activated carbon, molecular-imprinted polymers, bentonites and nanometer-sized materials have been employed. Among these, nanometer-sized materials have gained more attention due to their special properties.

Layered double hydroxides (LDHs) are a class of two-dimensional nano-structured anionic clays consisting of positively charged layers with charge balancing anions between the layers. LDHs can be represented by the general formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}[A_{x/n}{}^{n-} \cdot mH_2O]^{x-}$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively; the value of x is equal to the molar ratio of $M^{3+}/(M^{2+} + M^{3+})$, whereas A is the interlayer anion of valence n [32,33]. Due to their permanent layer positive charge, high anion-exchange capacity, large surface area, good thermal stability, water resistant structure and rapid regeneration, LDHs are considered as new class of green nano-sorbents for SPE of organic and inorganic anions [34].

Recently, LDHs have been successfully applied as inorganic sorption materials in SPE procedures [35,36]. However, to the best of our knowledge, there is no report on the use of the any LDHs for speciation analysis of metal ions. Thus, in this study, a simple SPE system based on the Ni–Al($NO_3{}^-$) LDH nano-sorbent was developed for the efficient retention and pre-concentration of Cr(VI) and Mn(VII), and coupled to FAAS detection. The presented method was applied to the speciation of Cr and Mn in different water samples with satisfactory results.

2. Experimental

2.1. Apparatus and instruments

A Varian model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer, equipped with a deuterium lamp background correction and an air–acetylene burner, was utilized for the analysis. The chromium and manganese hollow cathode lamps were used according to the manufacturer's recommendations (Table 1). All data acquisition was made in integrated absorbance mode with the equipment software. A 2 mL polypropylene cartridge (30 mm × 7 mm i.d.) (Shafa Co., Iran) packed with 0.2 g of Ni–Al($NO_3{}^-$) LDH was applied for column preparation. The flow rate of solution through the column was controlled with an air-driven fluid pump model P34112 (Taiwan). Electrical furnace model Ex.1200-4L (Exciton Co., Iran), Beckman centrifuge (USA) model GS-6 and N_2 gas (99.9995%, Azaroxide Co., Iran) were used in LDH preparation process. Oxidation of Cr(III) and Mn(II) was performed in a thermostatic water bath (Julabo, GMBH D-77960, Germany). The pH values were measured with a Metrohm pH-meter (model 827, Switzerland), supplied with a glass-combined electrode. An electronic analytical balance (Mettler Toledo, PB303, Switzerland) was used for weighting the solid materials.

Table 1
Instrumental and experimental conditions for Mn and Cr determination.

	Unit	Mn	Cr
FAAS conditions			
Wavelength	nm	279.5	357.9
Lamp current	mA	4	7
Spectral bandpass	nm	1	1
Acetylene flow rate	$L\,min^{-1}$	1.5	1.5
Air flow rate	$L\,min^{-1}$	3.5	3.5
Integration time	s	0.1	0.5
Solid phase extraction conditions			
Working pH	–	6	6
Concentration	$ng\,mL^{-1}$	30.0	30.0
Amount of sorbent	mg	200	200
Sample volume	mL	100.0	100.0
Loading flow rate	$mL\,min^{-1}$	3.0	3.0

2.2. Standard solutions and reagents

All chemicals used were of analytical-reagent grade and all solutions were prepared with high purity deionized water (Shahid Ghazi Co., Tabriz, Iran). The pipettes and vessels used for the trace analysis were kept in 10% (v/v) nitric acid at least overnight and subsequently rinsed with deionized water prior to use. Stock standard solutions of Cr(VI) and Cr(III) (1000 $mg\,L^{-1}$) were prepared by dissolving appropriate amounts of K_2CrO_4 and $Cr(NO_3)_3{\cdot}9H_2O$ (Merck, Darmstadt, Germany) in deionized water, respectively. Similarly, stock standard solutions containing 1000 $mg\,L^{-1}$ of Mn(VII) and Mn(II) were prepared by dissolving appropriate amounts of $KMnO_4$ and $Mn(NO_3)_2{\cdot}6H_2O$ (Merck) in deionized water, respectively. Working standard solutions were obtained daily by suitable stepwise dilution of the stock solutions with deionized water and shaking them just before to use. Hydroxylamine hydrochloride solution was prepared by dissolving sufficient amount of $OHNH_3Cl$ in deionized water. A 5% (m/v) of KIO_4 solution was prepared by dissolving 5 g of KIO_4 reagent in 20% (v/v) nitric acid. HNO_3 and NaOH (0.01–2.0 $mol\,L^{-1}$) were used for pH adjustment.

All salts used for the interference study, HNO_3 (65%), KIO_4, NaOH, NaCl, KBr, Na_2CO_3, $OHNH_3Cl$, N_2H_4, $C_6H_6O_6$ and LDH precursors, i.e., $Ni(NO_3)_2{\cdot}6H_2O$ (99%) and $Al(NO_3)_3{\cdot}9H_2O$ (99%) were purchased from Merck. The accuracy of the method was assessed by analyzing of a standard reference material, SRM 1643e (Trace Elements in Water), from National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA.

2.3. Preparation and characterization of Ni–Al($NO_3{}^-$) LDH

Ni–Al($NO_3{}^-$) LDH was synthesized as described method in our previous works [35,36]. In brief, the synthesis was carried out under a N_2 atmosphere, and all of the solutions were prepared using deionized water to avoid contamination. In the present work, 0.581 g $Ni(NO_3)_2{\cdot}6H_2O$ and 0.375 g $Al(NO_3)_3{\cdot}9H_2O$ were added into 30 mL deionized water under vigorous stirring at room temperature for the preparation of the Ni–Al($NO_3{}^-$) LDH with molar ratio (Ni^{2+}:Al^{3+}) of 2:1. The reaction mixture pH was adjusted to 9.6 by the addition of 2 $mol\,L^{-1}$ NaOH solution. Then, the obtained slurry was subjected to hydrothermal treatment at a constant temperature of 100 °C for about 24 h. Afterward, the resulting precipitate was separated by centrifugation at 4000 rpm for 10 min and washed three times with deionized water, and dried at 60 °C for 6 h.

In order to get better insight into the structural properties of the Ni–Al($NO_3{}^-$) LDH, a set of characterization was performed using powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The obtained results from XRD patterns, FT-IR spectrum and SEM image of the Ni–Al(NO_3^-) LDH are in agreement with the previously results reported by the authors [35,36].

2.4. Column preparation

Ni–Al(NO_3^-) LDH was employed to create the solid phase extraction column as follows: the column was prepared by introducing 200 mg of Ni–Al(NO_3^-) LDH into an empty 2 mL polypropylene cartridge using the dry packing method. In order to retain the nano-sorbent in the column, a small portion of cotton was placed on both ends of the column. Before loading the sample, the micro-column was cleaned with 1 mL of eluent solution and conditioned by passing only 2 mL of deionized water through the column prior to each use. Then, a 100.0 mL of sample solution was passed through the column at a flow rate of 3.0 mL min^{-1} controlled by an air-driven fluid pump.

2.5. Sample preparation

Tap water sample (Laboratory tap water), seawater (Caspian Sea), lake water (Urmia Lake), electroplating water (Iran Piston Manufacturing Co.) and different industrial wastewater samples (local Dye works and Chocolate Manufacturing Co.) were collected in pre-washed (with detergent, deionized water, dilute HNO_3 and deionized water, respectively) polyethylene bottles. After sampling, they were filtered through Rund filter paper (Blue band, No. 300210), and then the samples were stored in refrigerator at 4 °C and aliquots of 100.0 mL from each sample solution were analyzed within 24 h of collection without previous treatment by following the procedure described in Section 2.6. In the case of NIST SRM 1643e (trace elements in water), suitable aliquot of this sample was diluted with deionized water prior to sample loading.

2.6. General procedure

Aliquots of 100.0 mL sample or aqueous standard solution containing Cr(VI) or Mn(VII) in the range of 1–100 ng mL^{-1} ($pH \approx 6$) was passed through the Ni–Al(NO_3^-) LDH nano-sorbent in a micro-column at a flow rate of 3.0 mL min^{-1}. After loading, the retained analyte on the micro-column was stripped with 1 mL of hydroxylamine hydrochloride solution, at an elution rate of 1.5 mL min^{-1}, which acts as both reducing agent and eluent. Complete elution of the retained Mn(VII) and Cr(VI) from the column was carried out by using 1 mL of 5 and 10% (m/v) of hydroxylamine hydrochloride solution, respectively. The concentration of eluted analyte was determined by FAAS. After oxidation of Cr(III) and Mn(II), total Cr and Mn were evaluated by applying the pre-concentration procedure described above. The levels of Cr(III) and Mn(II) species were obtained by respectively subtracting Cr(VI) and Mn(VII) from the total Cr and the total Mn. A blank solution was run under the same conditions without adding analyte. The instrumental and optimized experimental conditions are listed in Table 1.

2.7. Oxidation of Cr(III) and Mn(II) species

As the presented procedure is based on the retention of Cr(VI) on the LDH-packed column, oxidation of Cr(III) to Cr(VI) was needed in order to allow Cr(III) retention on the column as Cr(VI) species. Oxidation procedure was performed using the method given in the literature [26] with minor modifications. For this purpose, a 100.0 mL of the sample solution was transferred into a 250.0 mL volumetric flask and 5 mL of 3% (v/v) H_2O_2 was added. This solution was heated on a thermostatic water bath for 40 min at 80 °C, and then boiled on a heating plate for 10 min in order to remove any excess of hydrogen peroxide. After cooling the solution to room temperature, the sample was transferred into a 100.0 mL volumetric flask, and then made up to 100.0 mL with deionized water.

To allow Mn(II) retention on the LDH-packed column as Mn(VII) species, oxidation of Mn(II) to Mn(VII) is necessary. Because, Mn(II) is a cation and could not be adsorbed on the Ni–Al(NO_3^-) LDH and/or exchanged with LDH interlayer NO_3^- ions. Oxidation procedure was performed according to the literature [37]. A 100.0 mL sample solution was oxidized with 2 mL of 5% (m/v) KIO_4 solution and 4 mL concentrated HNO_3 at 100 °C for 15 min.

3. Results and discussion

3.1. Selection of LDH

Recently, increasing interest has been diverted to evaluating the ability of LDHs to remove inorganic contaminants such as monoatomic anions and oxyanions from aqueous solutions by the process of adsorption and ion exchange. The structure of LDHs is based on positively charged brucite-like sheets of metal hydroxide and the positive charges are balanced by intercalation of anions in the hydrated interlayer regions. Distance between the hydroxide layers depends on the width of the brucite-like layers, interlayer hydration, size of the interlayer anion and, for non-spherical anions, its orientation within the interlayer space. On the other hand, the charge density and the anion exchange capacity of the LDHs may be controlled by varying the M^{2+}/M^{3+} ratio. According to authors' experience, among interlayer anions like Cl^-, NO_3^- and CO_3^{2-}, NO_3^- is a suitable interlayer anion for LDH-packed column SPE procedures [35,36]. However, as mentioned above, M^{2+}/M^{3+} ratio is important and can affect the retention efficiency. Therefore, three LDHs with the same NO_3^- interlayer anions, different M^{2+}/M^{3+} or $M^{2+}/(M^{3+}+M^{4+})$ molar ratios such as 1:1, 2:1, 3:1, and 4:1 and different metals, i.e., Ni–Al(NO_3^-) LDH, Mg–Al–Fe(NO_3^-) LDH and Ni–Al–Zr(NO_3^-) LDH were synthesized and tested for the extraction of Cr(VI) and Mn(VII) oxyanions. Based on the obtained results, the maximum extraction efficiency was obtained in the case of Ni–Al(NO_3^-) LDH with 2:1 (Ni^{2+}/Al^{3+}) molar ratio and this LDH was then employed as a nano-sorbent in SPE procedures.

3.2. Optimization of loading variables

3.2.1. Effect of pH

In the solid phase extraction studies, pH is the first important factor for the quantitative recoveries of analytes. Cr(III) and Mn(II) cations could not retain on the Ni–Al(NO_3^-) LDH due to positively charged brucite-like sheets of metal hydroxide in LDH structure. Therefore, the effects of pH on the recovery of Cr(VI) and Mn(VII) oxyanions on Ni–Al(NO_3^-) LDH were investigated in the pH range of 4–10. The recovery was calculated based on a difference between the amount of the analyte in the starting sample and the solution from the column. The effects of pH value on the recovery of the analytes are shown in Fig. 1. It can be seen that Cr(VI) and Mn(VII) were retained quantitatively (recovery higher than 95%) on Ni–Al(NO_3^-) LDH at pH range of 5.5–7.0, while the recoveries of Cr(III) and Mn(II) are rather low (<5%). This point could make it possible to separate Cr(VI) from Cr(III) and Mn(VII) from Mn(II) at the pH range of 5.5–7.0. In order to separate and pre-concentrate of Cr(VI) or Mn(VII), pH 6.0 was selected for further experiments. Any buffer solution was not used for pH adjusting, because this may affects the retention of the analytes due to the competition of the anionic species for the active sites of the nano-sorbent.

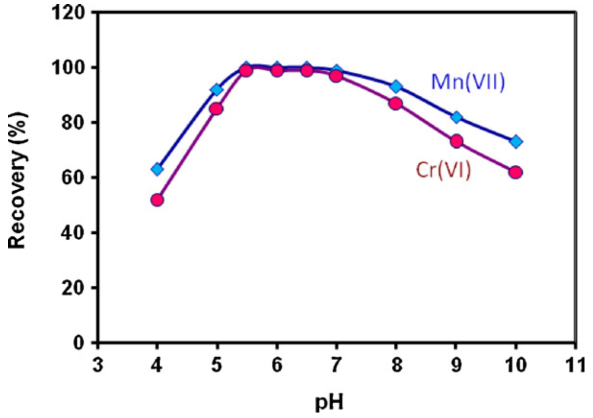

Fig. 1. Effect of pH on retention of Mn(VII) and Cr(VI) oxyanions on Ni–Al(NO_3^-) LDH nano-sorbent.

3.2.2. *Effect of the amount of Ni–Al(NO_3^-) LDH nano-sorbent*

To test the effect of the amount of Ni–Al(NO_3^-) LDH nano-sorbent on the quantitative retention of Cr(VI) and Mn(VII) oxyanions, the extraction was conducted by varying the amounts of the Ni–Al(NO_3^-) LDH from 150 to 350 mg. The results indicated that the quantitative recoveries of Cr(VI) and Mn(VII) oxyanions were obtained by using 200 mg of nano-sorbent. Therefore, 200 mg of nano-sorbent was employed in this work.

3.2.3. *Reusability of the Ni–Al(NO_3^-) LDH nano-sorbent*

The column could be reused after regenerating with 1 mL of 10% (m/v) hydroxylamine hydrochloride and 2 mL deionized water, respectively. Moreover, it was observed that the Ni–Al(NO_3^-) LDH nano-sorbent stable up to at least 150 retention–elution cycles and could be repeatedly used without significant loss of uptake capacity.

3.2.4. *Effect of sample loading flow rate*

The influence of Cr(VI) and Mn(VII) oxyanions retention on Ni–Al(NO_3^-) LDH nano-sorbent was investigated by varying the flow rate of the sample solution in the range of 0.5–6.0 mL min^{-1}. Based on the obtained results, the retention of the Cr(VI) and Mn(VII) oxyanions was practically not changed up to 3.0 mL min^{-1} of flow rate. However, at flow rates higher than 3.0 mL min^{-1} the recovery values were reduced. Hence, a flow rate of 3.0 mL min^{-1} was selected as the optimum flow rate for the subsequent work.

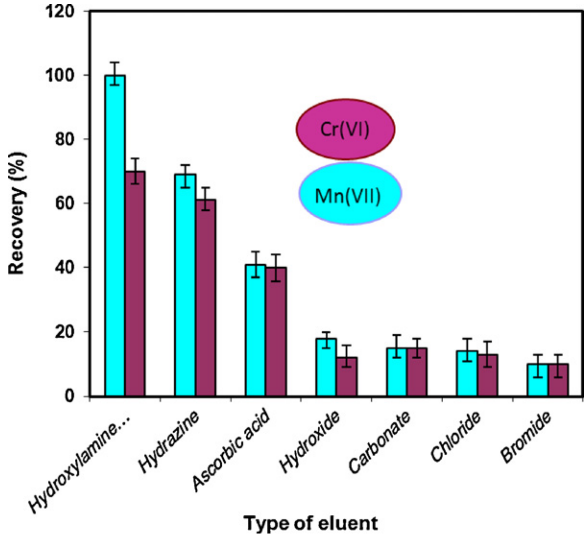

Fig. 2. Effect of various eluent on recovery of Mn(VII) and Cr(VI) oxyanions from Ni–Al(NO_3^-) LDH nano-sorbent.

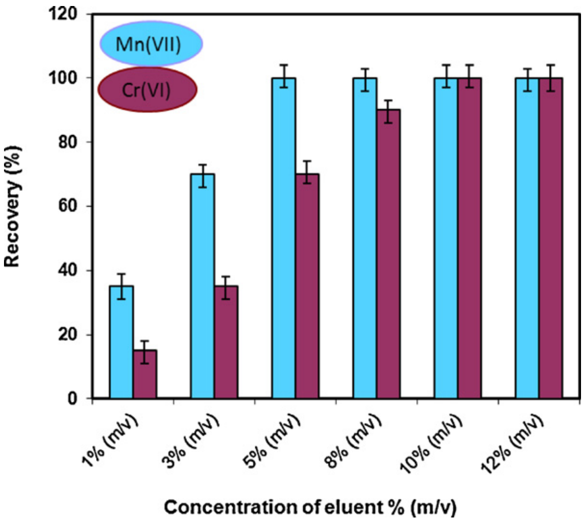

Fig. 3. Effect of hydroxylamine hydrochloride concentration on stripping of Mn(VII) and Cr(VI) oxyanions from Ni–Al(NO_3^-) LDH nano-sorbent.

3.3. *Optimization of elution variables*

The choice of elution reagent and its optimum concentration should be carefully taken into account. Some experiments were carried out in order to select a proper eluting reagent for stripping of the retained Cr(VI) and Mn(VII) oxyanions from the Ni–Al(NO_3^-) LDH nano-sorbent. For this purpose, various stripping reagents such as NaOH, NaCl, Na_2CO_3 and KBr were tested in different concentrations ranging from 1 to 5% (m/v). It was found that the recovery values were lower than 20% concerning the all tested reagent solutions.

It is obvious that the stripping of Cr(VI) and Mn(VII) oxyanions from the LDH-packed column could be very easy if they are converted to their cationic forms. Therefore, the possibility of the using a reducing agent for stripping of the analytes from the column via the respectively reduction of Cr(VI) and Mn(VII) to Cr(III) and Mn(II) was investigated. For this purpose, several reducing agents such as ascorbic acid, hydroxylamine hydrochloride and hydrazine were tested. As can be seen in Fig. 2, the maximum recoveries could be achieved when hydroxylamine hydrochloride was employed as both reducing agent and eluent. The concentration of the hydroxylamine hydrochloride solution was also optimized.

Table 2
Tolerance limits of interfering ions in the retention of 30 ng mL^{-1} of Cr(VI) and Mn(VII).

Ions	Foreign ion to Cr(VI) weight ratio
Li^+, Na^+, K^+, Ca^{2+}, NH_4^+, Mg^{2+}, Al^{3+}, Co^{2+}, Cu^{2+}, Mn^{2+}, NO_3^-, Ag^+, I^-, F^-, Br^-, Cl^-, IO_3^-, IO_4^-, OH^-	1000:1
CH_3COO^-, CO_3^{2-}	500:1
PO_4^{3-}, SO_4^{2-}, ClO_4^-, BrO_3^-	250:1
Mo(VI), V(V), Mn(VII)	100:1

Ions	Foreign ion to Mn(VII) weight ratio
Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+}, NH_4^+, Mg^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Cr^{3+}, Al^{3+}, Cl^-, Br^-, OH^-, IO_4^-, NO_3^-, SO_4^{2-}, CO_3^{2-}	1000:1
I^-, Fe^{3+}, Cd^{2+}	700:1
F^-, CH_3COO^-, PO_4^{3-}	500:1
Mo(VI), V(V), Cr(VI)	100:1

Table 3
Analytical characteristics of the method for Mn(VII) and Cr(VI).

Analytical parameters	Mn(VII)		Cr(VI)	
	Without preconcentration	With preconcentration	Without preconcentration	With preconcentration
Linear range (ng mL^{-1})	100–8000	1–100	100–10,000	1–100
Intercept	0.0471	0.088	0.0264	0.015
Slope	0.0001	0.01	0.00005	0.005
Detection limit (ng mL^{-1})	50.2	0.47	44.5	0.51
Correlation coefficient	0.993	0.991	0.999	0.995
Relative standard deviation (RSD %) ($n = 6$)[a]	2.1 (3000), 1.6 (7000)	3.2 (30), 2.6 (70)	2.2 (3000), 1.8 (7000)	2.5 (30), 2.1 (70)
Enhancement factor	–	100	–	100

[a] Values in parentheses are the analyte concentrations (ng mL^{-1}) for which the RSD was obtained.

Table 4
Speciation analysis of chromium in real samples (results of recoveries of spiked samples and standard reference material analysis).

Sample	Added (ng mL^{-1})		Found (ng mL^{-1})[a]		Recovery (%)[b]	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tap water[c]	–	–	5.2 ± 0.7	<LOD	–	–
	25.0	25.0	29.0 ± 0.6	23.9 ± 0.6	95.2	95.6
Sea water[d]	–	–	8.2 ± 0.9	2.5 ± 0.9	–	–
	25.0	25.0	33.4 ± 0.5	26.5 ± 0.5	100.8	96.0
Lake water[e]	–	–	11.6 ± 0.9	6.3 ± 0.2	–	–
	25.0	25.0	36.5 ± 0.8	31.3 ± 0.5	99.6	100.0
Electroplating water[f]	–	–	46.3 ± 0.8	12.3 ± 0.4	–	–
	25.0	25.0	70.9 ± 0.8	36.2 ± 0.7	98.4	95.6
Wastewater[g]	–	–	21.0 ± 0.5	9.2 ± 0.6	–	–
	25.0	25.0	45.9 ± 0.5	33.3 ± 0.5	99.6	96.4
Wastewater[h]	–	–	16.7 ± 0.8	6.5 ± 0.9	–	–
	25.0	25.0	41.1 ± 0.7	30.4 ± 0.4	97.6	95.6
NIST SRM	Certified values (ng mL^{-1})		Assayed values[a] (ng mL^{-1})		Relative error (%)	
1643e	20.40 ± 0.24		19.89 ± 0.34		−2.5	

[a] Mean of three experiments ± standard deviation.
[b] Recovery (%) = [(found − base)/added] × 100.
[c] From drinking water system of Tabriz, Iran.
[d] Collected from Caspian sea, Nowshahr, Iran.
[e] Collected From Urmia lake, Urmia, Iran.
[f] Electroplating water of Piston Manufacturing Co., Tabriz, Iran.
[g] Industrial waste water of Arko Dye works, Tabriz, Iran.
[h] Industrial waste water of Ghafari Dye works, Tabriz, Iran.

For this reason, various concentrations (1–12% (m/v)) of hydroxylamine hydrochloride were studied for the elution of the retained analytes from the column. As shown in Fig. 3, 5 and 10% (m/v) hydroxylamine hydrochloride were sufficient for complete elution of the retained Mn(VII) and Cr(VI) oxyanions from the column, respectively. Thus, 5 and 10% (m/v) hydroxylamine hydrochloride solutions were selected as optimum.

The effect of eluent volume on the recovery of the analytes was also studied. It was found that quantitative recovery could be accomplished with 1.0 mL of eluent. Therefore, optimum volume of the eluent was chosen as 1.0 mL. Moreover, based on the obtained results, the recoveries of the retained analytes from the column were quantitative and constant in the range of 0.5–2.0 mL min^{-1}

Table 5
Speciation analysis of manganese in real samples (results of recoveries of spiked samples and standard reference material analysis).

Sample	Added (ng mL^{-1})		Found (ng mL^{-1})[a]		Recovery (%)[b]	
	Mn(II)	Mn(VII)	Mn(II)	Mn(VII)	Mn(II)	Mn(VII)
Tap water[c]	–	–	8.6 ± 0.5	<LOD	–	–
	10.0	10.0	18.8 ± 0.5	10.0 ± 0.5	102.0	100.0
Wastewater[d]	–	–	23.8 ± 0.5	42.8 ± 0.7	–	–
	10.0	10.0	33.7 ± 0.4	52.5 ± 0.4	99.0	97.0
Wastewater[e]	–	–	26.1 ± 0.5	38.4 ± 0.5	–	–
	10.0	10.0	36.2 ± 0.4	48.0 ± 0.4	101.0	96.0
Wastewater[f]	–	–	22.3 ± 0.7	14.4 ± 0.6	–	–
	10.0	10.0	32.1 ± 0.6	24.0 ± 0.4	98.0	96.0
NIST SRM	Certified values (ng mL^{-1})		Assayed values[a] (ng mL^{-1})		Relative error (%)	
1643e	38.97 ± 0.45		38.74 ± 0.58		−0.6	

[a] Mean of three experiments ± standard deviation.
[b] Recovery (%) = [(found − base)/added] × 100.
[c] From drinking water system of Tabriz, Iran.
[d] Industrial waste water of Arko Dye works, Tabriz, Iran.
[e] Industrial waste water of Ghafari Dye works, Tabriz, Iran.
[f] Industrial waste water of Aydin Chocolate Manufacturing Co., Tabriz, Iran.

of elution flow rates. Hence, elution flow rate of 1.5 mL min^{-1} was selected.

3.4. *Sample volume and pre-concentration factor*

The sample volume influence was examined on the recoveries of Mn(VII) and Cr(VI) by passing 10–200 mL sample solutions containing 3.0 μg of the analytes at a flow rate of 3.0 mL min^{-1} according to the recommended procedure. The results show that the quantitative recoveries were obtained up to 100 mL of sample volume for the analytes. The pre-concentration factor was calculated by the ratio of the highest sample volume and the lowest final volume. So, by analyzing 1.0 mL of the final solution after the pre-concentration of 100 mL of sample solution, a pre-concentration factor was found as 100.

3.5. *Sorption capacity*

The sorption capacity of the Ni–Al(NO_3^-) LDH nano-sorbent was obtained by the batch technique. For this process, 200 mg of the sorbent was added to 50.0 mL of solution containing 50 mg L^{-1} of the analytes and stirred for 60 min with magnetic stirrer and filtered through a filter paper. Enriched Mn(VII) and Cr(VI) onto LDH nano-particles were stripped with 5 mL of 5 and 10% (m/v) hydroxylamine hydrochloride, respectively, and concentration of Cr and Mn were determined by FAAS after appropriate dilution. The sorption capacity (q, mg g^{-1}) was calculated as

$$q = V(C_o - C_e)m^{-1}$$

where V is the volume of analyte solution (L), m is the mass of Ni–Al(NO_3^-) LDH nano-sorbent (g), C_o and C_e are the initial and equilibrium concentration (mg L^{-1}) of the analyte in the solution, respectively. Eventually, capacity of the Ni–Al(NO_3^-) LDH for Mn(VII) and Cr(VI) were found to be 7.2 and 6.5 mg g^{-1} or 6.05×10^{-5} and 5.60×10^{-5} mol g^{-1}, respectively.

3.6. *Effect of divers ions*

The effect of some important divers ions on the recoveries of Mn(VII) and Cr(VI) oxyanions was examined in this study. Different concentrations of matrix ions were tested and maximum values were determined. In this experiment, the solutions of 30 ng mL^{-1} of Mn(VII) or Cr(VI) oxyanions containing the added interfering ions were treated according to the recommended procedure. The content of target analyte in the effluent was determined in order to calculate the recovery of the studied elements. The tolerance limit was considered if it resulted in a ±5% variation in retention efficiency of Mn(VII) and Cr(VI). As can be seen in Table 2, most of examined cations and anions did not interfere with the extraction and determination. This results show that this procedure could be applied to successfully for the speciation of chromium and manganese in real samples.

3.7. *Analytical characteristics*

The analytical performance of the procedure for manganese and chromium species were calculated on those results obtained from flame atomic absorption spectrometric measurements. The analytical characteristics can be found in Table 3. Under the optimized conditions, linear calibration graphs were obtained in the range of 1–100 ng mL^{-1} of Mn(VII) and Cr(VI), with correlation coefficients of 0.991 and 0.995, respectively. The limit of detection (LOD), evaluated as $3S_b/m$ (where S_b and m are standard deviation of the blank and slope of the calibration equation, respectively) was found to be 0.47 ng mL^{-1} for Mn(VII) and 0.51 ng mL^{-1} for Cr(VI). The relative

Table 6
Comparison of the presented method with some recent studies on chromium speciation reported in the literature.

Technique	Speciation system	Media	Detection system	Linear range (ng mL^{-1})	PF	LOD (ng mL^{-1})	RSD (%)	Ref.
FPC	Cr(VI)–Llama (*lama glama*) fiber, *oxidation of Cr(III)*	Animal fiber	FAAS	Up to 50	–	0.3	4.3	[38]
SPE	Cr(III)–Diphenylcarbazone complex, *oxidation of Cr(III)*	Amberlite XAD-1180	FAAS	Up to 250	75	7.7–8.6	5.7	[25]
MMCPE	Cr(VI)–1,5-Diphenylecarbazid complex, *oxidation of Cr(III)*	Triton X-114	ETAAS	0.003–3	92	0.001	3.5	[23]
SFODME	Cr(III)–1-Undecanol containing 2-thenoyltrifluoroacetone complex, *reduction of Cr(VI)*	–	GFAAS	0.03–0.13	333	0.006	5.1	[20]
DLLME	Cr(VI)–Ammonium pyrrolidinedithiocarbamate complex, *oxidation of Cr(III)*	[Hmim][PF6]	ETAAS	0.5–8.0	300	0.07	9.2	[39]
CPE	Cr(III)–1-Phenyl-3-methyl-4-benzoylpyrazol-5-one complex, *reduction of Cr(VI)*	Triton X-114	GFAAS	Up to 100	42	0.021	3.5	[40]
CEFC	Cr(III)–CFMEPI complex, *reduction of Cr(VI)*	–	FAAS	–	40	0.7	5	[41]
SPE	Cr(III)–Sorption on SWCNTs	Modified SWCNTs	ICP-MS	0.1–100	63	0.01	<5.0	[42]
Coprecipitation	Cr(III)–Ni^{2+}/2-Nitroso-1-naphthol-4-sulfonic acid, *reduction of Cr(VI)*	–	FAAS	–	50	1.33	<7	[43]
SPE	Cr(VI)–Retention on LDH, *oxidation of Cr(III)*	Ni–Al(NO_3^-) LDH	FAAS	1–100	100	0.51	2.5	This work

PF: pre-concentration factor; FPC: fiber-packed column; SPE: solid phase extraction; MMCPE: mixed-micelle cloud point extraction; SFODME: solidified floating organic drop micro-extraction; DLLME: dispersive liquid–liquid micro-extraction; CPE: cloud point extraction; CEFC: carrier element-free co-precipitation; FAAS: flame atomic absorption spectrometry; ETAAS: electrothermal atomic absorption spectrometry; GFAAS: graphite furnace atomic absorption spectrometry; [Hmim][PF6]: 1-hexyl-3-methylimidazolium hexafluorophosphate; CFMEPI: 5-chloro-3-[4-(trifluoromethoxy)phenylimino]indolin-2-one; SWCNTs: single-walled carbon nanotubes.

standard deviations resulting from the analysis of six replicates of 100 mL solution containing 30 ng mL^{-1} Mn(VII) and Cr(VI) were 3.2 and 2.5%, respectively. As the amount of Mn(VII) and Cr(VI) in the sample solution was measured after a final volume of 1.0 mL, the solution was concentrated by a factor of 100.

3.8. *Analysis of real samples*

To explore the feasibility of the presented speciation procedure, the procedure was applied to determination of manganese and chromium species in different water samples, i.e., tap water, seawater, lake water, electroplating water and industrial wastewaters. In order to verify the accuracy of the established procedure, recovery experiments were carried out by spiking the samples with different amounts of manganese/chromium species before any pretreatment. The recovery value was calculated from the equation $R\ (\%) = [(C_a - C_b)/A] \times 100$, where A is the added analyte concentration, C_a and C_b are the analyte concentration in real sample after and before spiking, respectively. Tables 4 and 5 show the obtained results. As can be seen, recoveries between 95.2 and 102.0% were obtained, which confirm the accuracy of the presented method. The accuracy of the method was further checked by applying the procedure for the determination of manganese and chromium in a certified reference material (SRM 1643e). The obtained values for total Mn and Cr are in good agreement with the certified concentrations. Statistical analysis of these results using Student's *t*-test showed that there was no significant difference between actual and found concentrations at 95% confidence level. It can be concluded that the presented speciation method is accurate and free from systematic errors. As shown in Tables 4 and 5, the method could be applied successfully for the speciation and pre-concentration of trace amounts of manganese and chromium in different water samples.

3.9. *Comparison with other methods*

A comparison of the represented method with other reported speciation methods for manganese and chromium are shown in Tables 6 and 7. Comparison of the presented SPE procedure with the previously reported SPE procedures for the speciation analysis of manganese and chromium indicates that the present procedure has the comparable or better LOD and higher pre-concentration factor than those reported previously. Higher sorption capacity, higher pre-concentration factor, lower detection limits and good RSD values are some of the advantages of the proposed method. These characteristics are of key interest for routine laboratories in trace metal ion analysis.

4. Conclusions

In this research, a novel nano-sorbent (Ni–Al(NO_3^-) LDH) was developed for the separation, pre-concentration and determination of inorganic manganese and chromium species in different water samples by FAAS. The experimental results indicate that Mn(VII) and Cr(VI) oxyanions were almost quantitatively retained on the Ni–Al(NO_3^-) LDH, while Mn(II) and Cr(III) cations remained in the solution. The retained analytes on the solid phase extraction column can be easily stripped with hydroxylamine hydrochloride and no carryover is observed in the next analysis. Comparison of the presented method with other procedures reported in the literature shows that the RSD and LOD of the presented method are comparable or better than others. The presented method is characterized with mild separation conditions, sensitive, reproducible, simple, low cost and environment-friendly technique that could be used

Table 7
Comparison of the presented method with some recent studies on manganese speciation reported in the literature.

Technique	Speciation system	Media	Detection system	Linear range (ng mL^{-1})	PF	LOD (ng mL^{-1})	RSD (%)	Ref.
SPE	Mn(VII)–Adsorption on CCTS, *oxidation of Mn (II)*	CCTS	FAAS	–	50	1.98	6.6	[37]
SIA	Mn(II)–4-(2-Pyridylazo) resorcinol complex, *reduction of Mn(VII)*	–	UV–vis	20–500	–	5	0.27	[44]
SPE	$[Mn–EDTA]^{n-}$ complex	AG-1 X-8 resin	ICP-OES	5–1000	–	1.5	3	[45]
CPE	Mn(II)–1-Phenyl-3-methyl-4-benzoylpyrazol-5-one complex, *reduction of Mn(VII)*	Triton X-100	GFAAS	–	31	0.02	3.5	[46]
Coprecipitation	Mn(II)–Zirconium(IV) hydroxide, *reduction of Mn(VII)*	–	FAAS	–	50	0.75	<7	[15]
SPE	Mn(VII)–Retention on LDH, *oxidation of Mn(II)*	Ni–Al(NO_3^-) LDH	FAAS	1–100	100	0.47	3.2	This work

PF: pre-concentration factor; SPE: solid phase extraction; SIA: sequential injection analysis; CPE: cloud point extraction; FAAS: flame atomic absorption spectrometry; CCTS: cross-linked chitosan; ICP-OES: inductively coupled plasma-optical emission spectrometry; GFAAS: graphite furnace atomic absorption spectrometry.

for the speciation of manganese and chromium in various water samples.

Acknowledgment

The financial support from the Research Council of Azarbaijan University of Tarbiat Moallem (AUTM, Iran) is gratefully acknowledged.

References

[1] M. Stoeppler, Hazardous Metals in the Environment, Amsterdam, Elsevier, 1992.
[2] G.F. Nordberg, B.A. Fowler, M. Nordberg, L. Friberg, Handbook on the Toxicology of Metals, Academic Press, Burlington, 2007.
[3] C.D. Pereira, J.G. Techy, S.P. Quinaia, E.M. Ganzarolli, Can. J. Anal. Sci. Spectrosc. 53 (2009) 275–281.
[4] Guidelines for Drinking-water Quality, Recommendations, vol. 1, 3rd ed., WHO Press, World Health Organization, Geneva, Switzerland, 2008, pp. 334–335.
[5] X. Guan, D. He, J. Ma, G. Chen, Front. Environ. Sci. Eng. China 4 (2010) 405–413.
[6] J.J. Chen, H.H. Yeh, Water Res. 39 (2005) 4420–4428.
[7] S.B. Goldhaber, Regul. Toxicol. Pharm. 38 (2003) 232–242.
[8] G.B. Gerber, A. Leonard, P. Hantson, Crit. Rev. Oncol. Hematol. 42 (2002) 25–34.
[9] Guidelines for Drinking-water Quality, vol. 1, 3rd ed., WHO Press, World Health Organization, Geneva, Switzerland, 2008, pp. 397–399.
[10] T.E. Gunter, C.E. Gavin, M. Aschner, K.K. Gunter, Neurotoxicology 27 (2006) 765–776.
[11] A. Beyer, M. Biziuk, Food Chem. 108 (2008) 669–680.
[12] F. Pena-Pereira, I. Lavilla, C. Bendicho, Spectrochim. Acta B 64 (2009) 1–15.
[13] S.S. Albaseer, R. NageswaraRao, Y.V. Swamy, K. Mukkanti, J. Chromatogr. A 1217 (2010) 5537–5554.
[14] A. Karatepe, E. Korkmaz, M. Soylak, L. Elci, J. Hazard. Mater. 173 (2010) 433–437.
[15] D. Citak, M. Tuzen, M. Soylak, J. Hazard. Mater. 173 (2010) 773–777.
[16] B. Galan, D. Castaneda, I. Ortiz, Water Res. 39 (2005) 4317–4324.
[17] C. Sarzanini, O. Abollino, E. Mentastri, Anal. Chim. Acta 435 (2001) 343–350.
[18] A. Beni, R. Karosi, J. Posta, Microchem. J. 85 (2007) 103–108.
[19] Y. Okamoto, Y. Nomura, H. Nakamura, K. Iwamaru, T. Fujiwara, T. Kumamaru, Microchem. J. 65 (2000) 341–346.
[20] M.R. Moghadam, S. Dadfarnia, A.M. Haji Shabani, J. Hazard. Mater. 186 (2011) 169–174.
[21] J.L. Manzoori, M. Amjadi, J. Abulhassani, Talanta 77 (2009) 1539–1544.
[22] L.-L. Wang, J.-Q. Wang, Z.-X. Zheng, P. Xiao, J. Hazard. Mater. 177 (2010) 114–118.
[23] M. Ezoddin, F. Shemirani, R. Khani, Desalination 262 (2010) 183–187.
[24] V.A. Lemos, P.X. Baliza, A.L. Carvalho, R.V. Oliveira, L.S.G. Teixeira, M.A. Bezerra, Talanta 77 (2008) 388–393.
[25] I. Narin, A. Kars, M. Soylak, J. Hazard. Mater. 150 (2008) 453–458.
[26] K.O. Saygi, M. Tuzen, M. Soylak, L. Elci, J. Hazard. Mater. 153 (2008) 1009–1014.
[27] T. Shamspur, A. Mostafavi, J. Hazard. Mater. 168 (2009) 1548–1553.
[28] E. Kendüzler, A.R. Türker, Ö. Yalçinkaya, Talanta 69 (2006) 835–840.
[29] P.M. Paquet, J.F. Gravel, P. Nobert, D. Boudreau, Spectrochim. Acta B 53 (1998) 1907–1917.
[30] R.E. Wolf, J.M. Morrison, M.B. Goldhaber, J. Anal. At. Spectrom. 22 (2007) 1051–1060.
[31] P. Kubáň, P. Kubáň, V. Kubán, Electrophoresis 24 (2003) 1397–1403.
[32] P.S. Braterman, Z.P. Xu, F. Yarberry, in: S.M. Auerbach, K.A. Carrado, P.K. Dutta (Eds.), Handbook of Layered Materials, Marcel Dekker, Inc., New York, 2004, pp. 509–540.
[33] C. Forano, T. Hibino, F. Leroux, C. Taviot-Gueho, F. Bergaya, B.K.G. Theng, L. Gerhard, in: B.K.G. FaïzaBergaya, G. Theng, Lagaly (Eds.), Developments in Clay Science, Elsevier, Amsterdam, 2006, pp. 1021–1095.
[34] V. Rives, Layered Double Hydroxides: Present and Future, Nova Science Publishers, New York, 2001.
[35] H. Abdolmohammad-Zadeh, Z. Rezvani, G.H. Sadeghi, E. Zorufi, Anal. Chim. Acta 685 (2011) 212–219.
[36] H. Abdolmohammad-Zadeh, S. Kohansal, G.H. Sadeghi, Talanta 84 (2011) 368–373.
[37] A.X. Shahua Qian, G.H. Fei He, X. Han, Analyst 126 (2001) 239–241.
[38] R.P. Monasterio, J.C. Altamirano, L.D. Martínez, R.G. Wuilloud, Talanta 77 (2009) 1290–1294.
[39] H. Chen, P. Du, J. Chen, S. Hu, S. Li, H. Liu, Talanta 81 (2010) 176–179.
[40] G.D. Matos, E.B. dos Reis, A.C.S. Costa, S.L.C. Ferreira, Microchem. J. 92 (2009) 135–139.
[41] V.N. Bulut, D. Ozdes, O. Bekircana, A. Gundogdu, C. Durana, M. Soylak, Anal. Chim. Acta 632 (2009) 35–41.
[42] S. Chen, L. Zhu, D. Lu, X. Cheng, X. Zhou, Mikrochim. Acta 169 (2010) 123–128.
[43] O.D. Uluozlu, M. Tuzen, M. Soylak, Food Chem. Toxicol. 47 (2009) 2601–2605.
[44] J.F. van Staden, L.V. Mulaudzi, R.I. Stefan, Anal. Chim. Acta 499 (2003) 129–137.
[45] O. Abollino, M. Aceto, M.C. Bruzzoniti, E. Mentasti, C. Sarzanini, Anal. Chim. Acta 375 (1998) 299–306.
[46] P. Liang, Z. Sun, J. Cao, At. Spectrosc. 28 (2007) 62–66.