

# Solid phase extraction of chromium(VI) from aqueous solutions by adsorption of its diphenylcarbazide complex on an Amberlite XAD-4 resin column

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## Abstract

A method has been developed for the solid phase extraction of chromium(VI) based on the adsorption of its diphenylcarbazide complex on an Amberlite XAD-4 resin column. The influence of acidity, stability of the column, sample volume, flow rate and interfering ions were studied in detail. The adsorbed complex could be eluted using acetone–sulfuric acid mixture and the concentration of chromium was determined using visible spectrophotometry. A detection limit of  $6 \mu\text{g L}^{-1}$  could be achieved. A preconcentration factor of 27 could be obtained for 400 mL sample volume. The validity of the method was checked in spiked water samples and electroplating wastewater.

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## 1. Introduction

The considerable emphasis on the removal of toxic metal ions led to the development of a variety of analytical methodologies. Hence, there has been considerable growth in the analytical chemistry of various metal ions. Chromium is not an exception to this. Among the stable oxidation states of chromium, Cr(III) is an essential dietary mineral in low doses, whereas Cr(VI) is carcinogenic [1].

In view of the toxic nature of chromium(VI), development of methods in order to establish their levels in the environment and industrial quality control are quite significant. Solid phase extraction has been explored for the preconcentration of many metal ions [2–5]. A variety of adsorbents have been used for the preconcentration of chromium [6–14].

A survey of the literature for the preconcentration of chromium(VI) reveals that solid phase extraction is one of the versatile methods. The major advantage of solid phase extraction is the high selectivity and enrichment factor that could be achieved in this method. Among the various adsorbents, silica and alumina have been extensively studied for the adsorption of chromium. Amberlite XAD resins have been widely used for the solid phase extraction of many metal ions [15,16]. Amberlite XAD-4 is a cross linked polymer which derives its adsorptive properties from its macroporous structure and higher surface area. This structure imparts excellent physical, chemical and thermal stability and is a good choice for the removal of a variety of metal ions.

In this paper, a simple methodology is proposed for the solid phase extraction of chromium based on the adsorption of its diphenylcarbazide complex on an Amberlite XAD-4 resin column. Diphenylcarbazide is a ligand that gives a very sensitive and selective color reaction with chromium(VI). The adsorbed complex could be eluted using acetone–sulfuric acid mixture and the concentration of chromium was determined using visible spectrophotometry. The influence of various experimental

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parameters such as sample volume, volume of eluent, flow rate, effect of diverse ions etc were studied in detail. The validity of the proposed method was checked in spiked water samples and electroplating wastewater.

## 2. Experimental

### 2.1. Instrumentation

A JASCO V-576 (Japan) model double beam UV–vis spectrophotometer fitted with tungsten lamp as the source was used for absorbance measurements. One centimeter matched quartz cells were used for measuring the absorbance. The pH measurements were performed with an Elico LI-120 (Hyderabad, India) digital pH meter.

### 2.2. Chemicals and reagents

Analytical grade reagents were used in the preparation of all solutions. Triple distilled water was used for the preparation of solutions. A stock solution of  $1000 \mu\text{g mL}^{-1}$  Cr(VI) was prepared by dissolving 0.372 g of potassium chromate (Qualigens Fine Chemicals, Mumbai, India) in 100 mL water. A working solution of  $10 \mu\text{g mL}^{-1}$  was prepared by appropriate dilution. Amberlite XAD-4 (Himedia Research Laboratories, Mumbai, India) of surface area  $735 \text{ m}^2/\text{g}$  and pore diameter 20–50 mesh was used for adsorption. Acetone (E. Merck) was used as such without further purification. 0.25 g of 1,5-diphenylcarbazide (Central Drug House Limited, Delhi, India) was dissolved in minimum amount of acetone and diluted to 100 mL. Sulfuric acid of the required concentration was prepared from concentrated sulfuric acid by appropriate dilution

### 2.3. Preparation of column

A glass column 1.5 cm in diameter and 15 cm in length was used for preconcentration. A slurry of 1.2 g of Amberlite XAD-4 resin in 25 mL triple distilled water was prepared and the column was packed to a height of 4 cm.

The column was washed using triple distilled water followed by conditioning it using  $0.1 \text{ mol L}^{-1}$  sulfuric acid. Glass wool was placed at the bottom and at the top of the column for allowing the adsorbent to settle properly.

### 2.4. Procedure for preconcentration

A 1 mL volume of  $10 \mu\text{g mL}^{-1}$  solution of Cr(VI) was mixed with 3 mL of  $0.5 \text{ mol L}^{-1}$  sulfuric acid followed by the addition of 3 mL of diphenylcarbazide and the resulting volume was maintained at 100 mL. The sample solution was loaded on to the column containing Amberlite XAD-4 resin maintaining a flow rate of  $2 \text{ mL min}^{-1}$ . The reddish violet complex was adsorbed on to the column, which was evident from the absorbance of the resulting solution that emerged out of the column. The adsorbed complex was then eluted using 15 mL of acetone– $2.5 \text{ mol L}^{-1}$

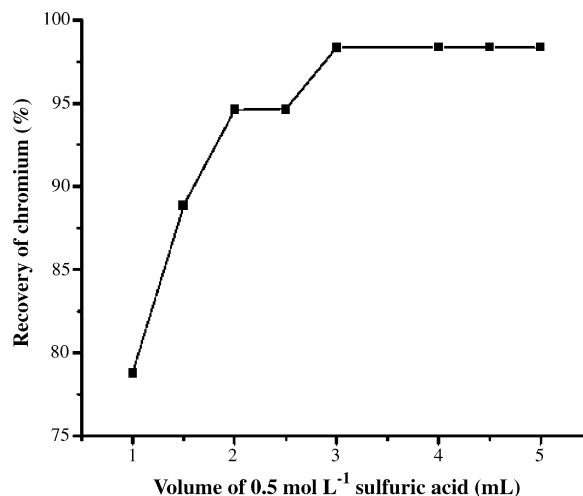


Fig. 1. Effect of variation of volume of  $0.5 \text{ mol L}^{-1}$  sulfuric acid.

sulfuric acid mixture and the concentration of chromium was determined by visible spectrophotometry at 580 nm.

## 3. Results and discussion

### 3.1. Effect of acidity

The effect of acidity plays a significant role in the preconcentration studies. The complex once prepared is stable even at moderately low pH. The volume of  $0.5 \text{ mol L}^{-1}$  sulfuric acid was varied from 1 to 5 mL in 100 mL sample volume. The adsorbed complex was eluted using 10 mL of acetone–sulfuric acid mixture. The results are presented in Fig. 1. As can be seen from the figure, it is evident that 3.0 mL of  $0.5 \text{ mol L}^{-1}$  sulfuric acid is required to achieve quantitative recovery of the chromium–diphenylcarbazide complex. Beyond 3 mL, there was no change in the percentage recovery of chromium.

### 3.2. Choice of eluent

A variety of reagents were tested in order to elute the adsorbed complex from the column. In order to choose the most effective eluent for quantitative recovery acetone, methanol, sulfuric acid, and acetone–sulfuric acid mixture were studied. The elution studies were carried out maintaining an overall Cr(VI) concentration of  $10 \mu\text{g}$  in 100 mL sample volume. The recovery of Cr(VI)–diphenylcarbazide complex was quantitative with acetone– $2.5 \text{ mol L}^{-1}$  sulfuric acid mixture as the eluting agent. Lower concentrations of sulfuric acid were not effective in the elution of the complex.

### 3.3. Effect of volume of the eluent

The volume of acetone–sulfuric acid mixture as the eluting agent was varied in the range 5–20 mL. It was observed that maximum recovery of chromium(VI) was observed with 15 mL of acetone– $2.5 \text{ mol L}^{-1}$  sulfuric acid mixture. The results are presented in Fig. 2. The use of acetone alone or sulfuric acid

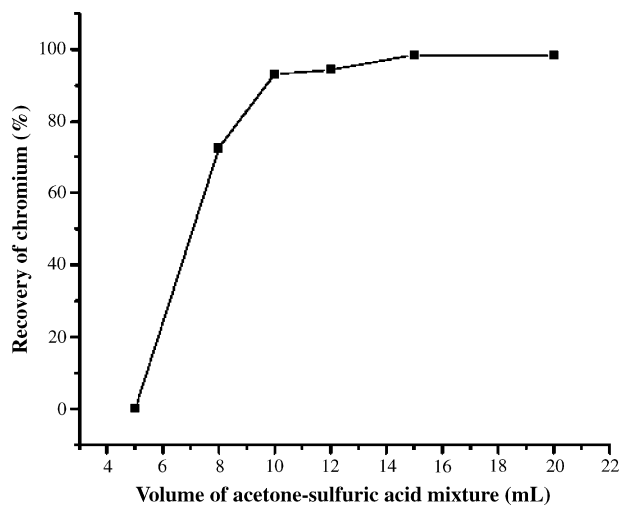


Fig. 2. Effect of variation of eluent volume.

of lower concentrations was not effective in the elution of the complex.

### 3.4. Effect of the amount of Amberlite XAD-4 resin loaded on the column

The amount of Amberlite XAD-4 resin loaded on the column was varied from 0.25 to 1.5 g. The concentration of chromium(VI) was maintained at 10  $\mu\text{g}$  in a 100 mL sample volume. Quantitative recovery of chromium(VI) could be attained in the range 0.8–1.5 g of Amberlite XAD-4. For amounts less than 0.8 g there was a significant reduction in the recovery of chromium beyond a sample volume of 100 mL.

### 3.5. Effect of sample volume

The effect of sample volume on the recovery of the analyte was investigated in the range 50–1000 mL maintaining on overall concentration of 0.025  $\text{mol L}^{-1}$  sulfuric acid. The resulting complex was eluted using 15 mL of acetone–sulfuric acid mixture. The results are presented in Fig. 3. As can be seen from the figure, it is evident that the recovery of chromium is quantitative (>95%) up to 400 mL sample volume. A preconcentration factor of 27 could be attained for quantitative recovery (>95%) of Cr(VI) when the sample volume was 400 mL.

### 3.6. Effect of flow rate

The flow rate of 1–4  $\text{mL min}^{-1}$  was found to be suitable for optimum loading of the Cr(VI)–diphenylcarbazide complex on the Amberlite XAD-4 column. At higher flow rates, there was a reduction in the percentage adsorption of chromium. This could be probably due to the insufficient contact time between the sample solution and the Amberlite XAD-4 resin column. A flow rate of 2  $\text{mL min}^{-1}$  was maintained for the elution of the complex.

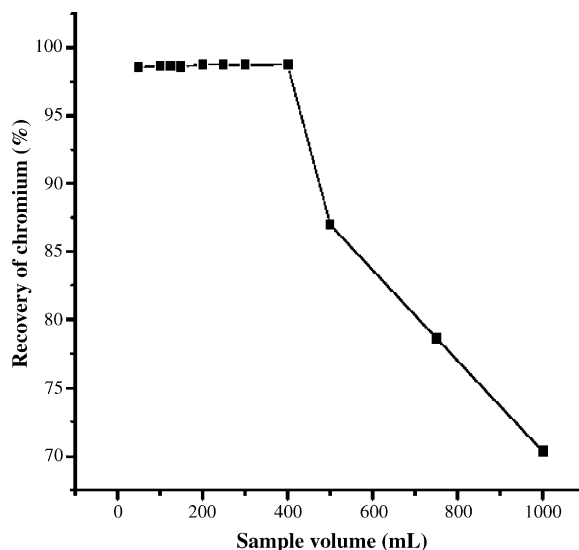


Fig. 3. Effect of variation of sample volume on the recovery of chromium.

### 3.7. Stability of the column

The stability of the column was tested using 10  $\mu\text{g}$  Cr(VI) maintaining a sample volume of 100 mL. The adsorbed Cr(VI)–diphenylcarbazide complex was eluted using 15 mL of acetone–sulfuric acid mixture. The column could be used with good precision and quantitative recovery (>95%) for seven cycles. Beyond seven cycles, there was a reduction in the recovery of chromium.

### 3.8. Adsorption capacity

The adsorption capacity was determined by passing increasing amounts of chromium through the column maintaining a sample volume of 100 mL. The concentration of chromium was determined as mentioned in Section 2.4. The adsorption capacity of the Amberlite XAD-4 resin for chromium was found to be 0.85  $\text{mg/g}$ .

### 3.9. Precision studies and limit of detection

The precision studies were carried out at 0.1  $\mu\text{g mL}^{-1}$  level of chromium by carrying out ten separate determinations using the above-mentioned procedure. The sample volume was maintained at 100 mL. The relative standard deviation of the method was found to be 3.6%. The sensitivity of the developed method is reflected by the limit of detection studies, defined as the lowest concentration of chromium(VI) below which quantitative sorption of the metal ion by Amberlite XAD-4 resin is not perceptibly seen. The limit of detection for Cr(VI) was found to be 6  $\mu\text{g L}^{-1}$ .

### 3.10. Effect of diverse ions

The effect of diverse ions was studied at varying concentrations. The solid phase extraction studies were carried out as

Table 1  
Effect of diverse ions on the recovery of 10  $\mu\text{g}$  chromium in a sample volume 100 mL (Eluent-15 mL acetone–sulfuric acid mixture, flow rate 2 mL min<sup>-1</sup>)

Ions	Amount ( $\mu\text{g}$ )	Recovery of chromium (%)
$\text{Mg}^{2+}$	500	98
	1000	98
	250	99
$\text{Ca}^{2+}$	500	98
	1000	98
	250	99
$\text{Ni}^{2+}$	1000	98
	500	99
	250	99
$\text{Cl}^-$	1000	99
	500	98
	250	99
$\text{NO}_3^-$	1000	98
	500	98
	250	98
$\text{SO}_4^{2-}$	1000	99
	500	99
	250	99
$\text{Co}^{2+}$	1000	99
	500	99
	250	99
$\text{Cu}^{2+}$	500	98
	250	98
	1000	98
$\text{Fe}^{2+}$	150	98
	500	75
	1000	73

mentioned above using 10  $\mu\text{g}$  Cr(VI) maintaining a sample volume of 100 mL. The studies indicated that  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cl}^-$   $\text{NO}_3^-$  did not cause any significant reduction in the recovery of chromium. The results are presented in Table 1 showing the recovery of chromium with varying concentrations of metal ions. Except  $\text{Fe}^{2+}$ , the recovery was found to be quantitative in the concentration range of the metal ions that was investigated. Since, the ions that are commonly present in water samples did not affect significantly the recovery of chromium the method was applied to study the recovery of chromium in tap water and well water samples.

Table 3  
Analysis of chromium(VI) in electroplating wastewater (Eluent 15 mL acetone–sulfuric acid mixture, flow rate 2 mL min<sup>-1</sup>)

Sample	Concentration of chromium(VI) added ( $\text{mg L}^{-1}$ )	Concentration of chromium(VI) found ( $\text{mg L}^{-1}$ )	Relative standard deviation (%)	% Recovery
Electroplating wastewater	0	82.7	3.7	–
	5.0	86.5	3.8	99
	10.0	91.5	3.4	99

Table 2  
Recovery studies in tap water and well water samples (Eluent 15 mL acetone–sulfuric acid mixture, flow rate 2 mL min<sup>-1</sup>)

Sample	Cr(VI) added ( $\mu\text{g}$ )	Cr(VI) found ( $\mu\text{g}$ )	Sample volume (mL)	Recovery of chromium (%)
Tap water	5.0	4.91	100	98
	2.0	1.95	250	98
	10	9.87	400	99
	10	9.86	350	99
	10	9.82	100	98
Well water	10	9.82	250	98
	5.0	4.90	350	98
	4.0	3.91	400	98
	2.0	1.94	250	97

### 3.11. Recovery study in spiked water samples

The proposed method was applied to study the recovery in tap water and well water samples by spiking known concentrations of chromium in varying sample volumes. The recovery of chromium was found to be quantitative with an average relative standard deviation of 3.8% on triplicate measurements and the results are shown in Table 2.

### 3.12. Analysis of chromium(VI) in electroplating wastewater

The proposed method was applied to study the recovery of chromium(VI) in electroplating wastewater sample. The electroplating wastewater sample had the following characteristics: pH 2.8, calcium: 65  $\text{mg L}^{-1}$ , magnesium: 40.5  $\text{mg L}^{-1}$ , chloride: 970  $\text{mg L}^{-1}$ , sulfate: 780  $\text{mg L}^{-1}$ . The wastewater sample was diluted to the required concentration and the preconcentration procedure was applied as mentioned above. The recovery of chromium was found to be quantitative and the results are presented in Table 3.

### 3.13. Comparison with other solid phase adsorbents

The proposed methodology was compared to a variety of solid adsorbents reported recently in the literature. The distinct features are summarized in Table 4. As can be seen from the table, it is evident that the preconcentration factor and the detection limit obtained with Amberlite XAD-4 resin is comparable to or even better than most of the other chelating matrices.

Table 4

Comparison of the proposed method in terms of preconcentration factor and detection limits with some of the recent methods reported in literature

SPE support/chelating agent	Method	Preconcentration factor	Detection limit ( $\mu\text{g L}^{-1}$ )	Reference
Amberlite XAD-16/1,5-diphenylcarbazone	FAAS	25	45	[8]
Naphthalene/potassiumethylxanthate	FAAS	100	0.5	[13]
Chitin/1,5-diphenylcarbazide	Spectrophotometry	–	50	[17]
C-18 bonded silica/CTABr	FAAS	45	20	[18]
Amborsorb-563/1,5-diphenylcarbazide	Spectrophotometry	30	3.4	[19]
Amberlite XAD-1180/chromotope 2R	FAAS	20	2.59	[20]
Chromosorb 108/dithizone	FAAS	71	0.75	[21]
Amberlite XAD-4/1,5-diphenylcarbazide	Spectrophotometry	27	6	Present work

FAAS—flame atomic absorption spectrometry.

#### 4. Conclusions

The proposed method for chromium is simple, and could be effectively used for the solid phase extraction of chromium. The preconcentration factor was 27 for a 400 mL sample volume. The method showed minimum interferences with commonly found ions in real samples and the recovery of chromium was quantitative. The quantitative recovery of chromium(VI) with a relative standard deviation of 3.8% reflects the validity and accuracy of the method when applied to spiked water samples and electroplating wastewater. The detection limit and the preconcentration factor obtained using Amberlite XAD-4 resin is comparable to most of the metal matrix combinations recently reported in the literature. The column exhibited good stability under the experimental conditions. The important features of the proposed method are its high sorption capacity with good preconcentration factor. The developed method is sensitive in detecting chromium(VI) at ppb levels.

#### References

- [1] D.M. Roundhill, Novel strategies for the removal of toxic metals from soils and waters, *J. Chem. Educ.* 81 (2004) 275–282.
- [2] V. Camel, Solid phase extraction of trace elements, *Spectrochim. Acta B* 58 (2003) 1177–1233.
- [3] A.M. Starvin, T. Prasada Rao, Removal and recovery of mercury(II) from hazardous wastes using 1-(2 thiazolyl-azo)-2-naphthol functionalized activated carbon as the solid phase extractant, *J. Hazard. Mater.* 113 (2004) 75–79.
- [4] C. Shuyu, Z. Zhifeng, Y. Huaming, Dithizone as chelator in the flow injection separation and preconcentration of trace metals in biological samples, *Anal. Chim. Acta* 451 (2002) 305–311.
- [5] J. Jakmunee, P. Sooksamiti, H. Geckies, K. Grudpan, Flow injection sample pretreatment for determination of lead by flame atomic absorption spectrophotometry, *Anal. Sci.* 17 (2001) 1415–1418.
- [6] H.W. Sun, W.J. Kang, S.X. Liang, J. HA, G. Shen, Determination of chromium(III) and total chromium in water by derivative atomic absorption spectrometry using flow injection on-line preconcentration with a double micro column, *Anal. Sci.* 3 (2003) 589–592.
- [7] M.J. Marques, A. Salvador, A. Morales Rubio, M. de la Guardia, Chromium speciation in liquid matrices: a survey of literature, *Fresen. J. Anal. Chem.* 367 (2000) 601–613.
- [8] A. Tunceli, R. Turker, Speciation of Cr(III) and Cr(VI) in water after preconcentration of its 1,5-diphenylcarbazone complex on amberlite XAD-16 resin and determination by FAAS, *Talanta* 57 (2002) 1199–1204.
- [9] S. Kocaoba, G. Akein, Removal and recovery of chromium and chromium speciation with MINTEQA2, *Talanta* 57 (2002) 23–30.
- [10] C. Raji, T.S. Anirudhan, Chromium(VI) adsorption by sawdust carbon: kinetics and equilibrium, *Indian J. Chem. Technol.* 4 (1997) 228–236.
- [11] Y.M. Scindia, A.K. Pandey, A.V.R. Reddy, S.B. Manohar, Selective preconcentration and determination of chromium(VI) using a flat sheet polymer inclusion sorbent, *Anal. Chem.* 74 (2002) 4204–4212.
- [12] E. Vassileva, K. Hadjiivanov, T. Stoychev, C. Daiev, Chromium Speciation analysis by solid-phase extraction on a high surface area  $\text{TiO}_2$ , *Analyst* 125 (2000) 693–698.
- [13] P. Gopikrishna, J. Mary Gladis, U. Rambabu, T. Prasada Rao, G.R.K. Naidu, Preconcentrative separation of chromium(VI) species from chromium(III) by co-precipitation of its ethylxanthate complex onto naphthalene, *Talanta* 63 (2004) 541–546.
- [14] J. Chawastowska, W. Skwara, E. Sterlinska, L. Psonicki, Speciation of chromium in mineral waters and Salinas by solid phase extraction and graphite furnace atomic absorption spectrophotometry, *Talanta* 66 (2005) 1345–1349.
- [15] G. Purnachandra Rao, S. Satya Veni, K. Pratap, Y. Koteswara Rao, K. Seshiah, Solid phase extraction of trace metals in sea water using morpholine dithiocarbamate loaded Amberlite XAD-4 and determination by ICP-AES, *Anal. Lett.* 39 (2006) 1009–1021.
- [16] M. Soylak, S. Saracoglu, L. Elci, M. Dogan, Determination of trace metals in sea-water by atomic absorption spectrometry after separation/preconcentration with calmagite on Amberlite XAD-1180, *Int. J. Environ. Anal. Chem.* 82 (2002) 225–231.
- [17] S. Hoshi, K. Konuma, K. Sugawara, M. Uto, K. Akatsuka, A simple and rapid spectrophotometric determination of trace chromium(VI) after preconcentration of its colored complex on chitin, *Talanta* 47 (1998) 659–663.
- [18] M.S. Tehrani, A.A. Ebrahmi, F. Rastegar, Chromium speciation by surfactant assisted solid-phase extraction and flame atomic absorption spectrometric detection, *Ann. Chim.* 94 (2004) 429–435.
- [19] I. Narin, Y. Surme, M. Soylak, M. Dogan, Speciation of Cr(III) and Cr(VI) in environmental samples by solid phase extraction on Amborsorb 563 resin, *J. Hazard. Mater.* 136 (2006) 579–584.
- [20] S. Saracoglu, M. Soylak, L. Elci, On-line solid phase extraction system for chromium determination in water samples by flow injection-flame atomic absorption spectrometry, *Anal. Lett.* 35 (2002) 1519–1530.
- [21] M. Tuzen, M. Soylak, Chromium speciation in environmental samples by solid phase extraction on chromosorb-108, *J. Hazard. Mater.* 129 (2006) 266–273.