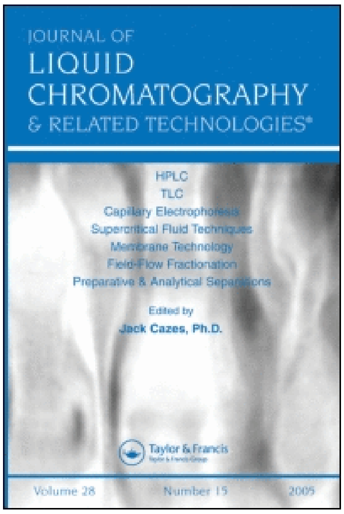

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Development of a Method for Chromium Speciation by Selective Solid Phase Extraction and Preconcentration on Alumina-Functionalized Thiosemicarbazide

Mohamed E. Mahmoud[a]; Amr A. Yakout[b]; Somia B. Ahmed[b]; Maher M. Osman[b]
[a] Medical Chemistry Department, Faculty of Medicine, King Abdullaziz University, Jeddah, KSA [b] Chemistry Department, Faculty of Sciences, Alexandria University, Alexandria, Egypt

To cite this Article Mahmoud, Mohamed E. , Yakout, Amr A. , Ahmed, Somia B. and Osman, Maher M.(2008) 'Development of a Method for Chromium Speciation by Selective Solid Phase Extraction and Preconcentration on Alumina-Functionalized Thiosemicarbazide', Journal of Liquid Chromatography & Related Technologies, 31: 16, 2475 — 2492

To link to this Article: DOI: 10.1080/10826070802319750

URL: http://dx.doi.org/10.1080/10826070802319750

Journal of Liquid Chromatography & Related Technologies®, 31: 2475–2492, 2008

ISSN: 1082-6076 print/1520-572X online
DOI: 10.1080/10826070802319750

Development of a Method for Chromium Speciation by Selective Solid Phase Extraction and Preconcentration on Alumina-Functionalized Thiosemicarbazide

Mohamed E. Mahmoud,[1] Amr A. Yakout,[2]
Somia B. Ahmed,[2] and Maher M. Osman[2]

[1]Medical Chemistry Department, Faculty of Medicine,
King Abdullaziz University, Jeddah, KSA
[2]Chemistry Department, Faculty of Sciences, Alexandria University,
Alexandria, Egypt

Abstract: A speciation method is developed for Cr(III) and Cr(VI) at selected medium pH range via solid phase extraction on three designed and synthesized chelating inorganic solid sorbents based on adsorption of thiosemicarbazide, as the nitrogen and sulfur containing chelating compound, on alumina surface [Al-TSC (I–III)]. The influence of various parameters including medium pH, time of contact, and interference of matrix and coexistent elements on the speciation and selective extraction processes of chromium species are studied and evaluated on the basis of determination of the metal adsorption capacity, distribution coefficient, and separation factor. Quantitative recovery of Cr(VI) was accomplished by [Al-TSC (I–III)] at $\text{pH} = 1.0$, while Cr(III) was found to be recovered on these sorbents at $\text{pH} = 7.0$ with minimal or no interference between these two species under the studied buffering conditions. The proposed method has been successfully applied for speciation, selective extraction, and preconcentration of Cr(III) and Cr(VI) in water samples with a preconcentration factor of 200.

Keywords: Alumina, Chromium, Solid phase extraction, Speciation, Thiosemicarbazide

Correspondence: Mohamed E. Mahmoud, Medical Chemistry Department, Faculty of Medicine, King Abdullaziz University, P.O. Box 80205, Jeddah 21589, KSA. E-mail: memahmoud10@yahoo.com

INTRODUCTION

Heavy metals and their species are the most dangerous and effective water pollutants due to their acute carcinogenicity and toxicity. Some of these metal species are characterized by their poisonous cumulative capabilities in organisms' tissues leading to adverse physiological effects.[1] In addition, trace heavy metals are well recognized for their direct and negative impact on the human health and ecological system.[2] It has been reported that the same heavy metal may be characterized by possessing different degrees of toxicity based on its various existing oxidation states, and generally the biological impact of heavy metals is mainly dependent on their chemical forms or species rather than total concentration of the element.[3] Therefore, metal speciation studies must be designed and established to identify and determine the actual concentration of each species. Metal speciation is usually defined in terms of experimental and procedural identification and quantification processes of different species, forms, or phases already existing in the matrix of interest.[4] Metal speciation may be also defined on the basis of species functionality, operational extraction, and specificity of components that are related to the oxidation states of the metal.[5] This speciation technique is highly demanded for some heavy metals such as mercury, arsenic, and chromium, as well as others owing to the fact that certain oxidation states of some metals are highly toxic to humans and associated with sever health problems, while other species are less toxic or even considered as essential trace elements.[6] Generally, chromium represents a typical example of an element forming species with different oxidation states that show opposite levels of toxicity to the environments, as well as humans, animals, and plants.[7] Chromium(VI) is highly soluble in water and the major toxicity effects of Cr(VI) are well documented.[8] It has been also reported that Cr(VI) compounds and species are approximately 100 times more toxic than Cr(III) salts due to the high oxidation potential and the ease of penetration into biological membranes.[9] On the other hand, trivalent chromium is the chemical species of naturally occurring chromium known as an essential trace element for metabolic processes including enzymes, proteins, and nucleic acids, as well as for proper metabolism of carbohydrates, lipids, and proteins.[10] The chemical industries, metallurgical, electroplating, pigments, tanning industries, oxidative dying, and cooling water towers are the major industrial sources for extensive uses and applications of chromium. These industrial activities are considered to be the major reasons for release of chromium species to numerous sites including drinking water supply systems. Therefore, both valence chromium forms in environmental samples have taken an important role in the analytical chemistry and due to these factors, accurate and facile speciation of these chromium forms must be established.[11,12]

Speciation of nanogram per milliliter levels or lower of chromium species must be started by an extraction procedure of one specific form as the initial step, followed by a preconcentration step. The final speciation procedures demand an instrumental analysis and determination of the isolated species. Various isolation and preconcentration procedures are recently reported, and these are mainly based on coprecipitation,[13] liquid–liquid extraction,[14] sorption,[15] ion-exchange,[16] electroanalytical techniques,[17] chelating sorbents, and solid phase extractors and preconcentrators.[18–20] These experimental procedures are critical in speciation analysis of real samples, because it strongly affect both the qualitative and quantitative evaluation of the collected data and a little agreement is reported between authors on the best choice of extraction technique.[21] Solid phase extraction and preconcentration techniques, based on designing and utilization of solid phases chemically or physically loaded chelating organic compounds, are now widely used and applied for speciation, separation, and preconcentration of trace constituents from various environmental matrices and natural water systems, due to their high separation efficiency, good kinetics, excellent reproducibility, and high sensitivity.[22–25] Several reports were recently published for determination and speciation of chromium in different samples and most of these methods are based on modified organic solid phases or resins.[26–29] These organic solid phase extractors and preconcentrators are experienced with some disadvantages if compared to inorganic modified solid phases such as alumina or silica.[30–35]

In this present work, we have successfully designed new stable chelating sorbents based on the immobilization of thiosemicarbazide on the surface of three alumina types. As a result, we have obtained three new sulfur and nitrogen containing chelating solid phases characterized with excellent selectivity parameters for chromium speciation via selective separation, extraction, and preconcentration in various water samples for the sake of satisfying the strong and growing needs for accurate and real determinations of Cr(III) and Cr(VI) species in their matrices separately, rather than total chromium content.

EXPERIMENTAL

Instrumentation

A Perkin–Elmer flame spectrophotometer model 2380 was used for metal analysis and determination. The concentration of chromium

(VI) and total chromium was determined by Hach digital UV-Vis spectrophotometer, model DR/2010 at $\lambda = 540\,\mathrm{nm}$. The pH measurement of metal ions and buffer solutions were carried out by an Orion 420A pH meter calibrated against potassium hydrogen phthalate at pH = 4.008. IR spectra of the active alumina and its modified phases were recorded from KBr pellets by using a Perkin–Elmer spectrophotometer, model 1430.

The electron impact mass spectra of active alumina, thiosemicarbazide, and modified alumina phases [Al-TSC (I–III)] were carried out by using a Varion MAT 212 mass spectrometer equipped with a direct insertion probe (DIP) in the Institute for Inorganic and Analytical Chemistry, Münster University, Germany.

Materials and Reagents

Thiosemicarbazide was purchased from Aldrich Chemical Company, USA and used as received. Three alumina types of analytical grade were used in this work (150 mesh size and 58 Å pore diameter) and purchased from Aldrich Chemical Company, USA. The pH values of aqueous suspensions of these three alumina phases were found to have pH ~ 6.0 ± 0.5, 7.0 ± 0.5, and 9.0 ± 0.5 for acidic, neutral, and basic alumina, respectively. The metal salts are all of analytical grade and purchased from Aldrich Chemical Company, USA and BDH limited, Poole, England.

Synthesis of Alumina Phases Physically Adsorbed-Thiosemicarbazide

Alumina phases physically adsorbed thiosemicarbazide were synthesized according to the following procedure. A sample of $10 \pm 0.1\,\mathrm{g}$ alumina, either acidic, neutral, or basic, was added to a solution of thiosemicarbazone (0.91 g, 10.0 mmol in 50 mL of ethyl alcohol). The reaction mixture was stirred for six hours and the newly modified [Al-TSC (I–III)] phases were filtered, washed with 50 mL ethyl alcohol, and finally, with 50 mL of diethyl ether, and allowed to dry in an oven adjusted to 60°C for eight hours.

Stability of [Al-TSC (I–III)] in Different Acidic Solutions

A sample of alumina phase (0.5 g) was mixed with 50 mL of different buffer solutions (pH 1–7) in a 100 mL volumetric flask and automatically shaken for one hour. The buffered alumina phase was filtered, washed with a 50 mL portion of the same pH solution, followed by doubly distilled water (DDW), and dried at 70°C. A sample of buffered alumina phase, 25.0 ± 1 mg, was then added to a solution containing 9.0 mL of buffer solution (pH = 6.0) and 1.0 mL of 0.1 M-Cu(II) solution, and this mixture was then shaken for 30 minutes by an automatic shaker. The percentage of hydrolysis of alumina phases [Al-TSC (I–III)] in different buffer solutions was determined from the metal uptake of Cu(II).

Determination of Surface Coverage

Thermal desorption method was used to determine the surface coverage values of alumina phases [Al-TSC (I–III)]. In this method, a sample of dry alumina phase (100 ± 1 mg) was ignited in a furnace at 550°C for one hour and left to cool down at 70°C. The sample was transferred to a desiccator and left to reach room temperature. The weight loss of thiosemicarbazide was determined by the difference in the sample masses before and after thermal desorption process. Blank samples of alumina phases were also subjected to the same procedure.

Determination of the Metal Adsorption Capacity

The metal adsorption capacity values (μmolg^{-1}) of the modified alumina phases for the extraction of different metal ions in various buffer solutions were determined in triplicate by the batch equilibrium technique. In this method, 50 ± 1 mg of dry phase was added to a mixture containing 1.0 mL of 0.1 M metal ion solution and 9.0 mL of the selected buffer solution into a 50 mL measuring flask. These were then shaken at room temperature for 30 minutes by an automatic shaker. The mixture was filtered and washed with 100 mL of DDW. The unbounded metal ion was determined by atomic absorption spectrophotometric analysis and/or complexometric EDTA titration.

The effect of shaking time intervals (1, 5, 10, 15, 20, 25, and 30 minutes) on the values of metal capacity and the percentage extraction of Cu(II) was also studied for some selected metal ions by the batch equilibrium technique according to the following procedure. A sample of dry alumina phase (50 ± 1 mg) was added to a mixture containing 1.0 mL of 0.1 M of Cr(III) and 9.0 mL of the selected buffer solution. The reaction mixture was then shaken by an automatic shaker for the selected time, filtered, washed with 100 mL DDW, and the unextracted metal ion was determined by flame atomic adsorption analysis.

Determination of the Distribution Coefficient

A solution containing 1.0 μg mL^{-1} of each tested metal ion was prepared and determined by flame atomic absorption spectrophotometry. Alumina phase (50 ± 1 mg) was mixed with 50 mL of this metal ion solution in a 100 mL measuring flask. The mixture was shaken for one hour by an automatic shaker, the solid phase was filtered, and the filtrate was subjected to atomic absorption analysis. Standard and blank metal ion solutions were also prepared and measured.

Applications of [Al-2PC-TSC (I–III)]

Speciation and percent extraction of Cr(III) and Cr(VI) from a (1:1) mixture

A 2.0 L sample of Alexandria drinking tap water was spiked to a concentration of ~1.0 μg mL^{-1} each of Cr(III) and Cr(VI). A 1.0 L of this water sample was adjusted to a pH 1.0 and passed over a micro column each packed with 100 mg of modified alumina phases [Al-TSC (I–III)] with a flow rate of 10 mL min^{-1}. The eluent solution was subjected to atomic absorption analysis and spectrophotometric determination of chromium species at $\lambda = 540$ nm. Another 1.0 L of this water sample was adjusted to a pH 7.0 and passed over a micro column each packed with 100 mg of modified alumina phases [Al-TSC (I–III)], with a flow rate of 10 mL min^{-1}. The eluent solution was subjected to the same analysis and determination procedures.

Selective extraction, preconcentration, and speciation of chromium in sea water samples

Speciation of chromium, selective extraction, and preconcentration of chromium species were performed according to the following procedures. A 1.0 L sample of sea water was spiked with ~5.0 ng mL^{-1} of Cr(VI), adjusted to a pH 1.0, and passed over a preconcentration microcolumn packed with 100 mg of the modified alumina phases [Al-TSC (I–III)], with a flow rate of 10 mL min^{-1} under air pressure. The adsorbed chromium species was eluted by 5.0 mL of concentrated HNO_3 as a preconcentration reagent and subjected to analysis by atomic absorption spectrophotometry and UV-Vis spectrophotometry.

RESULTS AND DISCUSSION

Characterization and Surface Coverage

Alumina phases, chemically or physically loaded organic compounds, can be tested for surface modification as well as thermal stability via their analysis by the mass spectrometric technique under electron impact ionization, with a heating range reaching 300°C in a way similar to that described and known for pyrolysis of polymer compounds by mass spectrometric technique. Alumina phases [Al-TSC (I–III)] were studied by the direct insertion probe under 70-eV EI-MS as previously reported.[36] The mass spectrum of thiosemicarbazide was found to exhibit the molecular ion peak as the base peak at m/z 91 (100%). In addition, two other peaks for fragment ions at m/z 60 (30%) and at m/z 44 (8%) are detected and corresponding to $[CSNH_2]^+$ and $[CS]^{+\bullet}$ fragment ions, respectively. The 70-eV EI–MS–DIP spectrum of acidic alumina—physically adsorbed—thiosemicarbazide [Al-TSC (I)], was found to exhibit few fragment ions at m/z 18, 44, and 60 corresponding to $[H_2O]^{+\bullet}$, $[CS]^{+\bullet}$, and $[CSNH_2]^+$, respectively. The other fragments ions are of low relative abundance and this trend is expected, owing to the low percentage value of immobilized thiosemicarbazide on the surface of acidic alumina (4.3%), which is calculated from the surface coverage of alumina phase [Al-TSC (I)]. The same trend and observations were identified and outlined from the 70-eV EI–MS–DIP spectra of modified neutral alumina phase [Al-TSC (II)] and basic alumina phase [Al-TSC (III)] concerning low relative abundance of the fragment ions due to the calculated surface coverage percentage values, which were found as 6.4% and 5.8%, respectively,[36] as given in Table 1.

The thermal desorption method[37] was used to determine the surface coverage of modified alumina phases [Al-TSC (I–III)]. In this method, alumina phases are heated at high temperatures in the range ~500–600°C and the obtained residue corresponds to the stable alumina matrix, which can then be used to calculate the surface coverage values expressed in $mmol\,g^{-1}$ and percentage as listed in Table 1.

Table 1. Surface coverage values of alumina phases [Al-TSC (I–III)]

	Thermal desorption	
Alumina phase	$mmol\,g^{-1}$	Coverage (%)
[Al-TSC (I)]	0.472	(4.3)
[Al-TSC (II)]	0.703	(6.4)
[Al-TSC (III)]	0.636	(5.8)

Stability of Surface Modified Alumina Phases [Al-TSC (I–III)]

The possible leaching and/or hydrolysis degree of the organic modifier from the surface of modified alumina phases [Al-TSC (I–III)] were tested in different buffer solutions (pH = 1–7) to identify their stability. The treated alumina phases were then used to determine the $\mu mol\,g^{-1}$ of adsorbed Cu(II) and the determined $\mu mol\,g^{-1}$ values of the hydrolyzed alumina phases were compared with those of the unhydrolyzed one to calculate the percentage of stability for each modified alumina phase in the tested solutions. Table 2 shows the results obtained for the stability towards hydrolysis and/or leaching process of the modified alumina phases [Al-TSC (I–III)]. It is evident that [Al-2PC-TSC (I)] and [Al-TSC (II)] are highly stable toward leaching or hydrolysis over the entire studied pH-range, judging from the percentage hydrolysis values of these two phases (96.0–97.0% and 95.0–96.0%), respectively, as listed in Table 2. In addition, modified basic alumina phase [Al-TSC (III)] was found to be completely and highly stable in buffer solutions with pH values equal 7.0 and 1.0. However, [Al-TSC (III)] was found to be less stable in the other studied pH-range 2–6, as given in Table 2.

The Metal Capacity Values

A series of metal ions was selected, viz. Mg(II), Ca(II), Mn(II), Fe(III), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Hg(II), Cu(II), Cr(III), and Cr(VI) to study and evaluate the metal adsorption and extraction processes by newly modified alumina phases [Al-TSC (I–III)]. This study is highly dependent on the medium pH, as well as the time of contact between the tested metal ion and solid sorbent. The influence of medium pH was examined for this series of metal ions by alumina phases [Al-TSC (I–III)] in various solutions of pH 1–7. However, buffer solutions in the basic range were excluded due to possible precipitation of most metal ions

Table 2. Stability of modified alumina phases [Al-TSC (I–III)]

	Stability in $\mu mol\,g^{-1}$							Percentage stability						
	pH							pH (%)						
Phase	1.0	2.0	3.0	4.0	5.0	6.0	7.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0
I	600	600	595	600	600	600	600	97	97	96	97	97	97	97
II	577	577	577	570	570	570	576	96	96	96	95	95	95	96
III	550	510	499	495	493	510	580	95	88	86	85	85	88	100

Table 3. Maximum metal capacity values under optimum buffering conditions

Metal ion	Max. μmol g^{-1} (pH)		
	Al-2PC-TSC (I)	Al-2PC-TSC (II)	Al-2PC-TSC (III)
Mg(II)	10 (7)	20 (7)	10 (7)
Ca(II)	20 (7)	10 (7)	10 (7)
Mn(II)	20 (7)	30 (7)	10 (7)
Fe(III)	340 (4)	330 (4)	340 (4)
Co(II)	10 (7)	10 (7)	10 (7)
Ni(II)	120 (6, 7)	120 (6, 7)	240 (6, 7)
Cu(II)	620 (7)	600 (7)	580 (7)
Zn(II)	60 (7)	80 (7)	120 (7)
Cd(II)	80 (7)	80 (7)	80 (7)
Hg(II)	160 (7)	200 (7)	320 (7)
Pb(II)	240 (6)	240 (6)	230 (5, 6)
Cr(III)	740 (7)	700 (7)	740 (7)
Cr(VI)	300 (1)	100 (1,2)	200 (1)

under these buffering conditions. The maximum metal capacity values (μmol g^{-1}) at the optimum pH-range are listed in Table 3.

For further confirmation of the effect of medium pH on the process of determination and speciation of chromium species, a comparison of the metal capacity for a mixture of Cr(III) and Cr(VI) in different buffer solutions, pH 1–7, was performed and the results are compiled in Table 4. The collected results of this study clearly refer to the strong affinity of modified alumina phases [Al-TSC (I–III)] toward selective binding and extraction of Cr(VI) from buffer solutions in the pH range 1.0–2.0. Maximum μmol g^{-1} metal uptake values of Cr(VI) were obtained for the three studied alumina phases [Al-TSC (I–III)] in the

Table 4. The influence of medium pH on the speciation adsorption capacity of Cr(III) and Cr(VI)

pH	[Al-TSC (I)]		[Al-TSC (II)]		[Al-TSC (III)]	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	0	300	0	100	0	200
2	0	200	0	100	0	100
3	20	200	100	0	20	0
4	70	100	100	0	50	0
5	440	100	460	0	460	0
6	500	0	520	0	550	0
7	740	0	700	0	740	0

buffer solution; pH = 1.0. Cr(III) was found to be highly extracted at higher pH buffer solutions (pH 5–7) leading to a reverse order and behavior as shown by Figure 1, as a representative for such opposite behavior. Thus, one can easily conclude from the results of this study that possible separation and speciation of Cr(III) and Cr(VI) can experimentally be accomplished by selecting the appropriate pH value of these two species.

The influence of contact time between the tested metal ion and the modified alumina phase on the metal adsorption capacity values was studied and evaluated for Cr(III) as the highest extracted metal ion by the three alumina phases [Al-TSC (I–III)]. This study is very important to identify the possible rapidness of binding process between the two interacting species, metal ion and modified solid phases. Figure 2 represents the adsorption capacity of Cr(III) versus time by the three newly alumina phases [Al-TSC (I–III)]. Figure 2 clearly refers to the high similarity between the studied alumina phases in their percentage extraction and binding processes with Cr(III).

Evaluation of the Distribution Coefficient Values

Evaluation of the capability of modified alumina phases for selective extraction of various metal ions from aqueous and organic solutions can be explored on the basis of distribution coefficients (K_d) determination.[38] The obtained results can be then used to provide a possible discrimination order between the various interfering metal ions. This method can be successfully applied for very low concentration ranges of metal ion, part per million (ppm) or part per billion (ppb).

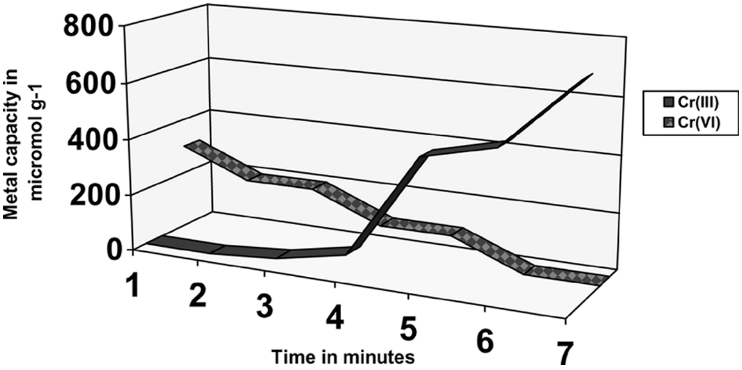

Figure 1. Speciation of Cr(III) and Cr(VI) in various buffer solutions by [Al-TSC (I)].

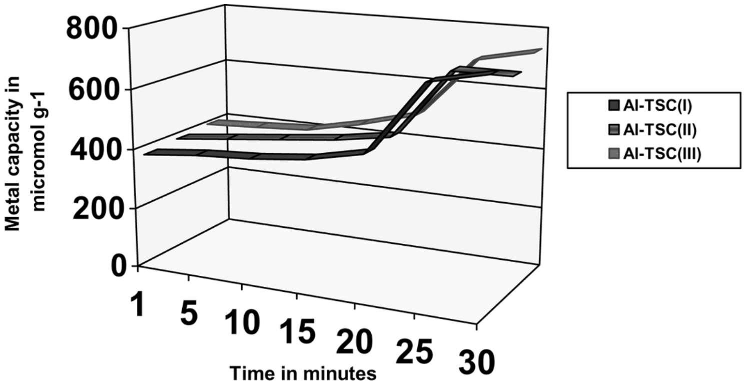

Figure 2. Effect of shaking time on the adsorption capacity values of Cr(III) by [Al-TSC (I–III)].

Evaluation of the distribution coefficient can lead to a more detailed series of values, which assists in further evaluation of the metal uptake trends as well as the selectivity incorporated into modified alumina phase. The K_d value is determined from the following equation:

$$K_d, \mathrm{mL\,g^{-1}} = \frac{C_{i,\mathrm{ex}}(\mu\mathrm{g\,g^{-1}})}{C_{i,\mathrm{sol}}(\mu\mathrm{g\,ml^{-1}})}$$

Table 5 compiles $\log K_d$ values for a series of tested metal ions by [Al-TSC (I–III)]. It is evident from the listed values that [Al-TSC (II)] and [Al-TSC (III)] are highly selective for Cr(III) judging from their determined $\log K_d$ values as 3.90 and 4.20 for the two phases, respectively. Cd(II) and Fe(III) were found to be the second and third

Table 5. Log K_d-values of metal ions determined by [Al-TSC (I-III)]

Metal ions	[Al-TSC (I)]	[Al-TSC (II)]	[Al-TSC (III)]
Ca(II)	1.00	2.00	2.11
Mg(II)	2.33	2.68	2.47
Mn(II)	1.00	1.00	2.91
Zn(II)	1.73	2.60	2.80
Ni(II)	1.00	3.27	2.82
Pb(II)	1.00	2.52	2.04
Co(II)	1.00	3.08	3.21
Fe(III)	3.98	3.27	3.42
Cu(II)	2.60	3.16	3.35
Cd(II)	3.25	3.55	3.75
Cr(III)	3.00	3.90	4.20

highest extracted metal ions by these two phases. [Al-TSC (I)] phase was found to exhibit its highest selectivity toward Fe(III), Cd(II), and Cr(III), providing K_d values of 3.98, 3.25, and 3.00, respectively. These values are pointing out to the role and selectivity incorporated into modified alumina phases for extraction and binding with Cr(III), as well as other heavy metal ions. Finally, the increasing orders of $\log K_d$ values for tested metal ions by modified alumina phases can be outlined in the following orders:

[Al-TSC (I)]: LogK_d: Ca(II), Mn(II), Co(II), Ni(II), Pb(II) < Zn(II) < Mg(II) < Cu(II) < Cr(III) < Cd(II) < Fe(III)

[Al-TSC (II)]: LogK_d: Mn(II) < Ca(II) < Pb(II) < Zn(II) < Mg(II) < Co(II) < Cu(II) < Ni(II) < Fe(III) < Cd(II) < Cr(III).

[Al-TSC (I-III)]: LogK_d: Pb(II) < Ca(II) < Mg(II) < Zn(II) < Ni(II) < Mn(II) < Co(II) < Cu(II) < Fe(III) < Cd(II) < Cr(III).

The incorporated selectivity into newly modified alumina phases [Al-2PC-TSC (I–III)] can also be evaluated and expressed in terms of the separation factor α, which can be derived from the measurements under static or dynamic condition. The separation factor $(\alpha_{A/B})$[38] of any two metal cations A and B is calculated from the distribution coefficients $K_{d(A)}$ and $K_{d(B)}$, respectively, as given in the following equation:

$$\alpha_{(A/B)} = \frac{K_{d(A)}}{K_{d(B)}}$$

The separation factors of Cr(III) versus other interfering metal ions are calculated for the three newly modified alumina phases [Al-TSC (I–III)]. A representation of these values is shown in Figure 3 for modified alumina phases [Al-TSC (III)]. It is evident that excellent separation factors for Cr(III) are attained by the studied alumina phases with no or minimum interference of most metal ions.

Applications of [Al-TSC (I–III)]

Speciation and Selective Solid Phase Extraction of Cr(III) from Water Samples

Table 6 summarizes the results of microcolumn applications for selective extraction and speciation of Cr(VI) and Cr(III) in Alexandria drinking tap water samples containing equal concentrations of both species by adjusting a sample of water to the optimum pH = 1 for selective

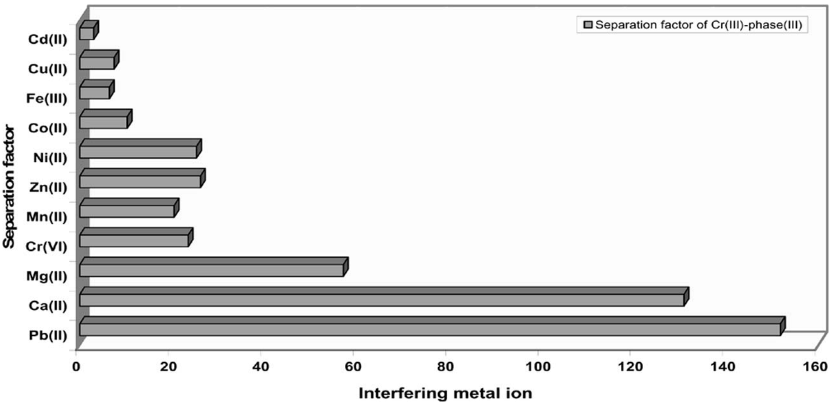

Figure 3. Separation factors of Cr(III) versus other interfering metal ions by alumina phase [Al-TSC (III)].

extraction of Cr(VI), and another sample to a pH = 7 for removal of Cr(III). It is evident from the results compiled in Table 6 of excellent recovery of Cr(VI) and Cr(III) by the three newly modified alumina phases [Al-TSC (I–III)] under the applied experimental buffering conditions. Non detected interference was identified in the process of Cr(III)/Cr(VI) speciation, judging from the results outlined in Table 6.

Speciation of Chromium via Selective Solid Phase Extraction

The ability of modified alumina phases [Al-TSC (I–III)] to selectively extract and preconcentrate Cr(VI) species from interfering metal ions

Table 6. Speciation and percent extraction of Cr(III) and Cr(VI) from Alexandria tap water

Phase	Mass of alumina	Adjusted pH	Spiked ($\mu g\,mL^{-1}$) Cr(III)	Cr(VI)	Percent extraction (%) Cr(III)	Cr(VI)
[Al-TSC (I)]	100 mg	1.0	1.00	1.00	0.00	100.0
[Al-TSC (I)]	100 mg	7.0	1.00	1.00	100.0	0.00
[Al-TSC (II)]	100 mg	1.0	1.00	1.00	0.00	100.0
[Al-TSC (II)]	100 mg	7.0	1.00	1.00	100.0	0.00
[Al-TSC (III)]	100 mg	1.0	1.00	1.00	0.00	100
[Al-TSC (III)]	100 mg	7.0	1.00	1.00	100.0	0.00

Values are based on triplicate analysis.

Table 7. Selective solid phase extraction and preconcentration of Cr(VI) from sea water by [Al-TSC (I–III)]

Phase	Mass of alumina	Preconcentration acid	Spiked ($\mathrm{ng\,mL^{-1}}$)	Detected ($\mathrm{\mu g\,mL^{-1}}$)	Percent extraction (%)
[Al-TSC (I)]	100 mg	5.0 ml of concentrated HNO_3	5.22	0.98	93.9 ± 2.0
[Al-TSC (II)]	100 mg	5.0 ml of concentrated HNO_3	5.22	1.01	96.7 ± 2.0
[Al-TSC (III)]	100 mg	5.0 ml of concentrated HNO_3	5.22	1.08	103.4 ± 3.0

Values are based on triplicate analysis.

and organic matters was studied as the final step to explore the potential applications of alumina phases [Al-TSC (I–III)] for direct speciation of Cr(VI) from sea water samples. The tested sea water samples were adjusted to a $pH = 1.0$ and passed over a microcolumn packed with the examined alumina phase. Concentrated nitric acid was used as a preconcentrating reagent with a preconcentration factor of 200. The results of atomic absorption analysis and UV-Vis spectrophotometric determination are listed in Table 7. The percentage recovery values of Cr(VI)-speciation were found to be $93.9 \pm 2.0\%$, $96.7 \pm 2.0\%$, and $103.4 \pm 3.0\%$, as determined by [Al-TSC (I)], [Al-TSC (II)] and [Al-TSC (III)], respectively. It is also evident from this study that no, or minimum interference and contribution of the sea water matrix caused by dissolved metal ions or organic matters in the process of Cr(VI)-speciation judging from the percentage recovery values.

CONCLUSION

The newly designed chelating alumina phases were found to be highly stable in buffer solutions, pH 1.0 and 7.0, and successfully applied for chromium speciation, preconcentration, and selective extraction by simply controlling and tuning the medium pH value. Cr(III) was completely extracted at pH 7.0 via possible chelation with the N and S donor atoms containing thiosemicarbazide, while Cr(VI) was quantitatively sorbed at pH 1.0. The presented method was potentially applied for the speciation of chromium in real water samples without matrix interference.

REFERENCES

1. Chardin, B.; Chaspoul, F.; Gallice, P.; Bruschi, M. Chromium speciation in bacterial culture medium by combined strong anion exchange liquid chromatography with inductively coupled plasma mass spectrometry. Applications to the reduction of Cr(VI) by sulfate-reducing bacteria. J. Liq. Chromatogr. & Rel. Technol. **2002**, *25*, 877–887.
2. Narukawa, T.; Riley, K.W.; French, D.H.; Chiba, K. Speciation of chromium in Australian fly ash. Talanta **2007**, *73*, 178–184.
3. Derbyshire, M.; Lamberty, A.; Gardiner, P.H.W.E. Optimization of the simultaneous determination of Cr(III) and Cr(VI) by ion chromatography with chemiluminescence detection. Anal. Chem. **1999**, *71*, 4203–4207.
4. Marques, M.J.; Salvador, A.; Morales-Rubio, A.E.; de la Guardia, M. Analytical methodologies for chromium speciation in solid matrices: A survey of literature. Fresenius J. Anal. Chem. **1998**, *362*, 239–248.

5. Fuentes, A.; Llorens, M.; Saez, J.; Aguilar, M.I.; Ortuno, J.F.; Meseguer, V.F. Comparative study of six different sludges by sequential speciation of heavy metals. Bioresource Technol. **2008**, *99*, 517–525.
6. Grandillo, V.A.; de Machado, L.P.; Romero, R.A. Determination of total chromium in whole blood, blood components, bone, and urine by fast furnace program electrothermal atomization AAS and using neither analyte isoformation nor background correction. Anal. Chem. **1994**, *66*, 3624–3631.
7. Kot, A.; Namiesnik, J. The role of speciation in analytical chemistry. Trends Anal. Chem. **2000**, *19*, 69–79.
8. Gomez, V.; Callao, M.R. Chromium determination and speciation since 2000. Trends Anal. Chem. **2006**, *25*, 1006–1015.
9. Tripathi, R.M.; Raghunath, R.; Kumar, A.V.; Krishnamoorthy, T.M. Separation and speciation of Cr(III) and Cr(VI) with Saccharomyces cerevisiae immobilized on sepiolite and determination of both species in water by FAAS. Talanta **2000**, *51*, 895–902.
10. Katz, S.A.; Salem, H. *The Biological and Environmental Chemistry of Chromium*; Wiley InterScience: 1994.
11. Yang, M.; Li, J.X.; Wang, J.H. Field speciation of chromium with a sequential injection lab-on-valve incorporating a bismuthate immobilized micro-column. Talanta **2007**, *72*, 1710–1716.
12. Pramanik, S.; Dey, S.; Chattopadhyay, P. A new chelating resin containing azophenolcarboxylate functionality: Synthesis, characterization and application to chromium speciation in wastewater. Anal. Chim. Acta **2007**, *584*, 469–476.
13. Krishna, P.G.; Gladis, J.M.; Rambabu, U.; Rao, T.P.; Naidu, G.R.K. Preconcentrative separation of chromium(VI) species from chromium(III) by coprecipitation of its ethyl xanthate complex onto naphthalene. Talanta **2004**, *63*, 541–546.
14. Subramanian, K.S. Determination of chromium(III) and chromium(VI) by ammonium pyrrolidinecarbodithioate-methyl isobutyl ketone-furnace atomic absorption spectrometry. Anal. Chem. **1998**, *60*, 11–15.
15. Demirata, B. Preconcentration of Cr(VI) ion on melamine formaldehyde resin. Fresenius J. Anal. Chem. **1992**, *343*, 357–359.
16. Johnson, C.A. Rapid ion-exchange technique for the separation and preconcentration of chromium(VI) and chromium(III) in fresh waters. Anal. Chim. Acta **1990**, *238*, 273–278.
17. Lin, L.; Lawrence, N.S.; Thongngamdee, S.; Wang, J.; Lin, J. Catalytic adsorptive stripping determination of trace chromium(VI) at the bismuth film electrode. Talanta **2005**, *65*, 144–148.
18. Narin, I.; Soylak, M.; Kayakirilmaz, K.; Elci, L.; Dogan, M. Speciation of Cr(III) and Cr(VI) in tannery wastewater and sediment samples on Ambersorb 563 resin. Anal. Lett. **2002**, *35*, 1437–1452.
19. Krishna, M.V.B.; Chandrasekaran, K.; Rao, S.V.; Karunasagar, D.; Arunachalam, J. Speciation of Cr(III) and Cr(VI) in waters using immobilized moss and determination by ICP-MS and FAAS. Talanta **2005**, *65*, 135–143.
20. Melaku, S.; Cornelis, R.; Vanhaecke, F.; Dams, R.; Moens, L. Method development for the speciation of chromium in river and industrial wastewater using GFAAS. Microchim. Acta **2005**, *150*, 225–231.

21. Ruiz-Chancho, M.J.; Sa'nchez, J.F.L.; Schmeisser, E.; Goessler, W.; Francesconi, K.A.; Rubio, R. Arsenic speciation in plants growing in arsenic-contaminated sites. Chemosphere **2008**, *71*, 1522–1530.
22. Mahmoud, M.E.; Al-Saadi, M.S.M. Preconcentration of cadmium, mercury and lead from natural water samples by silica gel functionalized purpald as a new chelating matrix for metal sorption. Annali di Chimica **2005**, *95*, 465–471.
23. Black, F.J.; Bruland, K.W.; Flegal, A.R. Competing ligand exchange-solid phase extraction method for the determination of the complexation of dissolved inorganic mercury(II) in natural waters. Anal. Chim. Acta **2007**, *598*, 318–333.
24. Bezerra, M.A.; dos Santos, W.N.L.; Lemos, V.A.; Korn, M.A.; Ferreira, S.L.C. On-line system for preconcentration and determination of metals in vegetables by Inductively Coupled Plasma Optical Emission Spectrometry. J. Hazard Mater. **2007**, *148*, 334–339.
25. Ahn, Y.G.; Shin, J.H.; Kim, H.Y.; Khim, J.; Lee, M.K.; Hong. Application of solid-phase extraction coupled with freezing-lipid filtration clean-up for the determination of endocrine-disrupting phenols in fish. J. Anal. Chim. Acta **2007**, *603*, 67–75.
26. YalÇin, S.; Apak, R. Chromium speciation analysis by separation of Cr(III) from Cr(VI) on a XAD sorbent derivatized with shellac: A natural polymer. Intl. J. Environ. Anal. Chem. **2006**, *86*, 915–929.
27. Ma, H.M.; Zhu, Z.L.; Zhang, R.H.; Zhao, J.F. Separation of Cr(VI) and organic Cr(III) in natural water by weak basic anion exchange resin and determination by ICP-AES. Spectrosc. Spectral. Anal. **2007**, *27*, 165–168.
28. Saygi, K.O.; Tuzen, M.; Soylak, M.; Elci, L. Chromium speciation by solid phase extraction on Dowex M 4195 chelating resin and determination by atomic absorption spectrometry. J. Hazard. Mater. **2007**, *156*, 1009–1014.
29. Tuzen, M.; Soylak, M. Chromium speciation in environmental samples by solid phase extraction on Chromosorb 108. J. Hazard Mater. **2006**, *129*, 266–273.
30. Mahmoud, M.E.; Soliman, E.M. A compartive study of the reactivity and selectivity characters of three silica gel phases-immobilized-8-hydroxyquinoline for separation and pre-concentration of chromium (III) from water samples. J. Liq. Chromatogr. & Rel. Technol. **2003**, *26*, 3045–3056.
31. Mahmoud, M.E.; Massoud, M.S.; Maximous, N.N. Synthesis, characterization, and selective metal binding properties of physically adsorbed 2-thiouracile on the surface of porous silica and alumina. Mikrocim. Acta **2004**, *147*, 111–115.
32. Mahmoud, M.E.; Elessawi, M.M.; Kholeif, S.A.; Fathallah, E.I. Aspects of surface modification, structure characterization, thermal stability, and metal selectivity properties of silica gel phases-immobilized-amine derivatives. Anal. Chim. Acta **2004**, *525*, 123–132.
33. Karve, M.; Rajgor, R.V. Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Cyanex302 and determination by flame atomic absorption spectrometry. J. Hazard. Mater. **2007**, *141*, 607–613.

34. Mahmoud, M.E. Surface modification of silica gel for selective extraction of metal ions. *Encyclopedia of Chromatography*; Marcell Dekker: 2006; on-line.
35. Mahmoud, M.E.; Haggag, S.S.; Abdel-Fattah, T.M. Synthesis, characterization and metal chelating properties of silica-physisorbed and chemisorbed-2,5-dioxypiperazine. Polyhedron **2007**, *26*, 3956–3962.
36. Mahmoud, M.E.; Haggag, S.S.; Hegazi, A.H. Synthesis, characterization and sorption properties of silica gel-immobilized-pyrimidine derivative. J. Colloid Interf. Sci. **2006**, *300*, 94–99.
37. Mahmoud, M.E. Study of the selectivity characteristics incorporated into physically adsorbed alumina phases-2-mercaptonicotinic acid and potential applications as selective stationary phases for separation, extraction and pre-concentration of lead(II) and copper(II). J. Liq. Chromatogr. & Rel. Technol. **2002**, *25*, 1187–1199.
38. Mahmoud, M.E.; Kenawy, I.M.M.; Soliman, E.M.; Hafez, M.A.; Akl, M.A.A.; Lashein, R.R.A. Selective preconcentration of uranyl Ion (UO22+) by silica gel phases-modified-chelating compounds as inorganic polymeric ion exchangers. Anal. Sci. **2008**, *24*, 381–387.

Received January 20, 2008
Accepted February 23, 2008
Manuscript 6306