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Chromium speciation by solid phase extraction on Dowex M 4195 chelating resin and determination by atomic absorption spectrometry

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Abstract

A solid phase extraction procedure has been established for chromium speciation in natural water samples prior to determination by atomic absorption spectrometry. The procedure is based on the solid phase extraction of the Cr(VI)- Dowex M 4195 chelating resin. After oxidation of Cr(III) to Cr(VI) by using H_2O_2, the presented method was applied to the determination of the total chromium. The level of Cr(III) is calculated by difference of total chromium and Cr(VI) levels. The procedure was optimized for some analytical parameters including pH, eluent type, flow rates of sample and eluent, matrix effects, etc. The presented method was applied for the speciation of chromium in natural water samples with satisfactory results (recoveries >95%, RSDs <10%). In the determinations of chromium species, flame atomic absorption spectrometer was used. The results were checked by using NIST SRM 2711 Montana soil and GBW 07603 Bush branched and leaves.
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1. Introduction

Chromium is one of the most abundant elements on Earth. The amount of chromium in the environment has gradually been increased predominantly by industrial activities especially from tanneries, mines and incinerators [1]. Chromium exists in Cr(III) and Cr(VI) oxidation states in aqueous solutions [2–4]. The properties of these species are different [1]. Trivalent chromium, the main chemical form found in foods, is essential for maintaining normal glucose metabolism [4,5]. Cr(VI) oxidation state is detrimental to health as it may be involved in the pathogenesis of some diseases like liver, kidney, lung and gastrointestinal cancers. Industrial processes such as plating, tanning, paint production, pigment production and metallurgy involve the use of Cr(VI) compounds and are therefore the most frequent source of hexavalent chromium [5,6]. The importance of chromium speciation is governed by the fact that the toxicity and reactivity depend on the chemical form or oxidation state of chromium [7–10]. A direct measurement of chromium species is not feasible with atomic absorption spectrometry and other atomic spectroscopic techniques. There are only a few analytical techniques available that have sufficient sensitivity and selectivity for the direct determination and speciation of trace levels of chromium in environmental samples [1,8,11,12]. Separation of chromium species using various separation-preconcentration procedures including liquid–liquid extraction, solid phase extraction, coprecipitation, etc. combined with flame and/or graphite furnace atomic absorption spectrometry often results in inadequate sensitivity for trace concentrations of chromium in real samples [8,13–17].

In the presented work, a speciation system for chromium(III), chromium(VI) and total chromium in natural water samples

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based on solid phase extraction on Dowex M 4195 chelating resin. The analytical parameters for optimal speciation conditions for chromium were investigated.

2. Experimental

2.1. Instruments

A Perkin-Elmer AAnalyst 700 atomic absorption spectrometer with deuterium background corrector, equipped with a chromium hollow cathode lamp operated at 25 mA, was used throughout this work. The wavelength and spectral band pass were set at 357.9 nm and 0.7 nm, respectively. A 10 cm long slot-burner head and an air–acetylene flame were used. The nebulizer uptake rate was adjusted to give the optimum response for conventional sample introduction, the resulting rate being 6.0 mL min^{-1}. An acetylene flow rate of 2.5 L min^{-1} was used with an air flow rate of 17.0 L min^{-1}. A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase.

Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used. Digestion conditions for microwave system for NIST SRM 2711 Montana soil, GBW 07603 Bush branched and leaves, sediment from Green river from Tokat and black tea samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [18–20].

2.2. Reagents and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionised water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1 + 9) and were rinsed with distilled water prior to use. Hydrogen peroxide solution (3%, w/v) was prepared in dilute sodium hydroxide solution (pH 10). The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg L^{-1} of the given element supplied by Sigma–Aldrich. Stock solutions of diverse elements were prepared from high purity compounds.

Dowex M 4195 chelating resin (Sigma, St. Louis, USA) is a macroporous divinylbenzene copolymer with bis-picolylamine functional group [21]. It was washed successively with methanol, water, 1 mol L^{-1} HNO_3 in acetone, water, 1 mol L^{-1} NaOH and water, sequentially. A glass column containing 500 mg of Dowex M 4195 chelating resin in water suspension was 10 cm long and 1.0 cm in diameter. The bed height in the column was approximately 2.5 cm.

Phosphate buffer solutions ($H_2PO_4^-/H_3PO_4$) were prepared by mixing of appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and phosphoric acid solutions for pH 2–3. Acetate buffer solutions (CH_3COO^-/CH_3COOH) were prepared by mixing of appropriate volumes of 0.1 mol L^{-1} acetic acid and 0.1 mol L^{-1} sodium acetate solutions for pH 4 and 6. For pH 7, a 250 mL of borate buffer was prepared by use of 2.5 mL of 1 mol l^{-1} HCl and 0.445 g $NaBO_2$. Ammonium buffer solution (NH_4^+/NH_3) was prepared by mixing of appropriate amounts of 0.1 mol L^{-1} ammonia and 0.1 mol L^{-1} ammonium chloride solutions for pH 8.

2.3. Model studies

Ten millilitres of buffer solution (to give the desired pH between 2 and 8) was added to 30 mL of solution containing 20 μg of chromium(VI). The column was preconditioned by passing buffer solution. The solution was passed through the Dowex M 4195 column at a flow rate of 5 mL min^{-1}. After passing of this solution, the column was rinsed twice with 10 mL of water. The adsorbed chromium on the column was eluted with 10 mL portion of 4 mol L^{-1} NH_3. The eluent was analysed for the determination of chromium(VI) concentrations by an atomic absorption spectrometry.

Oxidation of Cr(III) to Cr(VI) has been performed by using the procedure given in literatures [22,23]. After adjustment of the pH of the solution to pH 10, 10 mL of 3% hydrogen peroxide was added. The solution was heated at 80 °C for 40 min. Then the solution was boiled for 10 min in order to remove any excess of H_2O_2. Then test procedure given above was applied to this solution. Chromium(VI) was determined by FAAS.

After oxidation of Cr(III) to Cr(VI) by using H_2O_2 in basic media, the method was applied to the determination of the total chromium. The level of Cr(III) is calculated by difference of total chromium and Cr(VI) concentrations.

2.4. Procedure for real samples

The procedure was applied to the speciation of chromium in a tap water, river water and electroplating water. Various amounts of chromium species were also spiked to these samples. Then the procedures given in Section 2.3 were applied.

Water samples analyzed were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 2.0 with buffer solution. Then the procedure given above was applied. The levels of chromium in the samples were determined by flame atomic absorption spectrometry.

Total chromium in natural water samples was determined as chromium(VI) after oxidation of chromium(III) to chromium(VI) in the natural waters. The oxidation of Cr(III) to Cr(VI) was performed by the procedure given in literatures [22,23].

NIST SRM 2711 Montana soil, GBW 07603 Bush branched and leaves (250 mg) were digested with 6 mL of HCl (37%), 2 mL of HNO_3 (65%) in closed microwave digestion system and diluted to 50.0 mL with deionized water. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions.

For the microwave digestion of sediment from Green river from Tokat and black tea samples, 1.0 g of sample from Tokat was digested with 6 mL of HCl (37%), 2 mL of HNO_3 (65%) in microwave system. After digestion of the samples,

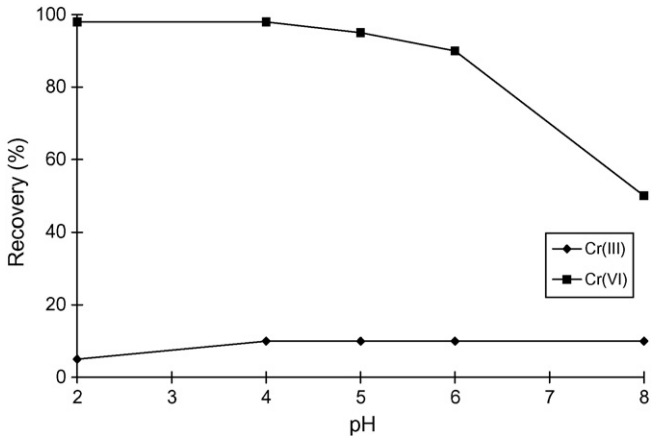

Fig. 1. Relation between pH and chromium species ($N = 3$, eluent: 4 mol L^{-1} NH_3).

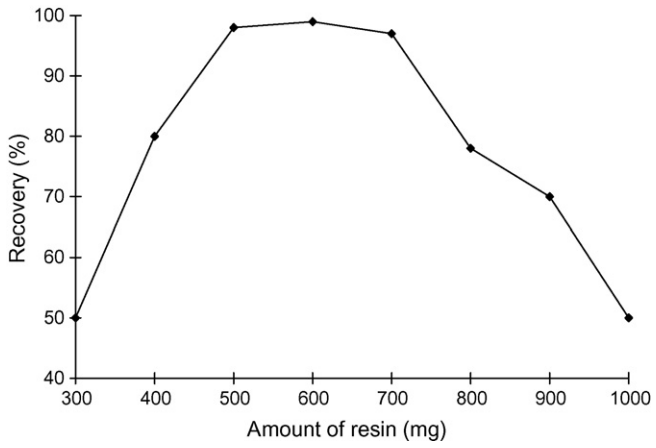

Fig. 2. Influences of amounts of the resin on the recoveries ($N = 3$, pH = 2, eluent: 4 mol L^{-1} NH_3).

the volume of the digested sample was made up to 50.0 mL with distilled water. The blank solutions were prepared in the same way as the real sample, but omitting the sample. The preconcentration procedure given above was applied to the samples.

3. Results and discussion

3.1. Effects of pH

In the solid phase extraction studies, pH is the first important factor for the quantitative recoveries of analytes [23–29]. The influences of pH of the working media on the recoveries of both Cr(III) and Cr(VI) on Dowex M 4195 chelating resin were investigated in the pH range of 2–8 (Fig. 1) by using model solutions that were prepared according to Section 2.3. Chromium(VI) was quantitatively recovered at the pH range of 2.0–5.0. The recovery values for chromium(III) were below 10% all the investigated pHs. The separation and speciation of chromium(III) and chromium(VI) are possible at pH range of 2.0–5.0. In order to speciation of Cr(III) and Cr(VI), pH 2 was selected for further studies by using phosphate buffer.

3.2. Eluent

The effects of some eluents on the recoveries of Cr(VI) from Dowex M 4195 column were also investigated at pH 2. The results are given in Table 1. Cr(VI) was quantitatively recovered only by using 8 mL of 4 mol L^{-1} NH_3.

Table 1
Effects of various eluents on the recoveries of Cr(VI) ($N = 3$)

Eluent type	Recovery (%)
1 mol L^{-1} HCl	30 ± 2[a]
2 mol L^{-1} HCl	40 ± 2
2 mol L^{-1} NH_3	75 ± 3
4 mol L^{-1} NH_3	98 ± 3

[a] Mean ± S.D.

3.3. Flow rates of sample and eluent

The influences of the flow rate of the sample and eluent solutions on the recoveries of Cr(VI) was examined in the range of 1.0–10.0 mL min^{-1} under optimal conditions. The flow rate of the sample and eluent solutions had no obvious effect on the quantitative recoveries of chromium(VI) at the range of 1.0–5.0 mL min^{-1}. Five millilitres per minute was chosen as the flow rate of the sample and eluent solutions in further works.

3.4. Amount of resin

The influences of the amounts of chelating resin on the adsorption of Cr(VI) were investigated at 5.0 mL min^{-1} flow rates of sample and eluent solutions at pH 2. The results were given in Fig. 2. The recovery values for analyte ions were found quantitative in the resin amounts of 500–700 mg. In all further studies, the short glass column was filled with 500 mg of chelating resin. If the amount of resin is more than 700 mg, the retained analytes cannot be eluted completely with 8 mL of 4 mol L^{-1} NH_3.

3.5. Sample volume

In order to study with high sample volumes, the effect of the sample volume on the recoveries of the analyte ions was also investigated in the sample volume range of 25–500 mL by using model solutions containing 20 μg of chromium(VI). The results are depicted in Fig. 3. Chromium(VI) was recovered quantitatively in the range of 25–250 mL. The preconcentration factor was 31, when the final volume was 8 mL.

3.6. Effect of divers ions

The effect of foreign ions which interfere with the determination of analytes by the presented method or/and often accompany them was examined with the optimized conditions to assess the possible applications of the procedure. Various salts and metal ions were added individually to a solution containing Cr(VI) and

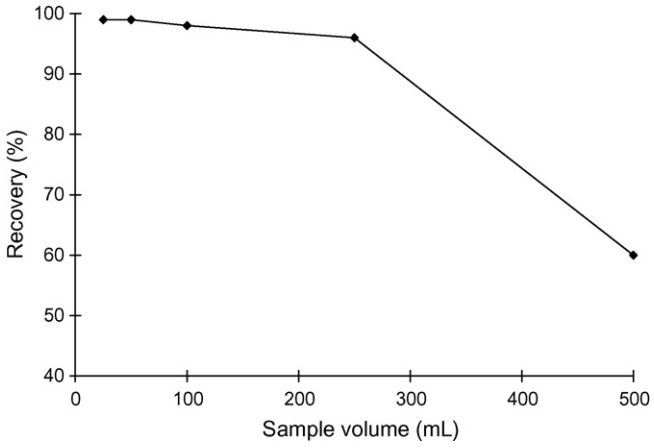

Fig. 3. Influences of sample volume on the recoveries of Cr(VI) ($N = 3$, pH = 2, eluent: 4 mol L^{-1} NH_3).

Table 2
Influences of some foreign ions on the recoveries of Cr(VI) ($N = 3$)

Ion	Added as	Concentration (mg L^{-1})	Recovery (%)
Na^+	NaCl	20,000	96 ± 2[a]
K^+	KCl	5,000	96 ± 2
Ca^{2+}	$CaCl_2$	2,000	95 ± 3
Mg^{2+}	$MgCl_2$	2,000	95 ± 3
Cl^-	NaCl	25,000	95 ± 3
F^-	NaF	1,000	97 ± 2
NO_3^-	KNO_3	2,000	95 ± 2
SO_4^{2-}	Na_2SO_4	3,000	97 ± 2
PO_4^{3-}	Na_3PO_4	3,000	98 ± 3
Mn^{2+}	$MnSO_4$	50	97 ± 2
Fe^{3+}	$FeCl_3$	50	95 ± 2
Cu^{2+}	$CuSO_4$	50	95 ± 3
Pb^{2+}	$Pb(NO_3)_2$	50	96 ± 2
Zn^{2+}	$ZnSO_4$	50	96 ± 3
Cd^{2+}	$Cd(NO_3)_2$	50	97 ± 3
Ni^{2+}	$NiSO_4$	50	98 ± 2
Co^{2+}	$CoSO_4$	50	95 ± 2
Cr^{3+}	$Cr(NO_3)_3$	500	98 ± 2

[a] Mean ± S.D.

the test procedure given in Section 2 was applied. The recoveries of analytes were higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte ions by the combination of presented procedure and the flame atomic absorption spectrometric determination methods. The results are summarized in Table 2. As it is seen, large numbers of ions used have no considerable effect on the determination of analyte ions.

3.7. Capacity of the resin

For this purpose batch technique was used. 0.1 g Dowex M 4195 was added 50 mL of solution containing 1.0 mg of Cr(VI) at pH 2.0. After shaking for 30 min, the mixture was filtered to study the adsorption capacity of the resin. Ten millilitres of the supernatant solution was diluted to 100 mL and determined by flame atomic absorption spectrometry. The capacity of Dowex M 4195 for Cr(VI) was 29.7 mg g^{-1}.

3.8. Limit of detection and qualification

The limit of detection (LOD) and limit of qualification (LOQ) of the present work were calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The limit of detection for chromium(VI) based on three times the standard deviations of the blank ($k = 3$, $N = 11$) was 1.94 μg L^{-1}. Limit of qualification (LOQ) value was found as 6.47 μg L^{-1}.

3.9. Determination of total chromium

In order to determination of total chromium by the presented solid phase extraction method, model solutions that contain different amounts Cr(VI) and Cr(III) (Table 3) were prepared. Then Cr(III) ions in the model solutions were oxidized to Cr(VI) by using H_2O_2 in basic media. The pH of the basic solution was adjusted to pH 2.0. Then the procedure given in Section 2 was applied to these solutions. The results are given in Table 3. The results show that the proposed method could be applied for the determination of total chromium.

3.10. Applications of the presented procedure

The presented speciation procedure was applied to the speciation of chromium in a tap water, river water and electroplating water. Various amounts of chromium species were also spiked to these samples. Then the procedures given in Section 2 were applied. The results were given in Table 4. A good agreement was obtained between the added and measured analyte amounts. These results confirmed the validity of the proposed method.

The method was applied to NIST SRM 2711 Montana soil and GBW 07603 Bush branched and leaves certified reference materials; sediment from Green river from Tokat and black tea for total chromium. The results were given in Table 5. The results were in good agreement with the certified values for chromium.

Table 3
Total chromium determinations in spiked test solutions (volume: 100 mL, $N = 4$)

Added (μg)		Found (μg)			Recovery (%)[a]			Relative error (%)		R.S.D. (%)	
Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
0	30	–	29.1 ± 0.8	29.1 ± 0.8	–	97 ± 1	97 ± 2	–	−3.0	–	2.7
10	20	9.9 ± 0.4	19.5 ± 0.7	29.4 ± 0.7	99 ± 2	98 ± 2	98 ± 2	−1.0	−2.5	4.0	3.6
20	10	19.2 ± 0.5	9.8 ± 0.3	29.0 ± 0.6	96 ± 3	98 ± 2	97 ± 3	−4.0	−2.0	2.6	3.1
30	0	28.9 ± 0.9	–	28.9 ± 0.9	96 ± 2	–	96 ± 2	−3.7	–	3.1	–

[a] Mean ± S.D.

Table 4
Speciation of Cr(III) and Cr(VI) and total chromium in some natural and waste water samples[a] (sample volume: 100 mL, $N = 4$)

Samples	Added (μg)		Found (μg)			Recovery (%)			Relative error (%)		R.S.D. (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tap water	–	–	1.2 ± 0.1	BDL	1.2 ± 0.1	–	–	–	–	–	8.3	–
	5.0	5.0	6.1 ± 0.3	4.9 ± 0.2	11.0 ± 0.5	98 ± 2	98 ± 2	98 ± 2	−1.6	−2.0	4.9	4.1
	10.0	10.0	10.9 ± 0.8	9.8 ± 0.7	20.7 ± 0.7	97 ± 2	98 ± 2	98 ± 2	−2.7	−2.0	7.3	7.1
River water	–	–	6.9 ± 0.3	2.2 ± 0.1	9.1 ± 0.4	–	–	–	–	–	4.3	4.5
	5.0	5.0	11.4 ± 0.4	6.9 ± 0.2	18.3 ± 0.5	96 ± 1	96 ± 1	96 ± 1	−4.2	−4.2	3.5	2.9
	10.0	10.0	16.2 ± 0.7	11.8 ± 0.8	28.0 ± 1.1	96 ± 2	97 ± 2	96 ± 2	−4.1	−3.3	4.3	6.8
Electro plating water	–	–	45.1 ± 1.7	10.3 ± 0.5	55.4 ± 2.1	–	–	–	–	–	3.8	4.9
	10.0	10.0	53.4 ± 2.5	19.8 ± 1.1	73.2 ± 2.9	97 ± 2	98 ± 2	97 ± 2	−3.1	−2.5	4.7	5.6
	30.0	30.0	72.6 ± 3.1	38.9 ± 1.5	111.5 ± 5.2	97 ± 2	97 ± 2	97 ± 2	−3.3	−3.5	4.3	3.9

[a] Mean ± S.D., BDL: below detection limit.

Table 5
The level of total chromium in certified reference materials and some samples after application of the presented procedure ($N = 4$)

Reference material	Certified value	Our value	Relative error (%)
NIST SRM 2711 Montana soil (μg g^{-1})	(47)[a]	45.5 ± 1.5	−3.2
GBW 07603 Bush branched and leaves (μg g^{-1})	2.6	2.5 ± 0.2	−3.8
Sediment from Green river from Tokat (μg g^{-1})	–	15.2 ± 1.1	–
Black tea (μg g^{-1})	–	1.7 ± 0.1	–

[a] The value in the parenthesis is not certified. Mean expressed as 95% tolerance limit.

4. Conclusion

The procedure presented for Cr(III) and Cr(VI) is simple, facile and economic for their speciation and preconcentration. Dowex M 4195 resin can be used all throughout the works without any loss in recovery values. The procedure presented is comparable for the procedure in the literatures [7,8,25–27] with quantitative recovery values and lower detection limit for chromium speciation.

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