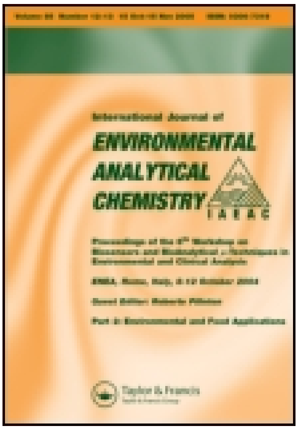

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Speciation, separation and enrichment of Cr(III) and Cr(VI) in environmental samples by ion-pair solvent extraction using a β-diketone ligand

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Speciation, separation and enrichment of Cr(III) and Cr(VI) in environmental samples by ion-pair solvent extraction using a *β*-diketone ligand

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A simple speciation, separation and enrichment method has been developed for the determination of Cr(III) and Cr(VI) ions in different samples by ion-pair solvent extraction with a β-diketone ligand, 2-(4-methoxybenzoyl)-N'-benzylidene-3-(4-methoxyphenyl)-3-oxo-N-phenyl-propono hydrazide (MBMP). Cr(III) was separated from Cr(VI) as Cr(III)-(MBMP)-perchlorate ternary ion-pair complex. The influences of various analytical parameters including pH, amount of reagent, shaking time, sample volume and ionic strength on the recovery of Cr(III) and/or Cr(VI) were investigated. Total chromium was obtained after reducing Cr(VI) to Cr(III) with $NH_2OH \cdot HCl$. Recoveries were found to be higher than 95% and the relative standard deviation (RSD) was less than 2%. The method detection limit based on 3σ criterion for Cr(III) was found to be $0.32\,\mu g\,L^{-1}$. The formed ternary ion-pair complex, Cr(III) : MBMP : $2ClO_4$, has a molar ratio of 1 : 1 : 2. The developed method has been applied successfully to the speciation of chromium in various natural water, soil, sediment and hair samples with satisfactory results.

Keywords: speciation; chromium(III/VI); ion-pair; solvent extraction; atomic absorption spectrometry

1. Introduction

Chemical speciation is one of the most interesting areas of research in the field of environmental science, toxicology, nutritional sciences, environmental and occupational medicine and analytical sciences, since the toxicity and reactivity of an element depends on its chemical form [1,2]. Speciation analysis of trace heavy metals yields information on the individual concentrations of the various chemical forms of that element in environmental samples, and also concerns their presence in various oxidation states, in different protonated and polymerised forms, in complexes with various ligands as well as homogeneous and heterogeneous association with constituents of natural samples [3,4].

Chromium is used in various fields of technology [5]. For example, it is also found in wastewater and airborne particulate matter from industries, which use Cr for metallurgical purposes in the production of alloys and stainless steel and so on [6–8]. Its two primary oxidation states in natural waters are Cr(III) and Cr(VI) and they differ from each other in their biological, geochemical, and toxicological properties [9–11]. Namely, Cr(III) is

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considered to be an essential trace element, since it can coordinate several amino-acids ligands in a human body [12,13]. On the other hand, Cr(VI) diffuses as CrO_4^{2-} or $HCrO_4^-$ through cell membranes and oxidise biological molecules, causing toxic results, such as chronic ulcers and corrosive action in nasal septum, in the body [14,15]. These facts show that speciation analysis of Cr, as well as its determination, is very important for its biological and environmental evaluations.

Therefore, it is necessary to control the level of Cr(VI) in natural and drinking water, where typical concentrations of total chromium are in the range 0.1–0.5 $\mu g\,L^{-1}$ [11,12,16,17].

The high separation efficiency, the broad range of experimental conditions that can be used, the simplicity and the low-cost make solvent extraction a good choice for determination of chromium speciation [18]. Solvent extraction prior to the instrumental analysis of trace metal provides a method of improving the sensitivity and reducing the interference from the matrix [19,20]. Ion-pair recognition of cationic and anionic guest species by bifunctional receptors is a topic in molecular recognition chemistry [21]. In ion-pair extractive separation of metal cations using a complexation reagent and a counter anion, use of a higher selective complexation reagent is one of the most important factors to realise their mutual separation [22–26].

In this study, we evaluated a method which can be employed for the determination of Cr(III) and also for preconcentration and speciation of Cr(III) and Cr(VI). Here, the MBMP reagent (see Figure 1) was used as an extractant for the ion-pair extraction of Cr(III) into MIBK. After these evaluations, the proposed method was applied for the determination and/or speciation of Cr(III) and Cr(VI) in natural waters, soil, sediment and hair samples, giving satisfactory results. To the best of our knowledge, the proposed solvent extraction of Cr(III) with the MBMP reagent has not been reported to date.

2. Experimental

2.1 *Instruments*

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Norwalk, CT, USA) was used for determining the concentration of Cr(III) in aqueous phase after back-extraction. Atomic absorption measurements were carried out in an air/acetylene flame and without any background correction. The instrument settings were made according to manufacturer's instructions. Absorbance measurements were made using a Hitachi 150-20 model UV-vis spectrophotometer (Hitachi, Tokyo, Japan) with 1.00 cm quartz cells. The Fourier Transform Infrared (FTIR) spectra was recorded on a Jasco FTIR 460 plus spectrophotometer (Jasco Co., Tokyo, Japan) using KBr pellet. Elemental analysis was

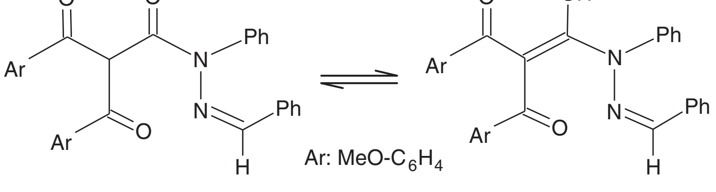

Figure 1. Keto-enol tautomerism of the MBMP reagent.

performed on a Carlo Erba CHNS-O EA 1108 apparatus (Carlo Erba Instruments, Milan, Italy). A Buchi 510 melting point apparatus (Büchi, Flawil, Switzerland) was used. A pH-meter with a glass-combined electrode, Nel pH 900 (Nel pH 900, Ingold-Nedherland), was employed for measuring pH values.

2.2 *Synthesis of the MBMP reagent*

The MBMP reagent was synthesised according to the literature [27]. Elemental analysis results for the reagent, $C_{31}H_{26}N_2O_5$, were in good agreement to each other; i.e. calculated: $C = 73.51$, $H = 5.13$, $N = 5.53\%$, and found: $C = 73.29$, $H = 5.29$, $N = 5.63\%$. The synthesised compound was characterised by melting point, FT-IR and elemental analyses. The characterisation results achieved were in agreement with the published information [27].

2.3 *Reagents and standard solutions*

All chemicals were of analytical reagent grade and obtained from Merck (Darmstadt, Germany). Cr(III) and Cr(VI) stock solutions ($1000\,mg\,L^{-1}$) were prepared from $Cr(NO_3)_3 \cdot 9H_2O$ and K_2CrO_4. From these solutions, dilute working solutions were prepared on a daily basis. The MBMP solution (0.08%, w/v) was prepared daily by dissolving the required amounts of the reagent in methyl isobutyl ketone (MIBK) immediately before use. The density of MIBK is $0.8\,g\,mL^{-1}$ and it dissolves 1.9 g in 100 mL of water only. $H_2NOH \cdot HCl$ solution (5%, w/v) was prepared in water. NH_3/NH_4Cl buffer ($1\,mol\,L^{-1}$) was prepared by adding an appropriate amount of NH_3 to NH_4Cl solution to obtain a solution of pH 8.0. A solution of sodium perchlorate ($0.01\,mol\,L^{-1}$) was used as the counter ion for the ion-pair extraction. The glassware used was cleaned by soaking overnight in aqueous HNO_3 (1 : 1 v/v) and then rinsed with distilled water several times before use.

2.4 *Recommended extraction procedures*

The method was tested with model solutions before its application to various samples. For the determination of Cr(III), to the model solution of 200 mL containing 4 µg of Cr(III), $0.01\,mol\,L^{-1}$ $NaClO_4$ for constant ionic strength and 8 mL of 0.08% (w/v) MBMP reagent solution were added and the pH was adjusted to the desired value by adding 2 mL of $1\,mol\,L^{-1}$ NH_3/NH_4Cl solution. In all cases, a phase ratio (aqueous/organic) of 25 was used. The solution was then transferred to a separatory funnel. The ion-pair compound was extracted by shaking the mixture for 3 min. The two phases were allowed for 3 min to separate and then the organic phase was transferred into a new separatory funnel and the ion-pair compound was back-extracted from 8 mL of MIBK into 10 mL of $2\,mol\,L^{-1}$ HNO_3 solution while thoroughly shaking. The $2\,mol\,L^{-1}$ HNO_3 extract was evaporated to near dryness on a hot plate. The residue was diluted to 2 mL with $1\,mol\,L^{-1}$ HNO_3. The final solution was analysed for the determination of Cr(III) concentration.

Total chromium was determined as Cr(III) by using the proposed method, after reducing Cr(VI) to Cr(III) by the addition of 10 mL of 5% (w/v) $H_2NOH \cdot HCl$ solution in acidic medium. To adjust the pH of this solution to 1.0, concentrated H_2SO_4 was used [28–30]. The beaker was covered with a watch glass and heated at ~80°C for 30 min to complete the reduction. After cooling, 8 mL of MBMP reagent and $0.01\,mol\,L^{-1}$ $NaClO_4$

solutions were added to the mixture and then pH was adjusted to 8.0. The subsequent procedure applied for this solution was as described just above. The content of Cr(VI) was calculated by difference of the total chromium and Cr(III) concentrations. The results are given in Table 1.

2.5 *Analytical application*

The method was extended for the separation, speciation and determination of Cr(III) in real samples. Tap water, rain water, wastewater, snow water and tannery wastewater samples were collected in prewashed (with anionic liquid detergent, doubly deionised distilled water (Elga LabWater/VWS, UK), dilute HNO_3 and doubly deionised distilled water, respectively) polyethylene bottles. The water samples were filtered through a cellulose membrane filter (Millipore Co., Billerica, MA, USA) of 0.45 μm pore size. The pH of the samples was adjusted to 8.0 with about 2–3 mL of $1\,mol\,L^{-1}$ of NH_3/NH_4Cl buffer solution. Then the preconcentration procedure given above was applied to the samples.

The procedure was also applied for soil, river sediment and hair samples. For this purpose, the samples were dried in an oven at 105°C and homogenised. Then 0.5 g of soil, sediment and/or hair sample was digested with a mixture of 6 mL of HNO_3 (65%, w/w) and 3 mL of H_2O_2 (30%, w/w) in 100 mL of beakers covered with glass watches on a hot plate in a hood. After the evolution of NO_2 fumes had ceased, the mixture was evaporated near to dryness. After the evaporation, 25 mL of distilled water was added and the sample was mixed. The resulting mixture was filtered through a cellulose filter paper. The filtrate was made up to 200 mL with distilled water. The proposed procedure given above was applied to these sample solutions. Blank analyses were carried out in the same way without sample. The final volume was 2 mL.

In order to ascertain the validation of the proposed procedure, the method was put into practice for the analysis of Cr(III) ions in two certified reference materials (LGC6019 River water, Middlesex, UK and RTC-CRM044 Soil, Laramie, WY, USA). The pH of the reference sample (50 mL of LGC6019 River water) was adjusted to 8.0 with 2 mL of $1\,mol\,L^{-1}$ NH_3/NH_4Cl buffer solution after neutralisation with $1\,mol\,L^{-1}$ NaOH. The extraction procedure given above was applied to the sample.

Secondly, 0.1 g of RTC-CRM044 Soil sample was digested with a mixture of 4 mL of HNO_3 (65%) and 2 mL of H_2O_2 (30%) just mentioned above and the other procedures

Table 1. Determination of chromium species in spiked test solutions (sample volume = 200 mL, $n = 5^a$).

Added (μg)		Found (μg)[b]		Recovery (%)	
Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
5.0	–	5.1 ± 0.1	–	102 ± 2	–
5.0	2.5	4.9 ± 0.1	2.5 ± 0.6	98 ± 2	100 ± 2
7.5	–	7.3 ± 0.8	–	97 ± 2	–
7.5	2.5	7.3 ± 0.8	2.5 ± 1.0	97 ± 2	100 ± 3
10.0	–	9.9 ± 0.4	–	99 ± 2	–
10.0	2.5	9.9 ± 0.4	2.5 ± 0.7	99 ± 2	100 ± 3

[a] Number of replicate analyses.
[b] Mean ± standard deviation.

applied were similar to that in the preparation of soil and/or sediment samples. Analyses for blank samples were carried out in the same way without sample.

3. Results and discussion

In order to obtain quantitative recoveries of the Cr(III) ions using the MBMP reagent in the absence of other metal ions, the enrichment/separation procedure was optimised for various analytical parameters such as pH, sample volume, amount of MBMP, shaking time, ionic strength, and matrix effects. The percentage extraction of the metal was calculated using the amounts of metal in the initial and final sample solutions.

3.1 *Characterisation of the ion-pair complex*

The stoichiometry of the developed complex, ion-pair of Cr(III) : MBMP : $2ClO_4$ in MIBK, was determined by the Job's method [31]. The MBMP reagent has a maximum absorbance at 331 nm. Cr(III) : MBMP ternary ion-pair complex is colourless and has a maximum absorbance at 388 nm. The reagent blank does not show any absorbance at this wavelength. The pH of the aqueous phase was 8 and sodium perchlorate concentration was 0.01 mol L^{-1}. The amount of Cr(III) in the organic phase was determined spectrophotometrically at 388 nm. The obtained regression equations relevant to the Job's plot were as follows:

$$\text{Absorbance} = -0.0014 + 0.512 \cdot X_{Cr}\,(R^2 = 0.9996) \tag{1}$$

$$\text{Absorbance} = +0.4764 - 0.462 \cdot X_{Cr}\,(R^2 = 0.9924) \tag{2}$$

where, X_{Cr} is the mol fraction for chromium. After combining Equations (1) and (2), the mol fraction for X_{Cr} is obtained as 0.491 or more approximately ≈0.5. A Job's plot of the absorbance of the complex versus the mole fraction of the Cr(III) gave a graph that indicated the formation of an ion-pair complex having a Cr(III) to the reagent ratio of exactly 1 : 1, which was assumed to be a Cr(III) : MBMP ternary complex.

For determination of the chemical composition, the ion-pair complex was isolated from the organic phase after the evaporation of the solvent. The obtained compound was purified using dry diethyl ether. Then, the produced ternary ion-pair complex was characterised by elemental analysis: Cr(III) : MBMP : $2ClO_4$ required (%); C = 49.22, H = 3.33, N = 3.70, and found (%); C = 49.40, H = 3.55, N = 3.80. In addition, while the melting point of the MBMP reagent was 211°C [26], the same property for Cr(III) : MBMP : $2ClO_4$ ternary ion-pair complex was 296°C.

The IR spectrum of the extracted ion-pair complex shows that the stretching frequency of the carbonyl groups in the MBMP reagent has shifted from 1690, 1674 and 1658 to 1686, 1670 and 1654 cm^{-1}, respectively [31,32]. This indicates that the carbonyl groups are involved in bonding during the complex formation.

3.2 *The pH of the aqueous phase*

The pH is a very important parameter for the extraction studies [33]. Much of the selectivity achieved in these extractions depends on adequate control of pH [34]. The effect of pH of the aqueous phase on the extraction recovery was examined by varying the pH with NH_3/NH_4Cl buffer solution of 200 mL of model solution in which the aqueous-to-organic phase ratio (V_{aq}/V_{org}) was 25. These model solutions always contained 4 µg Cr(III) and 4 µg Cr(VI) species. The results are shown in Figure 2. The influences of pH on the quantitative recoveries of chromium species were studied in the pH range of 1.0–10.0. The recoveries of Cr(III) were quantitative in the pH range of 7.5 – 8.7. Cr(VI) was not recovered at the optimal pH range for Cr(III). These results show that chromium species can be quantitatively separated in the pH range of 7.5–8.7. In all the subsequent studies for the separation/preconcentration of Cr(III), pH 8.0 was used.

3.3 *Amount of the MBMP reagent*

The effect of the amount of the MBMP reagent on the extraction of Cr(III) was investigated. The recovery values increased with the increasing amounts of the reagent. It was observed that 8 mL of 0.08% (w/v) of the MBMP solution was required. The quantitative values were obtained between 7.9×10^{-4} (0.04%) – 3.0×10^{-3} (0.15%) mol L^{-1} MBMP. For this reason, 8 mL of 1.6×10^{-3} M (0.08%) MBMP was used in all the further studies (see Figure 3).

3.4 *Amounts of HNO_3 for back-extraction*

Several aqueous solutions were tested for back-extraction of Cr(III) from the organic phase. From the loaded organic phase, back-extraction of Cr(III) was investigated using HNO_3 and HCl solutions having concentrations from 0.2 to 14.5 and from 0.1 to 12.0 mol L^{-1}, respectively. HCl solutions did not give a satisfactory recovery for the back-extraction of Cr(III) ions. It could be completely back-extracted with 10 mL of 2 mol L^{-1} HNO_3 solution. With the increasing acid concentration in the back-extraction medium, the acid protons may attack toward to the ligand (MBMP) and consequently the Cr(III) ions may be free, i.e. they pass through from the organic phase (MIBK) to the aqueous acidic phase. After the concentration of 3.4 mol L^{-1} HNO_3, the recoveries (%) for

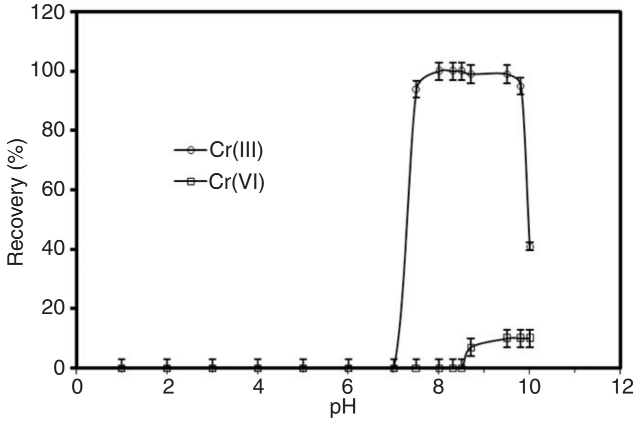

Figure 2. Effect of pH on the recoveries of chromium species ($n = 5$).

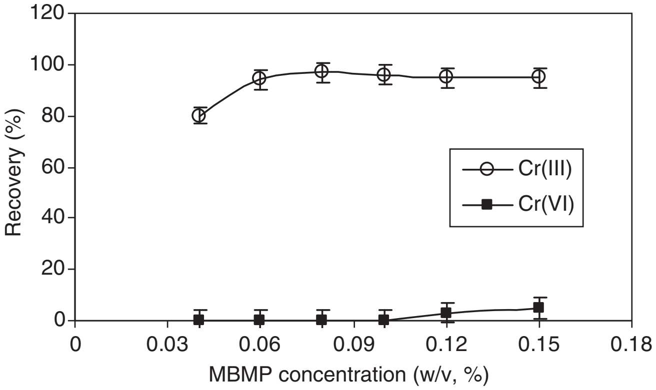

Figure 3. Effect of concentration of the MBMP reagent ($n = 5$).

Table 2. Effect of HNO_3 and Cr(VI) concentrations on the back-extraction of Cr(III) in model solutions (200 mL of model solution, $n = 3^a$).

HNO_3 concentration, mol L^{-1}	Found (μg L^{-1})		Found (μg L^{-1})		Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Total Cr
0.2	4.00	–	3.40 ± 0.03[b]	–	85 ± 1	–
1.1	4.00	–	3.60 ± 0.04	–	90 ± 1	–
2.0	4.00	–	4.00 ± 0.03	–	100 ± 1	–
3.4	4.00	4.00	4.00 ± 0.03	4.4 ± 0.1	100 ± 2	110 ± 1
4.7	4.00	4.00	2.60 ± 0.05	3.0 ± 0.1	65 ± 2	75 ± 1
6.7	4.00	4.00	2.60 ± 0.08	3.0 ± 0.1	65 ± 2	75 ± 1
14.5	4.00	–	2.60 ± 0.10	–	65 ± 1	–

[a] Number of replicate analyses.
[b] Mean ± standard deviation.

Cr(III) were decreased, probably due to the excess H^+ and/or H_3O^+ ions may attack to the organic solvent molecules (MIBK), and therefore they may form protonated solvent ions (MIBK-H^+). As a consequence, the extraction of Cr(III) from the organic phase to the aqueous acidic phase decreases in concentrated acidic media. For this reason, 10 mL of 2 mol L^{-1} HNO_3 solution was used in all the further studies. The results are summarised in Table 2.

3.5 *Shaking time*

The influence of shaking time on the efficiency of the extraction and back-extraction was tested by evaluating shaking times from 0.5 to 10 min. It was found that a 3 min shaking time was required for the quantitative extraction of Cr(III). When shorter shaking times were used, the Cr(III) was not quantitatively extracted. So, when a sample containing the two ions is treated with the present extraction procedure, only Cr(III) will be extracted into the organic phase.

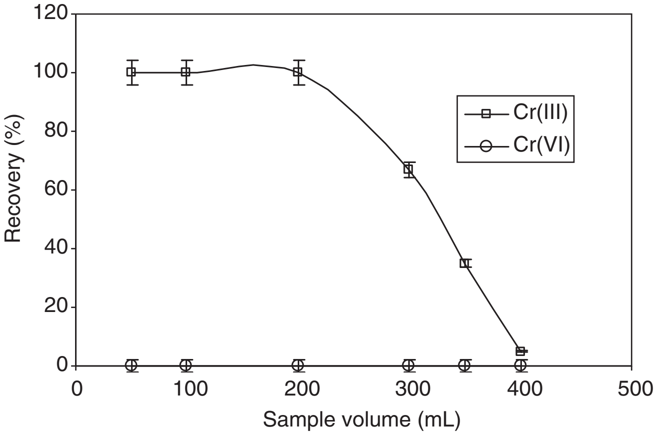

Figure 4. Effect of sample volume ($n = 3$).

3.6 *Pairing anions*

Sample solutions containing 4 μg Cr(III) in the presence of 0.01 mol L^{-1} solutions of KI, NH_4SCN, Na_2SO_4, $NaNO_3$, CH_3COONa and $NaClO_4$ were subjected to the present separation/preconcentration procedure. The results showed that 0.01 mol L^{-1} $NaClO_4$ was the most efficient medium for ion-pair extraction [35]. The recovery obtained with $NaClO_4$ was $98 \pm 1\%$, whereas recoveries (%) for NH_4SCN and KI were 49 and 47, respectively, and were found $\leq 18\%$ for the others.

3.7 *Aqueous phase volume*

In the analysis of water samples using a separation/preconcentration method, a convenient sample volume is an important parameter. For this purpose, the maximum applicable sample volume must be determined. The effect of aqueous phase volume on the extraction of Cr(III) : MBMP : $2ClO_4$ ternary ion-pair complex into MIBK was studied using 50–400 mL aliquots of the aqueous sample solutions. The obtained results indicate that the quantitative preconcentration of Cr(III) was observed up to 200 mL of sample solutions and thus enables to get an enrichment factor of ~100, with the final volume at 2 mL. The results are shown in Figure 4.

3.8 *Choice of diluents*

Various solvents were tested for the dissolution of Cr(III) : MBMP : $2ClO_4$ ternary ion-pair complex. It is essential to select a solvent in which the Cr(III) : MBMP : $2ClO_4$ ternary ion-pair complex is highly soluble. The solid material is insoluble in ordinary organic solvents such as toluene, 1,2-dichloroethane, n-hexane, nitrobenzene, iso-amylalcohol, but is readily soluble in MIBK, chloroform and benzene. MIBK was preferred because of the high solubility of the complex. Solvents containing hydroxyl and ketone functional groups were found to solvate the ion-paired chromium complex effectively [35]. MIBK has been reported as a suitable extraction solvent for chromium complexes [36]. Also, MIBK is considered to be a better solvent for FAAS, producing higher and sharper signals, because of more intensive enhancement of the flame atomisation [35]. $CHCl_3$ and benzene did not give quantitative results for Cr(III) and Cr(VI) ions. By adding different volumes of MIBK to 200 mL of chromium solutions and measuring the amount of the extracted Cr(III), it was found that the extraction with 8 mL of MIBK was found to be optimum extraction volume.

3.9 *Interference of various major and trace ions*

In order to assess the possibility of selective recovery in analytical applications of the recommended speciation/preconcentration procedure, the effect of some foreign ions which interfere in the ion-pair extraction of Cr(III) and/or often accompany analyte ions in various real environmental samples was examined at the optimised conditions. The sample solutions containing 0.02 µg mL^{-1} of Cr(III) in the presence of 10 mg L^{-1} of Fe(III), Fe(II), Cu(II), Zn(II), Pb(II), Ni(II), Co(II), Cd(II), Pd(II), Mn(II), Au(III) and Ag(I) were subjected to extractive preconcentration. No adverse effects originating from these metal ions were observed on the determination of Cr(III). The results have proved that the Cr(III) recoveries were almost quantitative ($\geq$95%) in the presence of 10 mg L^{-1} levels of the possible interfering metal ions. The tolerance limit was defined as the ion concentration causing a relative error higher than ±5% related to the determination of analytes. The separation of the metal ions based on the pH adjustment was assisted by the observation that some of the metals were quantitatively extracted at certain pH values at which others were extracted minimally or not at all. The Pd(II), Fe(II), Au(III) and Ag(I) ions remained in the aqueous phase at all pHs. Fe(III), Ni(II), Pb(II), Co(II), Mn(II), Cd(II), Zn(II), Cr(III) and Cu(II) ions were quantitatively extracted in the pH range of 9.0–10.0. This situation did not affect the performance of the proposed method due to its optimum working pH of 8.0.

On the other hand, a number of common major anions and cations like Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and NO_3^- were tested and found that they did not interfere significantly at concentrations from 1,000 to 50,000 mg L^{-1}. The recoveries for Cr(III) were quantitative ($\geq$95%), except for K^+ (92%) and SO_4^{2-} (90%) (see Table 3). These results show that it was possible to predict the separability of Cr(III) from the other metal ions in the pH range of 7.5–8.7.

3.10 *Reduction of Cr(VI) to Cr(III)*

The effect of reducing agents was studied to obtain rapid conversion of Cr(VI) to Cr(III). In this work, some reducing agents, such as sodium sulfite, ascorbic acid, hydrazine sulfate, sodium iodide, potassium iodide, sodium nitrite and hydroxylammonium chloride were examined [37]. After adding a reducing agent to a sample solution containing Cr(VI), it was heated at ~80°C for 30 min. $NH_2OH \cdot HCl$ resulted in highest effiency for the conversion of Cr(VI) to Cr(III). Hydroxylammonium chloride gave a recovery of 100 ± 2%, whereas sodium sulfite gave only a recovery of 40% and the others $\leq$10%, for 0.02 µg mL^{-1} Cr(VI) in 200 mL of sample solution ($n = 5$).

3.11 *Calibration curve, detection limit, precision and accuracy of the method*

For this purpose, the general procedure was performed successively. The calibration line was linear up to 5 mg L^{-1} of Cr(III) with a correlation coefficient of 0.9993. The detection

Table 3. Influences of various major and trace ions on the recovery of $0.02\,\mu g\,mL^{-1}$ Cr(III) (sample volume = 200 mL, $n = 5^a$).

Ions	Added as	Concentration ($mg\,L^{-1}$)	Recovery of Cr(III) (%)
Na^+	NaCl	20 000	99 ± 2^b
K^+	KCl	2 500	92 ± 1
Ca^{2+}	$CaCl_2$	1 000	95 ± 2
Mg^{2+}	$MgCl_2$	5 000	96 ± 1
Cl^-	NaCl	50 000	94 ± 1
SO_4^{2-}	Na_2SO_4	2 500	90 ± 1
SO_4^{2-}	Na_2SO_4	2 250	96 ± 1
NO_3^-	$NaNO_3$	5 000	98 ± 4
Pb^{2+}	$Pb(NO_3)_2$	10	98 ± 1
Ni^{2+}	$Ni(NO_3)_2$	10	95 ± 2
Cu^{2+}	$Cu(NO_3)_2$	10	96 ± 2
Cd^{2+}	$Cd(NO_3)_2$	10	95 ± 1
Zn^{2+}	$Zn(NO_3)_2$	10	98 ± 3
Mn^{2+}	$Mn(NO_3)_2$	10	97 ± 3
Fe^{3+}	$Fe(NO_3)_3$	10	98 ± 2
Fe^{2+}	$Fe(NO_3)_2$	10	96 ± 2
Ag^+	$AgNO_3$	10	95 ± 2
Au^{3+}	Au	10	96 ± 2
Pd^{2+}	Pd	10	96 ± 2

[a] Number of replicate analyses.
[b] Average ± standard deviation.

limit based on the 3σ criterion was $0.32\,\mu g\,L^{-1}$ for Cr(III) by using 200 mL of blank solutions ($n = 20$). The relative standard deviation (RSD) evaluated by repeated analysis of the standard solutions of Cr(III) with a concentration of $20\,\mu g\,L^{-1}$ was 1.9% ($n = 8$).

In order to estimate the accuracy of the procedure, different amounts of Cr(III) were spiked to aliquots of 200 mL of tap and/or waste water samples and the resulting solutions were submitted to the preconcentration procedure. The results are given in Table 4. A good agreement was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were between 97 and 101%, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed method.

3.12 *Applications of the presented procedure*

The method was applied to LGC6019 River water and RTC-CRM044 Soil standard reference materials for the separation and preconcentration of Cr(III). The results of analyses for LGC6019 River water (certified value: $0.78 \pm 0.20\,\mu g\,L^{-1}$) and RTC-CRM044 Soil standard reference (certified value: $84.1 \pm 5.8\,\mu g\,g^{-1}$) materials were found to be $0.81 \pm 0.10\,\mu g\,L^{-1}$ and $86.4 \pm 1.8\,\mu g\,g^{-1}$, respectively, at 95% confidence level ($n = 3$). The results were in good agreement with the certified values for chromium.

The proposed method was applied to the untreated and treated real samples taken from Asil Leather Plant in Develi, 80 km from Kayseri (Central Turkey), for the speciation

Table 4. Determination of Cr(III) in the water samples ($n = 5^a$).

Samples	Added (μg)	Found (μg)	Recovery (%)
Tap water	0.0	1.70 ± 0.09[b]	–
	1.0	2.70 ± 0.06	100 ± 1
	3.0	4.60 ± 0.05	97 ± 2
	6.0	7.6 ± 0.9	98 ± 1
Wastewater	0.0	18.8 ± 1.2	–
	9.0	27.9 ± 0.6	101 ± 2
	18.0	36.3 ± 0.8	97 ± 3
	36.0	54.5 ± 1.2	99 ± 2

[a] Number of replicate analyses.
[b] Average ± standard deviation.

Table 5. Concentrations of the chromium species in various samples ($n = 5^a$).

	Concentration ($\mu g\,L^{-1}$)		
Sample	Cr(III)	Cr(VI)	Total chromium
Tap water	1.68 ± 0.04[b]	–[c]	1.68 ± 0.04
Wastewater	18.8 ± 0.9	4.4 ± 0.5	23.2 ± 1.0
Rain water	0.70 ± 0.01	–	0.70 ± 0.01
Snow water	1.08 ± 0.03	–	1.08 ± 0.03
			Total chromium ($\mu g\ g^{-1}$)
Hair samples			0.90 ± 0.04
Soil			25.1 ± 1.7
Sediment			29.5 ± 2.8

[a] Number of replicate analyses.
[b] At 95% confidence level (mean ± t·s /√5).
[c] Below the detection limit.

and determination of chromium species. Analyses were performed as soon as possible after sampling (about 2 hours). Firstly, Cr(III) level was determined and then the total amount of chromium was determined after the reduction of Cr(VI) to Cr(III) with $NH_2OH{\cdot}HCl$. The content of Cr(VI) was calculated by the difference between the total chromium and Cr(III) contents. The concentrations of Cr(III) and Cr(VI) species were found to be 6.90 ± 0.06 and 18.4 ± 0.2 $\mu g\,L^{-1}$, respectively, in the influent tannery wastewater samples while their contents in the effluent samples were 0.70 ± 0.03 and 3.6 ± 0.1 $\mu g\,L^{-1}$ in the same sequence ($n = 5$). The relative standard deviations were found to be lower than 1%.

The method was extended for the separation, speciation and determination of Cr(III) in various natural water samples. In order to determine total chromium in the samples the proposed procedure was applied to soil, river sediment and hair samples after the reduction of chromium(VI) to chromium(III) in the sample solutions. The results are given in Table 5. The results show that the proposed method can easily be applied to different aqueous and solid samples for the determination of total chromium.

Table 6. Comparative data from some recent studies involved Cr(III) and Cr(VI) speciation.

Technique	System	Media	Detection system	PF[a]	DL (μg L^{-1})[b]	RSD (%)[c]	Reference
Solvent extraction	Cr(III)-MBMP and reduction of Cr(VI)	MIBK	FAAS	100	0.32	<2	Present work
Solvent extraction	Cr(VI)-DPC and oxidation of Cr(III)	MIBK	Spectrophotometry	20	2.22	<1	[38]
Coprecipitation	Cr(VI)-ethyl xanthate complex and oxidation of Cr(III)	–	FAAS	100	0.5	3.1	[39]
SPE[d]	Cr(III)-1,1,1-trifluoroacetyl-acetone and reduction of Cr(VI)	Polyimide-coated silica fiber	GC[e]	–	2	<7	[40]
SPE	Cr(VI)-diphenylcarbazide	XAD-4	Spectrophotometry	27	6	3.6	[41]
Ion exchange	Cr(III)- ion exchange resin	–	FI-FAAS[f]	–	10	3.63	[42]
SPE	Cr(VI)-ADPC	Dianinon HP-2MG	GF-AAS[g]	–	0.3	<9	[25]
CPE[h]	Cr(III)-1-phenyl-3-methyl-4-benzoylpyrazol-5-one and reduction of Cr(VI)	Triton X-100	ICP-AES[i]	20	0.81	3.2	[43]
Ion-pair extraction	Cr(VI)-1,5-diphenylcarbazide	1-Butanol	Spectrophotometry	3	0.5–1.5	<10%	[44]
	Cr(VI)-tetrabutylammonium	4-Methyl-2-pentanone	ET-AAS		0.2	<30%	
Ion-pair extraction	Cr(VI)-tribenzylamine	Toluene	Spectrophotometry	6	0.08	4.5	[45]

[a] PF: Preconcentration factor.
[b] DL: Detection limit.
[c] RSD: Relative standard deviation.
[d] SPE: Solid phase extraction.
[e] GC: Gas chromatography.
[f] FI-FAAS: Flow injection – flame atomic absorption spectrometry.
[g] GF-AAS: Graphite furnace – atomic absorption spectrometry.
[h] CPE: Cloud point extraction.
[i] ICP-AES: Inductively coupled plasma – atomic emission spectrometry.

4. Conclusions

The results of this study show that the ion-pair extraction procedure results in good separation of Cr(III) and Cr(VI). In principle, by using the MBMP reagent in combination with perchlorate in a slightly basic media (pH 8.0), we demonstrated that the proposed method has extraction capability and efficiency to remove and separate Cr(III) from a mixture containing Cr(VI). The speciation of Cr(III), Cr(VI) and total chromium in the natural waters, soil, sediment, hair and certified reference material were successfully performed in the present study. The method is suitable for speciation measurement without separation of Cr(III) from Cr(VI). The MBMP reagent was used for the first time in this study for the speciation, preconcentration and determination of chromium (III, VI) species. Comparative data from some recent studies on Cr(III) and Cr(VI) speciation are given in Table 6. The procedure presented here was comparable with the procedures given in the literature [25,38–45] with quantitative recovery values and lower detection limit for chromium.

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