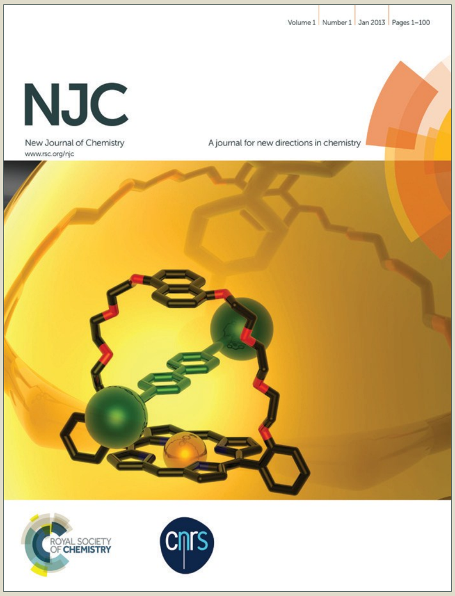
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On-line speciation of chromium using modified chelating resin and determination in industrial water samples by flame atomic absorption spectrometry

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Abstract

A flow injection- flame atomic absorption spectrometry (FI-FAAS) system for speciation of Cr(III)/Cr(VI) based on solid phase extraction (SPE) has been proposed. A newly synthesized resin, Amberlite XAD-16 modified with α-benzoin oxime was used as a solid phase extractor for speciation of chromium. The sorbed Cr(III) on the resin was desorbed with 0.2 mol L^{-1} HNO_3. The influence of various chemical and flow parameters on Cr(III) sorption were investigated. The selectivity of proposed method towards Cr(III) sorption in the presence of interfering ions was also studied. The preconcentration factor and limit of detection for the preconcentration time of 300 s were 76 and 0.14 ng mL^{-1}, respectively. The relative standard deviation was 1.0 % (n = 6). The determination of total chromium was done after reducing Cr(VI) to Cr(III) using hydroxylamine hydrochloride. The concentration of Cr(VI) was then calculated by subtracting Cr(III) concentration from total chromium concentration. The proposed system was applied to industrial water samples and recoveries of spiked samples were > 95%. The accuracy of the proposed method was studied by analyzing standard reference material (SRM 1643e, Trace Elements in Water) supplied by NIST, USA.

Keywords: Flow injection, Chromium, Solid phase extraction, flame atomic absorption spectrometry, Amberlite XAD-16, preconcentration

INTRODUCTION

The toxicological and biochemical properties of an element depend on the chemical form it is present in. In the last few years the presence of chromium in water has gained much attention. Chromium is distinguished by its different oxidation states that exhibit opposite level of toxicity to environment, plants, animals and humans. Cr(III) is considered as an essential micronutrient which plays an important role in glucose and protein metabolism in humans[1]. On the other hand, Cr(VI) is carcinogenic and toxic as it can diffuse as CrO_4^{2-} through cell membrane and can oxidize biological material. The permissible limit for total chromium in water sample given by WHO is 0.05 mg L^{-1}. [2] Due to the importance of Cr(III) for humans and toxic nature of Cr(VI) analytical methods related to the determination and speciation of these species have been significantly developed in last decade So far, many analytical techniques have been used for speciation of chromium species like electro thermal atomic absorption spectrometry (ET-AAS)[3], flame atomic absorption spectrometry[4] (FAAS), inductive coupled plasma-atomic emission spectrometry[5] (ICP-AES), and inductive coupled plasma –mass spectrometry(ICP-MS)[6]. Flame atomic absorption spectrometry is a popular technique with considerable accuracy and precision. In order to bring the analyte concentration into the range of detector a preconcentration step is required before the final measurement. This step is also important to separate the ion of interest from the interfering ions. The determination of chromium species in water samples is governed by several factors such as low concentration of metal ion in sample or loss of analyte ion during sampling. Thus, a preconcentration step such as liquid-liquid extraction[7] coprecipitation[8], electrochemical separation[9], ion exchange[10] and solid-phase extraction[11] is required. However, the disadvantages associated with these methods such as solvent loss, low concentration of analyte ion, prefiltration problem limits the application of most of these techniques.

Solid phase extraction is an efficient separation-preconcentration technique for trace metal analysis[12]. SPE offers advantages like flexibility, economic, more importantly environment friendly. Other then all these advantages, SPE can be time-consuming, large sample or reagent consumption and contamination and loss of analyte during analysis[13]. The combination of flow injection on-line solid phase extraction(SPE) with FAAS has proven to be an effective system for trace element determination in various systems as it provides better sensitivity, effective removal of interfering ions, low cost and offers high sampling rate[14].

Various on-line systems have been proposed for determination of chromium like polystyrene[15], alumina[16], biosorbents[17], nanomaterials[18] etc. In recent years supports based on polymers has found application in speciation analysis because of the advantages like hydrophobic character and high surface area. Chemical modification of polymers with various chelating resins can also be done to ensure selectivity towards certain metal ions. Chelating agents like xylenol orange[19], salicylic acid[20], 8-Hydroxyquinoline[21], dithizone[22] etc have already been chemically loaded on different polymers for speciation of metal ions. The commercially available polymeric supports based on Amberlite XAD series have been chemically modified and used for preconcentration of metals ions[23]. In this work α-Benzoin oxime has been used to preconcentrate Cr(III) ions. It is a spectrophotometric reagent used for the preconcentration of heavy metal ions present in natural waters and other samples. This chelating agent has been used in various preconcentrative systems which include solvent extraction, cloud point extraction and solid phase extraction[24, 25]. Thus**,** the aim of present work is to synthesize α-benzoin oxime functionalized Amberlite XAD-16 (ABO-16) resin as SPE for speciation and determination of chromium in industrial water samples by flow injection-solid phase extraction-FAAS (FI-SPE-FAAS) method.

EXPERIMENTAL

Instrumentation

AAnalyst400 (PerkinElmer) flame atomic absorption spectrometer (FAAS) flow rates of acetylene and air used were 3.46 and 9.56 L min^{-1}, respectively was used as detector. A chromium hollow cathode lamp (PerkinElmer Lumina HCL) operated at 10mA was used as the light source with wavelength set at 357.9 nm. The flow injection system (FIAS 400, PerkinElmer) consisting of two peristaltic pumps (P1 and P2), a 5-port 2-positional injection valve and a mini-column for preconcentration, was coupled with the FAAS. The entire on-line system was controlled by Winlab32TM (version 6.5.0.0266) application software through a personal computer. Infrared spectra were recorded on a PerkinElmer FT-IR spectrometer Model Spectrum RX-1 (resolution 4 cm^{-1}, number of scans 16 and range 400–4000 cm^{-1}). SEM images were recorded using Scanning Electron Microscope model FEI Quanta 200F. Thermogravimetric analysis was done using a PerkinElmer Diamond DSC. pH adjustments were done by a pH meter Model LI-614 (ELICO Ltd., India).

Reagents and materials

All reagents used were of analytical grade. Water with resistivity 18.2 MΩ obtained from Milli-Q water purification system (Merck Millipore) was used for all dilutions and working solutions. Amberlite XAD-16 (Sigma-Aldrich) was used as the polymeric support. α-benzoin oxime used was obtained from Thomas Baker and was used as the chelating agent. All standard solutions of chromium were prepared by appropriate dilution of 1000 mg L^{-1} standard Cr(III) and Cr(VI) solutions traceable to NIST (Fluka). 0.1 mol L^{-1} HCl, phosphate buffer (pH 6-8) and trisodium phosphate buffer (pH 11.7) were used for pH adjustments,. Polypropylene apparatus (POLYLAB) used were washed with 10%(v/v) nitric acid, rinsed thoroughly with 18.2 MΩ water and dried before use.

Synthesis of chelating resin

The synthesis of the chelating resin followed the procedure given in literature[26] and was modified accordingly. In the first step of synthesis the nitration of styrene–divinylbenzene copolymer takes place, which is followed by its reduction to give an aromatic amine. The amine thus formed was then diazotized to form a diazonium salt. This diazotized salt was then filtered and washed with cold water. In next step it was reacted with 2 g of α-benzoin oxime dissolved in 50 mL of water and 25 mL of glacial acetic acid and was kept at 0–5 ^{o}C for 24 h. the beads thus obtained were then filtered, washed and stored in a desiccator until further use. The scheme of the synthesis is given in Fig. 1.

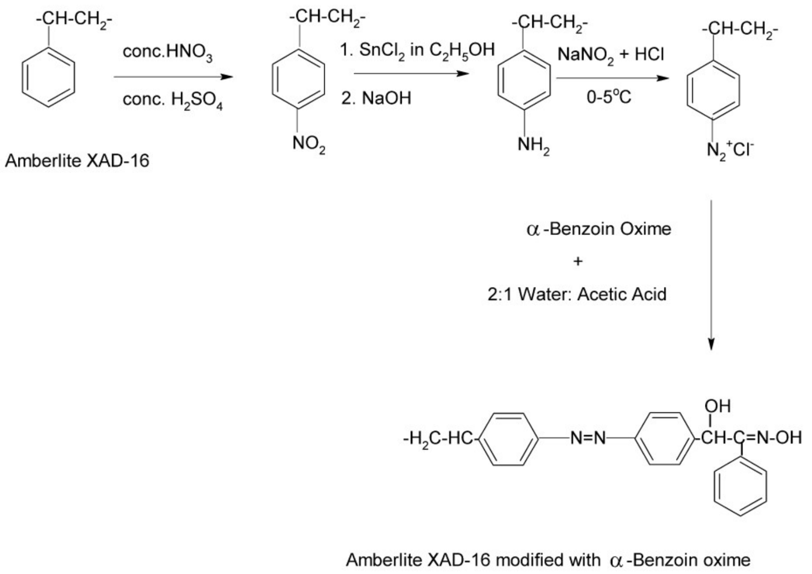

Fig. 1 Synthesis of Amberlite XAD-16 functionalized with α-benzoin oxime and its proposed structure.

Packing of minicolumn

The synthesized ABO-16 resin ~75mg was packed in a mini glass column (3.0 cm length and 3.0 mm internal diameter). The slurry of the resin was injected into the minicolumn using a syringe. The ends of the column were closed with cotton to retain the resin. The column was then washed with 2.0 mol L^{-1} HNO$_3$ and after that with doubly distilled water. The column had a constant performance during all experiments, thus there was no need for any regeneration or repacking.

On-line preconcentration procedure for determination of Cr(III)

The working of on-line preconcentration system is a two step process involving loading and elution. A schematic representation of flow injection analysis system coupled to FAAS is given in Fig. 2. It is a computer controlled program operated in a time based mode provided with operational steps optimized for chromium retention. Every preconcentration cycle starts with a prefill step to fill the tubes. 50 μg L^{-1} Cr(III) solution at pH 5 and flow rate of 2 mL min^{-1} was pumped through Pump 1 with preconcentration time of 150s. During the elution step, 0.2 mol L^{-1} HNO_3 was passed through Pump 2 for 30 s. The analytical signal was recorded as the height of the analytical signal. A blank check was done before every measurement. For all standard and sample solutions three replicate of measurements were taken. Table 1 represents the on-line flow injection program for preconcentration of Cr(III) ions.

Table 1: On-line flow injection program for preconcentration of Cr(III) ions.

STEP	TIME (s)	PUMP 1	PUMP 2	VALVE POSITION	READING
Prefill	1	+	+	Elute	-
1	10	+	-	Load	-
2	20	-	+	Elute	-
3	90	+	-	Load	-
4	50	+	-	Load	-
5	10	+	+	Load	-
6	30	-	+	Elute	+

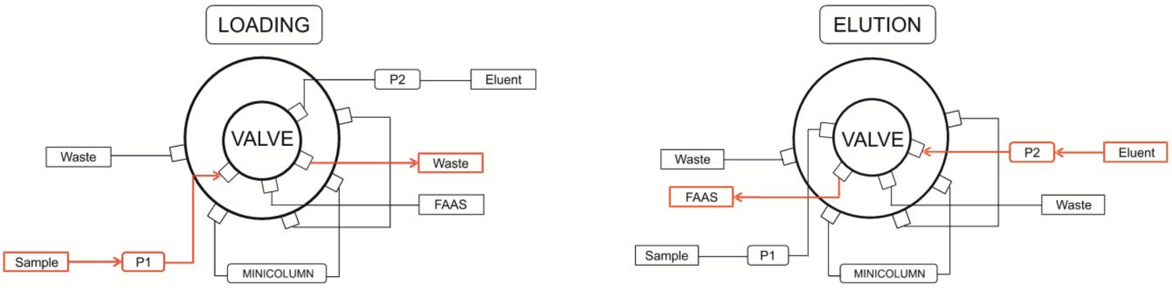

Fig. 2 Schematic representation of FIA-FAAS system

Total chromium determination

The determination of Cr(VI) was done by its reduction to Cr(III)[27]. 0.1 mL of 5% hydroxylamine hydrochloride was added to 25 mL of 50 µg L^{-1} Cr(VI) solution and was left at room temperature for 45 min. It was then analyzed according to the optimized preconcentration procedure for Cr(III). The concentration of Cr(VI was calculated by subtracting Cr(III) concentration from total chromium concentration..

General procedure for analysis of industrial water samples

The applicability of synthesized chelating resin for Cr(III) determination was checked by analyzing industrial water samples collected from three different places– Anand Parbat, Wazirpur and Seelampur industrial areas. The collected water samples were acidified and stored in clean polypropylene bottles. Prior to preconcentration, 25 mL of each water sample was filtered through a 0.45 µm pore size filter paper (Miilipore) to remove any particulate matter, if present. After filtration water samples were analysed by the suggested preconcentration method. The water samples were spiked with certified Cr(III) solution traceable to NIST to perform recovery studies. The determination of Cr(VI) was done by the reduction procedure. The water samples were spiked with certified Cr(VI) solution traceable to NIST, reduced again and analysed to study the recovery.

RESULTS AND DISCUSSION

The chemical immobilization of the chelating agent α -benzoin oxime on to the polymeric solid support Amberlite XAD-16 was done. Chemical modification of the solid support was confirmed by characterizing the synthesized solid phase extractant (ABO-16) using FT-IR, TGA and SEM. To achieve maximum preconcentration of Cr(III) on this solid phase extractant, various chemical and flow variables were optimized.

Characterization of α–benzoin oxime functionalized Amberlite XAD-16 chelating resin

FT-IR band assignments

The FT-IR spectrum of synthesized chelating resin was recorded. It has bands of Amberlite XAD-16 and α-benzoin oxime which supports the loading of chelating agent on polymeric surface. ABO-16 resin has bands at 3458 (O–H stretching), 2924 (C–H stretching), 1631 (C=N), 1528 (–N=N–), 1443 (C=C stretching), 1350 (C–N), 1028 (N–O) and 960 cm^{-1} (C–O). The presence of band at 1528 cm^{-1} confirms the loading through diazotized coupling as shown in Fig. 3a. After the sorption of Cr(III) shifting in the peaks of O-H, C-N, N-O by 5-10 cm^{-1} and were observed at 3445, 1325, 952 cm^{-1} respectively. The presence of peaks at 538 and 440 cm^{-1} corresponding to Cr-O and Cr-N (Fig. 3b) has supported complexation of Cr(III) with α-benzoin oxime.

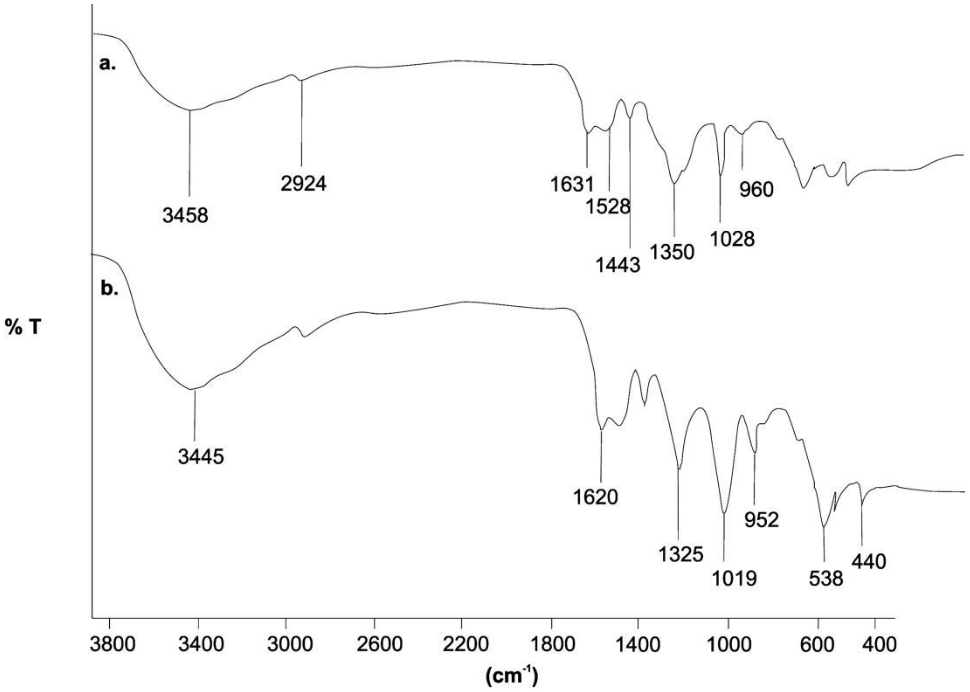

Fig. 3 Infrared spectra of a, Amberlite XAD-16 functionalized with α- benzoin oxime (ABO-16), b, Amberlite XAD-16 functionalized with α-benzoin oxime after sorption of Cr(III)

Thermo Gravimetric Analysis (TGA)

The thermo gravimetric analysis (TGA) curve of freshly prepared ABO-16 resin showed a very slow but steady weight loss up to 615°C. The observed weight loss was 24.85% up to

120 ^oC. This was due to physiosorbed water on the resin, which supported the presence of six water molecules per repeating unit in the chelating resin.

Surface morphology

Scanning electron microscope (SEM) uses a focused beam of electrons for scanning to produce three dimensional images of a thin flat sample. Fig. 4a shows that pure Amberlite XAD-16 resin has a flat and smooth surface whereas the modified chelating resin (Fig. 4b) has granular microstructures. This supports that Amberlite XAD-16 has been loaded with the chelating agent, α-benzoin oxime.

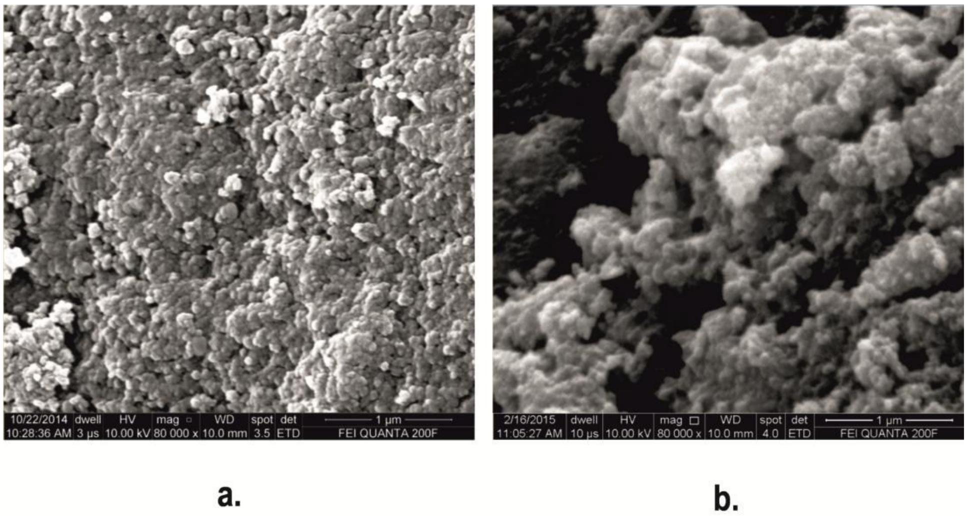

Fig. 4 SEM images of a, Amberlite XAD-16, b, ABO-16 resin

Optimization of chemical and flow variables

Due to the σ – donor N and π – acceptor O atoms present in α-benzoin oxime, the ligand acts as a hard base and Cr(III) acts as a hard acid. The complexation of Cr(III) with α-benzoin oxime loaded on Amberlite XAD-16 is based on the σ – donor π – acceptor interaction between N atom and Cr(III) as well as the ion-dipole interaction between O atom and Cr(III) [24]. The optimization of the preconcentration procedure is a crucial step as it influences the enrichment of Cr(III) via complexation and its recovery. The influence of pH, eluent concentration, sample and eluent flow rate was studied on Cr(III) sorption and desorption to ensure maximum recovery of Cr(III) ions.

Selection of optimum pH for Cr(III) preconcentration

pH of the sample plays an important role on the retention of Cr(III) on the sorbent. Cr(III) is known to form different complexes with many naturally occurring organic molecules in the pH range of 4 – 7. In these pH conditions present in natural waters, Cr(III) forms complexes with macromolecular compounds and thus is removed from the solution.[28] The sorption of Cr(III) ions on the minicolumn was thus studied in the pH range of 2-10. The maximum retention of Cr(III) on the minicolumn was achieved at pH 5 (Fig. 5a). At pH 5, Cr(III) is known to exist as $Cr(OH)^{2+}$ in natural water samples[29] Thus, pH 5 was chosen for all successive studies.

Selection of eluent for Cr(III) desorption

To elute sorbed Cr(III) ions both HNO_3 and HCl were studied. The signals achieved with HNO_3 were better and sharp and so it was used as an eluent. The effect of the concentration of HNO_3 on desorption of Cr(III) ions was studied in the range of 0.01-2.0 mol L^{-1}. It was observed that maximum desorption was obtained with in 0.2 mol L^{-1} HNO_3 [Fig. 5(b)]. Thus, 0.2 mol L^{-1} HNO_3 was chosen as the eluent for maximum recovery of Cr(III).

Selection of optimum sample flow rate

For optimum retention of Cr(III) on the minicolumn, effect of sample flow rate was studied in the range of 2.0-7.0 mL min^{-1}. The results are shown in Fig. 5(c). It was observed that at flow rate of 2.0 mL min^{-1} maximum absorbance was obtained at, beyond which the absorbance decreased. Thus, sample flow rate was kept at 2.0 mL min^{-1} for all subsequent studies.

Selection of optimum eluent flow rate

To ensure maximum desorption of Cr(III), the effect of eluent flow rate was studied in the range of 2-7 mL min^{-1} . Maximum absorbance was obtained at flow rate of 5.0 mL min^{-1}, as shown in Fig. 5(d). Thus eluent flow rate of 5 mL min^{-1} was maintained for all subsequent analysis.

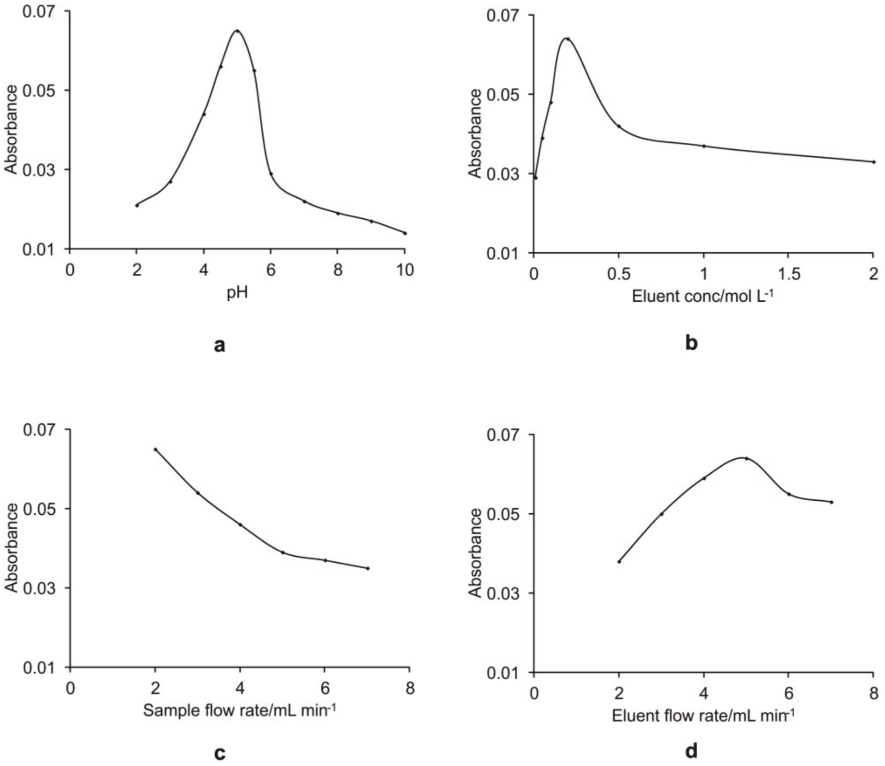

Fig. 5 Optimization of the preconcentation procedure of Cr(III). a, influence of pH, b, influence of eluent concentration, c, influence of sample flow rate, d, influence of eluent flow rate

Effect of commonly present interfering ions on Cr(III) sorption

The effect of commonly present ions in water on the selectivity of preconcentration of 100 µg L^{-1} of Cr(III) by the resin ABO-16 under the optimized conditions was studied. The existence of ions such as nitrate, sulphate, chloride, etc. can result in decreased preconcentration efficiency of the chelating resin towards Cr(III). The effect of any such species is considered to be interfering if its presence results in deviation of the analytical signal by more than ± 5%. The results show that there is negligible effect on Cr(III) preconcentration even in the presence of high concentration of ions reported in Table 2.

Table 2 Effect of interfering ions on the recovery of Cr(III) using ABO-16 resin

Interfering Ion	**Tolerance Limit (mg L^{-1})**
NO_3^-	9000

Cl^-	5500
Na^+	5000
CH_3COO^-	900
I^-	900
Br^-	800
NH_4^+	420
K^+	300
Pb^{2+}	175
SO_4^{2-}	110
Zn^{2+}	70
Cu^{2+}	65
Ca^{2+}	55
Mg^{2+}	55
Cd^{2+}	50
Al^{3+}	40

Analytical figures of merit for Cr(III) preconcentration

The analytical figures of merit of the proposed FI-SPE-FAAS system for Cr(III) preconcentration with ABO-16 resin under the optimum conditions are shown in Table 3. Preconcentration factor is defined as the ratio of the slopes of the calibration curves with and without preconcentration and was found to be 35 and 76, for preconcentration time of 150 and 300 s, respectively. The limit of detection (LOD), calculated as three times of standard deviation of the blank was 0.22 and 0.14 ng mL^{-1}. The relative standard deviation (% RSD) is a measure of precision of the measurements and was found to be 1.12% and 1.03% for 50 and 100 µg L^{-1} of Cr(III), respectively.

Sorption capacity of synthesized resin

The sorption capacity of synthesized resin was determined by shaking 50 mL of 100 mg L^{-1} of Cr(III) solution at pH 5 with 50 mg of resin for 5 hours. After this, the resin was filtered and the sorbed Cr(III) ions were desorbed by adding 30 mL of 2 mol L^{-1} HNO_3. Then the filtrate was diluted and analyzed by using pre-calibrated FAAS system. The sorption capacity of ABO-16 resin was 27.6 mg g^{-1}, which is much better in comparison to other systems[27, 30-37].

Resin stability and reusability

The loading and elution of Cr(III) ions in a single run involves one cycle of sorption-desorption. To check the reusability of resin the sorption capacity of unused resin was compared with that of the used resin. It was observed that the sorption capacity of used and unused resin varied by <5% and the measurements were reproducible even after ~300 cycles. This can be explained by the fact that the concentration and the volume of eluent used for each cycle were low. Another factor which supports this is the chemical immobilization of α-benzoin oxime on Amberlite XAD-16 preventing leaching of the chelating agent from the column.

Application of proposed method to industrial water samples

The proposed on-line method using the synthesized chelating resin ABO-16 was applied to industrial water samples according to the procedure described earlier. The spike recovery tests gave good recoveries for Cr(III) and Cr(VI). The results are discussed in Table 4.

Table 3 Analytical performance of FI-SPE-FAAS system for Cr(III) determination using ABO-16 resin

Parameter	Optimum Conditions
pH	5.0
Eluent	0.2 mol L^{-1} HNO_3
Sample flow rate (mL min^{-1})	2.0
Eluent flow rate (mL min^{-1})	5.0
Preconcentration Time (PT, s)	150 300

Sample Consumption (mL)	5.0	10.0
Linear range (µg L^{-1})	0.74 – 550	0.46 – 300
Limit of detection (ng mL^{-1})	0.22	0.14
Limit of quantification (µg L^{-1})	0.74	0.46
Sample Throughput (h^{-1})	17	9
Preconcentration factor	35	76
Correlation coefficient	0.9999	0.9996
Regression equation (6 standards, Cr(III)/µg L^{-1})	A_{150} = 0.00246[Cr(III)] - 0.00090	A_{300} = 0.00535[Cr(III)] - 0.00607
Regression equation (6 standards, Cr(III)/ µg L^{-1}) (without preconcentration)	A = 0.00007[Cr(III)] - 0.00023	A = 0.00007[Cr(III)] + 0.00025
Precision (% R.S.D.)	1.12, [Cr(III)] = 50 µg L^{-1} 1.03, [Cr(III)] = 100 µg L^{-1}	

Table 4 Results of application of the proposed system to industrial water samples

Sample	Added		Found			Recovery (%)[c]	
	Cr(III)[a]	Cr(VI)[b]	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)
Anand Parbat Industrial Area, Delhi, India	-	-	24.9 ± 1.1	5.6 ± 1.2	31.1 ± 2.7	96.9	99.4
	20	20	43.5 ± 1.2	25.4 ± 1.6			
Seelampur Industrial Area, Delhi, India	-	-	20.8 ± 2.5	4.6 ± 2.5	25.5 ± 3.4	97.3	95.1
	20	20	39.7 ± 1.7	23.4 ± 2.3			
Wazirpur Industrial Area, Delhi, India	-	-	26.1 ± 1.5	9.8 ± 1.4	35.9 ± 1.7	96.5	95.9
	20	20	44.5 ± 2.2	28.54 ± 3.6			

[a] Spiking with Cr(III) solution traceable to NIST

[b] Spiking with Cr(VI) solution traceable to NIST

[c] Confidence Interval 95%

Accuracy of the proposed on-line preconcentration method

The accuracy of the suggested system for Cr(III) preconcentration was studied using NIST standard reference material 1643e (Trace Elements in Water). It was observed that there was no significant difference between the Cr(III) concentration obtained from proposed method and the standard results at the 95% confidence interval. The recovery of Cr(III) was found to be > 95%.

Comparison of the suggested on-line preconcentration method with other on-line SPE methods for Cr(III) determination

The analytical figures of merit of the proposed on-line preconcentration method were compared with other selected on-line SPE preconcentration FAAS methods reported in the literature. ABO-16 chelating resin has proven to be a better system for Cr(III) preconcentration in terms of sensitivity (detection limit), better precision (% R.S.D.) and high preconcentration factor over other on-line preconcentration methods. Table 5 gives a comparison of the figures of merit of some reported on-line SPE methods for chromium speciation.

Table 5 Comparison of reported on-line SPE methods with proposed system for Cr(III) determination

Support	**Chelating agent**	**Eluent**	**PT(s)**	**Sample volume (mL)**	**R.S.D. (%)**	**DL (ng mL^{-1})**	**PF**	**Ref.**
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	36
Chitosan-FeC nanoparticles		HCl	4000	100	2.5	0.0524	100	35

Llama Fibres	--	NaOH	750	25	4.3	0.3	32	39
MWCNTs	--	HNO_3	180	6	1.7	1.15	22	40
Silica	Al_2O_3/TiO_2	HCl	--	20	2.4	0.66	17.62	41
Silica gel	Niobium(V) oxide	HNO_3	120	15	4.6	0.34	23	42
Silica gel	Zirconium oxide	HNO_3	225	15	3	1.9	20.8	42
UVM-7	Amino silane	NaOH	-	100	-	1.2	66.7	44
Amberlite XAD-16	***α-Benzoin oxime***	***HNO_3***	***300***	***10***	***1.03***	***0.14***	***76***	***This work***

PT: Preconcentration Time; RSD: Relative Standard Deviation; DL: Detection Limit; PF: Preconcentration factor

Conclusion

The performance of the on-line preconcentration system involving the use of a mini column packed with Amberlite XAD-16 modified with α-benzoin oxime has been described. The synthesized resin was used to determine chromium species in different industrial water samples with good recoveries of 95%. Flow injection system hyphenated with FAAS reduces analysis time and consumption of reagents. In the presence of commonly present ions the developed system has shown selectivity towards Cr(III) ions. Cr(VI) can also be determined after reducing it to Cr(III). Once synthesized the resin can be used for ~300 cycles of sorption and desorption. The proposed method has better preconcentration factor, selectivity and detection limits in comparison to other reported on-line FAAS methods (Table 6). The accuracy of the method was tested by analyzing NIST Standard Reference Material 1643e and the certified and observed results were found to be in good agreement with each other.

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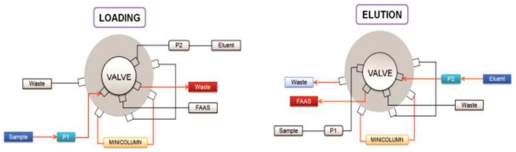

Preconcentrative speciation of chromium in industrial water samples using a flow injection – FAAS system with synthesized chelating resin in minicolumn.