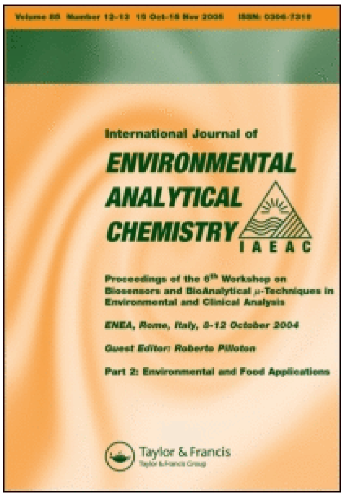

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Preconcentration of total chromium on Dowex 50W-X8 resin loaded with 2-amino-benzenethiol

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Application of Dowex 50W-X8 loaded with 2-amino-benzenethiol for preconcentration of total chromium (Cr(VI) and Cr(III)) in water samples and subsequent determination by inductively coupled plasma-atomic emission spectrometry was studied. The reagent 2-amino-benzenethiol loaded onto the resin effectively reduced Cr(VI) to Cr(III) and total chromium (both Cr(VI) and Cr(III)) formed chelate complex with the reagent in the Cr(III) valence state. Experimental parameters such as preconcentration time, solution flow rates, pH, and concentration of the eluent were optimized. The method has been applied for the determination of total chromium in seawater samples in the range of 0.1–200 $\mu g\,L^{-1}$. A detection limit of 0.3 $\mu g\,L^{-1}$ was achieved, and the relative standard deviation was about 5%.

Keywords: Chromium; 2-Amino-benzenethiol; Inductively coupled plasma-atomic emission spectrometry; Preconcentration

1. Introduction

Heavy metals are generally biorefractory, cannot be degraded or detoxified biologically, and tend to accumulate in living organisms, thus causing various diseases and disorders [1]. Effluents discharged from major industries like chromoplating, textile, leather tanning, electroplating, pigment and dyes, metallurgical, metal finishing, photography, and wood-preserving industries contain chromium which is one of several very toxic metals. Due to its high toxicity and persistence, its disposal in landfill sites is considered as an environmental hazard because it may be leached into drinking-water samples [2]. It is reported that in the UK and other EU states, concentrations of total chromium in drinking water are monitored for compliance with a limit concentration of 0.05 $mg\,L^{-1}$ [3].

Chromium exists in two predominant forms, trivalent and hexavalent, in industrial wastewaters [4]. The speciation of chromium has attracted a great deal of interest

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in view of the properties of Cr(VI) as compared with the much less toxic Cr(III). Dietary intake of Cr(VI) in mg L^{-1} levels produces chronic toxicity, causing erosion of the gastrointestinal tract and kidney lesions. Human health is affected when exposed to Cr(VI) in excess of the recommended level. Cr(VI) can generate serious disorders and diseases (skin ulcerations and lung cancer) when accumulated at high levels and ultimately can become lethal [5]. Cr(VI) compounds are strong oxidizers and highly soluble in anionic forms, so they are very mobile in soil–water systems.

Distribution coefficients for 43 cations in various concentrations of hydrochloric acid using the cation exchange sulphonated polystyrene AG 50W-X8 resin have been reported by Strelow *et al.* [6]. Dowex 50W-X8 is a cationic ion exchanger, and its application for the preconcentration of several trace metals and cations in water and wastewater has been studied by several workers [7–13]. There are studies on chromium determination using various sorbents like *Lemna Minor* [14], 5-palmitoyl oxine-functionalized XAD-2 resin [15], Amberlite XAD-7 resin impregnated with aliquat 336 [16]. Coedo *et al.* [17] studied the preconcentration, speciation, and determination of chromium species after leaching and dissolving the sample by combining retention of the analytes on Dowex 1-X8 and Dowex 50W-X8 ion-exchange resins. Yalcin and Apak [18] studied the Cr(III,VI) speciation analysis with preconcentration on maleic acid functionalized XAD sorbent. In this method, Cr(VI) was first reduced to Cr(III) using Na_2SO_3 and then preconcentrated. All these studies revealed that Cr(VI), which exists as dichromate ($Cr_2O_7^{2-}$) in acidic medium or chromate (CrO_4^{2-}) in alkaline medium, is not exchanged by the cationic ion exchanger Dowex 50W-X8. The determination of Cr(VI) using Dowex 50W-X8 is difficult because Cr(VI) compounds are strong oxidizers and highly soluble as anionic forms. Hence, preconcentration of Cr(VI) along with other trace metals is not possible with simple Dowex 50W-X8 resin. In view of this, preconcentration of Cr(VI) along with Cr(III) (total chromium in the sample) has been carried out by loading Dowex 50W-X8 with 2-amino-benzenethiol. In this method, the thiol group of 2-amino-benzenethiol effectively reduced from Cr(VI) to Cr(III). The Cr(VI) which was reduced to Cr(III) sorbed onto the resin by forming a chelate complex with the reagent 2-amino-benzenethiol. Based on these studies, we report a simple and sensitive method for preconcentration of total chromium (Cr(VI) and Cr(III)) using Dowex 50W-X8 loaded with 2-amino-benzenethiol and subsequent determination by ICP-AES. The 2-amino-benzenethiol has a strong metal-binding property by forming a chelate complex because it contains two binding sites as sulphur and nitrogen. Metal complexes of 2-amino-benzenethiol are highly insoluble in water. These are the advantages for the high preconcentration factor in the determination of metals in natural waters using 2-amino-benzenethiol.

2. Experimental

2.1 *Reagents*

All the reagents used were of analytical reagent grade. Doubly distilled water was used throughout the experiments.

Dowex 50W-X8 (200 mesh, cation exchanger) resin was used in the H^+ form. The resin was washed several times with doubly distilled water and then treated with

Table 1. ICP-AES operating parameters.

Photomultiplier tube voltage (V)	700
Plasma glass flow (L $\min^{-1}$)	15.0
Auxiliary gas flow (L $\min^{-1}$)	1.5
Incident power (kW)	1.1
Observation height (mm)	14.0
Sample uptake time (s)	30
Pump rate (rpm)	15
RF generator (MHz)	27.12
Wavelength of chromium (nm)	267.716

1 M HCl for 4 h and finally with doubly distilled water until the washing was free from chloride (5 mL of it did not precipitate with 1 mL of 1 M $AgNO_3$ solution). Then, it was air-dried and stored in a polyethylene container.

A standard solution of chromium(VI) (100 µg mL^{-1}) was prepared from the dilution of ICP standard (Merck, Germany), and the working standards were prepared by diluting the standard solution.

Standard reference materials NIST SRMs and 3112a and 1643e were used in the experiment, and the compositions (µg L^{-1}) of the two reference samples were as follows:

- 3112a: Al 9.94, Bi 9.93, Cd 9.97, Co 9.95, Ni 9.96, V 9.94, Mn 9.94, Zn 10, Cu 9.98, Na 9.94, K 9.93, Mg 9.94, Ca 9.98.
- 1643e: Al 141.8, Bi 14.09, Cd 6.568, Co 27.06, Ni 62.41, Mo 121.4, Mn 38.97, V 37.86, Zn 78.5, Cu 22.76, Na 20740, K 2034, Mg 38.97, Ca 32 300.

2.2 *Apparatus*

An atomic emission spectrometer (ICP-AES Varian, Liberty Series II, Australia) with a Wipro Acer computer was used. The operating conditions and wavelengths of the emission lines selected are given in table 1. The analyte lines were selected on the basis of net and background intensities as well as their freedom from spectral overlaps. An Elico model LI-129 pH meter with a combined glass electrode was used for pH measurements.

2.3 *Preparation of the Dowex 50W-X8 resin loaded with 2-amino-benzenethiol*

The Dowex 50W-X8 resin was dried at 115°C to attain a constant weight. The resin (20 g) was added to 100 mL of ethanol containing 3 mL of 2-amino-benzenethiol, and the mixture was shaken at room temperature for 1 h. The reagent was loaded by the physical adsorption of 2-amino-benzenethiol from organic solvent on to the Dowex 50W-X8 resin surface. The resin loaded with reagent was filtered off, washed with ethanol and water, and dried at room temperature for 24 h in a vacuum dry oven.

2.4 *Procedure for the sorption of Cr(VI) on Dowex 50W-X8*

The glass column (0.90 cm i.d., length of 15 cm) was fitted with 0.5 g of resin loaded with 2-amino-benzenethiol. In the lower part of the column, the resin was held by a glass ball and a fine layer of glass wool. In the upper part, another layer of glass wool was put into place. The sample solution containing 100 mL of Cr(VI) in the concentration range 0.1–200 µg L^{-1} was transferred into a 250 mL beaker. The solution pH was adjusted to 7.0 ± 0.5 with HCl (1 : 1) or dilute ammonia (1 : 1) and 2 mL borate buffer solution. The solution was allowed to pass through the column at a flow rate of 1.5 mL min^{-1}. After passing the solution, the column was washed with 10 mL of distilled water, and then the retained chromium was eluted with 10 mL of 6 mol L^{-1} HNO_3 at a flow rate of 1.0 mL min^{-1}. The eluent was collected in a 25 mL volumetric flask and diluted to the mark using double-distilled water. The eluents were nebulized into the plasma of ICP-AES. The operating parameters for chromium determination are given in table 1.

2.5 *Preconcentration of chromium in seawater samples*

A 500 mL seawater sample filtered through a 0.45 µm membrane filter was taken, and the pH was adjusted to 7 ± 0.2 with HCl (1 : 1) or dilute ammonia (1 : 1) and 2 mL of borate buffer solution. The solution was passed through the column containing 0.5 g of resin loaded with 2-amino-benzenethiol, at a flow rate of 1.5 mL min^{-1}. Then, the column was rinsed by passing 10 mL of doubly distilled water. The standard addition method was followed, and the sorbed metal ion was eluted with 10 mL of 6 mol L^{-1} HNO_3 at a flow rate of 1.0 mL min^{-1}, diluted to 25 mL with doubly distilled water, and determined by ICP-AES.

3. Results and discussion

3.1 *Effect of pH*

The effect of pH on the preconcentration of chromium ion on Dowex 50W-X8 loaded with 2-amino-benzenethiol resin was studied by taking 50 µg of metal ion in the pH range of 2.0–9.0. The pH of solution was adjusted using 1 mol L^{-1} of HCl, pH 1.0, acetate buffer, pH 2.0–6.0, borate buffer, pH 7.0, and ammonium buffer, pH 8.0–10.0. The solution was allowed to pass through the column, and then the procedure described in section 2.4 followed. The data are presented in figure 1. As can be seen from figure 1, the recovery of chromium with resin loaded with 2-amino-benzenethiol was higher at pH 4.5–8.0, with a maximum at about pH 7.0. The elution was performed with 10 mL of 6 mol L^{-1} HNO_3. The recovery of chromium was maximum at about pH 7.0, so pH 7.0 ± 0.5 was chosen for the determination of chromium ion in water samples.

3.2 *Sorption capacity of resin and preconcentration factor*

The sorption capacity of the resin was calculated by passing increasing concentrations of chromium solution through the column containing 1.0 g of Dowex 50W-X8 loaded with 2-amino-benzenethiol. The sorbed chromium was eluted with 10 mL of 6 mol L^{-1} HNO_3 at a flow rate of 1.0 mL min^{-1} and determined as described in section 2.4. The results are presented in table 2.

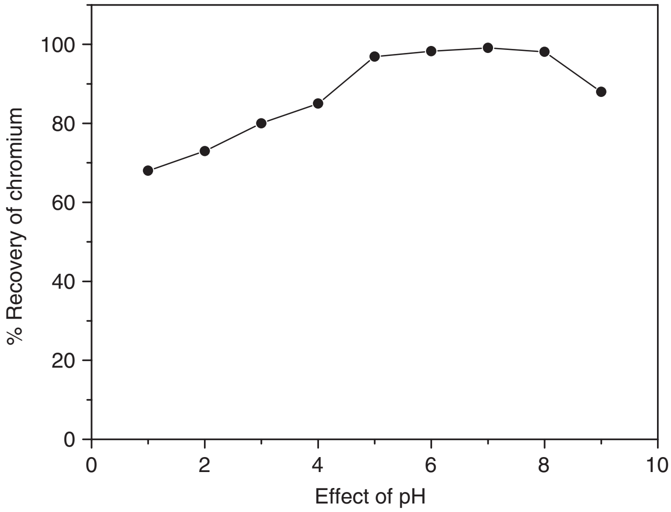

Figure 1. Effect of pH on complexation of chromium on resin loaded with 2-amino-benzenethiol.

Table 2. Experimental results of modified Dowex 50W-X8 resin.

Experimental parameter	Experimental results of chromium
Sorption capacity (mmol g^{-1})	0.19
Preconcentration factor	150
Detection limit (µg L^{-1})	0.3
Loading half time ($t_{1/2}$) (min)	3.6
Sample flow rate (mL min^{-1})	1.5
Eluent flow rate (mL min^{-1})	1.5

The preconcentration factor was evaluated by passing increasing volumes of chromium solution containing 10 µg of Cr(VI) through the column containing 0.5 g of Dowex 50W-X8 resin loaded with 2-amino-benzenethiol and following the procedure described in section 2.4. The results showed that the recovery values were above 95% up to 1500 mL of sample volume. The results are presented in table 2. The recoveries from further diluted solutions were not quantitative. The resin can be reused two or three times with little change in the sorption capacity (<5%).

3.3 *Effect of flow rate and eluent acid concentration*

One-hundred-millilitre solutions containing 50 µg of chromium at pH 7.0 were passed through the column at different flow rates, and the recoveries of chromium were >95% when the flow rate was <3.0 mL min^{-1}. However, when this limiting flow rate was exceeded, there was a decrease in percentage retention. Thus, the retention flow rate was selected as 1.5 mL min^{-1} in further studies. The chromium retained on Dowex 50W-X8 resin loaded with 2-amino-benzenethiol column was quantitatively eluted with 10 mL

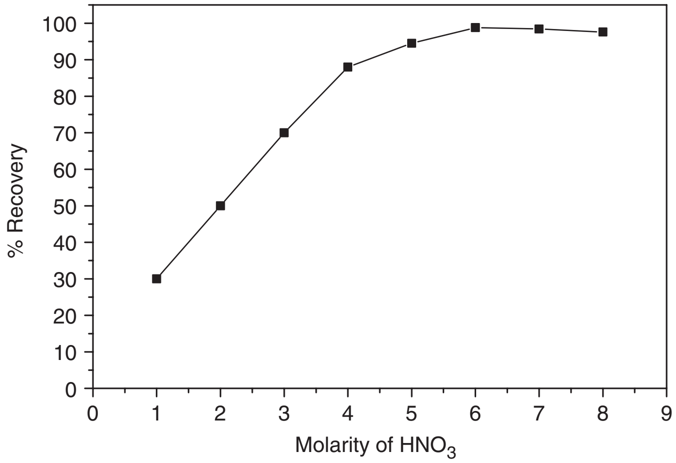

Figure 2. Effect of HNO_3 concentration on elution of chromium.

of 6 mol L^{-1} HNO_3 solution at a flow rate of 1.0 mL min^{-1}. The effect of HNO_3 concentration on elution of chromium is shown graphically in figure 2.

3.4 *Kinetics of sorption*

Sorption kinetics is one of the parameters currently being studied in solid-phase extraction methods because it provides the rate of sorption of metals onto resin loaded with a reagent in the dynamic column mode for routine analysis of water. The rate of uptake of chromium on Dowex 50W-X8 resin loaded with 2-amino-benzenethiol was studied by the batch method. Ten milligrams of chromium was added to 100 mL of distilled water, followed by the addition of 0.5 g of resin and then stirred for 2, 5, 10, 20, 30, 40, 50, and 60 min at room temperature. The remaining chromium in supernatant liquid was determined after the appropriate dilution. The amount of chromium sorbed onto resin loaded with 2-amino-benzenethiol was obtained by mass balance. The loading half time ($t_{1/2}$), defined as the time needed to reach 50% of the resin total loading capacity, was obtained from figure 3. The loading half time ($t_{1/2}$) is reported in table 2.

3.5 *Determination of chromium in standard reference materials and spiked water samples*

The accuracy of the method was investigated by determining the chromium in standard reference materials (NIST-SRM) 1643e, 3112a, and spiked water samples. The results are presented in tables 3 and 4, respectively. The detection limit defined as the concentration of metal (μg L^{-1}) giving an emission reading equal to the mean of the blank plus three times the standard deviation of the blank was determined and reported in table 2. The method was used for the determination of total chromium in seawater samples by the standard addition method, and the results are presented in table 5.

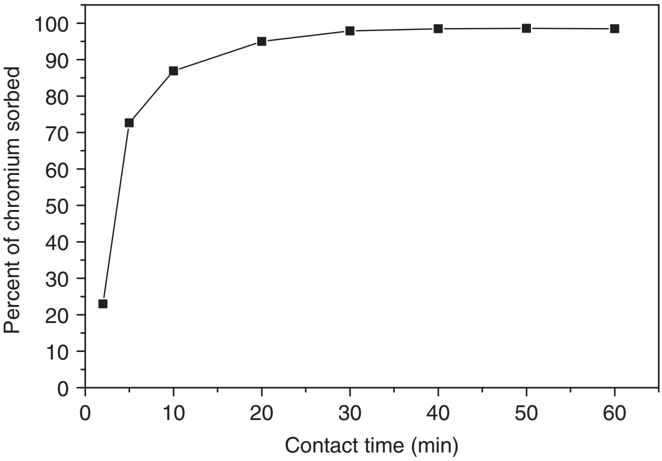

Figure 3. Effect of contact time on sorption of chromium on resin loaded with 2-amino-benzenethiol.

Table 3. Recovery of chromium from standard reference samples after preconcentration on Dowex 50W-X8 resin loaded with 2-amino-benzenethiol.

Name of the SRM	Certified value	After preconcentration on 2-amino-benzenethiol coated resin
1643e	20.4	20.2 ± 0.7
3112a	10.0	9.9 ± 0.4

All values are in μg L^{-1}. The values reported are a mean of five readings ± SD.

Table 4. Recovery of chromium from spiked distilled water samples after preconcentration on Dowex 50W-X8 resin loaded with 2-amino-benzenethiol.

Spiked chromium concentration (μg L^{-1})	Found (μg L^{-1})	Recovery (%)[a]
10	9.9 ± 0.3	99.2
25	24.8 ± 0.8	99.4
50	49.6 ± 1.6	99.2
100	99.2 ± 3.2	99.2

[a] Percentage recovery and percentage RSD for five determinations.

Table 5. Determination of total chromium in seawater samples.[a]

Sample 1[b]			Sample 2[b]		
Added (μg L^{-1})	Found (μg L^{-1})	RSD (%)[c]	Added (μg L^{-1})	Found (μg L^{-1})	RSD (%)[c]
0.0	1.2	4.6	0.0	0.9	4.8
5.0	6.1	3.2	5.0	5.9	3.4
10.0	11.3	3.8	10.0	11.1	3.1
15.0	16.3	3.5	15.0	15.8	3.4

[a] Sample volume: 500 mL.

[b] Samples 1 and 2 were two different seawater samples.

[c] Percentage RSD for five determinations.

Table 6. Tolerance limits of matrix ions for the recovery of chromium.

Matrix ion	Tolerance limit ($\mu g\,mL^{-1}$)
Co^{2+}	45
Cu^{2+}	40
Fe^{3+}	55
Ni^{2+}	65
Mo(VI)	160
V(V)	80
Ca^{2+}	45 000
Mg^{2+}	35 000
K^{+}	55 000
Na^{+}	50 000
SO_4^{2-}	40 000
Cl^{-}	55 000
NO_3^{-}	35 000

3.6 *Effect of matrix ions*

The effect of matrix ions on the sorption of chromium was studied. Different amounts of various cations and electrolytes were added to the 50 µg of chromium solution in 100 mL, and this solution was passed into a column containing 0.5 g of 2-amino-benzenethiol-loaded Dowex 50W-X8 resin. The concentrations causing ±5% error are given in table 6. Alkali and alkaline earth metals did not form complexes with the reagent, and so they were not retained by the column. Transition metal ions also formed complexes with the reagent, but there was no significant effect on the emission signal at the selected analyte wavelengths by their presence in the eluates. However, the maximum limit of transition metals should not exceed the concentrations specified in table 6. The results in table 6 demonstrate that the listed anions and cations did not affect the sorption of chromium under the reported conditions.

4. Conclusions

The reported studies demonstrate that the 2-amino-benzenethiol loaded with Dowex 50W-X8 resin has a good enrichment factor for preconcentration of total chromium (Cr(VI) and Cr(III)) in water samples. The results of sorption capacity, detection limits, and RSD values showed that resin loaded with 2-amino-benzenethiol can be used as an effective preconcentration technique for the determination of total chromium in water samples by ICP-AES. The method has high tolerance limits from the matrix ions. The results of the standard addition method revealed that the proposed method has a good accuracy. The proposed method was applied for the determination of total chromium in seawater samples.

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