

Chromium Speciation in Contaminated Water Samples Using PTFE Beads Packed Minicolumn and FI-FAAS Determination

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INTRODUCTION

Metal pollutants are non-bio-degradable in nature. Thus, once they enter the environment, the toxicity caused by them mainly depends on the chemical form they exist in. Chromium is one of the common pollutants introduced into water sources as a result of various industrial processes.

The toxicity of chromium depends on its oxidation state. Cr(III) is considered biologically essential to mammals as it is responsible for the glucose, lipid and protein metabolism. Cr(VI) ions are highly toxic because of their high oxidation potential and small size which allows them to penetrate through cell membranes and thus leads to the oxidation of bio-molecules (1). The toxic effects of Cr(VI) are chronic ulcers, dermatitis, lung and skin cancers. The World Health Organization (WHO) has decided the permissible limit for chromium in water to be 0.05 mg L⁻¹ (2).

The development in the industrial sector has amplified the problems associated with environmental pollution. Therefore, remediation of chromium species from industrial effluents has become extremely important. It is due to these two distinct effects that the precise and accurate determination of Cr(III) and Cr(VI), especially at ultra-trace levels, in environmental samples is urgently required.

Speciation is defined as the determination of the individual con-

ABSTRACT

A spectroanalytical method for remediation of chromium species from contaminated water samples based on flow injection hyphenated to a flame atomic absorption spectrometer is proposed. Iminodiacetic acid (IDA) was used as the chelating agent, and the chromium-IDA complex was preconcentrated on the minicolumn filled with polytetrafluoroethylene (PTFE) beads. The chemical and flow variables were optimized. The effect of commonly occurring matrix ions on the recovery of the chromium species was also studied. For a preconcentration time of 120 s, preconcentration factors and detection limits achieved for Cr(III)/Cr(VI) were 68/59, 0.11/0.13 µg L⁻¹, respectively. The relative standard deviation for 5 replicates of measurements for 100 µg L⁻¹ level was 1.2/1.4% for Cr(III)/Cr(VI), respectively. Real water samples collected from industrial sites and the Yamuna river were analyzed and spike recovery tests were performed. The method validation was done by analyzing the chromium concentration in NIST SRM 1640a Trace Elements in Natural Water.

centrations of the various chemical forms of an element that together make up the total concentration of that element in a given matrix (3). Spectrometric techniques are most commonly used for trace Cr determination (4). Flame atomic absorption spectrometry (FAAS) is a popular technique with considerable accuracy and precision. However, in practice for complex matrices, quantification is often very difficult due to the presence of

interfering effects, comprised of spectroscopic and non-spectroscopic interferences. Moreover, in some cases, the concentration of the analyte might be too low to be directly analyzed.

The most effective way to avoid these problems is to perform appropriate sample pretreatment aimed at improving the limits of detection (LODs) by removal of interferences as well as preconcentration of the analyte into a smaller sample volume, thus effectively increasing its concentration (5). In order to bring the analyte concentration into the detection range of the detector, a preconcentration step is required before the final measurement. Solid phase extraction (SPE) is an efficient separation-preconcentration technique for trace metal analysis (6) SPE offers the advantages of flexibility, is economical and, more importantly, is environmentally friendly. Despite these advantages, SPE can be time-consuming, requires large sample or reagent volume, and the risk of contamination and loss of analyte during analysis is common (7).

The combination of flow injection preconcentration using SPE with FAAS determination in an on-line method (FI-SPE-FAAS) has proven to be an effective system for trace element determination in various systems. It provides better sensitivity, effective removal of interfering ions, low cost, and offers high sampling rate (8). The various on-line systems proposed for the determination of chromium include polymeric support (9), alumina (10), biosorbents (11), and nano-materials (12). In recent years, polymer-based systems have gained considerable attention in speciation

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analysis because of the advantages of hydro-phobic character, ease of surface modification, thermal stability, and high surface area (13-15).

In the present study, polytetrafluoroethylene (PTFE) beads have been used as the solid phase extractant for the preconcentration of chromium species. PTFE beads possess properties such as swelling and chemical inertness, low friction coefficient, etc., which makes them appropriate for solid phase extraction studies (16, 17). Iminodiacetic acid (IDA) was used as a chelating agent to complex both Cr(III) and Cr(VI) at a different pH. Studies have reported that IDA can be used as a complexing agent for both Cr(III) and Cr(VI) (18, 19). The optimized method was applied for chromium determination in industrial and river water samples, and spike recovery tests were carried out. The method was validated by analyzing standard reference material (SRM) NIST 1640a Trace Elements in Natural Water (National Institute of Science and Technology, Gaithersburg, MD, USA).

EXPERIMENTAL

Instrumentation

Chromium determination was performed using the AAnalyst™ 400 flame atomic absorption spectrometer (FAAS) (PerkinElmer, Inc. Shelton, CT, USA), equipped with an air-acetylene burner and deuterium background correction. The on-line preconcentration studies were performed by coupling the FIAS 400 flow injection system (PerkinElmer, Inc., USA) fitted with a glass minicolumn of 3 cm x 3 mm (length x i.d.) to the FAAS system. The on-line system was controlled by a personal computer using Winlab32™ (version 6.5.0.0266, PerkinElmer, Inc., USA) application software. Tygon® and PTFE materials were used for all tubing and connection purposes. All pH adjustments were carried out with pH meter Model

LI-614 (ELICO, India). Ultrapure water (Merck Millipore Corporation, USA resistivity 18.2 MΩ·cm) for all studies was obtained from Milli-Q® water purification system.

Reagents and Standard Solutions

The chemicals used were of analytical reagent grade. All working standard solutions were prepared daily by dilution from 1000 mg L⁻¹ Cr(III) and Cr(VI) standard solutions (TraceCERT®, Sigma-Aldrich, USA) using ultrapure water. PTFE beads (Sigma-Aldrich) and Iminodiacetic acid (Thomas Baker) were used as the solid support and chelating agent, respectively. The pH of the solutions was maintained using 0.5 mol L⁻¹ HCl, phosphate buffer (pH 6-8), and trisodium phosphate buffer (pH 12).

Column Packing

The PTFE beads suspended in water were packed into the glass minicolumn by injecting them with a syringe. The ends of the columns were sealed with cotton. Prior to use, the PTFE bead-packed glass minicolumn was rinsed with 2.0 mol L⁻¹ HNO₃, then with ultrapure water.

Flow Injection Preconcentration Procedure for Chromium Determination

The on-line preconcentration of the chromium species using the FI-SPE-FAAS system is controlled by a computer program which involves

separate steps for filling, preconcentration and elution as given in Table I (20). The coupling is an efficient and easy procedure as both systems operate in continuous mode. The sample introduction capillary of the FAAS is connected to the output capillary of the FI system. Thus, the FI preconcentration with FAAS detection improves the nebulization efficiency of FAAS since the flow rate of the reagents can be optimized by flow injection. The first step enables filling of both sample and eluent carrier tubes with their respective solutions. This step is followed by the preconcentration step in which the sample solution is preconcentrated on the minicolumn containing the PTFE beads as shown in Figure 1. In the last step, elution of the retained species with the appropriate eluting agent takes place. The eluent containing the desorbed chromium species is directly sent to the nebulizer of the FAAS system for its detection (21). Peak height of the analytical signal is taken as the absorbance. Prior to all measurements, blank measurements were recorded and saved. Triplicate sets of all readings were taken for all solutions.

Real Water Analysis

The water samples were collected from industrial areas (Anand Parbat, Seelampur and Wazirpur) and the Yamuna River. The water samples were acidified and stored in cleaned polypropy-

TABLE I
Flow Injection Program for Preconcentration of Cr(III) and Cr(VI) Ions Using PTFE Minicolumn and IDA as Complexing Agent

Step	Time (s)	Pump 1	Pump 2	Valve Position	Reading
Prefill	1	+	+	Elute	-
1	10	+	-	Load	-
2	20	-	+	Elute	-
3	50	+	-	Load	-
4	10	+	+	Load	-
5	30	-	+	Elute	+

lene bottles below 4 °C. Before analysis, all solutions were filtered with 0.45 μm pore size filter paper (Merck Millipore Corporation) in order to remove suspended particulate matter if present. The water samples were then analyzed for Cr(III) and Cr(VI) according to the optimized preconcentration procedure, and spike recovery tests with standard Cr(III) and Cr(VI) solutions (TraceCERT®) were performed.

RESULTS AND DISCUSSION

Optimization of Chemical and Flow Variables for Preconcentration of Cr(III) and Cr(VI)

To ensure maximum recovery of the chromium species using the preconcentration system, the influence of both the chemical (effect of sample acidity, concentration of eluting and chelating agent) and flow variables (effect of sample and eluent flow rates) were studied.

Effect of Sample Acidity

Sorption of the analyte is dependent on the acidity of the sample solutions. For this purpose, pH studies were done in the range of 2–10 for Cr(III) and Cr(VI). It was found that maximum sorption for Cr(III) and Cr(VI) took place at pH 3 and 8, respectively (Figure 2a) (18, 22).

Effect of Eluent Concentration

Optimization of eluent concentration is a crucial step as it affects removal of the retained species from the column. The acidic and basic eluents were studied for desorption of the chromium species. It was observed that HNO₃ gave the most stable and highest absorption signals. Thus, the influence of HNO₃ concentration was studied for the effective removal of the sorbed Cr(III) and Cr(VI) species in the range of 0.1–2.0 mol L⁻¹. The results obtained in Figure 2b show that for both Cr(III) and Cr(VI) species, 0.5 mol L⁻¹ HNO₃ solution gave maximum absorbance. Thus, 0.5 mol L⁻¹ HNO₃ was chosen as the eluent for all subsequent studies.

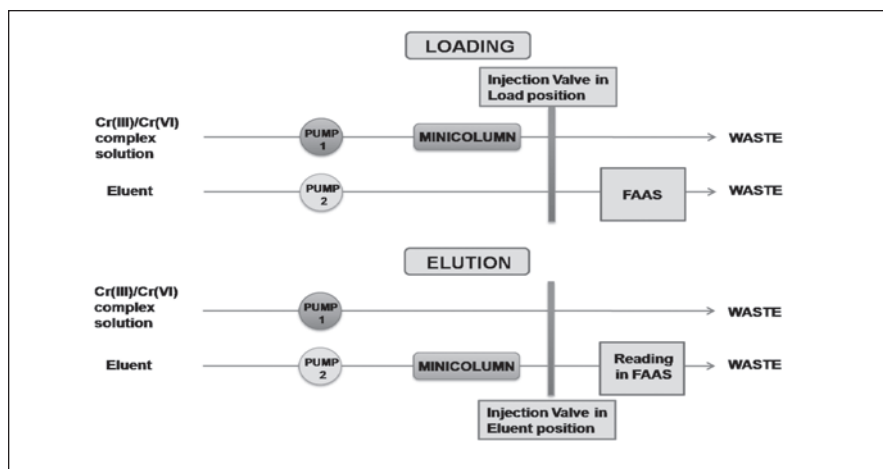


Fig. 1. On-line preconcentration system incorporated with PTFE filled minicolumn for sorption of Cr(III)/Cr(VI) complex.

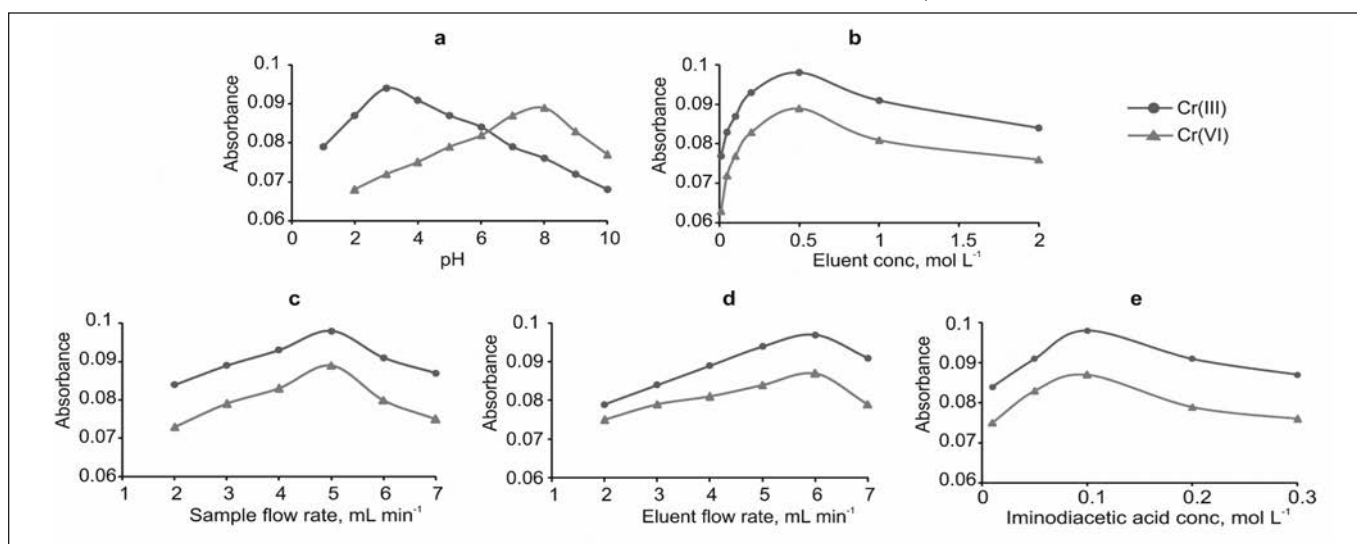


Fig. 2. Optimization of preconcentration procedure of Cr(III) and Cr(VI) using PTFE minicolumn and IDA as complexing agent. (a) influence of pH, (b) influence of eluent concentration, (c) influence of sample flow rate, (d) influence of eluent flow rate, and (e) influence of chelating agent concentration.

Effect of Chelating Agent

Sample solutions of iminodiacetic acid solution containing 50 µg L⁻¹ each of Cr(III) and Cr(VI) were prepared in the concentration range of 0.01– 0.3 mol L⁻¹. It was observed that maximum absorbance was obtained with 0.1 mol L⁻¹ iminodiacetic acid solution (Figure 2e). Thus, for all studies, the Cr(III) and Cr(VI) solutions were prepared in 0.1 mol L⁻¹ iminodiacetic acid solution.

Effect of Eluent and Sample Flow Rates

The contact time between sample/eluent and solid phase extractant is directly related to sample and eluent flow rate. Sample and eluent flow rate studies were done in the range of 2–7 mL min⁻¹. The results showed that the sample and eluent flow rates of 5 mL min⁻¹ and 6 mL min⁻¹ gave maximum absorbance for both Cr(III) and Cr(VI) species (Figures 2c and 2d).

TABLE II
Effect of Interfering Ions on Recovery of Cr(III) and Cr(VI)

Interfering Ion	Tolerance Limit (mg L ⁻¹)	
	Cr(III)	Cr(VI)
NO ₃ ⁻	2100	1600
Na ⁺	1100	850
Br ⁻	900	750
Cl ⁻	900	700
SO ₄ ²⁻	910	990
I ⁻	700	850
K ⁺	700	710
NH ₄ ⁺	530	580
Ca ²⁺	275	300
CH ₃ COO ⁻	260	250
Zn ²⁺	8	4
Al ³⁺	8	3
Cd ²⁺	3	2
Pb ²⁺	1	0.5
Cu ²⁺	1.0	0.5
Mg ²⁺	0.5	0.5

Effect of Interfering Ions

Nitrates, chlorides, sulphates, etc., are some of the most commonly found ions in environmental water samples. If present, these ions can interfere in the preconcentration procedure of chromium species. Thus, the effect of the presence of these ions towards the preconcentration of chromium species according to the optimized system was studied. An ion is considered to be interfering if it deviates the analytical signal by more than ± 5%. Table II lists the tolerance limits of different interfering ions towards Cr(III) and Cr(VI) preconcentration.

Analytical Performance of On-Line Preconcentration System

The analytical performance of the proposed method under optimum conditions was studied and the results are given in Table III. The preconcentration factor was calculated as the ratio of the calibration curve obtained with and without preconcentration. The precision of the method was studied by calculating the relative standard

deviation of five replicates of the measurements of 50 and 100 µg L⁻¹ Cr(III) and Cr(VI) solutions. For seven blank replicates, the limit of detection and limit of quantification were calculated according to the 3σ and 10σ criteria, respectively.

Analysis of Real Water Samples and Method Validation

The proposed method under optimized conditions was applied to real water samples (industrial water and Yamuna river water) for the determination of the Cr(III) and Cr(VI) species. Spike recovery tests were also performed and recoveries greater than 95% were observed for both species. The results are given in Table IV. Method validation was performed by analyzing NIST SRM 1640a Trace Elements in Natural Water. The observed results (40.12 ± 1.50 µg L⁻¹) were in good agreement with the certified values (40.54 ± 0.30 µg L⁻¹) and recovery of 98.9% was achieved.

TABLE III
Analytical Figures of Merit for Cr(III) and Cr(VI) Preconcentration

Parameters	Figures of Merit			
	Cr(III)		Cr(VI)	
Preconcentration Time (s)	60	120	60	120
Sample Consumption (mL)	5	10	5	10
Linear Range (µg L ⁻¹)	0.80 - 120	1.11 - 110	0.93 - 100	1.3 - 90
Limit of Detection (µg L ⁻¹)	0.24	0.11	0.28	0.13
Limit of Quantification (µg L ⁻¹)	0.80	1.1	0.93	0.43
Sample Throughput (h)	30	20	30	20
Preconcentration Factor	33	68	28	59
Correlation Coefficient	0.9992	0.9996	0.9998	0.9997
Regression Equation (6 standards, Cr(III)/mg L ⁻¹) (with preconcentration)	A ₆₀ =2.29[Cr(III)] - 0.00212	A ₁₂₀ =4.74[Cr(III)] - 0.00579	A ₆₀ =1.95[Cr(VI)] - 0.00116	A ₁₂₀ =4.13[Cr(VI)] - 0.00628
Regression Equation (6 standards, Cr(III)/mg L ⁻¹) (without preconcentration)	A=0.07[Cr(III)] - 0.00023		A=0.07[Cr(VI)] + 0.00025	
Precision (% R.S.D.)	1.5, [Cr(III)] = 50 µg L ⁻¹ 1.2, [Cr(III)] = 100 µg L ⁻¹		1.8, [Cr(VI)] = 50 µg L ⁻¹ 1.4, [Cr(VI)] = 100 µg L ⁻¹	

TABLE IV
Analysis of Industrial Water and Yamuna River Water Samples

Sample	Added ($\mu\text{g L}^{-1}$) ^a		Found ($\mu\text{g L}^{-1}$) ^b		Total Cr	Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)		Cr(III)	Cr(VI)
Anand Parbat Industrial Area, Delhi, India	-	-	27.3 ± 1.21	10.5 ± 0.78	37.8 ± 1.60	98.1	101
	20	20	46.4 ± 3.07	30.8 ± 0.66			
Seelampur Industrial Area, Delhi, India	-	-	22.9 ± 2.02	7.07 ± 0.82	30.1 ± 2.40	97.9	98.3
	20	20	42.0 ± 3.22	26.6 ± 2.47			
Wazirpur Industrial Area, Delhi, India	-	-	31.4 ± 1.53	12.8 ± 2.0	44.2 ± 2.48	99.4	97.6
	20	20	51.1 ± 1.56	32.0 ± 0.62			
Yamuna River Water	-	-	36.5 ± 1.68	28.0 ± 1.70	64.5 ± 3.17	98.6	98.7
	20	20	55.7 ± 3.64	47.4 ± 0.82			

^a Spiking with Cr(III) and Cr(VI) solutions traceable to NIST.

^b Confidence Interval 95%.

TABLE V
Comparison of Reported On-Line Methods with Proposed System For Cr(III) Determination

Support	Chelating Agent	Eluent	PT (s)	Sample Volume (mL)	RSD (%)	LOD ($\mu\text{g L}^{-1}$)	PF	Ref. No.
Chitosan-FeC nanoparticles	-	HCl	4000	100	2.5	0.0524	100	(23)
Chloromethylated polystyrene	N,N-bis (naphthylideneimino) diethylenetriamine	HCl	225	10	2.5	0.6	74	(24)
Divinyl benzene	Poly 2-(5-methylisoxazol) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid	HNO ₃	210	5.8	2.3	0.05	48	(25)
MWCNTs	-	HNO ₃	180	6	1.7	1.15	22	(26)
Poly(methacrylic acid)	-	HNO ₃	-	87	1.46	0.84	47.3	(27)
Silica	Al ₂ O ₃ /TiO ₂	HCl	-	20	2.4	0.66	17.6	(28)
Silica gel	Niobium(V) oxide	HNO ₃	120	15	4.6	0.34	23	(29)
Silica gel	Zirconium oxide	HNO ₃	225	15	3.0	1.90	20.8	(30)
PTFE beads	Iminodiacetic acid	HNO ₃	120	10	1.2	0.11	68	<i>This work</i>

PT: preconcentration time; RSD: relative standard deviation; LOD: limit of detection; PF: preconcentration factor.

Comparison of Proposed Method with Reported On-Line Methods

The analytical performance of the proposed method was compared with on-line methods reported in the literature. The reported method has proven to be

better in terms of preconcentration factor, detection limit, reagent consumption, sample throughput and reproducibility. In Tables V and VI a comparison of the method reported with some recent on-line methods for Cr(III) and Cr(VI) preconcentration is given.

CONCLUSION

The hyphenated FI-SPE-FAAS system was successfully applied for the preconcentrative speciation of chromium species. The iminodiacetic acid complex of both Cr(III) and Cr(VI) species was retained on a

TABLE VI
Comparison of Reported On-Line Methods with Proposed System For Cr(VI) Determination

Support	Chelating Agent	Eluent	PT (s)	Sample Volume (mL)	RSD (%)	LOD ($\mu\text{g L}^{-1}$)	PF	Ref. No.
Chloromethylated polystyrene	N,N-bis (naphthylideneimino) diethylenetriamine	Buffer Solution of 25 M NH_4NO_3 and 1.0M NH_3	225	10	2.2	2.5	30	(24)
Dowex 21K	-	HNO_3	17	5.8	4	0.3	30	(25)
Llama Fibres	-		750	25	4.3	0.30	32	(31)
Poly vinyl imidazole	-	HNO_3	-	87	2.0	1.58	8.6	(27)
SBA-15 mesoporous silica	Aminopropyl-triethoxysilane	HNO_3	300	-	2.1	0.2	44	(32)
UVM-7	Amino silane	NaOH	-	100	-	1.2	66.7	(33)
Silica	[3-(2-aminoethyl-amino)propyl]trimethoxysilane	HCl	-	20	2.4	0.27	32.98	(28)
Silica gel	Zirconium phosphate	0.1 M tris (hydroxymethyl) methylamine (THAM)	225	15	2.1	2.3	24.9	(30)
PTFE beads	Iminodiacetic acid	HNO_3	120	10	1.4	0.13	59	<i>This work</i>

PT: preconcentration time; RSD: relative standard deviation; LOD: limit of detection; PF: preconcentration factor

mini-column filled with PTFE beads. The reported system involves no chemical modification and is based on the physical adsorption of the chromium complex with iminodiacetic acid which further eliminates the step of regeneration since at the end of each cycle the beads are free of the chromium complex. The study on effect of interfering ions revealed that the proposed system shows sufficient tolerance towards the commonly occurring interfering ions. As can be seen in Tables V and VI, the method reported has proven to be better than other reported methods in terms of preconcentration factor, sample consumption, sensitivity, and reproducibility. The method validation was performed by analyzing NIST SRM 1640a Trace Elements in Natural Water.

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