

# Selective Preconcentration and Determination of Chromium(VI) Using a Flat Sheet Polymer Inclusion Sorbent: Potential Application for Cr(VI) Determination in Real Samples

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**A method for sorption preconcentration of Cr(VI) from aqueous samples was developed using a polymer inclusion sorbent (PIS). The PIS used in this method was prepared by physical inclusion of Aliquat-336 in the matrix formed by cellulose triacetate and 2-nitrophenyl octyl ether. This sorbent was found to be stable, cost-effective, efficient for preconcentration of Cr(VI) present in the aqueous samples, and amenable to direct quantitative analysis of Cr(VI) held in it by neutron activation analysis and spectrophotometry. The quantifying of Cr(VI) in PIS by spectrophotometry was carried out by developing color directly on the PIS after reacting it with 1,5-diphenylcarbazide. The distinct color developed on the PIS even at very low concentrations of Cr(VI) suggests its possible use for field determination of Cr(VI). The composition of PIS was optimized to obtain maximum uptake of Cr(VI) without sacrificing uniformity in terms of thickness and distribution of ion-exchange sites, stability, and time required for quantitative sorption of Cr(VI) from aqueous samples. The Cr(VI) species held in the PIS, mainly  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ , were found to vary as a function of pH of the aqueous samples from which Cr(VI) was preconcentrated. A close agreement was found in the abundances of Cr(VI) species held in the PIS with those reported in the literature for aqueous solutions at different pH. The variation of Cr(VI) species as a function of pH was found to have a significant impact on the tolerance to anions on the uptake of Cr(VI) in the PIS. The high selectivity of PIS toward Cr(VI) from aqueous solution at pH = 2 was explained on the basis of hydration of anions. The uptake of Cr(VI) was found to be fairly constant ( $88 \pm 3\%$ ) up to nearly complete exchange of counterions present in the PIS. The method developed in the present work was successfully used for the preconcentration of Cr(VI) from tap water and seawater samples containing low levels of Cr(VI).**

Chromium is known to occur widely in nature. However, the concentration of chromium in the aquatic systems is increasing as a result of effluent discharge from some of the processes such

as steel works, electroplating, tanning, chemical industries, oxidative dyeing, and cooling water towers.<sup>1</sup> Chromium may also enter drinking water from the corrosion inhibitors used in water pipes and containers.<sup>1</sup> The most common oxidation states of chromium in the aqueous medium are Cr(III) and Cr(VI). The hexavalent form of chromium can persist unchanged in solution for a long time. The Cr(VI) anions such as  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$ , and  $\text{Cr}_2\text{O}_7^{2-}$  are not strongly sorbed in many soils under alkaline to slightly acidic conditions.<sup>2</sup> Thus, they can be mobile in the subsurface environment. The hexavalent chromium anions are known to be toxic for biological systems.<sup>3</sup> Therefore, investigation on the fate of Cr(VI) anions in different environmental systems is required. This calls for the development of analytical techniques that are able to differentiate Cr(VI) from other oxidation states of chromium in a variety of matrixes.

Analytical techniques such as atomic spectrometry,<sup>4–6</sup> spectrophotometry,<sup>7,8</sup> fluorometry,<sup>9</sup> chemiluminescence,<sup>10</sup> and isotope dilution mass spectrometry<sup>11</sup> have been applied for the quantitative determination of the chromium species after their preconcentration or separation. The preconcentration step used in these analytical methods resulted in enhancing the sensitivity to sub-pb levels.

The major problem in establishing a reliable methodology for chromium speciation is related to the preservation of natural species present in the sample.<sup>12,13</sup> Also, the methodology involving prolonged sample manipulation may affect the distribution of

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chromium species significantly.<sup>14</sup> Thus, there is a need for the preconcentration methods that can be used under dynamic conditions with minimum sample manipulation. The selective speciation of chromium through micelle-mediated preconcentration can be used on-line with minimum sample manipulation.<sup>15</sup> Preconcentration methods involving solid sorbents are considered superior to liquid–liquid extraction systems in terms of simplicity, rapidity, and ability to obtain a high enrichment factor. In sorption preconcentration methods, solid sorbents such as activated alumina,<sup>16</sup> tributyltin chloride immobilized on C<sub>18</sub> cartridges,<sup>17</sup> ion-exchange column,<sup>18</sup> or diphenylcarbazide immobilized on silica<sup>19</sup> have been employed for on-line preconcentration of Cr(VI) from water. This is followed by its determination with atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry. Most of these methodologies require elution of Cr(VI) species from the solid sorbent. Solid-phase spectrophotometry offers the possibility of direct quantification of Cr(VI) species held in the solid sorbents.<sup>20–22</sup> In this method, a higher degree of sensitivity and accuracy can be expected due to direct determination of Cr(VI) in the solid phase by absorption spectrophotometry. The disadvantage in this approach appears to be the difficulty in preparing a reference resin layer that has the same optical background as the colored resin. A possible approach to overcome this difficulty would be to replace the resin with a thin flat sheet polymer sorbent for sorption of Cr(VI) from aqueous medium.

There are two possible routes to form the flat sheet sorbents. The first one involves the grafting of a suitable monomer into the pores of a microporous membrane and subsequent incorporation of desirable functional groups by chemical modification of the grafted polymeric chains. Most of the ion-exchange membranes are prepared using such an approach.<sup>23</sup> In the other route, the sorbent is formed by physical inclusion of the required ligands or ion-exchange molecules into the polymer matrix. The Zn(II)-imprinted microspheres were prepared by physical trapping of 1,12-dodecanediol-*O,O*-diphenylphosphonic acid in the highly cross-linked polymer matrix formed by in situ polymerization of trimethylolpropane trimethylacrylate.<sup>24</sup> The physical inclusion of extractants into the polymer matrixes can also be achieved by using preformed polymers such as poly(vinyl chloride) and cellulose triacetate, which are extensively used in potentiometric sensors<sup>25</sup> and polymer inclusion membranes, respectively.<sup>26,27</sup> This

approach of preparing polymer inclusion substrates is very simple and cost-effective. The hydrophobicity of the polymer inclusion sorbent provides stability to this substrate in the aqueous medium.

In this paper, we report the possibility of using a well-defined polymer inclusion sorbent (PIS) for the sorption preconcentration of Cr(VI) from aqueous medium. The PISs have been formed by physical inclusion of a liquid anion exchanger, Aliquat-336, into a matrix formed by cellulose triacetate and 2-nitrophenyl octyl ether. The PISs have been optimized for the sorption preconcentration of Cr(VI) from aqueous media. The analyses have been carried out to evaluate the species of Cr(VI) held in the PIS samples as a function of pH of aqueous medium. The tolerance to various anions, commonly present in the aquatic environmental samples, on Cr(VI) sorption in PIS is also reported here. An attempt has been made to understand the selectivity of PIS for Cr(VI) based on hydration of anions. The method developed in the present work has been employed for preconcentration of Cr(VI) from tap water and seawater samples. Neutron activation analysis (NAA) and spectrophotometry were used for quantitative determination of Cr(VI) sorbed on PIS.

## EXPERIMENTAL SECTION

**Reagents and Apparatus.** Analytical reagent grade chemicals (KCl, KI, Na<sub>2</sub>SO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, KMnO<sub>4</sub>, NaNO<sub>3</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, CHCl<sub>3</sub>) from BDH, ultrapure water (18 MΩ/cm, gradient A-10 model, Milli-Q), and suprapure grade HCl (Merck) were used throughout the present studies. Cellulose triacetate (molecular weight 72 000–74 000; acetyl value 43.2%) (Alfa Biochem), 2-nitrophenyl octyl ether (Fluka, purity 99%), and 1,5-diphenylcarbazide (Merck, purity 98%) were used as obtained. Trioctylmethylammonium chloride (Aliquat-336, mixture of C<sub>8</sub>–C<sub>10</sub>; C<sub>8</sub> is dominating) (Fluka) was used as such. Aliquat-336 was found to contain 85 mol % exchange sites as estimated by chlorine analysis using NAA.

A UV–visible spectrophotometer (Cary 500 Scan, Varian), a FT-IR (FT-IR-420 Jasco), a viscometer (AU-250, DJ Scientific), and a pH meter (PHAN Lab) were used for measurements. The pH meter was calibrated using pH = 4.01, pH = 7, and pH = 9.01 standard buffer solutions (Merck). The radiotracer <sup>51</sup>Cr(VI) was prepared by irradiating known amounts of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for the appropriate time in the Dhruva research reactor (BARC, Mumbai, India). The stock solution of <sup>51</sup>Cr(VI) radiotracer was prepared by dissolving the irradiated K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in a known volume of ultrapure water. Therefore, the amount of Cr(VI) represents the total amount of Cr(VI) including the amount of <sup>51</sup>Cr(VI) radiotracer. The radioactivity of <sup>51</sup>Cr(VI) (320 keV) was monitored by γ-ray spectrometry using a HPGe detector coupled to a 4k channel analyzer (MCA) or a well-type NaI(Tl) detector connected to a single channel analyzer.

**Safety Considerations.** Chloroform used for casting PIS presents a moderate risk to health by inhalation, ingestion, or skin absorption. Although the activity used in the present work is low, all radioactive materials can be hazardous if they are not handled correctly. Physical handling of low-level radioactive materials was carried out inside a fume hood connected to an exhaust system and using disposable latex gloves.

**Preparation and Characterization of PIS.** A solution of cellulose triacetate (CTA) was prepared by dissolving an appropri-

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ate amount of CTA in 15 mL of chloroform. A separate chloroform solution containing known amounts of 2-nitrophenyl octyl ether (NPOE) and Aliquat-336 was prepared. These solutions were mixed (total volume, 25 mL) and ultrasonicated for 2 min to form the casting solution of PIS. Finally, this casting solution was spread on a 9-cm-diameter flat-bottom glass Petri dish which was kept on a leveled surface. The Petri dish was covered in such a way to allow aeration and prevent any cross-contamination. Chloroform was allowed to evaporate slowly over a period of 12 h. After evaporation of chloroform, the PIS was peeled off the Petri dish. The weight of PIS was found to be identical ( $\pm 1\%$ ) as expected from the total weights of CTA, NPOE, and Aliquat-336 used for casting PIS. The PIS was washed with water and equilibrated in 0.2 mol/L KCl before use.

The thickness of the PIS samples was measured using a digital micrometer (Mitutoyo) with an accuracy of  $\pm 0.001$  mm. The dimensions of the PIS samples used throughout the studies were maintained as  $2 \times 2$  cm unless otherwise mentioned. The water uptake capacity of the PIS was measured from the weight difference of PIS before and after equilibration with 0.2 mol/L KCl for 48 h. The chloride and iodide content in the PISs were determined by NAA to obtain their ion-exchange capacities. The PIS samples were equilibrated with 0.2 mol/L KCl and KI solutions, respectively. The chlorine and iodine analyses were carried out by irradiating PIS samples for 10 min in a neutron flux of  $5 \times 10^{11}$  n cm $^{-2}$  s $^{-1}$  at the APSARA reactor in BARC, Mumbai, India. Known amounts of KCl and KI were irradiated along with the PIS samples as standards for chlorine and iodine, respectively. The radioactivity of  $^{38}\text{Cl}$  and  $^{128}\text{I}$  isotopes in the samples were measured by counting them on a 40% HPGe detector coupled to a 4K MCA, in an identical sample to detector geometry. The areas under the 1642- and 443-keV  $\gamma$ -ray peaks were used to arrive at the amounts of  $\text{Cl}^-$  and  $\text{I}^-$ , respectively, by a standard comparison method. The amount of chlorine from the residual chloroform left after evaporation was obtained by irradiating PIS in  $\text{I}^-$  form and also the PIS made up of only CTA and NPOE.

The stability of PIS was tested by monitoring the loss of  $^{51}\text{Cr(VI)}$  radiotracer and  $\text{Cl}^-$  ions from the PIS samples kept in contact with aqueous solution over a period of one month. The losses of Cr(VI) and  $\text{Cl}^-$  ions from the sample were monitored by radiometry and NAA, respectively. The dimensions and weight were also monitored over the same period.

For optimizing the amounts of CTA, NPOE, and Aliquat-336 in PIS, initial Cr(VI) uptake studies were carried out using 15 mL of pH = 2 Clark-Lubs buffer solution containing  $3.5 \times 10^{-3}$  mmol of Cr(VI) with  $^{51}\text{Cr}$  radiotracer. The Clark-Lubs buffer solution was prepared using 0.2 mol/L KCl, and pH was adjusted with HCl. The PIS samples were immersed in this solution overnight, and the Cr(VI) uptake in them was estimated from radioactivity balance, which was obtained from the measured radioactivity before and after the experiment. The uptake of Cr(VI) in the PIS as a function of time was studied by placing the PIS sample in 25 mL of stirred Clark-Lubs buffer solution having the same chemical conditions as that used for optimization of PIS composition. The amount of radiotracer  $^{51}\text{Cr(VI)}$  diffusing in the PIS sample was monitored by periodically taking out 100- $\mu\text{L}$  samples of the equilibrating solution kept in contact with PIS as a function of time.

**Analyses of Cr(VI) in PIS.** The ion-exchange sites occupied by Cr(VI) in the PIS were estimated by NAA from the difference in the amount of  $\text{Cl}^-$  ions in PIS before and after loading Cr(VI). The experimental method used for chlorine analysis in the PIS samples by NAA was same as that described above for measuring ion-exchange capacities of the PIS samples. The amount of Cr(VI) present in these PIS samples was obtained by using the  $^{51}\text{Cr}$  radiotracer. Although the  $^{51}\text{Cr}$  radiotracer could be produced by neutron irradiation, the time of irradiation was too short to produce a sufficient amount of  $^{51}\text{Cr}$ . This necessitated adding  $^{51}\text{Cr}$  radiotracer to monitor the amount of Cr(VI) present in the PIS samples. The vast difference in half-lives of  $^{38}\text{Cl}$  (37.2 min) and  $^{51}\text{Cr}$  (27.7 days) requires short and long durations of irradiations for sufficient production of  $^{38}\text{Cl}$  and  $^{51}\text{Cr}$  radioisotopes, respectively. Therefore, instead of irradiating the PIS samples twice for short and long durations, the Cr(VI) content in the PIS was monitored by using  $^{51}\text{Cr}$  radiotracer.

**Cr(VI) Uptake in PIS as a Function of pH.** The effect of pH on Cr(VI) uptake in PIS was studied by equilibrating PISs with 20-mL aqueous solutions of pH = 2–8. The equilibrating aqueous solutions contained a constant amount of Cr(VI) ( $1.78 \times 10^{-3}$  mmol). The pH adjustments were carried out using HCl and  $\text{NH}_4\text{OH}$ . The uptake of Cr(VI) at different pH was obtained by radioactivity balance. The same experimental procedure was used for studying the variation of Cr(VI) uptake as a function of the amount of Cr(VI) in the aqueous solution at constant pH.

**Tolerance to Anions on the Cr(VI) Sorption in PIS.** The tolerance to anions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{MnO}_4^-$  on Cr(VI) sorption in the PIS was studied using a constant amount of  $^{51}\text{Cr(VI)}$  radiotracer ( $3.5 \times 10^{-3}$  mmol) and a fixed size of PIS. Solutions of the appropriate salts containing known concentration of anions were mixed with  $^{51}\text{Cr(VI)}$  radiotracer solution, and the pH of this resulting solution was adjusted using HCl and  $\text{NH}_4\text{OH}$ . Care was taken to account for the  $\text{Cl}^-$  ions added for pH adjustment. The total volume of the solution kept in contact with PIS was 20 mL. The uptake of Cr(VI) was measured from the difference in radioactivity of  $^{51}\text{Cr}$  before and after immersing the PIS samples in the solutions.

**Preconcentration of Cr(VI) from Aqueous Solution.** The preconcentration of Cr(VI) in the PIS was carried out by spiking  $3.4 \times 10^{-3}$  mmol of  $^{51}\text{Cr(VI)}$  radiotracer in 25, 100, and 250 mL of tap water. The pH of tap water was found to be 6.3. A PIS sample was immersed in tap water spiked with  $^{51}\text{Cr(VI)}$  radiotracer and vigorously stirred (300 rpm) using a Teflon-coated magnetic stirrer. The uptake of Cr(VI) in PIS as a function of time was monitored by taking out the PIS sample from the equilibrating solution at regular time intervals and measuring the intensity of  $\gamma$ -rays (320 keV) of  $^{51}\text{Cr}$ . To find the lower level of Cr(VI) that could be preconcentrated, experiments were carried out with two identical pieces of PIS placed in 250 mL of tap water containing  $3.36 \times 10^{-6}$  mmol of Cr(VI).

The preconcentration of Cr(VI) from seawater was also carried out by spiking it with  $1.78 \times 10^{-3}$  mmol of  $^{51}\text{Cr(VI)}$  radiotracer and keeping other experimental conditions similar to those used for tap water. The pH of seawater was found to be 8.2. The experiments were carried out at natural pH of seawater and at pH 7 and 2, which was adjusted by adding HCl to seawater.



Table 1. Composition and Properties of Different PIS

| mem   | composition (mg/cm <sup>2</sup> ) |             |      | thickness<br>( $\mu$ m) | ion-exchange<br>capacity (mmol/g) | Cr(VI)<br>uptake <sup>a</sup> (mol %) |
|-------|-----------------------------------|-------------|------|-------------------------|-----------------------------------|---------------------------------------|
|       | CTA                               | Aliquat-336 | NPOE |                         |                                   |                                       |
| PIS-1 | 1.67                              | 0.84        | 0.97 | 31 $\pm$ 3              | 0.51 $\pm$ 0.01                   | 85 $\pm$ 3                            |
| PIS-2 | 1.60                              | 0.85        | 1.62 | 37 $\pm$ 2              | 0.44 $\pm$ 0.01                   | 88 $\pm$ 2                            |
| PIS-3 | 1.63                              | 0.86        | 2.09 | 45 $\pm$ 3              | 0.39 $\pm$ 0.01                   | 86 $\pm$ 2                            |
| PIS-4 | 1.64                              | 0.86        | 3.18 | 50 $\pm$ 2              | 0.32 $\pm$ 0.01                   | 89 $\pm$ 3                            |
| PIS-5 | 1.65                              | 0.85        | 3.52 | 52 $\pm$ 3              | 0.30 $\pm$ 0.01                   | 88 $\pm$ 3                            |
| PIS-6 | 1.64                              | 0.85        | 5.14 | 66 $\pm$ 3              | 0.23 $\pm$ 0.01                   | 87 $\pm$ 2                            |
| PIS-7 | 1.68                              | 0           | 3.15 | 40 $\pm$ 3              | 0                                 | 0                                     |
| PIS-8 | 1.68                              | 3.33        | 1.10 | 56 $\pm$ 6              | 1.15 $\pm$ 0.03                   | 87 $\pm$ 3                            |

<sup>a</sup> Area of PIS sample, 2  $\times$  2 cm; amount of Cr(VI) in the aqueous solution, 3.5  $\times$  10<sup>-3</sup> mmol in Clark-Lubs buffer with pH = 2; equilibration time, 4 h.

**Quantifying of Cr(VI) in PIS.** The direct spectrophotometric determination of Cr(VI) held in the PIS was carried out by developing color on PIS with a 0.25 wt % solution of 1,5-diphenylcarbazide (DPC). The varying amounts of Cr(VI) (0.6–25  $\mu$ g) were loaded in the PIS samples from 20 mL of tap water. The amounts of Cr(VI) in the PIS samples were obtained by radiometry as described above. The DPC solution was prepared by dissolving a known amount of DPC in methanol. For color development, 0.2 mL of freshly prepared 0.25 wt % DPC solution was added to 15 mL of water whose pH was adjusted to 3 using HCl. The PIS sample (1  $\times$  3 cm) containing a known amount of Cr(VI) was placed in this solution. The solution was stirred to develop uniform color on the PIS sample. A stirring time of 15 min was found to be sufficient to develop uniform color on the PIS. After development of color, absorption measurements of the PIS samples were carried out by mounting PIS on to the inside wall of a 1  $\times$  1  $\times$  3 cm quartz cell. The fixed wavelength ( $\lambda_{\text{max}}$  = 555 nm) was used for spectrophotometric determinations of the Cr(VI)–DPC complex held in the PIS samples. Repeatability was established by measuring the absorbance of the same PIS sample after mounting the PIS in the cell.

Calibration graph for NAA was obtained by irradiating the PIS samples loaded with varying amounts of Cr(VI) in the Dhruva reactor (BARC, India) having a flux of 2  $\times$  10<sup>13</sup> n cm<sup>-2</sup> s<sup>-1</sup> for 24 h. The samples of identical shape and geometry were doubly wrapped in a 0.0025-cm-thick high-purity aluminum foil and cold sealed in an aluminum container. The variation of radioactivity of <sup>51</sup>Cr as a function of Cr(VI) amount in the PIS was obtained by counting the irradiated PIS using a HPGe detector coupled to a MCA.

## RESULTS AND DISCUSSION

The fabrication of PIS was based on the physical inclusion of a good extractant for Cr(VI) in the polymer matrix. It is essential that extractant trapped in the polymer matrix should not be leached out into the aqueous medium. The network of overlapping chains of CTA polymer provides mechanical support to the PIS. CTA is an inert and highly hydrophobic polymer. The strong interactions between the CTA polymer chains make PIS stable in the aqueous medium and prevent leaching out of the extractant. Hence, the chemical cross-linking of the polymer chains is not necessary for PIS made with a CTA matrix. The amount of CTA was fixed based on the required thickness of PIS (~50  $\mu$ m). Aliquat-336 is known to be a good extractant for anionic species

of Cr(VI) present in the aqueous medium.<sup>28</sup> NPOE is also hydrophobic and nonvolatile and intimately mixes with CTA and Aliquat-336. The high affinity between NPOE and CTA allows retention of more liquid fraction in the PIS. These characteristics of NPOE are suitable for using it as a plasticizer in the preparation of uniform PIS with good optical properties for spectrophotometric analysis.

In accordance with diffusion theories, the plasticizer (NPOE) may have a significant role in the kinetics of Cr(VI) sorption in the PIS. There are two known types of mechanisms of diffusion in the solid medium: fixed site jumping and carrier diffusion. In the first case, negligible transport below a critical carrier concentration in the polymer inclusion membrane has been observed.<sup>29</sup> This threshold concentration corresponds to a minimum distance between fixed sites required to allow ion jumping. In the carrier diffusion mechanism, the ions diffuse through the liquid medium present in the solid matrix as carrier–ion pairs.<sup>30</sup> Hence, the rate of ionic diffusion in the medium is mainly governed by the viscosity and tortuosity factors. The tortuosity factor is a parameter to account for the obstruction in the diffusion path of the carrier–ion pair in the medium. The tortuosity factor is expected to decrease with increase in the liquid fraction in the PIS. Thus, the optimization of the amounts of extractant (Aliquat-336) and plasticizer (NPOE) requires the knowledge of the diffusion mechanism dominating in the PIS. One of the reported methods to establish the diffusion mechanism in the PIS is to monitor the diffusion rate in the PIS samples having varying amounts of plasticizer and extractant.<sup>27</sup>

PISs with varying amount of NPOE and fixed amounts of CTA and Aliquat-336 were made. The ultrasonication of the casting mixture (CTA, NPOE, and Aliquat-336 dissolved in chloroform) was found to improve the uniformity of the PIS. The PISs made in the present work were transparent. The properties of these PISs are summarized in Table 1. The complete evaporation of chloroform during the casting of PIS was checked by chlorine analysis of PIS samples containing I<sup>-</sup> counterions as described in the Experimental Section. This analysis indicated that the amount of chloroform in the PIS samples was the order of 0.05 wt %. No significant amount of chlorine was observed in the PIS made up

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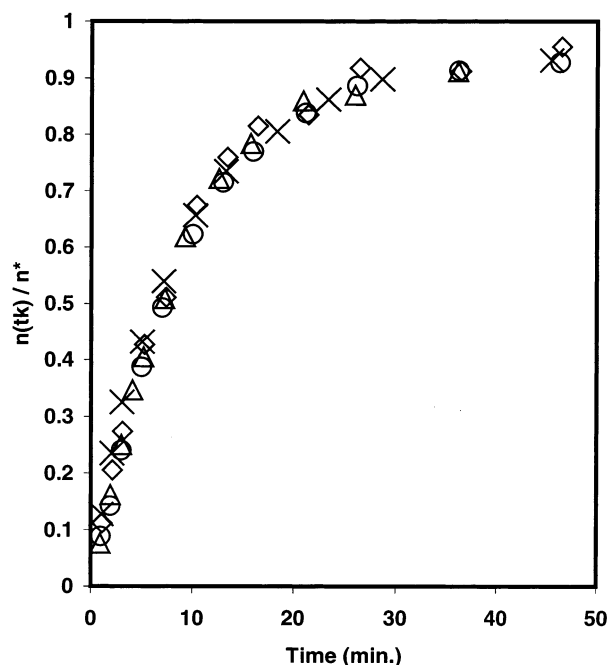


Figure 1. Variation of fractions of the  $^{51}\text{Cr(VI)}$  radiotracer in the PIS as a function of time ( $t$ ). The term  $n(t_k)$  represents the activity of  $^{51}\text{Cr(VI)}$  ions at time  $t_k$  and  $n^*$  represents the activity of  $^{51}\text{Cr(VI)}$  ions at saturation time ( $t = \infty$ ). Symbols  $\diamond$ ,  $\circ$ ,  $\triangle$ , and  $\times$  represent PIS-1, PIS-3, PIS-5, and PIS-8, respectively.

of only CTA and NPOE (PIS-7). Therefore, it was assumed that the evaporation of chloroform was almost complete. The composition of PIS samples given in Table 1 was arrived at based on the amounts of CTA, NPOE, and Aliquat-336 used for casting the PIS. The ion-exchange capacities of the PIS samples were determined by the chlorine (corrected for contribution from chloroform) and iodine analyses. The PIS used in the present work was found to be selective for Cr(VI). This is based on the fact that no uptake of Cr(III) from aqueous solutions containing Cr(III) radiotracer was observed in any of the PIS used in the present studies. Cr(VI) sorption was not observed in the PIS-7 having only CTA and NPOE, indicating that Cr(VI) sorption in the PIS occurs only through interaction of Cr(VI) with Aliquat-336.

As can be seen from Table 1, the thickness of PIS samples (PIS-1–PIS-6) increases as a function of the amount of NPOE. The uptake of Cr(VI) in the PISs with varying amounts of NPOE was found to be  $88 \pm 3\%$ . The variations in the sorption of Cr(VI) in the PIS samples made up of varying amounts of NPOE and Aliquat-336 were studied as a function of time over a period of 1 h. As shown in Figure 1, the time required for attaining maximum sorption of Cr(VI) did not change in the PISs having different compositions. It is expected that the liquid fraction of the PIS samples increases with increase in the amount of NPOE. This, in turn, results in the decrease of both viscosity and tortuosity factors of the PIS. The constant time for maximum uptake of Cr(VI) in the PIS samples having varying amounts of NPOE seems to suggest that the increase in the thickness of PIS samples nullifies the effects of decrease in viscosity and tortuosity factor. The time required for maximum uptake of Cr(VI) was also found to be same in the PIS-8. In this case, the diffusion of carrier–ion pair (Aliquat-336 with Cr(VI) counterion) is expected to face more resistance due to reduction in the liquid fraction in the PIS. It is likely that

the increase in the resistance is offset by the exchange of Cr(VI) among the Aliquat-336 molecules, leading to the same time for maximum uptake of Cr(VI) for PIS-8.

The final composition of PIS was kept as follows:  $[\text{CTA}] = 1.65 \pm 0.08 \text{ mg/cm}^2$ ,  $[\text{NPOE}] = 3.15 \pm 0.05 \text{ mg/cm}^2$ , and  $[\text{Aliquat-336}] = 0.78 \pm 0.04 \text{ mg/cm}^2$  based on (i) uniform distribution of Aliquat-336 as indicated by the  $\text{Cl}^-$  counterions analysis in different PIS samples from the same batch and also from different batches, (ii) uniform thickness,  $48 \pm 3 \mu\text{m}$ , and density,  $0.93 \pm 0.08 \text{ g/cm}^3$ , (iii) dimensional stability in the aqueous medium with negligible water uptake, and (iv) stability of Cr(VI) held in the PIS as indicated by negligible loss of  $^{51}\text{Cr}$  tracer from the PIS in the aqueous solution over a period of 7 days and 5% over a period of one month. The leaching out of the extractant (Aliquat-336) and plasticizer (NPOE) from the PIS was found to be negligible over a period of one month as observed from chlorine analysis and loss in weight of PIS, respectively. The ion-exchange capacity of this PIS was found to be  $0.28 \text{ mmol/cm}^3$ . The volume of the liquid fraction in this PIS was 74 vol %. The volume of the liquid fraction in the PIS was computed from the knowledge of density and weight of the liquid phase comprising NPOE and Aliquat-336 in the PIS. The density of the liquid phase was obtained by measuring the density of the solution having a composition of NPOE and Aliquat-336 identical to that in the PIS. To select appropriate counterions in the PIS, the PIS samples were converted into  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  forms by equilibrating the PIS samples in the appropriate salt solutions of 0.5 mol/L concentration. The sorption experiments as a function of time were carried out to find the possible effect on the sorption of Cr(VI) in the PIS with counterions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ . In this study, no significant change in the sorption of Cr(VI) as a function of time was observed. Hence, the PIS samples in  $\text{Cl}^-$  form were used for further studies.

**Analyses of Cr(VI) Species in PIS.** The IR spectra in the wavenumber range of  $4000\text{--}400 \text{ cm}^{-1}$  of PISs loaded with Cr(VI) at different pH were used to find out the anionic species of Cr(VI) present in the PIS. The IR spectra of all the samples of PIS loaded with Cr(VI) at pH = 2 and 7 were found to be identical to that of the blank PIS spectrum, except for the appearance of one new absorption band at  $945$  and  $937 \text{ cm}^{-1}$  at pH = 2 and 7, respectively. This new band in the PIS samples loaded with Cr(VI) at pH = 2 and 7 corresponds to an antisymmetric  $\text{CrO}_3$  stretching vibration.<sup>31</sup> The absence of stretching Cr–O–Cr vibrations in the IR spectrum of PIS loaded with Cr(VI) indicates the presence of only monomeric Cr(VI) species. This excludes the presence of  $\text{Cr}_2\text{O}_7^{2-}$  species and thus the possible species of Cr(VI) held in the PIS samples could be either  $\text{CrO}_4^{2-}$  or  $\text{HCrO}_4^-$ .

Neutron activation analyses were carried out to obtain the total ion-exchange sites and ion-exchange sites occupied by Cr(VI) in PISs at different pH. The ion-exchange sites in the fixed size sample were estimated by the amount of  $\text{Cl}^-$  counterions present in PIS by NAA. The PIS samples were equilibrated with aqueous solution containing Cr(VI) at different pH. The amount of Cr(VI) in aqueous solution was kept at 0.64 times the ion-exchange sites of the PIS. The amount of Cr(VI) sorbed in the PIS samples at different pH was monitored by using radiotracer  $^{51}\text{Cr(VI)}$  ions.

(31) Stammreich, H.; Bassi, D.; Sala, O.; Siebert, H. *Spectrochim. Acta* **1958**, *13*, 192–196.

Table 2. Analysis of Cr(VI) Present in the PIS and Probable Species

| pH | total IES of PIS <sup>a</sup><br>( $\times 10^{-3}$ mmol) | Cr(VI) loaded in PIS <sup>b</sup><br>( $\times 10^{-3}$ mmol) | residual $\text{Cl}^-$ in PIS <sup>c</sup><br>( $\times 10^{-3}$ mmol) | IES occupied by Cr(VI) in PIS <sup>d</sup><br>( $\times 10^{-3}$ mmol) | Cr(VI)/IES occupied by Cr(VI) | probable Cr(VI) species                         |
|----|---|---|--|--|-------------------------------|---|
| 2  | $5.4 \pm 0.1$   | $2.92 \pm 0.09$   | $2.44 \pm 0.05$  | $2.9 \pm 0.1$  | $1.00 \pm 0.050$              | 100% $\text{HCrO}_4^-$                          |
| 2  | $5.3 \pm 0.1$   | $2.80 \pm 0.09$   | $2.70 \pm 0.05$  | $2.6 \pm 0.1$  | $1.06 \pm 0.050$              | 100% $\text{HCrO}_4^-$                          |
| 7  | $5.3 \pm 0.1$   | $2.92 \pm 0.09$   | $0.32 \pm 0.01$  | $5.0 \pm 0.1$  | $0.58 \pm 0.020$              | 28% $\text{HCrO}_4^-$ , 72% $\text{CrO}_4^{2-}$ |
| 7  | $5.3 \pm 0.1$   | $2.89 \pm 0.09$   | $0.20 \pm 0.01$  | $5.1 \pm 0.1$  | $0.57 \pm 0.020$              | 25% $\text{HCrO}_4^-$ , 75% $\text{CrO}_4^{2-}$ |
| 8  | $5.4 \pm 0.1$   | $2.68 \pm 0.09$   | $0.25 \pm 0.01$  | $5.2 \pm 0.1$  | $0.52 \pm 0.020$              | 8% $\text{HCrO}_4^-$ , 92% $\text{CrO}_4^{2-}$  |

<sup>a</sup> Ion-exchange sites as measured by NAA, <sup>b</sup> Cr(VI) sorption in PIS as obtained by the radiometry, <sup>c</sup> Residual  $\text{Cl}^-$  in PIS left after Cr(VI) sorption was estimated by NAA, <sup>d</sup> Ion-exchange sites occupied by Cr(VI) were computed from the difference of total ion-exchange sites and residual  $\text{Cl}^-$  left after Cr(VI) sorption. The standard deviation given in the table corresponds to the value obtained by the three determinations.

The radiotracer  $^{51}\text{Cr}$  was used with an assumption that the radiation dose during neutron irradiation in the production of radiotracer may not significantly alter the chemical state of the Cr(VI) in the compound ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) used in the present studies as the Szilard–Chalmers effect responsible for the change in the chemical state was reported to be negligible in this compound.<sup>32</sup> The balance of  $\text{Cl}^-$  counterions left after sorption of Cr(VI), as estimated by NAA, was used to calculate the ion-exchange sites occupied by Cr(VI) in the PIS. The data obtained in these analyses are summarized in Table 2. The abundance of  $\text{CrO}_4^{2-}$  in the PIS samples was estimated by charge balance. The difference in the ion-exchange sites occupied by Cr(VI) in the PIS and moles of Cr(VI) present in the PIS was assumed to be the extent of the ion-exchange sites neutralized by divalent Cr(VI) anions. This assumption was based on the fact that only monovalent and divalent anionic species of Cr(VI) are expected to be present in the aqueous solution.<sup>33</sup> The reason for considering only one kind of divalent ion of Cr(VI) was based on the IR spectra, which indicated the presence of only monomeric species in the PIS. Based on these facts, the following equation was used to compute the abundance of  $\text{CrO}_4^{2-}$  held in the PIS.

$$\text{abundance of } \text{CrO}_4^{2-} \text{ present in PIS} = \frac{(\text{IES}_{\text{Cr}} - n_{\text{Cr}})/\text{IES}_{\text{Cr}} \times 100}{(1)}$$

where  $\text{IES}_{\text{Cr}}$  is moles of ion-exchange sites in the PIS occupied by Cr(VI) and  $n_{\text{Cr}}$  is moles of Cr(VI) held in the PIS. The abundance of monovalent Cr(VI) species  $\text{HCrO}_4^-$  was computed from the difference of total ion-exchange sites occupied by Cr(VI) ions and ion-exchange sites occupied by  $\text{CrO}_4^{2-}$ . The comparison of abundances of  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  in the PIS samples and aqueous solutions<sup>33</sup> at different pH is shown in Figure 2. It is evident from Figure 2 that there is an excellent correlation of species of Cr(VI) present in the PIS with that expected in the aqueous medium.<sup>33</sup> From this analysis, it is obvious that  $\text{HCrO}_4^-$  is a major hexavalent chromium species present in the PIS at pH less than 6 and  $\text{CrO}_4^{2-}$  is the dominating species in the PIS above pH = 7. The limits for maximum uptake of Cr(VI) in the PIS calculated from the abundance of Cr(VI) species in the aqueous solution and amount of ion-exchange sites were found to be 0.28 and 0.18 mmol/cm<sup>3</sup> at pH = 2–5 and 6.5, respectively.

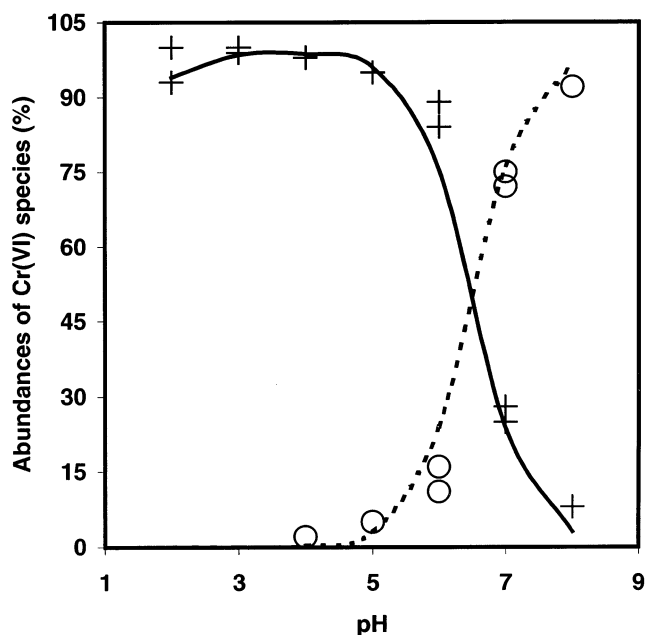


Figure 2. Variation of Cr(VI) species in the aqueous solution and held in PIS as a function of pH. The dashed line and solid line represent  $\text{CrO}_4^{2-}$  and  $\text{HCrO}_4^-$  species, respectively, in the aqueous solution (taken from ref 33). The symbols  $\circ$  and  $+$  represent the abundances of  $\text{CrO}_4^{2-}$  and  $\text{HCrO}_4^-$  species observed experimentally in the PIS. Each data point is an average of triplicate measurements.

**Cr(VI) Uptake in PIS as a Function of pH.** As seen by chemical analyses of Cr(VI) held in PIS, the maximum uptake of Cr(VI) in the PIS should be equal to its ion-exchange capacity in the range of pH = 2–5, where  $\text{HCrO}_4^-$  is the main species. However, the maximum uptake of Cr(VI) at pH above 6 would depend on the extent of  $\text{CrO}_4^{2-}$  present in the aqueous solution. To study the effect of pH on Cr(VI) sorption, the Cr(VI) was loaded in PIS samples from aqueous solutions at different pH. The amount of Cr(VI) was kept at one-third the number of ion-exchange sites in the PIS samples to ensure an excess of ion-exchange sites. As shown in Figure 3, the uptake of Cr(VI) was fairly constant at ~88% in the pH range of 2–7. However, Cr(VI) uptake in the PIS has decreased to 80% at pH = 8, at which  $\text{CrO}_4^{2-}$  is the main Cr(VI) species. This indicates that  $\text{CrO}_4^{2-}$  uptake in the PIS was less than  $\text{HCrO}_4^-$  even though excess of exchange sites were available. The high extraction efficiency of Aliquat-336 toward monovalent chromate and perrhenate anions was also observed by Strzelbicki et al.<sup>28</sup> The use of Clark-Lubs buffer solution with pH = 2 did not alter the sorption of Cr(VI) in the

(32) Muxart, R.; Daudel, P.; Daudel, R.; Haissinsky, M. *Nature* **1947**, 159, 538–539.

(33) Tandon, R. K.; Crisp, P. T.; Ellis, J.; Baker, R. S. *Talanta* **1984**, 31, 227–228.

Table 3. Tolerance to Some Anions on Cr(VI) Sorption in the PIS

| anion                         | $-\Delta G_h^a$<br>(kJ/mol) | concn of<br>anions <sup>b</sup> (mol/L) | uptake of Cr(VI) (mol %) <sup>c</sup>           |  |  |
|-------------------------------|-----------------------------|---|---|--|--|
|                               |                             |   | pH = 2<br>(94% HCrO <sub>4</sub> <sup>-</sup> ) | pH = 6.3<br>(59% HCrO <sub>4</sub> <sup>-</sup> + 41% CrO <sub>4</sub> <sup>2-</sup> ) | pH = 7<br>(24% HCrO <sub>4</sub> <sup>-</sup> + 76% CrO <sub>4</sub> <sup>2-</sup> ) |
| Cl <sup>-</sup>               | 340                         | 0.2                                     | 88 ± 3  | 43 ± 1   | 11 ± 1   |
| NO <sub>3</sub> <sup>-</sup>  | 300                         | 0.0001                                  | 90 ± 3  | 90 ± 3   | 69 ± 2   |
|                               |                             | 0.001                                   | 90 ± 3  | 71 ± 2   | 29 ± 1   |
|                               |                             | 0.005                                   | 88 ± 3  | 60 ± 2   | 23 ± 1   |
|                               |                             | 0.01                                    | 82 ± 3  | 0  | 0  |
| SO <sub>4</sub> <sup>2-</sup> | 1080                        | 0.05                                    | 87 ± 2  | 85 ± 3   | 41 ± 2   |
|                               |                             | 0.1                                     | 86 ± 2  | 71 ± 2   | 22 ± 1   |
|                               |                             | 0.2                                     | 89 ± 2  | 0  | 0  |
|                               |                             | 0.1                                     | 89 ± 3  | 84 ± 2   |  |
| PO <sub>4</sub> <sup>3-</sup> | 2765                        | 0.1                                     | 90 ± 2  | 90 ± 3   |  |
| MnO <sub>4</sub> <sup>-</sup> | 235                         | 0.0001                                  | 90 ± 2  | 90 ± 3   |  |
|                               |                             | 0.001                                   | 90 ± 3  | 21 ± 1   |  |

<sup>a</sup> Experimental molar Gibbs energy of hydration of ions ( $-\Delta G_h$ ) taken from ref 35. The  $-\Delta G_h$  for CrO<sub>4</sub><sup>2-</sup> is 950 kJ/mol. The experimental  $-\Delta G_h$  for HCrO<sub>4</sub><sup>-</sup> is unknown. The  $-\Delta G_h$  for HCrO<sub>4</sub><sup>-</sup> was calculated based on the Marcus model<sup>35</sup> and found to be 184 kJ/mol. <sup>b</sup> The moles of Cr(VI) in the equilibrating aqueous solution were kept as half of the ion-exchange sites in the PIS ( $0.14 \times 10^{-3}$  mol of Cr(VI)/L). <sup>c</sup> Abundances of Cr(VI) species in aqueous solution (taken from ref 33).

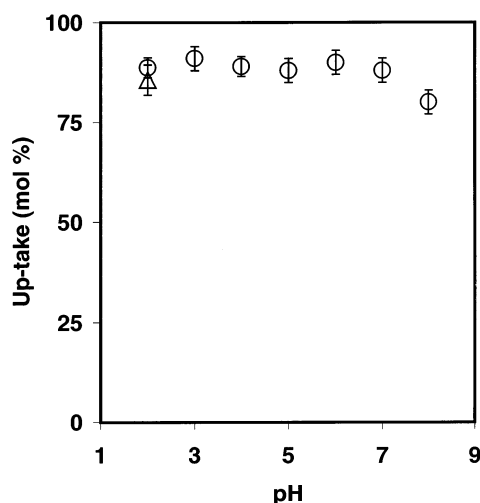


Figure 3. Uptake of Cr(VI) by the PIS as a function of pH. Symbols  $\Delta$  and  $\circ$  represent the uptake of Cr(VI) from Clark-Lubs buffer solutions and from aqueous solutions whose pH was adjusted with HCl and NH<sub>4</sub>OH. The ion-exchange sites in the PIS were 3 times the total moles of Cr(VI) in the equilibrating aqueous solution. Triplicate measurements were carried out for each data point.

PIS. The maximum limit of Cr(VI) uptake in the PIS at pH = 2 and 6.3, as obtained from the analysis of Cr(VI), was confirmed by varying the amount of Cr(VI) in aqueous solution kept in contact with PIS samples with fixed ion-exchange capacity (0.28 mmol/cm<sup>3</sup>). As shown in Figure 4, Cr(VI) uptake in the PIS is fairly constant ( $\sim 88\%$ ) up to  $5 \times 10^{-3}$  mmol of Cr(VI) in the aqueous solution at pH = 2. This limit corresponds to the ion-exchange capacity of the PIS. Thereafter, the percentage uptake of Cr(VI) in the PIS starts decreasing due to lack of availability of sites for Cr(VI) exchange in the PIS. At tap water pH = 6.3, the Cr(VI) sorption in the PIS remains constant up to  $3.5 \times 10^{-3}$  mmol (0.18 mmol/cm<sup>3</sup>) of Cr(VI). This experimental capacity for the uptake of Cr(VI) in the PIS is also in good agreement with that expected from the ion-exchange sites and ionic charge of chromium species. Thus, Cr(VI) anions present in the aqueous solution replace counterions completely in the PIS. This means 88% uptake of Cr(VI) in the PIS from aqueous solution could be due to H<sub>2</sub>CrO<sub>4</sub> or any such neutral species of hexavalent chromium that are not sorbed in the PIS.

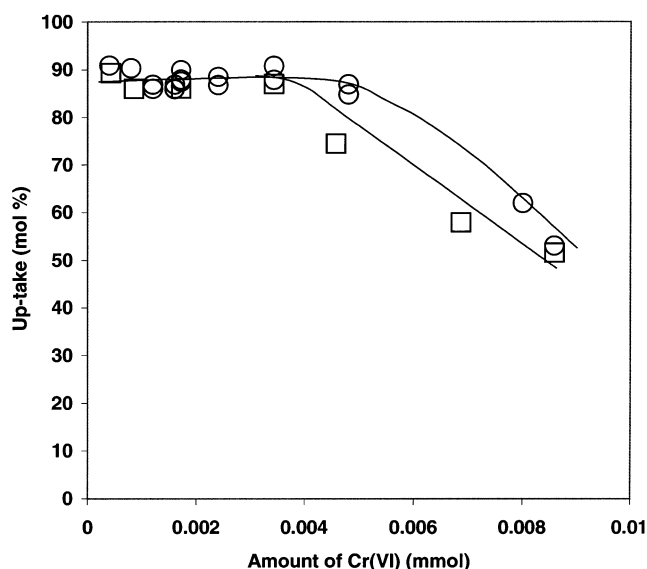


Figure 4. Variation of Cr(VI) uptake in PIS as a function of amount of Cr(VI) in the aqueous solution. Symbols  $\circ$  and  $\square$  represent the uptake from aqueous solution at pH = 2.0 and 6.3, respectively. The ion-exchange capacity of the PIS samples used for this experiment was  $5.35 \times 10^{-3}$  mmol.

**Tolerance to Anions on the Cr(VI) Sorption in PIS.** The tolerance to anions commonly present in the natural aqueous systems on Cr(VI) sorption in the PIS were studied at pH = 2, 6.3, and 7, and data are summarized in Table 3. It appears from this table that the PIS is highly selective for Cr(VI) at pH = 2. However, the tolerance limits for most of the anions present in aqueous solution at pH = 6.3 and 7 on Cr(VI) sorption in the PIS under identical experimental conditions were considerably reduced. This behavior of PIS toward Cr(VI) seems to be based on two factors: (i) hydrophobicity and nucleophilicity of the extractant present in the PIS (Aliquat-336) lead to increase in quaternary ammonium–monovalent anion complex stability,<sup>28</sup> and (ii) the solubility of anions in the hydrophobic organic medium of PIS is dependent on the hydration of anions.<sup>34</sup> The Cr(VI) at lower pH

(34) Sata, T.; Yamaguchi, T.; Matsusaki, K. *J. Phys. Chem.* **1995**, *99*, 12875–12882.



(pH = 2) exists mainly as  $\text{HCrO}_4^-$ , which is the least hydrated monovalent anion listed in Table 3. Thus, PIS is highly selective for  $\text{HCrO}_4^-$  anions. The order of tolerance limits for monovalent ions on the sorption of  $\text{HCrO}_4^-$  (pH = 2) is as follows:  $\text{Cl}^-$  (0.2 mol/L) >  $\text{NO}_3^-$  (0.005 mol/L) >  $\text{MnO}_4^-$  (0.001 mol/L). This order of tolerance limits seems to correlate with the molar Gibbs energy of hydration ( $-\Delta G_h$ )<sup>35</sup> given in Table 3. Thus, the tolerance limits of anions on  $\text{HCrO}_4^-$  sorption in the PIS is governed mainly by hydration of the anions.

The tolerance limits to anions on Cr(VI) sorption in PIS decreases with increase in pH. This is probably related to the decrease in the abundance of  $\text{HCrO}_4^-$ . For example, the order of uptake of Cr(VI) in the PIS at pH = 2, 6.3, and 7 is as follows: 88, 43, and 11% in the presence of 0.2 mol/L  $\text{Cl}^-$ , respectively, and 88, 60, and 23% in the presence of 0.005 mol/L  $\text{NO}_3^-$ , respectively. The abundances of  $\text{HCrO}_4^-$  in aqueous solution at pH = 2, 6.3, and 7 are: 94, 59, and 24%, respectively.<sup>33</sup> Therefore, similar trends in uptake of Cr(VI) in the PIS and the abundances of  $\text{HCrO}_4^-$  seem to indicate that the  $\text{CrO}_4^{2-}$  species is not sorbed in the PIS when other monovalent anions (>0.0001 mol/L) compete for the ion-exchange sites in the PIS. The lack of selectivity for divalent Cr(VI) anionic species may be related to both its relatively greater hydration and the decrease in the stability of Aliquat-336-divalent anion complex in the PIS. However, it should be noted that the equilibrium between  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  may be changed depending upon chemical conditions or selective removal of one of the ions. The shift in  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  equilibrium would alter the abundances of these species in the aqueous solution at different pH.

**Sorption Preconcentration of Cr(VI) from Aqueous Solution.** The sorption preconcentration of Cr(VI) in the PIS sample was carried out from the 25, 100, and 250 mL of tap water having a pH = 6.3 and spiked with  $3.4 \times 10^{-3}$  mmol of  $^{51}\text{Cr(VI)}$  radiotracer. The sorption of Cr(VI) in the PIS was monitored by measuring the radioactivity of  $^{51}\text{Cr(VI)}$  radiotracer in the PIS. As shown in Figure 5, the time required for  $88 \pm 3\%$  sorption of Cr(VI) in the PIS from the 25-, 100-, and 250-mL volume of tap water was found to be 45 min, 6 h, and 15 h, respectively. This variation of time as a function of volume of the aqueous solution is related to the buildup of concentration gradient in the aqueous solution in contact with PIS.<sup>36</sup> Hence, the time required for the optimum sorption of Cr(VI) from larger volumes of aqueous solutions can be reduced by using a better stirring procedure to decrease the concentration gradient in the aqueous solution and by increasing the surface area of the PIS. To find the lowest amount of Cr(VI) that could be preconcentrated in the PIS, two pieces of PIS each having  $2 \times 2$  cm area were placed in the 250 mL of tap water containing  $3.36 \times 10^{-6}$  mmol of Cr(VI). This corresponds to  $0.7 \mu\text{g/L}$  Cr(VI). A time period of 15 h was found to be sufficient for preconcentrating 88% of Cr(VI) in the PIS. Below this concentration, the experiment could not be carried out due to lack of sufficient radioactivity required for monitoring the uptake of Cr(VI).

The Cr(VI) uptake in the PIS was also tested from seawater. The chromium concentration in natural seawater was  $96.9 \mu\text{g/L}$ , which was determined by atomic absorption spectroscopy. The

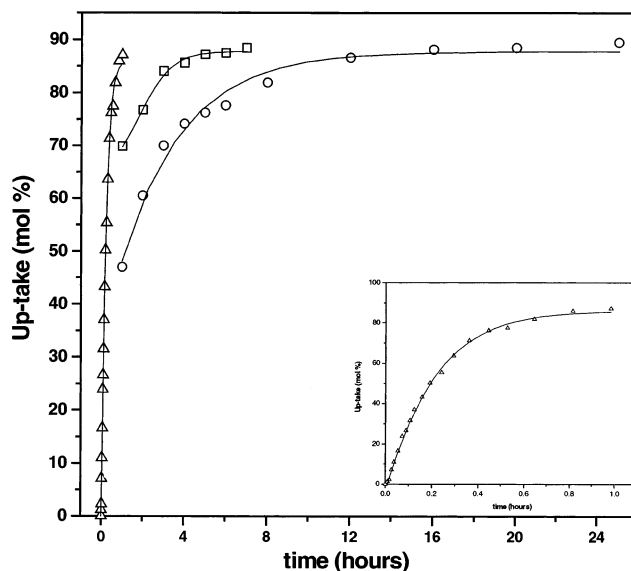


Figure 5. Preconcentration of Cr(VI) in the PIS from varying volumes of aqueous solutions as a function of time. The symbols  $\Delta$ ,  $\square$ , and  $\circ$  represent 25, 100, and 250 mL of aqueous phase, respectively. Inset in figure is expanded graph representing 25-mL volume.

pH of seawater was 8.2. A PIS sample was placed in 25 mL of this seawater spiked with  $1.72 \times 10^{-3}$  mmol of Cr(VI) radiotracer. The ion-exchange capacity of the PIS was 3 times the moles of Cr(VI) in the aqueous solution. The uptake of Cr(VI) was found to be only 4%. The uptake of Cr(VI) could be improved only to 33% by lowering the pH of seawater to 7. However, quantitative sorption of Cr(VI) in the PIS (88%) could be achieved from seawater when the pH was adjusted to 2. The close correspondence between the sorption of Cr(VI) from seawater as a function of pH and abundance of  $\text{HCrO}_4^-$  in the aqueous medium at different pH (see Figure 2) seems to suggest that  $\text{HCrO}_4^-$  is the only form of Cr(VI) that is sorbed in the PIS from seawater.

**Quantifying of Cr(VI) in PIS.** The direct determination of Cr(VI) in the PIS samples was carried out by two different methods, i.e., spectrophotometry and neutron activation analysis. For spectrophotometric determination of Cr(VI) held in the PIS, color development was based on the formation of a Cr(VI) cationic complex with DPC.<sup>37</sup> The determination of Cr(VI) by solid-phase spectrophotometry is generally based on the measurement of the absorption of the Cr(VI)–DPC complex on the cation-exchange resin.<sup>20–22</sup> In the present work, the Cr(VI) was first sorbed in the PIS, which is essentially an anion-exchange sorbent. This was followed by color development directly on the PIS. To find out whether the Cr(VI)–DPC complex can be retained in the PIS, PIS-2 and PIS-5 samples of  $1 \times 3$  cm area were loaded with the  $^{51}\text{Cr(VI)}$  radiotracer. For color development, DPC was dissolved in methanol instead of acetone as it was found to degrade PIS. The PIS samples were placed in an aqueous solution of DPC at pH = 3, and loss of radiotracer was monitored as a function of time. The losses of Cr(VI) tracer from PIS-2 and PIS-5 were found to be within 0.5 and 2%, respectively, over 30 min of duration. The time required for complete development of color on PIS containing Cr(VI) was found to be 10 min. The PIS-2 was selected

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(36) Pandey, A. K.; Gautam, M. M.; Shukla, J. P.; Lyer, R. H. *J. Membr. Sci.* **2001**, 190, 9–20.

(37) Pflaum, R. T.; Howick, L. C. *J. Am. Chem. Soc.* **1956**, 78, 4862–4866.



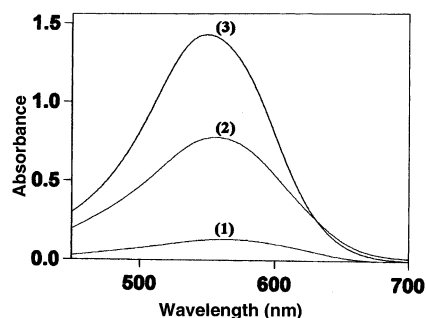


Figure 6. Absorbance spectra of Cr(IV)-DPC complex held in the PIS. Samples loaded with (1) 1.42, (2) 7.09, and (3) 17.33  $\mu\text{g}$  of Cr(VI), respectively.

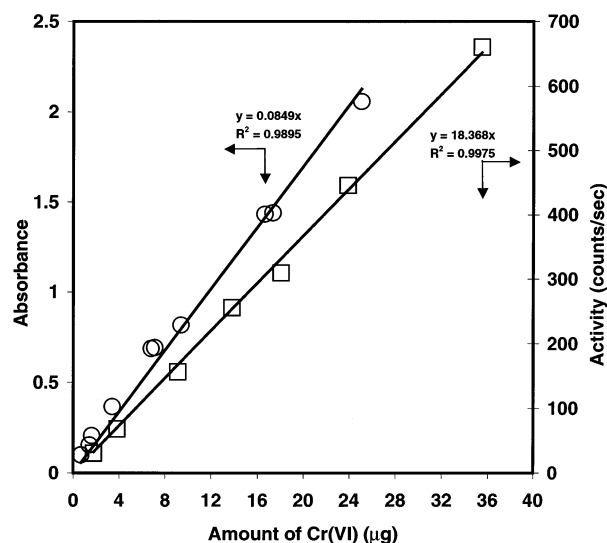


Figure 7. Calibration graph as obtained by spectrophotometry (○) and by neutron activation analysis (□).

for spectrophotometric studies of the Cr(VI)-DPC complex. This PIS after color development was mounted on the inner wall of a  $1 \times 1 \times 3$  cm cell. The absorption spectrum of Cr(VI)-DPC in the PIS, shown in the Figure 6, indicates that the maximum absorption occurs at a wavelength of 555 nm. The absorption at this wavelength was found to be negligible for the blank PIS reacted with DPC. All further measurements were carried out at this wavelength. The color developed on the PIS containing even 0.6  $\mu\text{g}$  of Cr(VI) was found to be distinct from the blank PIS. This distinct color difference is amenable for field application to detect and measure Cr(VI) by color matching. A calibration graph was made by loading 0.6–25  $\mu\text{g}$  of Cr(VI) in PIS samples. As can be seen from Figure 7, the absorption increases linearly with the amount of Cr(VI) in the PIS samples. The detection limit based on  $3\sigma$  of the blank PIS was found to be 0.28  $\mu\text{g}$ .

NAA cannot distinguish the different oxidation states of an element. However, NAA is useful to estimate the Cr amounts in different matrixes unambiguously with high sensitivity. The use of PIS provides a tool for differentiating Cr(VI) from other

oxidation states of chromium. NAA was used to validate our methodology. In the present studies, NAA was used to estimate the speciated Cr(VI) and total Cr in separate experiments. Since the element of interest is preconcentrated in a small matrix, it helps in enhancing the sensitivity. Matrix interferences are absent too as the PIS is made of light elements. The PIS samples loaded with 0.6–25  $\mu\text{g}$  of Cr(VI) were irradiated in the reactor for 24 h as described in the Experimental Section. The measured activities were used to construct the calibration plot (Figure 7). Cr(VI) loaded in the PIS was determined by using the calibration plot. The values obtained are in good agreement with those obtained by spectrophotometry.

The detection limit (LOD) was calculated using Curries<sup>38</sup> formula

$$\text{LOD} = 2.71 + 3.29 \sqrt{\text{Cb}} \quad (2)$$

where Cb represents the number of counts in the region of interest ( $^{51}\text{Cr}$ , 320 keV) for a given period of counting, which is the signal in the absence of actual sample. The number of counts in this blank were low because of interference-free conditions (selective preconcentration of Cr(VI)). The LOD computed from this equation was converted to the amount of Cr(VI) using the slope obtained from the calibration graph given in Figure 7. The LOD was found to be 1.36 ng in an interference-free condition. However, it should be noted that LOD is dependent on the irradiation time, cooling time, and detection efficiency of the  $\gamma$ -spectrometer used.

## CONCLUSION

Polymer inclusion sorbent was prepared by inclusion of Aliquat-336 in the matrix of preformed polymer cellulose triacetate and with 2-nitrophenyl octyl ether. These PIS samples were found to be stable and robust. It was used to preconcentrate Cr(VI) from tap water and seawater samples. It was found that these PISs selectively take up Cr(VI) over a pH range of 2–7 in the presence of Cr(III). Retention of Cr(VI) on the PIS samples was excellent over a period of one week. Radiotracer  $^{51}\text{Cr}$  was used to estimate the uptake of Cr(VI), and the value obtained was reproducible ( $88 \pm 3\%$ ). The analysis of Cr(VI) loaded in PIS at different pH suggests that main chemical forms of Cr(VI) at pH below 6 and above 7 are  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ , respectively. The selectivity of PIS was found to be governed by the hydration of anions. This makes the PIS highly selective for  $\text{HCrO}_4^-$  ions. The sorption preconcentration and determination of Cr(VI), carried out on tap water and seawater, demonstrate the potential application of PIS for quantitative determination of Cr(VI) in aqueous environmental samples. Cr(VI) from tap water samples even at the levels of 0.7  $\mu\text{g/L}$  Cr(VI) was quantitatively preconcentrated in the PIS. The PIS was found to be amenable for direct quantification of Cr(VI) by spectrophotometry and NAA. The distinct color developed on the PIS even at very low concentrations of Cr(VI) suggests its possible use for field determination of Cr(VI).

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