Separation of Cr(III) and Cr(VI) in river and reservoir water with 8-hydroxyquinoline immobilized polyacrylonitrile fiber for determination by inductively coupled plasma mass spectrometry

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Abstract

A rapid and simple method has been developed for the separation of chromium (III) and Cr(VI) species in river and reservoir water. Chromium (III) can be chelated with 8-hydroxyquinoline immobilized polyacrylonitrile (PAN) fiber, whereas Cr(VI) cannot. Chelated Cr(III) can be eluted with $2 \text{ mol l}^{-1} \text{ HCl}$ – $0.1 \text{ mol l}^{-1} \text{ HNO}_3$. Cr(VI) in the filtrate and Cr(III) in the eluant were determined by inductively coupled plasma mass spectrometry. The effect of pH, sample flow rate, eluant type and its volume on the concentration effectiveness of Cr(III) was investigated. The recommended method has been applied for the separation and determination of Cr(III) and Cr(VI) in river and reservoir water. The results indicated that the recovery of each individual Cr species ranged from 96 to 107% and the R.S.D. were found to be $< 10\%$ at the level of ng ml^{-1} . The effect of HNO_3 added in the sampling procedure was also evaluated. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 8-Hydroxyquinoline immobilized polyacrylonitrile fiber; Chromium(III); Chromium(VI); Inductively coupled plasma mass spectrometry; River and reservoir water

1. Introduction

With wide application, more and more chromium enters the natural water through the effluents from the electroplating, tanning and dye-

ing industry [1]. In solution, Cr exists in the oxidation states +3 and +6. Speciation of trace amount of Cr(III) and Cr(VI) ions in river water is of importance because of their different bioavailability and toxicity. Cr(III) is considered as an essential element in mammals. It can maintain the metabolism of glucose, lipid and protein [2]. Whereas, Cr(VI) is reported to be toxic to the biological system and can easily permeate biological membrane [3].

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In order to determine the low levels of the individual Cr species, speciation separation are always required. Due to the lack of sufficient sensitivity of the determination techniques available, many investigations focus not only on the separation, but also on the preconcentration goal. Because of its excellent sensitivity, precision and accuracy, inductively coupled plasma mass spectrometry (ICP-MS) has occupied an invaluable position in the modern analytical laboratory. It is also ideally suitable for speciation analysis as a detector. The normal concentrations of chromium in natural water are in the range of $0.3\text{--}6\text{ g l}^{-1}$ [4]. For somewhat polluted water, it is one or two times higher than that in natural waters, which is also higher than the detection limit of ICP-MS. Therefore, only a separation procedure is required in the sample pretreatment processes in order to determine individual Cr species.

Traditionally, chromium species were separated and enriched by coprecipitation [5,6], liquid–liquid [7,8] and liquid–solid extraction [9–12] methods. It is recognized that 8-hydroxyquinoline is a well-characterized chelating organic ligand which can form covalent compounds with over 60 metal ions under controlled pH conditions. It is especially suitable for complex bivalent and trivalent ions [13]. Beceiro-Gonzalez et al. [3] used 8-hydroxyquinoline in methyl alcohol to chelate Cr(III) and then extracted the chelates with isobutyl methyl ketone. The total chromium was then determined by electrothermal atomic absorption spectrometry (ETAAS) and Cr(VI) was obtained by the difference between the total and Cr(III). Isshiki et al. [14] selectively collected Cr(III) using a column packed with macroporous polystyrene-divinylbenzene resin after complexation with quinolin-8-ol. Cr(VI) was collected by a similar method after reducing it to Cr(III) with hydroxylamine. Paleologos et al. [15] used 8-hydroxyquinoline in a micellar medium to form a hydrophobic complex with Cr(III) and subsequently trapped the complex in the surfactant micelles and separated it from the aqueous phase before being injected to the flow-injection analysis. Cr(VI) was determined based on its reduction to Cr(III) by sulfite, which subsequently reacted with 8-hydroxyquinoline in a similar manner. All

these methods introduced additional laborious and time-consuming sample manipulation steps with the associated well-known sources of errors. Milosavljevic et al. [16] reported the on-line flow-injection preconcentration of Cr(III) on a column packed with quinolin-8 ol immobilized on porous glass. The pH values of the samples should be adjusted to 10, however under this pH condition the precipitation of Cr(III) may occur. By these methods, 8-hydroxyquinoline is well demonstrated as a characteristic organic ligand which can complex Cr(III) selectively.

In our previous work, 8-hydroxyquinoline was immobilized on polyacrylonitrile (PAN) hollow fiber membrane and employed to preconcentrate trace elements in sea water successfully [17,18]. However, due to its brittleness, the modified hollow fiber membrane is difficult to execute and maintain. In this study, glass column packed with 8-hydroxyquinoline immobilized PAN fiber was applied for the separation of Cr(III) from river and reservoir water. Then, the chelated Cr(III) was eluted with $2\text{ mol l}^{-1}\text{ HCl}$ – $0.1\text{ mol l}^{-1}\text{ HNO}_3$. Total Cr in the sample, Cr(III) in the eluant and Cr(VI) in the filtration were determined by ICP-MS, separately.

2. Experimental

2.1. Instrument

A Plasma-Quad 3 (VG Elemental, Winsford, UK) inductively coupled plasma-mass spectrometer was used for the determination of Cr. The optimum instrumental operating parameters are given in Table 1.

2.2. Reagent and solution

The stock solutions of Cr(III) and Cr(VI), 1000 g ml^{-1} , were prepared by dissolving appropriate amounts of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ (Specpure, Johnson Matthey Chemicals Ltd.) in 0.1 mol l^{-1} nitric acid, respectively. Standard solutions of 10, 50 and 100 ng ml^{-1} were prepared daily before use by serial dilution with dilute HNO_3 from the stock solution. The final acid concentration of all

standard solutions was fixed at $0.1 \text{ mol l}^{-1} \text{ HNO}_3$.

All other reagents were of analytical grade or better. High purity water ($18 \text{ M}\Omega \text{ cm}^{-1}$) was prepared by double distillation of deionized water in a fused quartz still (Westdeutsche Quarzschmelze, Geesthacht, Germany). Nitric acid was purified by sub-boiling distillation in a quartz still using ultrapure grade HNO_3 as feed. All other acids used were of ultrapure grade (Beijing Chemicals, People's Republic of China). Indium was added as an internal standard at the level of $10 \mu\text{g l}^{-1}$ in final solution to monitor matrix effects and signal drift.

Polyacrylonitrile fiber was obtained from Beijing Chemical Factory and rinsed with nitric acid (1 + 1), hydrochloric acid (1 + 1) and double distilled deionized water sequentially before use.

Prior to use, all beakers, funnels, calibrated flasks and other glassware were cleaned sequentially with tap water, neutral detergent, tap water, then soaked in nitric acid (1 + 1) for 48 h and cleaned with double deionized distilled water before use.

2.3. Immobilization procedure

The details of the immobilization procedure have been described elsewhere [17], where PAN

hollow fiber membrane was replaced by PAN fiber. The color of 8-hydroxyquinoline immobilized PAN fiber is yellow-orange.

2.4. Fiber capacity

The chelating capacity of 8-hydroxyquinoline immobilized PAN fiber was determined by batch technique for Cr(III) and Cr(VI). Fiber ($\approx 100 \text{ mg}$) was equilibrated with Cr(III) and Cr(VI) separately, by shaking for 24 h at pH 6 in an excess of metal ion solutions (10 ml , 50 g ml^{-1}). The fiber was then isolated from the solution by filtration and the concentrations of the metal ion that remained in the solutions were determined by ICP-MS.

2.5. Packing of columns

Columns were packed by placing a small glass wool plug treated with 1% HNO_3 at the bottom end of a glass column (i.d. 4 mm, 50 mm high). The column was then drained and rinsed several times with double deionized distilled water. Fiber (100 mg) suspended in water was then slurry-packed into the column. Another small glass wool plug was inserted on the top of the fiber bed. The column was rinsed first with 100 ml of distilled water, then with 100 ml of $2 \text{ mol l}^{-1} \text{ HCl}$ – $0.1 \text{ mol l}^{-1} \text{ HNO}_3$ and finally with double deionized distilled water until the pH of the eluant was neutral.

2.6. Sampling of water

The polyethylene bottles (10 l) used for sampling river and reservoir water were precleaned with detergent, double deionized distilled water, dilute HNO_3 and double deionized distilled water, successively. River and reservoir water samples were taken at a depth of 1 m at six locations in April, 2001. The sample localities were situated at Yong-ding River and Guanting Reservoir, Beijing, People's Republic of China. High-purity HNO_3 (10 ml) was added to keep the final acidity of the water at about pH 2 after sampling. In order to make a comparison, another pre-cleaned polyethylene bottle was applied with no HNO_3

Table 1
ICP-MS operating conditions

<i>ICP system</i>	
Forward power	1350 W
Reflected power	<5 W
Coolant argon flow rate	14 l min^{-1}
Auxiliary argon flow rate	0.9 l min^{-1}
Nebulizer argon flow rate	0.8 l min^{-1}
Sample uptake rate	1.0 ml min^{-1}
Sampling depth	15 mm
<i>Mass spectrometer</i>	
Sampler (nickel) orifice	1.0 mm
Skimmer (nickel) orifice	0.7 mm
Third stage pressure	$1.7 \times 10^{-1} \text{ m Pa}$
Data acquisition	Range-scanning mode
Mass range	m/z 9–210
Total acquisition time	20 s
Cr	52

added. The pH of this sample was ≈ 7 . The samples were filtered through a Millipore cellulose membrane with pore size of 0.45 μm immediately after sampling and stored at 4 $^{\circ}\text{C}$. The non-acidic samples were analyzed immediately after filtration with 0.45 μm membrane.

2.7. Determination of total and individual species of Cr in river and reservoir water

River and reservoir water samples (10 ml) was adjusted to the desired pH 6 using high purity of ammonium hydroxide and nitric acid, then introduced to the column using a peristaltic pump at a flow rate of 0.6 ml min^{-1} . The eluate was collected, acidified with a small amount of HNO_3 and the concentration of Cr(VI) in the elute was determined by ICP-MS. After washing with 10 ml double deionized distilled water, Cr(III) retained in the column was eluted with 5 ml of 2 mol l^{-1} HCl –0.1 mol l^{-1} HNO_3 at a flow rate of 0.5 ml min^{-1} and then determined by ICP-MS. In the meantime, total Cr in water samples was also determined by ICP-MS.

3. Results and discussion

3.1. Fiber capacity

The adsorption capacity of fiber is an important factor because it determines how much fiber is required to quantitatively concentrate the analyte of interest from water. Following the procedure described in Section 2, the capacity of the fiber for Cr(III) was found to be 41.7 $\mu\text{mol g}^{-1}$ at pH 6, while no Cr(VI) was sorbed. Therefore, 8-hydroxyquinoline immobilized PAN fiber can be used to separate Cr(III) from Cr(VI). In the meantime, the capacity of the fiber for Cr(III) is relatively high and preconcentration of Cr(III) is feasible.

3.2. Optimum conditions for the separation of Cr(III) from water

To achieve quantitative recovery of Cr(III) from the column, the experimental parameters of

Fig. 1. Effect of sample pH on concentration efficiency of Cr(III) (sample volume: 10 ml, concentration of Cr(III): 10 $\mu\text{g l}^{-1}$, eluant: 5 ml 2 mol l^{-1} HCl –0.1 mol l^{-1} HNO_3 , $n = 5$).

pH, sample flow rate, eluant type and its volume were carefully optimized. The concentration of Cr(III) in sample solution used for this purpose was 10 $\mu\text{g l}^{-1}$.

3.2.1. Effect of pH on the sorption efficiency

The effect of sample pH on the sorption efficiency was studied. The results are graphically shown in Fig. 1. It is obvious that the optimum acidity condition for the sorption of Cr(III) was in the range of pH 5–8. Therefore, pH 6 was used for the remainder of this study.

3.2.2. Effect of flow rate

The effect of different flow rates of sample solutions on the concentration efficiency of Cr(III) was tested at flow rates from 0.1 to 2 ml min^{-1} under the condition of pH 6 (Fig. 2). It can be seen that the recoveries of Cr(III) were 90% at a flow rate of $< 0.6 \text{ ml min}^{-1}$. Although our previous work recommended a faster exchange reaction of the immobilized PAN hollow fiber membrane for other heavy metal ions [18], it seems that the sorption speed of the immobilized PAN fiber for Cr(III) is relatively slow. In aquatic solution, Cr(III) often forms hydroxy ions, such as $\text{Cr}(\text{OH})_2^{2+}$ and $\text{Cr}(\text{OH})_2^+$ [19], which probably ascribe to a low reaction rate between Cr(III) and organic ligands [20].

Fig. 2. Effect of the sample flow rate on the concentration efficiency of Cr(III) (sample volume: 10 ml, concentration of Cr(III): $10 \mu\text{g l}^{-1}$, eluant: 5 ml $2 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$, $n = 5$).

3.2.3. Effect of eluant type and volume

In our previous work, $1 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$ was used as an eluant [17,18], while, $2 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$ were employed by Landing et al. [21] to elute transition metal ions adsorbed on 8-hydroxyquinoline immobilized on vinyl polymer agglomerate. In this study, the elution efficiencies of 1 and $2 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$ were compared. As shown in Fig. 3, lower recovery was obtained when $1 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$ was used as an eluant. However, when 4 ml or more volume of $2 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$ was applied to elute the

Fig. 3. Elution efficiency of Cr(III) as a function of the eluent type and volumes (sample volume: 10 ml, Cr(III) concentration: 10 g l^{-1} , eluent: $1 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$ (■), $2 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$ (◆)).

adsorbed Cr(III), the recovery was found to be 98–100%. Therefore, 5 ml of $2 \text{ mol l}^{-1} \text{HCl}$ – $0.1 \text{ mol l}^{-1} \text{HNO}_3$ was used in the following experiments.

3.3. Blank and detection limits

The blank value for Cr determination was obtained by performing $0.1 \text{ mol l}^{-1} \text{HNO}_3$ as a sample. The detection limits of the method were calculated based on three times the S.D. of 11 runs of the blank solution. The blank value for Cr was $0.67 \mu\text{g l}^{-1}$ and the detection limit was $0.06 \mu\text{g l}^{-1}$. Compared with the concentration of individual Cr species present in the samples (Table 3), the concentration of all individual Cr species in the real samples are much greater than the detection limits.

3.4. Effect of the HNO_3 added in the sampling procedure

Pavel et al. [8] found that in water solution, Cr(VI) showed the best long-term stability at pH 9, whereas it decreased sharply within 1 day at pH 2. Sperling et al. [20] also reported that the conventional sample conservation technique with nitric acid, which was typically used for trace element determination, should be avoided for the speciation analysis of Cr. However, results obtained by Bergmann and Ludwig [22] showed that the Cr(III) in acidified water samples were stable over 32 days with an experimental error within 10%, and the loss of Cr(VI) was $< 20\%$. In order to examine the effectiveness of HNO_3 addition on Cr speciation analysis, a comparison was made using two water samples with and without HNO_3 addition during sampling stage. The results (Table 2) revealed that no distinct dissimilarity existed between different sampling methods.

3.5. Determination of trace Cr(III) and Cr(VI) in river and reservoir water

Because no certified reference standard water materials were available for individual Cr species, trace species of Cr equal to the same levels of Cr(III) and Cr(VI) present in river water were

Table 2

Effect of HNO₃ added in the sampling procedure on chromium speciation analysis ($\mu\text{g l}^{-1}$)

Sample	With HNO ₃ added		Without HNO ₃ added	
	Cr(III) found	Cr(VI) found	Cr(III) found	Cr(III) found
Zhuwo	4.35 $\pm$ 0.24	1.42 $\pm$ 0.05	4.45 $\pm$ 0.29	1.35 $\pm$ 0.07
Zhaitang	2.58 $\pm$ 0.13	0.81 $\pm$ 0.06	2.47 $\pm$ 0.21	0.73 $\pm$ 0.07
Guihe	4.51 $\pm$ 0.35	1.05 $\pm$ 0.07	4.63 $\pm$ 0.33	1.03 $\pm$ 0.05
Hekou	8.04 $\pm$ 0.72	1.39 $\pm$ 0.07	8.01 $\pm$ 0.56	1.41 $\pm$ 0.06

Seven measurements for each sample.

Table 3

Determination of chromium species in river and reservoir waters ($\mu\text{g l}^{-1}$)

Sample	Cr(III)				Cr(VI)				Total	
	Found	Added	Total found	Recovery %	Found	Added	Total found	Recovery %	Found	Calculated
Zhaitang	2.58	2.50	5.10	101	0.81	1.00	1.88	107	3.44	3.39
Sanjiadian	3.42	3.00	6.56	105	1.19	1.00	2.23	104	4.59	4.61
Zhuwo	4.35	4.00	8.43	102	1.42	1.00	2.51	109	5.43	5.54
Qingshuihe	3.70	3.50	7.15	99	1.23	1.00	2.25	102	4.87	4.93
Luopoling	4.55	4.50	9.21	104	1.00	1.00	2.02	102	5.44	5.55
Yanhecheng	3.31	3.00	6.24	98	2.18	2.00	4.32	107	5.32	5.49
Guihe	4.51	4.50	9.00	100	1.05	1.00	2.10	105	5.56	5.56
Guihedaqiao	3.84	3.50	7.30	99	4.65	4.50	9.12	99	8.55	8.49
Bahaoqiao	4.25	4.00	8.20	99	0.52	0.50	1.05	106	4.89	4.77
1008	4.97	5.00	9.88	98	3.85	3.50	7.20	96	8.45	8.82
Hekou	8.04	8.00	16.00	100	1.39	1.50	2.98	106	9.12	9.43
1003	7.16	7.00	14.30	102	1.67	1.50	3.23	104	8.79	8.83

Seven measurements for each sample, the R.S.D. <10%.

spiked before matrix separation. The determination of individual species of Cr in river and reservoir water and the recovery of spikes are given in Table 3, showing high reliability, validity and sufficiently high recoveries (96–107%) of the method. In the meantime, total amount of Cr(III) and Cr(VI) calculated and determined compared well. Sperling et al. [20] deemed that in the speciation analysis of Cr, many sampling and analytical techniques might disturb the equilibria between the various species in solution, so that the analytical data did not reflect the actual situation in the original sample. The present study demonstrated that Cr(III) was the main species of Cr in river and reservoir water. This is consistent with the report of Yu et al. [9], who found that in three

NWRI certified reference water materials, chromium existed as Cr(III).

4. Conclusion

In this study, a new rapid technique was developed based on the 8-hydroxyquinoline immobilized PAN fiber for Cr(III) and Cr(VI) separation and differential determination. This method has the following advantages: only a single-stage process is required for Cr(III) and Cr(VI) separation and determination, no reduction or oxidation procedure is needed, which minimized the analytical time. Cr(III) can be sorbed at a wide pH-range, therefore no buffer is required for controlling

sample pH, which minimizes the contamination. Therefore, we can expect that the 8-hydroxyquinoline immobilized polyacrylonitrile fiber can be employed in the preconcentration of Cr(III) in a variety of waters.

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