CHAPTER 5

SEPARATION, PRECONCENTRATION AND TRACE DETERMINATION OF TOXIC METAL IONS Cr(VI), As(III) AND Tl(I) ON CALIX[4]ARENE-o-VANILLINTHIOSEMICARBAZONE BASED POLYMERIC CHELATING RESIN [RESIN B]
TABLE OF CONTENTS

5.1 INTRODUCTION 183
5.2 EXPERIMENTAL 185
5.2.1 Apparatus 185
5.2.2 Reagents 186
5.2.3 Procedure for Column Concentration and Determination of Cr(VI), As(III) and Tl(I) 189
5.3 RESULTS AND DISCUSSION 189
5.3.1 Parameters Optimized for Separation and Preconcentration of Cr(VI), As(III) and Tl(I) 189
5.3.1.1 Effect of pH 189
5.3.1.2 Effect of Flow Rate 190
5.3.1.3 Effect of Concentration of Eluting Agents 190
5.3.1.4 Total Sorption Capacity 191
5.3.1.5 Distribution Coefficient $K_d$ 191
5.3.1.6 Exchange Kinetics 192
5.3.1.7 Breakthrough Studies 192
5.3.1.8 Preconcentration of Cr(VI), As(III) and Tl(I) 193
5.3.1.9 Resin (B) Stability Tests 194
5.3.1.10 Effect of Electrolytes and Associated Cations 194
5.3.2 Separation Cr(VI), As(III) and Tl(I) 195
5.3.3 Analytical Performance (Calibration Graph, Detection Limit and Precision) 196
5.3.4 Application to Analysis of Water Samples 196
5.4 TABLES

5.4.1 Parameters Optimized for Sorption and Desorption of Cr(VI), As(III) and Tl(I) on Resin (B). 198

5.4.2 Effect of Concentration of Eluting Agents for Desorption of Cr(VI), As(III) and Tl(I) from Resin (B). 199

5.4.3 Preconcentration Factors for the Sorption of Cr(VI), As(III) and Tl(I) on Resin (B). 200

5.4.4 Effect of Commonly Associated Cations in Water Samples on the Sorption of Cr(VI), As(III) and Tl(I) on Resin (B). 201

5.4.5 Tolerance Limits of Electrolytes on the Sorption of Cr(VI), As(III) and Tl(I) on Resin (B). 202

5.4.6 Regression Analysis for the Calibration Graph, Linear Range, Detection Limit and Precision. 203

5.4.7 Determination of Cr(VI), As(III) and Tl(I) in Natural Water Samples on Resin (B). 204

5.4.8 Determination of Cr(VI), As(III) and Tl(I) in Standard Reference Material (SRM) Samples of NIST on the Resin B. 205

5.5 FIGURES

5.5.1 Effect of pH on Sorption of Cr(VI), As(III) and Tl(I) on Resin (B). 206

5.5.2 Effect of Flow Rate on Sorption of Cr(VI), As(III) and Tl(I) on Resin (B). 207

5.5.3 Plot of log K_d against pH for Sorption of Cr(VI), As(III) and Tl(I) on Resin (B). 208
5.5.4 Exchange Kinetics of Cr(VI), As(III) and Tl(I) on Resin (B).

5.5.5 Breakthrough Curves for Cr(VI), As(III) and Tl(I) on Resin (B).

5.5.6 Elution Profile of Cr(VI), As(III) and Tl(I) on Resin (B).

5.5.7 Evaluation of the Stability of Resin (B) for Cr(VI), As(III) and Tl(I) by Sorption and Elution.

5.5.8 Separation of Cr(VI), As(III) and Tl(I) on Resin (B).

REFERENCES
5.1 INTRODUCTION

The concentration of toxic metal ions like Cr(VI), Cu(II), Cd(II), As(III), Pb(II), Hg(II), Tl(I) etc. has increased beyond environmentally and ecologically sustainable levels due to the increase in industrial activity in the field of chemicals, dyes, colour chemicals, petrochemicals, electroplating, textiles and pharmaceuticals sectors over the years \[1\]. It has resulted in severe contamination of ground and surface water; for eg. rivers, lakes, rivulets etc. Especially in the developing countries, water and soil degradation generated by industrial effluents has been a serious issue \[2\]. In order to achieve balanced growth which is sensitive towards conservation of scarce natural resources, time-to-time analysis of these metal ions in natural water samples as well as in bio fluids is necessary. In natural water and biological systems Cr(VI), As(III) and Tl(I) are found in low levels and their separation and preconcentration are obligatory ahead of their trace quantification by instrumental or chemical methods of analysis. The metabolism and toxicology of Cr(VI), As(III) and Tl(I) are of great concern as they get accumulated in body systems \[3,4,5\]. Their determination in food, blood and tissues samples is also very important in order to identify cases of human intoxication leading to untold suffering in developing and least developed countries \[6,7,8\].

These metal ions, scheduled as environmental hazards by Environment Protection Agency (EPA) are essential dietary trace elements required for normal growth and development of animals and human beings and are essential to the human life with permissible limits. The metal ions, which have the adverse effect on human body, are known as toxic metal ions. Toxicity of these metal ions in human beings is outlined below \[1,2\].
Chromium: The potential symptoms on overexposure of chromium are dermatitis, skin ulcers, nasal inflammation, perforation of nasal septum, lung cancer etc.

Arsenic: Overexposure to arsenic and its compounds has been associated with acute and chronic toxicity due to ingestion or inhalation. It can cause local irritation, dermatitis and it increases the risk of skin, liver, bladder, kidney and lung cancer.

Thallium: The toxic effects of thallium, when exposed in larger quantities, cause nausea, diarrhea, abdominal pain, vomiting and pulmonary edema.

The extraction of these metal ions is a tedious process as they are associated with a variety of complex species present in the natural aquatic systems. Many times they are found in such a low concentration that even sophisticated instrumental techniques like FAAS and ICP-OES are not sensitive enough to detect and quantify these toxic metal ions in natural water samples and their prior separation and preconcentration is required. Polymeric chelating ion exchange resins, which can act as specific, sensitive and selective complexants for these types of metal ions have been found very useful by the researchers around the world. For the solid phase extraction of toxic metal ions, polymeric calixarenes can play a vital role due to their characteristics such as lower toxicity, affordability, ease of synthesis and operation. They are more eco-friendly compared to liquid-liquid extraction method where in disposal of organic waste has been a serious environmental hazard.

Various calixarene derivatives have been recently studied with Cr(VI), As(III) and Tl(I) as these cavitands have been found useful in the complexation of these metal ions. Beer and coworkers and Lambert et al have been working particularly on...
this subject as is observed from the number of publications and citations \(^{16-22}\). The thrust of the ongoing research programmes is on arsenic determination at trace and ultra trace levels and its speciation \(^{24-34}\).

As the sulfur containing o-vanillinthiosemicarbazone has proved to be a very good complexing agent for toxic metal ions \(^{35,36}\) we deliberated to introduce it on the calix[4]arene scaffold held by a polymeric backbone. In this chapter we report the synthesis of Merrifield resin supported calix[4]arene-o-vanillinthiosemicarbazone i.e. Resin B and its application to the separation, preconcentration and trace determination of Cr(VI), As(III) and Tl(I) in various natural water samples collected from Ahmedabad city.

5.2 EXPERIMENTAL

5.2.1 Apparatus

A Systronics digital pH meter Model 335 was used for the pH measurements. Flow rate in the column was adjusted with a Miclins peristaltic pump PP-10. Spectral measurements were done on a Hitachi 3210 UV-Vis spectrophotometer using 10 mm quartz cells. Atomic absorption measurements were performed on Perkin-Elmer model 420 atomic absorption spectrophotometer (AAS) pyrolytically coated HGA-76 graphite furnace (GF) for Cr(VI) and Tl(I). Total arsenic determination in the form of As(III) was done on a Chemito 201 AAS with a continuous flow hydride generator for arsine generation. The operating conditions for hydride generator were: argon flow rate - 70 cm\(^3\)/min; concentration of NaBH\(_4\) - 1 % w/v; concentration of HCl - 5 % v/v; sampling time - 25 seconds; reaction time - 25 seconds. The measurements were based on integrated absorbance.
Operating Conditions for Atomic Absorption Spectrophotometer

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<th>Thallium(I)</th>
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<tr>
<td>Burner (cm)</td>
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</table>

5.2.2 Reagents

All chemicals used in this work were of analytical grade of E. Merck or Lancaster. The solvents were purified by the method of Weissberger et al. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system. Standard stock solutions (2000 µg ml⁻¹) of Cr(VI), As(III) and Tl(I) were prepared as given below.

Standard Stock Solutions

1. Chromium(VI): 5.66 g K₂Cr₂O₇ was dissolved in water and then diluted with water to 1000 ml in volumetric flask.

2. Arsenic(III): 2.64 g As₂O₃ was dissolved in 20 ml NaOH. It was diluted with water, neutralized with 2 N HCl and then diluted with water to 1000 ml in volumetric flask.

3. Thallium(I): 2.606 g TlNO₃ was dissolved in water containing 2 ml concentrated HNO₃ and then diluted with water to 1000 ml. Their final concentrations were then standardized spectrophotometrically.

UV-Vis Spectrophotometric Determination of Cr(VI), As(III) and Tl(I)

1. Cr(VI) forms violet coloured water soluble complex with diphenyl
carbazide reagent.

\[ \text{pH} = 1.5, \lambda_{\text{max}} = 546 \text{ nm}, \varepsilon = 41700 \]

2. As(III) forms blue coloured n-butanol soluble arsenomolybdenum blue with ammonium molybdate reagent.

\[ \text{pH} = 6-7, \lambda_{\text{max}} = 800 \text{ nm}, \varepsilon = 30000 \]

3. Tl(III) forms red-violet fluorescent (Benzene+CCl₄:2+1) soluble complex with Rhodamine B reagent.

\[ \text{[Tl(I) oxidized to Tl(III) with Br₂ water in acidic condition.]} \]

\[ \text{In 1 N HCl, } \lambda_{\text{max}} = 560 \text{ nm}, \varepsilon = 97000 \]

The pH of solutions was maintained by adding 0.1 / 0.01 N HCl or NaOH and / or acetate buffer as described in the literature \(^{[40]}\). The glassware used were soaked in 10 % HNO₃ overnight before use and cleaned repeatedly with double distilled deionized water.

**Sample Preparation**

The water samples from Sabarmati river were isokinetically collected in clean polyethylene bottles from locations near thermal power station, Ahmedabad. The groundwater samples were collected from University area and Vatva industrial zone of Ahmedabad city. The standard reference materials (SRMs) procured from National Institute of Standards and Technology (NIST, USA) were digested and their aqueous solutions were prepared as described below.

1. **Standard Samples**

SRMs analyzed to determine the accuracy of the proposed method were in accordance with NIST guidelines. 1 g sample was transferred to 200 ml pyrex glass beaker and 25 ml concentrated HCl was added. Digestion on a sand bath was done for
1 hour and the solution was evaporated to dryness. The residue was dissolved in 15 ml concentrated HCl along with 0.5 g ammonium persulphate. The solution was diluted with double distilled water, filtered and diluted up to the mark in a 100 ml standard volumetric flask.

2. **Soil Samples**

   1 g sample of dried soil was digested with 50 ml concentrated HCl and 10 ml concentrated HNO₃ for 1 hour on a sand bath which was subsequently evaporated to dryness. The residue was moistened with 5 ml HF in a teflon beaker. It was digested on a water bath and evaporated to dryness. The residue was boiled with 50 ml 0.1 N HCl, filtered and the filtrate and the washings were evaporated to dryness. The residue was taken up and diluted to 100 ml with 0.1 N HCl.

3. **Plant, Pulp and Paper Samples**

   10 g sample was ashed at 450° C for 3 hours. 0.1 g of this ash was transferred to a 200 ml pyrex glass beaker and it was digested on a sand bath with 100 ml concentrated HCl and 20 ml concentrated HNO₃ for about 1 hour. The hot solution was centrifuged and the supernatant liquid was decanted from any silicious matter. The residue was boiled with 50 ml 0.1 N HCl and filtered. The supernatant liquid and the filtrated were then evaporated to dryness and the residue was taken in the standard volumetric flask and diluted accurately to 100 ml with 0.1 N HCl.

4. **Biological Sample**

   A known amount of biological sample (blood, body organ, urine, hair, skin etc.) was digested with 20 ml concentrated HCl and 0.25 g ammonium persulphate for 1 hour and then the mixture was diluted with water and filtered. The filtrate and the
washings were evaporated to dryness and the residue was taken in the standard volumetric flask and diluted up to the mark (100 ml) with 0.1 N HCl.

5.2.3 Procedure for Column Concentration and Determination of Cr(VI), As(III) and Tl(I)

A glass column (200 x 8.0 mm) was prepared by adding the slurry of the beads of same mesh size having 1 g Resin (B) in CH₃OH:H₂O::1:1. The height of the column section containing Resin (B) (bed height) was 15 mm. It was conditioned with different buffer solutions for the samples containing Cr(VI), As(III) and Tl(I) prior to their elution from the column. A suitable aliquot of the solution containing 0.01-3.03 μg ml⁻¹ Cr(VI), 0.065-7.2 μg ml⁻¹ As(III) and 0.023-4.9 μg ml⁻¹ Tl(I) was passed through the column after adjusting the appropriate pH at an optimum flow rate. The stripping of the metal ions from the resin bed was carried out by suitable eluting agents like HCl or HNO₃. The eluants were collected in a 25 ml volumetric flask, made to volume by double distilled water and determined spectrophotometrically as well as by GFAAS (Table 5.4.1).

5.3 RESULTS AND DISCUSSION

5.3.1 Parameters Optimized for Separation and Preconcentration of Cr(VI), As(III) and Tl(I)

5.3.1.1 Effect of pH

A glass column was packed with 1 g Resin (B). 100 ml solutions containing 3, 7 and 4.5 μg ml⁻¹ Cr(VI), As(III) and Tl(I) respectively were passed through the column at their optimum flow rate by varying pH. The percentage of metal sorption was measured by desorbing Resin (B) with suitable eluting agent and then determined
by both spectrophotometry and GFAAS. The optimum pH for Cr(VI), As(III) and Tl(I) were found to be 3.5, 5.0 and 6.0 respectively (Table 5.4.1, Figure 5.5.1). Their selectivity in pH of sorption suggests the possibility of separation of these metal ions in presence of each other in the column.

[Table 5.4.1, Figure 5.5.1]

5.3.1.2 Effect of Flow Rate

The effect of flow rate on the extent of metal ion sorbed on the resin was studied in the column packed with 1 g Resin (B) at 30° C. Feed solutions containing 3, 7 and 4.5 μg ml⁻¹ Cr(VI), As(III) and Tl(I) respectively were passed at different flow rates (0.5, 1.0, 1.5, 2.0 etc. ml min⁻¹) maintained by peristaltic pump. The flow rate of the liquid during chromatographic separation should be such that the working conditions are close to the equilibrium state as the flow rate depends upon the particle size and the temperature. Optimum flow rate may be defined as the rate of flow of the effluent through the column at which more than 98 % sorption takes place. The optimum flow rates obtained were 1.5, 1.0 and 1.0 ml min⁻¹ for Cr(VI), As(III) and Tl(I) respectively. An increase in flow rate resulted in decrease in sorption due to insufficient contact time between the resin phase and the metal ion solution (Table 5.4.1, Figure 5.5.2).

[Table 5.4.1, Figure 5.5.2]

5.3.1.3 Effect of Concentration of Eluting Agents

The effect of various eluting agents like HCl, HNO₃ and H₂SO₄ was studied by taking their different normal concentrations. 1 g Resin (B) in the column was conditioned at pH of maximum sorption and then fed with 100 ml solutions containing 3, 7 and 4.5 μg ml⁻¹ Cr(VI), As(III) and Tl(I) respectively. The metal ions
were desorbed with different mineral acids and then determined by spectrophotometry and GFAAS (Table 5.4.1 & 5.4.2). It was observed that quantitative elution was possible with 15 ml of 0.1 N H2SO4, 0.5 N HCl and 1 N HNO3/3 N HCl for Cr(VI), As(III) and Tl(I) respectively.

5.3.1.4 Total Sorption Capacity

The total sorption capacity studies were carried out using the batch techniques for Cr(VI), As(III) and Tl(I). 1 g Resin (B) was equilibrated with 500 ml solution containing 100 μg ml⁻¹ metal ions at their optimum pH for 2 hours at 30° C. The amount of metal ions sorbed on Resin (B) was calculated from the difference in the metal ion concentration before and after desorption (Table 5.4.1). The total sorption capacities of the resin were found to be 11325, 15575 and 34397 μg g⁻¹ for Cr(VI), As(III) and Tl(I) respectively.

5.3.1.5 Equilibrium Distribution Coefficient Kd

Exchange equilibria are very often expressed in terms of the distribution coefficient Kd. This quantity is given by the ratio of the equilibrium concentrations of the same metal ion in the resin phase and in the solution. The distribution coefficient Kd of the metal ions between Resin (B) and aqueous phase was determined by batch experiment. 1 g resin (B) was equilibrated with 25 ml solution containing not more than 453, 623 and 1376 μg ml⁻¹ Cr(VI), As(III) and Tl(I) respectively for 2 hours at 30° C. The solution was filtered to remove Resin (B) and the filtrate was subjected to spectrophotometric and GFAAS determination of the metal ion content. The concentration of the eluted metal ion solution was also measured (Table 5.4.1). Kd for
CrvVI), As(III) and Tl(I) were found to be 3360, 2600 and 2128 respectively. The distribution coefficient \( K_d \) or efficiency of Resin (B) was measured using the equation,

\[
K_d = \frac{\text{Amount of the metal ion taken up by the resin}}{\text{Amount of the metal ion remaining in the solution}} \times \frac{\text{Volume of the solution}}{\text{Amount of resin taken}}
\]

The plots of \( \log K_d \) against pH (Figure 5.5.3) were straight lines with the slopes nearly equal to unity, indicating 1:1 stoichiometry between the metal ions and Resin (B) \[41\].

[Table 5.4.1, Figure 5.5.3]

**5.3.1.6 Exchange Kinetics**

The batch experiments were carried out to determine the rate of loading of Cr(VI), As(III) and Tl(I) on Resin (B). 1 g resin (B) was stirred with 100 ml feed solution containing 113, 156 and 344 \( \mu \)g ml\(^{-1}\) Cr(VI), As(III) and Tl(I) respectively at 30\(^\circ\) C. 5 ml of the feed solution was withdrawn at predetermined intervals and analyzed. The concentration of metal ion in aqueous phase was determined by spectrophotometry and GFAAS. The amount of metal ion loaded on the resin phase was calculated by measuring the concentration of metal ion in the feed solution (Table 5.4.1, Figure 5.5.4). The time taken for the sorption of 50 % of the metal ions (\( t_{1/2} \)) was found to be 6.5, 9.0 and 12.5 minutes for Cr(VI), As(III) and Tl(I) respectively, which indicated very good accessibility of these metal ions towards chelating sites.

[Table 5.4.1, Figure 5.5.4]

**5.3.1.7 Breakthrough Studies**

Breakthrough capacities are more significant and useful than total sorption capacities in ion exchange chromatographic applications as it gives actual working
capacity of the resin in the column. Breakthrough capacity or the effective capacity may be defined as the capacity at the moment when the adsorbed component has appeared in the effluent with an increased concentration. It is one of the most critical parameters when working under dynamic condition. Breakthrough studies were carried out by taking 1 g Resin (B) in the column having 200 mm length and 8.0 mm internal diameter with the bed height of 15 mm and passing 10 \( \mu \text{g ml}^{-1} \) of metal ions [Cr(VI), As(III) or Tl(I)] at their optimum pH and flow rate. An aliquot of 2.0 ml eluant was collected each time and analyzed by spectrophotometry and GFAAS for the metal ion content (Figure 5.5.5). Breakthrough capacities of Resin (B) for Cr(VI), As(III) and Tl(I) were found to be 2151, 2647 and 5503 \( \mu \text{g g}^{-1} \) respectively (Table 5.4.1). All the curves were steep at their breakthrough points at different times, indicating the possibility of separating these metal ions from their mixtures.

**Table 5.4.1, Figure 5.5.5**

### 5.3.1.8 Preconcentration of Cr(VI), As(III) and Tl(I)

The concentration of trace elements in natural water is too low for their direct determination. Therefore, preconcentration or enrichment step is unavoidable even with a sensitive detection method. Resin (B) was studied for column concentration of Cr(VI), As(III) and Tl(I) in terms of their preconcentration factor (PF).

\[
P F = \frac{\text{Concentration of metal in stripping solution}}{\text{Initial concentration of metal in feed solution}}
\]

1000 ml solutions containing 6, 9, 6 \( \mu \text{g l}^{-1} \) Cr(VI), As(III) and Tl(I) at pH 3.5, 5.0, 6.0 respectively, were passed through the column containing 1 g Resin (B). The preconcentrating ability of Resin (B) was assessed from the elution profile of metal ions by plotting the concentration of effluents as a function of the volume of stripping.
solutions: 8.5 ml, 0.1 N H₂SO₄ for Cr(VI); 11.1 ml, 0.5 N HCl for As(III); 9.5 ml, 1 N HNO₃ for Tl(I) respectively. The preconcentration factors were found to be 117, 90 and 105 for Cr(VI), As(III) and Tl(I) respectively with 98-99 % recovery (Table 5.4.1 & 5.4.3, Figure 5.5.6).

[Table 5.4.1, Table 5.4.3, Figure 5.5.6]

5.3.1.9 Resin (B) Stability Tests

The stability of Resin (B) was tested to evaluate its sustainability for repeated cycles of sorption and desorption with different mineral acids. It was observed that there was no detectable change in the physical and chemical properties of Resin (B) in concentrated acidic solutions of 5.0 N HCl, 3.0 N HNO₃ and 3.5 N H₂SO₄. To check the regenerating capacity of Resin (B), it was subjected to repeated sorption and desorption of Cr(VI), As(III) and Tl(I) at their optimum conditions in the column. 1 g resin (B) was taken in the column and 500 ml solution containing 100 µg ml⁻¹ metal ions was passed through it at 30°C. Resin (B) was then stripped off metal ions with 25 ml of suitable eluant. Resin (B) showed very good stability up to 15 repeated cycles of sorption and desorption (Figure 5.5.7), after which it showed 2-3 % decrease in efficiency, which may be due to hydrolysis of Resin (B) when treated with mineral acids.

[Figure 5.5.7]

5.3.1.10 Effect of Electrolytes and Associated Cations

The limit of tolerance of anions and cations on the sorption of Cr(VI), As(III) and Tl(I) is defined as that concentration which causes an error of 2-3 % in the recovery of these metal ions. The effect of commonly associated cations in natural water samples such as Fe(II), Fe(III), Co(II), Ni(II), Mn(II), alkali [Li(I), Na(I), K(I), Rb(I), Cs(I)]
and alkaline earth [Mg(II), Ca(II), Sr(II) and Ba(II)] had been studied under optimum conditions of metal ion sorption. Mn(II) did not affect the sorption of Cr(VI), As(III) and Tl(I) up to 4 mg, however, for other cations the tolerance limits were much higher (Table 5.4.4). The effect of anions and their limit of tolerance on the sorption of Cr(VI), As(III) and Tl(I) by Resin (B) was studied by taking different concentrations of some electrolytes like NaCl, NaF, NaBr, NaN[3]NO[2], NaNO[3], Na[2]SO[4], Na[3]PO[4] and CH[3]COONa. The results (Table 5.4.5) showed that except Na[3]PO[4], all other electrolytes did not interfere between 1.0-3.0 M concentration range, which further augments the potential application of Resin (B) for the analysis of real samples.

[Table 5.4.4, Table 5.4.5]

5.3.2 Separation of Cr(VI), As(III) and Tl(I)

Resin (B) was found useful for separating chromium, arsenic and thallium from the mixture due to favourable kinetics and different breakthrough capacities in the column. The Resin (B) was tested for simultaneous separation of their ternary mixture. Hence, the mixture of chromium, arsenic and thallium (each 100 μg in 25 ml buffer solution) was passed through the column at optimum pH and flow rate. The column effluents were analyzed for the metal ions by spectrophotometry and GFAAS.

In the separation of their ternary mixture containing 100 μg each of Cr(VI), As(III) and Tl(I) was passed through the column maintained at pH 3.0 at the flow rate of 1.0 ml min⁻¹. At this pH, most of As(III) and Tl(I) came out with the effluent while Cr(VI) was retained in the column. Cr(VI) was eluted with 0.1 N H[2]SO[4]. The small amounts of As(III) and Tl(I) (≤ 2 %) which were sorbed by Resin (B) were then separated on the basis of selective elution with different eluting agents. As(III) was eluted first with 0.5 N HCl followed by Tl(I) with 1 N HNO[3]. The effluent containing
As(III) and Tl(I) was then passed through a fresh column maintained at pH 5.5. Both the metal ions were retained in the column and As(III) was desorbed first with 0.5 N HCl followed by Tl(I) with 1 N HNO₃. Thus, quantitative separation was achieved as seen in the separation pattern in Figure 5.5.8.

5.3.3 Analytical Performance (Calibration Graph, Detection Limit and Precision)

In the preparation of the calibration standards for Cr(VI), As(III) and Tl(I), the standard stock solutions of these elements were used after appropriate dilution. The precision of the proposed method was examined based on the optimum condition for preconcentration in the column and expressed as R.S.D. (%), 1.3 % for Cr(VI), 1.2 % for As(III) and 1.1 % for Tl(I). The limit of detection (LOD) was defined as that analyte concentration giving a signal equal to three times the standard deviation of blank signal [42]. The limit of quantification (LOQ) was then set as ten times the standard deviation of the blank signal (Table 5.4.6).

5.3.4 Application to Analysis of Water Samples

The validity of the proposed method was verified by subjecting Resin (B) to the natural water samples and SRMs procured from NIST. The results obtained for the water samples by the proposed method were compared with that of standard addition method. The natural water samples and aqueous samples of reference standards were prepared as per the methods described in the experimental section and then passed through the column as explained in the general procedure for column concentration. The amount of the metal ions present in the water samples and their R.S.D. values are

196
given in Table 5.4.7 and the method validation with respect to NIST standards has been given in Table 5.4.8. Higher efficiency of separation curves with lower values of R.S.D., between 1.1-1.3 %, suggests the utility of Resin (B) for various analytical applications in the determination of Cr(VI), As(III) and Tl(I).

[Table 5.4.7]
### Table 5.4.1
Parameters Optimized for Sorption and Desorption of Cr(VI), As(III) and Tl(I) on Resin (B).

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<tr>
<td>4</td>
<td>Total Sorption Capacity (µg g(^{-1}) of Resin)</td>
<td>11325</td>
<td>15575</td>
<td>34397</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Distribution Coefficient (K(_d))</td>
<td>3360</td>
<td>2600</td>
<td>2128</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Preconcentration Factor (PF)</td>
<td>117</td>
<td>90</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Breakthrough Capacity (µg g(^{-1}) of Resin)</td>
<td>2151</td>
<td>2647</td>
<td>5503</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>R.S.D. (%)*</td>
<td>1.2-1.4</td>
<td>1.1-1.3</td>
<td>1.0-1.2</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Average Recovery (%)</td>
<td>98</td>
<td>99</td>
<td>97-98</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>t(_{1/2}) for Exchange (minutes)</td>
<td>6.5</td>
<td>9.0</td>
<td>12.5</td>
<td></td>
</tr>
</tbody>
</table>

*Average of ten determinations.
**Table 5.4.2**

**Effect of Concentration of Eluting Agents for Desorption**

of Cr(VI), As(III) and Tl(I) from Resin (B).

**Experimental Condition:**

- **Resin**: 1 g
- **Volume of Solution Passed**: 100 ml
- **Cr(VI)**: pH 3.5; 3 µg ml\(^{-1}\)
- **As(III)**: pH 5.0; 7 µg ml\(^{-1}\)
- **Tl(I)**: pH 6.0; 4.5 µg ml\(^{-1}\)

<table>
<thead>
<tr>
<th>Conc. (N)</th>
<th>HCl</th>
<th>HNO(_3)</th>
<th>H(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr(VI)</td>
<td>As(III)</td>
<td>Tl(I)</td>
</tr>
<tr>
<td>0.01</td>
<td>5.5</td>
<td>22.8</td>
<td>5.0</td>
</tr>
<tr>
<td>0.1</td>
<td>12.5</td>
<td>66.5</td>
<td>9.7</td>
</tr>
<tr>
<td>0.5</td>
<td>17.1</td>
<td>99.7</td>
<td>12.0</td>
</tr>
<tr>
<td>1.0</td>
<td>21.6</td>
<td>---</td>
<td>17.9</td>
</tr>
<tr>
<td>1.5</td>
<td>29.5</td>
<td>---</td>
<td>32.3</td>
</tr>
<tr>
<td>2.0</td>
<td>40.7</td>
<td>---</td>
<td>63.0</td>
</tr>
<tr>
<td>3.0</td>
<td>49.9</td>
<td>---</td>
<td>99.8</td>
</tr>
</tbody>
</table>

Values given are average of ten determinations.
Table 5.4.3

Preconcentration Factors for the Sorption of Cr(VI), As(III) and Tl(I) on Resin (B).

Experimental Condition:
Resin : 1 g
Cr(VI) : pH 3.5; Elution by 0.1 N H₂SO₄
As(III) : pH 5.0; Elution by 0.5 N HCl
Tl(I) : pH 6.0; Elution by 1 N HNO₃

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Volume of Solution Passed (ml)</th>
<th>Concentration of Solution Passed (µg l⁻¹)</th>
<th>Volume of Eluted Solution (ml)</th>
<th>Recovery (%)</th>
<th>Preconcentration Factor (PF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>1000</td>
<td>6</td>
<td>8.5</td>
<td>98.0</td>
<td>117</td>
</tr>
<tr>
<td>As(III)</td>
<td>1000</td>
<td>9</td>
<td>11.1</td>
<td>99.0</td>
<td>90</td>
</tr>
<tr>
<td>Tl(I)</td>
<td>1000</td>
<td>6</td>
<td>9.5</td>
<td>98.0</td>
<td>105</td>
</tr>
</tbody>
</table>

Values given are average of ten determinations.
Table 5.4.4

Effect of Commonly Associated Cations in Water Samples on the Sorption of 
Cr(VI), As(III) and Tl(I) on Resin (B).

Experimental Condition:
Resin: 1 g
Volume of Solution Passed: 100 ml
Cr(VI): pH 3.5
As(III): pH 5.0
Tl(I): pH 6.0

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Fe(II)</th>
<th>Fe(III)</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Mn(II)</th>
<th>Alkali Metal Ions</th>
<th>Alkaline Earth Metal Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>16</td>
<td>21</td>
<td>17</td>
<td>20</td>
<td>4</td>
<td>DNI</td>
<td>DNI</td>
</tr>
<tr>
<td>As(III)</td>
<td>14</td>
<td>17</td>
<td>16</td>
<td>15</td>
<td>4</td>
<td>DNI</td>
<td>DNI</td>
</tr>
<tr>
<td>Tl(I)</td>
<td>7</td>
<td>15</td>
<td>11</td>
<td>14</td>
<td>5</td>
<td>DNI</td>
<td>DNI</td>
</tr>
</tbody>
</table>

Values given are average of ten determinations. DNI: do not interfere.
Table 5.4.5

Tolerance Limits of Electrolytes on the Sorption of Cr(VI), As(III) and Tl(I) on Resin (B).

**Experimental Condition:**
- Resin: 1 g
- Volume of Solution Passed: 100 ml
- Cr(VI): pH 3.5
- As(III): pH 5.0
- Tl(I): pH 6.0

<table>
<thead>
<tr>
<th>Metal Ions (2.5 μg ml⁻¹)</th>
<th>Concentration of Electrolytes (mol l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaF</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>1.5</td>
</tr>
<tr>
<td>As(III)</td>
<td>2.0</td>
</tr>
<tr>
<td>Tl(I)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Values given are average of ten determinations.
Table 5.4.6

Regression Analysis for the Calibration Graph, Linear Range, Detection Limit and Precision.

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Linear Range (µg ml⁻¹)</th>
<th>Regression Equation</th>
<th>Correlation Coefficient</th>
<th>LOD (µg l⁻¹)</th>
<th>LOQ (µg l⁻¹)</th>
<th>R.S.D.* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>0.010 - 3.03</td>
<td>$A = C \times 0.599 - 0.0011$</td>
<td>1.0010</td>
<td>5.83</td>
<td>19.43</td>
<td>1.3</td>
</tr>
<tr>
<td>As(III)</td>
<td>0.065 - 7.20</td>
<td>$A = C \times 0.201 - 0.0076$</td>
<td>0.9979</td>
<td>8.48</td>
<td>28.26</td>
<td>1.2</td>
</tr>
<tr>
<td>Tl(I)</td>
<td>0.023 - 4.90</td>
<td>$A = C \times 0.3469 - 0.0006$</td>
<td>1.0110</td>
<td>5.56</td>
<td>18.56</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Average of ten determinations. $A =$ Absorbance, $C =$ Concentration (µg ml⁻¹)
Table 5.4.7

Determination of Cr(VI), As(III) and Tl(I) in Natural Water Samples on Resin (B).

Experimental Condition:
Resin: 1 g
Sample Volume: 1000 ml

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>Cr(VI)</th>
<th>As(III)</th>
<th>Tl(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount (µg l⁻¹)</td>
<td>R.S.D.* (%)</td>
<td>Amount (µg l⁻¹)</td>
<td>R.S.D.* (%)</td>
</tr>
<tr>
<td>Sabarmati River, Near Thermal Power Station, Ahmedabad</td>
<td>Present Method</td>
<td>42</td>
<td>1.0</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Standard Addition</td>
<td>43</td>
<td>1.1</td>
<td>38</td>
</tr>
<tr>
<td>Ground Water, University Area, Ahmedabad</td>
<td>Present Method</td>
<td>20</td>
<td>1.4</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Standard Addition</td>
<td>19</td>
<td>1.2</td>
<td>30</td>
</tr>
<tr>
<td>Ground Water, Vatva Industrial Zone, Ahmedabad</td>
<td>Present Method</td>
<td>94</td>
<td>1.2</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Standard Addition</td>
<td>96</td>
<td>1.3</td>
<td>69</td>
</tr>
</tbody>
</table>

*Average of ten determinations.
Table 5.4.8

Determination of Cr(VI), As(III) and Tl(I) in Standard Reference Material (SRM) Samples of NIST on the Resin B.

Experimental Condition:
Resin : 1 g
Sample: 1 g

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal ion Concentration* Found by GFAAS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr(VI) (µg g⁻¹)</td>
</tr>
<tr>
<td>SRM 361 (Low Alloy Steel)</td>
<td>6937.5 (6940)</td>
</tr>
<tr>
<td>SRM 2711 (Montana Soil)</td>
<td>47.2 (47)</td>
</tr>
<tr>
<td>SRM 1573a (Tomato Leaves)</td>
<td>1.99 (1.99)</td>
</tr>
<tr>
<td>SRM 1577b (Bovine Lever)</td>
<td>--</td>
</tr>
</tbody>
</table>

(Certified Values in the Brackets)

*Average of three determinations.
Fig. 5.5.1: Effect of pH on the Sorption of Cr(VI), As(III) and Tl(I) by the Resin B.

Amount of resin B in the column 1 g,
Volume of the metal ion solution passed. 100 ml,
Cr(VI) 3 μg ml⁻¹, Elution by 0.1 N H₂SO₄;
As(III) 7 μg ml⁻¹, Elution by 0.5 N HCl;
Tl(I) 4.5 μg ml⁻¹, Elution by 1 N HNO₃.
Fig. 5.5.2: Effect of Flow Rate on the Sorption of Cr(VI), As(III) and Tl(I) on the Resin B.

Amount of resin B in the column: 1 g;
Cr(VI): 3 µg ml⁻¹; pH 3.5;
As(III): 7 µg ml⁻¹; pH 5.0;
Tl(I): 4.5 µg ml⁻¹; pH 6.0.
Fig. 5.5.3: Plot of log\(K_d\) against pH for the Sorption of Cr(VI), As(III) and Tl(I) on the Resin B.

Amount of the resin B: 1 g;
Volume of the solution: 25 ml;
Cr(VI): 453 \(\mu g \text{ ml}^{-1}\);
As(III): 623 \(\mu g \text{ ml}^{-1}\);
Tl(I): 1376 \(\mu g \text{ ml}^{-1}\).
Fig. 5.5.4: Exchange Kinetics of Cr(VI), As(III) and Tl(I) on the Resin B.

Amount of the resin B: 1 g;
Volume of the feed solution: 100 ml;
Cr(VI): 113 µg ml⁻¹; pH 3.5;
As(III): 156 µg ml⁻¹; pH 5.0;
Tl(I): 344 µg ml⁻¹; pH 6.0.
Fig. 5.5.5: Breakthrough Curves for Cr(VI), As(III) and Tl(I) on the Resin B.

Amount of the resin B in the column: 1 g;
Concentration of the solution passed: 10 μg ml⁻¹;
Cr(VI): pH 3.5;
As(III): pH 5.0;
Tl(I): pH 6.0.
Fig. 5.5.6: The Elution Profile of Cr(VI), As(III) and Tl(I) on the Resin B.

Amount of resin B in the column: 1 g;
Volume of the solution passed: 1000 ml;
Cr(VI): 6 µg l⁻¹; pH 3.5; elution by 0.1 N H₂SO₄;
As(III): 9 µg l⁻¹; pH 5.0; elution by 0.5 N HCl;
Tl(I): 6 µg l⁻¹; pH 6.0; elution by 1 N HNO₃.
Fig. 5.5.7: Evaluation of the Stability of the Resin B for Cr(VI), As(III) and Tl(I) by Sorption and Elution.

Amount of resin B in the column: 1 g;
Volume of the feed solution: 500 ml;
Concentration of the feed solution: 100 μg ml$^{-1}$;
Cr(VI): pH 3.5; elution by 0.1 N H$_2$SO$_4$;
As(III): pH 5.0; elution by 0.5 N HCl;
Tl(I): pH 6.0; elution by 1 N HNO$_3$. 
Fig. 5.5.8: Separation of Cr(VI), As(III) and Tl(I) on the Resin B.

Amount of resin B: 1 g;
Column maintained first at pH 3.0 and than at pH 5.5;
Cr(VI): 100 µg in 25 ml buffer;
As(III): 100 µg in 25 ml buffer;
Tl(I): 100 µg in 25 ml buffer.
REFERENCES


