

# A novel method for speciation of Cr(III) and Cr(VI) and individual determination using Duolite C20 modified with active hydrazone

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## Abstract

Trivalent and hexavalent chromium have been successfully separated and estimated from different solutions using 1-(3,4-dihydroxybenzaldehyde)-2-acetylpyridiniumchloride hydrazone (DAPCH) loaded on Duolite C20 in batch and column modes. The obtained modified resin [DAPCH-Duolite C20] was identified by C, H and N analyses and infrared spectra. The presence of multi-active chelating sites gives the ability for DAPCH to bind more chromium, Cr(III) by forming stable complex and chromate by forming ion pair molecule  $[\text{H}_2\text{DAPCH-Duolite C20}]^{2+}[\text{Cr}_2\text{O}_7]^{2-}$  ( $\text{H}_2\text{DAPCH-Duolite C20}$  is the protonated form in acidic medium). The extraction isotherms were measured at different pH. The pH was found to be the backbone for the separation procedure in which the Cr(VI) and Cr(III) ions are sorbed selectively from aqueous solution at pH 2 and 6, respectively. The sorbed ions can be eluted using different concentrations of HCl. The saturation sorption capacity (41.6 and 20.05  $\text{mg g}^{-1}$ ), the preconcentration factor (150 and 200) and the detection limit (13.3 and 10.0 ppb) were calculated for Cr(III) and (VI). The loaded resin can be regenerated for at least 50 cycles. The utility of the modified resin was tested in aqueous samples and shows R.S.D. value of <4% reflecting its accuracy and reproducibility.

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## 1. Introduction

Chromium, especially Cr(VI), is important in environmental samples and must be preconcentrated for precise determination. Chromium is usually found in oxidation states III and VI and exists in environment as a result of the discharge of steel, electroplating, tanning industries and in tap water supply systems [1,2].

The physiological effect of chromium on the biological systems depends on its oxidation states. Cr(III) is essential in mammals for the maintenance of glucose, lipid and protein metabolism, whereas Cr(VI) is toxic [1,3–5] because of its ability to oxidize other species and its adverse impact on lung, liver and kidney. Owing to these effects, accurate determination of both species is essential. Due to the different properties and toxicity of the chemical forms of chromium, a great number of speciation methods have been performed [6].

The direct determination of chromium in water was carried out by analytical methods such as inductively coupled plasma-atomic emission spectrometry [7] or electrothermal atomic absorption spectrometry [8]. Various separation and preconcentration methods such as liquid–liquid extraction [9], coprecipitation [10,11] and solid-phase extraction [12,13] have been developed. Ion-exchange separation and preconcentration cover *ca.* 24% of all pretreatments employed for the speciation analysis of chromium [3]. The sorption of Cr(VI) has been achieved using column filled with melamine–formaldehyde [14], melamine–urea–formaldehyde [15], sodium dodecyl sulfate-coated alumina [16], C18-bonded silica reversed-phase sorbent with DDC [17] and Amberlite XAD-2010 [18]. On the other hand, Cr(III) may be sorbed selectively using polyaminophosphonic acid [19], quinolin-8-ol or imminodiacetate [20] and quinolin-8-ol complexed macroporous resin [21]. 2-Naphthol-3,6-disulfonic acid [22] and azophenylcarboxylate [23] functionalized polystyrene–divinylbenzene copolymer resins were reported to sorb Cr(III) and (IV) at different pH. Each method has many advantages but in general the time length of preparation, the lower sorption capacity and the use

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of expensive organic reagents [14–22] are the common disadvantages. The use of modified ion-exchange resins in separation and/or preconcentration solved these difficulties, but suffers from the presence of electrolytes [23]. In the present work, trial to overcome the above disadvantages by investigating the ability of Duolite C20 modified with 1-(3,4-dihydroxybenzaldehyde)-2-acetylpyridinium-chloride hydrazone (DAPCH) for the speciation of Cr(III) and (VI) from different media for precise determination of the two ions individually was done.

## 2. Experimental

### 2.1. Reagents and solutions

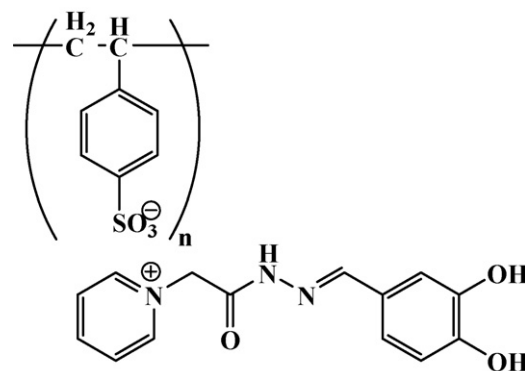
All chemicals were of analytical reagent grade and obtained from E Merck. Stock solutions ( $1 \text{ mg ml}^{-1}$ ) of Cr(VI) and Cr(III) were prepared by dissolving  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in 0.5 M HCl and distilled water, respectively. The colorimetric reagent diphenylcarbazide (DPC) was freshly prepared by dissolving 0.25 g in 99 ml acetone + 1 ml conc.  $\text{H}_2\text{SO}_4$ , and kept in a dark bottle. The pH adjustment was made with HCl and  $\text{CH}_3\text{COONa}$  (0.2 M). HCl (up to  $4 \text{ mol l}^{-1}$ ) was used as eluent. An aqueous solution of 5% (v/v)  $\text{H}_2\text{O}_2$ , prepared daily, was used as oxidant. Girard's reagent P (GP), NaCl and 3,4-dihydroxybenzaldehyde were purchased from Aldrich, Duolite C20 (Rohm and Hass Co.), HCl, NaOH and the other reagents were analytical grade (BDH). The glasswares were cleaned by soaking overnight in aqueous  $\text{HNO}_3$  (1:1) and then rinsing with distilled water several times.

### 2.2. Equipment

A PerkinElmer atomic absorption Spectrometer model 2380 (USA) was used. The IR spectra were carried out using Mattson 5000 FTIR spectrophotometer ( $4000\text{--}400 \text{ cm}^{-1}$ ) as KBr disk. The spectrophotometric measurements were performed on a UV<sub>2</sub> Unicam UV/vis spectrophotometer using 1 cm quartz cell. The pH values were measured using a pH-meter (Hanna Instruments, 8519, Italy) with accuracy of  $\pm 0.01$  and standardized at  $25^\circ\text{C}$ . The pH-metric titrations were performed using a Metrohm E536 potentiograph equipped with a 665 DOSIMAT (Metrohm, Herisau, Switzerland). The combined glass electrode was standardized using buffer solutions produced by Fisher's, NJ, USA.

### 2.3. Preparation of DAPCH

1-(3,4-Dihydroxybenzaldehyde)-2-acetylpyridiniumchloride hydrazone was prepared as previously reported [24] by heating under reflux 5 g of GP with 3.7 g 3,4-dihydroxybenzaldehyde in 10 ml absolute ethanol and few drops of glacial acetic acid on a water bath for 4 h till yellow precipitate, filtered off, recrystallized from ethanol and dried in a vacuum desiccator over anhydrous  $\text{CaCl}_2$ , m.p.,  $281\text{--}282^\circ\text{C}$ .



Scheme 1. DAPCH-Duolite C20.

### 2.4. Preparation of modified resin (DAPCH-Duolite C20)

In a bottle flask, introduce 1 g of Duolite C20 and 10 ml portion of  $10^{-3}$  M DAPCH in bidistilled water and mechanically stir the mixture at  $80^\circ\text{C}$  for 10 min. The mother liquor is decanted, replaced by another 10 ml of DAPCH solution and the process is repeated until saturation. The progress of the reaction is followed by taking 1 ml of the filtrate with buffer (pH 10) and measuring the intensity of the produced yellow color at 365 nm (the absorbance value is taken as a criterion for complete loading). The modified resin (Scheme 1) is filtered off, rinsed several times with bidistilled water, dried and stored. The amount of DAPCH sorbed on Duolite C20 is  $1.04 \text{ mmol g}^{-1}$ .

### 2.5. pH-metric titrations

All pH titrations were carried out at  $25 \pm 2^\circ\text{C}$ . The following solutions were titrated against 0.0052 M NaOH at ionic strength (0.1 M KCl):

- 1 ml of KCl + 2.5 ml HCl (0.0135 M).
- 1 ml of KCl + 2.5 ml HCl (0.0135 M) + 50 mg DAPCH-Duolite C20.
- 1 ml of KCl + 2.5 ml HCl (0.0135 M) + 50 mg DAPCH-Duolite C20 + 1 ml Cr(III) [ $1 \times 10^{-3}$  M].
- 1 ml of KCl + 2.5 ml HCl (0.0135 M) + 50 mg DAPCH-Duolite C20 + 1 ml Cr(VI) [ $1 \times 10^{-3}$  M].

The volume was completed to 25 ml with bidistilled  $\text{H}_2\text{O}$ , stirred and the pH was recorded.

### 2.6. Separation procedures

#### 2.6.1. Batch method

In a 250 ml glass-stoppered bottle, 100 ml solution containing  $50 \mu\text{g ml}^{-1}$  of Cr(III) and/or Cr(VI) ions were taken. After adjusting the pH to the optimum value, 100 mg of the modified resin was added. The mixture was shaken for 1 h, filtered, washed with bidistilled water and the sorbed metal ion was eluted with 5 ml of the suitable concentration of HCl and determined spectrophotometrically [25]. To confirm the results, 1 ml

of the desorbed solution was completed to 100 ml bidistilled water and the metal ion was determined by FAAS.

### 2.6.2. Column method

DAPCH-Duolite C20 (500 mg) was firstly swollen for 24 h, packed in a glass column (40 mm length and 6 mm diameter), treated with 20 ml (1 M) HCl at the optimum flow rate and washed with bidistilled water to become acid free. The metal ion (100 ml of  $100 \mu\text{g ml}^{-1}$ ) at the optimum pH was passed through the column at the optimum flow rate. The column was then washed with 100 ml bidistilled water to remove any uncomplexed metal ions from the resin bed. The metal ion was stripped from the resin using HCl, collected in a 100 ml calibrated flask and determined.

### 2.7. Oxidation of Cr(III) and determination of the total chromium

The spectrophotometric method with DPC was used to determine Cr(VI). Oxidation of Cr(III) to Cr(VI) may be carried out by the following two methods:

- Using  $\text{H}_2\text{O}_2$  in basic medium [18] as: after adjusting the solution to pH 10, 10 ml of 3%  $\text{H}_2\text{O}_2$  was added and heated for 50 min to complete oxidation and excess  $\text{H}_2\text{O}_2$  was removed, and then the total chromium was determined.
- Using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in acidic medium as: to 5 ml of the solution containing metal ions,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{AgNO}_3$  crystals were added and heated for boiling and finally the total chromium was measured [25].

The spectrophotometric measurement for chromium was confirmed by FAAS. The content of Cr(III) is calculated by the difference.

## 3. Results and discussion

The Cr-DAPCH reaction on the resin was confirmed by IR spectra. The bands of  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{N})$  were shifted to lower wavenumbers with lower intensity in the IR spectrum of the Cr(III) complex and not changed in Cr(VI) complex indicating that the hydrazone carbonyl and azomethine groups are taking part in coordination with Cr(III) only. The broad band centered at  $3540 \text{ cm}^{-1}$ , assigned to phenolic OH, decreased in intensity and shifted to lower wavenumber by  $10\text{--}15 \text{ cm}^{-1}$  in both complexes indicating that the phenolic OH is altered during the complex formation.

The pH-titration curves (Fig. 1) for HCl, modified resin and modified resin with Cr(III) and with Cr(VI) ions were taken as another support for the complex formation. It is shown that the curves of the modified resin with the metal ions are different from that of the modified resin alone which is taken as an evidence for the sorption of metal ions. The curve of Cr(VI) begins at pH higher than Cr(III) supporting the protonation of the phenolic hydroxyl groups.

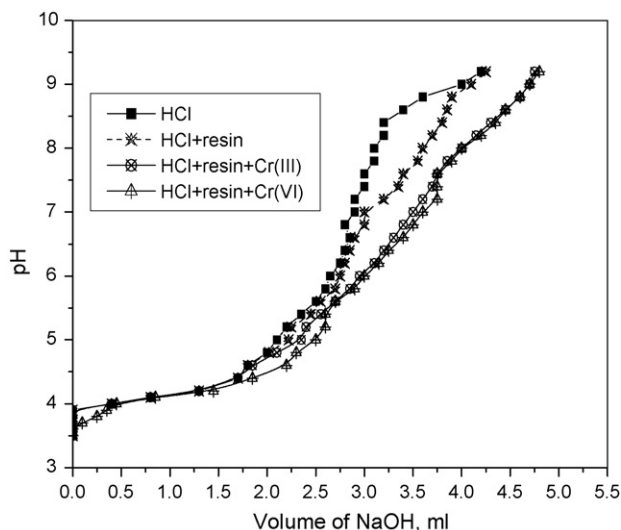


Fig. 1. The pH-metric titrations of HCl, HCl + resin, HCl + resin + Cr(III) and HCl + resin + Cr(VI) against  $0.0052 \text{ mol l}^{-1}$  NaOH.

### 3.1. Preliminary investigations

Batch and column preliminary experiments were carried out to investigate the quantitative sorption of the studied metal ions by Duolite C20 and DAPCH-Duolite C20. It was found that, Duolite C20 has no tendency for sorption of Cr(III) or Cr(VI) ions. On the other hand, DAPCH-Duolite C20 is efficient due to the strong interaction between Cr ions and the functional groups in the loaded hydrazone *via* complexation. The analytical variables have been studied through the batch and column techniques.

#### 3.1.1. Batch technique

**3.1.1.1. Effect of pH.** The sorption of Cr(III) and Cr(VI) ions has been investigated at interval pH (1–8) by batch equilibrium technique. The experiments were elaborated by shaking the solutions containing the metal ion with the modified resin at variable

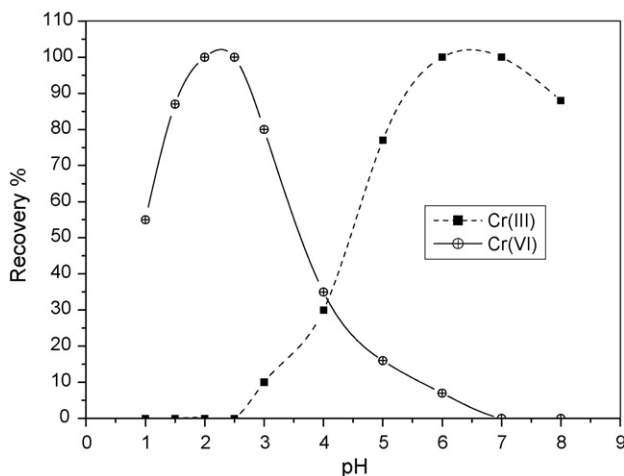


Fig. 2. Effect of pH on the recovery of Cr(III) and Cr(VI) ions using 100 mg resin; stirring time 30 min for Cr(VI) and 45 min for Cr(III) at  $25 \text{ }^\circ\text{C}$ .

pH for sufficient equilibrium time. Fig. 2 shows that the maximum sorption efficiency of DAPCH-Duolite C20 for Cr(VI) and Cr(III) ions was achieved at pH 2.0–2.5 and 6–7, respectively. For subsequent experiments, the working medium is adjusted at pH 6.0 for Cr(III) and 2.0 for Cr(VI). It is suggested that the sorption of chromium ions on the resin proceeds with participation of its hydroxyl groups. At higher pH, the hydroxyl groups become deprotonated and tend to attract the cation ( $\text{Cr}^{3+}$ ). In contrast, the positive charges (appear on the protonated hydroxyl groups) at low pH have the ability to sorb anions [ $\text{Cr}_2\text{O}_7^{2-}$ ]. This behavior indicates the possibility of separation of each species individually by controlling the pH. The sorption of only Cr(III) [26,27] or only Cr(VI) [28,29] were reported and the total chromium content was estimated either by reduction of Cr(VI) or oxidation of Cr(III).

### 3.1.2. Sorption capacity

The maximum capacity of the modified resin for sorption of Cr(III) and/or Cr(VI) ions was determined by shaking the solution containing excess ions with 100 mg of the resin under optimum conditions. The values are 41.6 and 25.05  $\text{mg g}^{-1}$  for Cr(III) and Cr(VI) ions, respectively. The higher capacity of Cr(III) may be due to its existence as  $\text{Cr}^{3+}$  (small size) where Cr(VI) exists as  $\text{Cr}_2\text{O}_7^{2-}$  (large size). Also, the IR spectral data support the coordination of DAPCH on the resin with two Cr(III) ions.

### 3.1.3. Amount of resin

The recovery of the metal ions was affected by the amount of the resin. To show its effect on the quantitative sorption of Cr(III) and Cr(VI), 25–500 mg of the resin were used. The recovery reached maximum at 50–200 mg. Thus, 100 mg of the resin has been used for subsequent experiments. Quantitative sorption is inaccurate for amount less than 50 mg. On the other hand, amount over 200 mg prevents the elution of the quantitative sorbed metal ion by a small volume of eluent. For this reason, the amount must be optimized.

### 3.1.4. Sorption kinetics of metal ions

The sorption rate curves (Fig. 3) of the resin towards Cr(III) and Cr(VI) were obtained by plotting the recovery (%) against the allowed sorption time. It shows that the  $t_{1/2}$  at 50% recovery for Cr(VI) and Cr(III) is 10 and 25 min, respectively. The sorption rate constants ( $k$ ) were calculated using Brykina equation [23]:

$$-\ln(1 - F) = kt, \quad F = \frac{Q_t}{Q}$$

where  $Q_t$  and  $Q$  are the sorption amounts at time  $t$  and at equilibrium, respectively. Putting the value of  $Q$  at  $t_{1/2}$  in the above equation, the calculated sorption rate constants ( $k$ ) are found to be  $6.54 \times 10^{-2} \text{ min}^{-1}$  for Cr(VI) and  $4.66 \times 10^{-3} \text{ min}^{-1}$  for Cr(III) at pH 2 and 6, respectively.

### 3.1.5. Effect of temperature

Temperature affects the equilibrium as well as the sorption of the metal ions. The sorption of Cr(III) and Cr(VI) ions was inves-

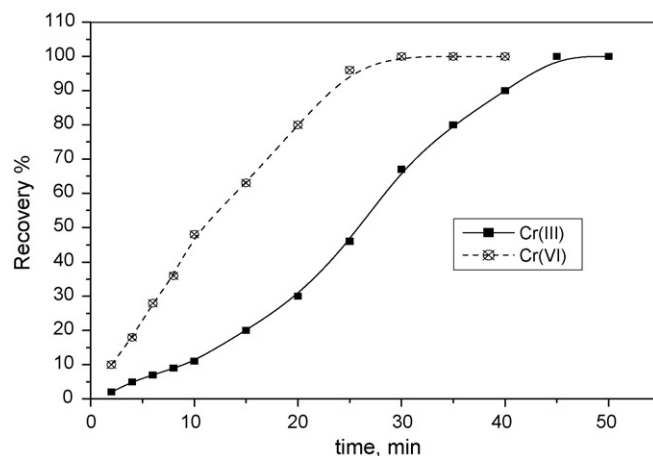


Fig. 3. Effect of stirring time on the recovery of Cr(III) and Cr(VI) ions using 100 mg resin at 25 °C.

tigated over a temperature range of 20–60 °C, which reflects the laboratory conditions. In general, the sorption capacity and the rate of sorption increase with increasing temperature (Fig. 4). The study was carried out at time 20 min for Cr(VI) and 30 min for Cr(III) at which the recovery is not maximum and the system is not in equilibrium. At maximum recovery, the temperature has no effect.

### 3.1.6. Resin stability and reusability

The modified resin (100 mg) was shaken with 100 ml of HCl with different concentrations (1–6) or 1 M of NaCl, KCl or  $\text{NaNO}_3$  and/or organic solvents (ethanol, acetone and chloroform) for 24 h, filtered, washed with bidistilled water and air dried. It was found that, no change in the sorption capacity of the resin reflect a stable nature of the modified resin. It was noticed that, the hydrazone moiety on the resin dissociates at  $\text{pH} > 9$  and the dissociation increases with the pH.

The sorption capacity of the modified resin was subjected to several cycles of sorption and desorption. The resin (100 mg)

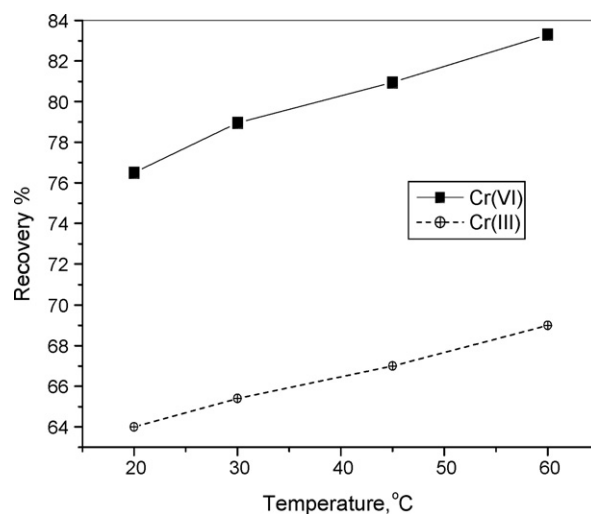


Fig. 4. Effect of temperature on the recovery of Cr(III) and Cr(VI) ion using 100 mg of the resin at pH 6 for Cr(III) and 2 for Cr(VI); stirring time 20 min for Cr(VI) and 30 min for Cr(III).

Table 1

Effect of eluent (5 ml) on the recovery (%) of Cr(III) and Cr(VI) ion from modified resin after separation of Cr(III) at pH 6 and Cr(VI) at pH 2

HCl (mol l <sup>-1</sup> )	Recovery (%)	
	Cr(III)	Cr(VI)
0.1	100	ND
0.2	100	ND
0.5	100	16
1		40
1.5		56
2		78
3		100
4		100

was stirred with 100 ml of 25 mg l<sup>-1</sup> solution containing Cr(III) and Cr(VI) ions for 1 h at room temperature. The concentration of the metal ion was determined after elution with 5 ml of appropriate concentration of HCl. Less than 3% decrease in sorption capacity for Cr(III) and Cr(VI) ions was found indicating that the modified resin is highly stable and may be used for several times. The modified resin when stored for 6 months under the laboratory conditions was found to have the same sorption capacity.

### 3.1.7. Choice of eluent

The effective eluent for the quantitative stripping of the retained metal ions on the resin is greatly selected. The metal sorbed can be eluted with acids or complexing agents such as sodium tartarate and EDTA. It was shown that the presence of a complex containing the analyte may cause severe suppression of the analyte signal. So the use of acid solution is analytically preferred. The data obtained (Table 1) indicate that Cr(III) is eluted with 5 ml of 0.1 M HCl while Cr(VI) with 5 ml of 3.0 M HCl. Elution of the metal ions with HCl has the advantage that, chloride ion is an acceptable matrix for the spectrophotometric and AAS techniques.

### 3.1.8. Effect of diverse ions

In order to assess the possible analytical applications of the recommended procedure, the effect of some foreign ions was examined. For this study, 25 µg Cr(VI) was taken with different amounts of foreign ions and the recommended procedure (batch) was followed. The results (Table 2) show no effect on the recovery of Cr(VI) in the presence of sodium, magnesium, calcium, potassium, chloride, sulphate, phosphate, nitrate and various metal ions.

## 3.2. Column technique

### 3.2.1. Effect of flow rate

The sorption of metal ions was investigated at different flow rates (0.5–10 ml min<sup>-1</sup>) under the optimum conditions. The maximum capacity of Cr(III) and Cr(VI) was found at flow rate of 2 and 5 ml min<sup>-1</sup>, respectively (less than 2 ml min<sup>-1</sup> gave long time). However, at flow rate >2 ml min<sup>-1</sup>, Cr(III) ions do not reach equilibrium. The faster sorption of Cr(VI) ion with the

Table 2

Influence of some ions on the recovery of Cr(III) and/or Cr(VI) on the resin by repeating the experiment three times ( $v = 50$  ml)

Ions	Concentration (mg l <sup>-1</sup> )	Recovery (%) <sup>a</sup>
Na <sup>+</sup>	1000	97 ± 2 <sup>b</sup>
K <sup>+</sup>	1000	95 ± 3
Ca <sup>2+</sup>	1000	96 ± 2
Mg <sup>2+</sup>	1000	95 ± 3
Cl <sup>-</sup>	1000	97 ± 2
PO <sub>4</sub> <sup>3-</sup>	1000	94 ± 4
SO <sub>4</sub> <sup>2-</sup>	500	96 ± 2
NO <sub>3</sub> <sup>-</sup>	500	95 ± 4
Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cd <sup>2+</sup> , Co <sup>2+</sup> , Pb <sup>2+</sup> , Zn <sup>2+</sup> , Mn <sup>2+</sup>	10	96 ± 2
Fe <sup>3+</sup> <sup>c</sup>	25	97 ± 2
Mixed <sup>d</sup>		93 ± 4

<sup>a</sup> Mean + R.S.D (relative standard deviation) which is equal to  $s \times 100/X$  where X is the experimental average and s is the standard deviation.

<sup>b</sup> The values mean both of Cr(III) and Cr(VI)

<sup>c</sup> In the presence of fluoride.

<sup>d</sup> The solution containing ions in this table together.

modified resin is taken as an indication for its higher reactivity with the resin.

### 3.2.2. Breakthrough capacity

To evaluate the amount of metal ion sorbed per gram on the modified resin under the optimum conditions, a breakthrough capacity is operated. The column was packed with 0.5 g of the modified resin and 50 µg ml<sup>-1</sup> of Cr(III) or Cr(VI) at the optimal pH and flow rate. The receiving effluent after 5 min was fractionalized into 5 ml portions and in each the metal ion was determined. The breakthrough capacity (Fig. 5) indicates that, the column is saturated with 42.5 and 25.0 mg g<sup>-1</sup> of Cr(III) and Cr(VI) ions, respectively.

### 3.2.3. Column reuse

To test the long-term stability of the column containing the modified resin, successive sorption and elution cycles were car-

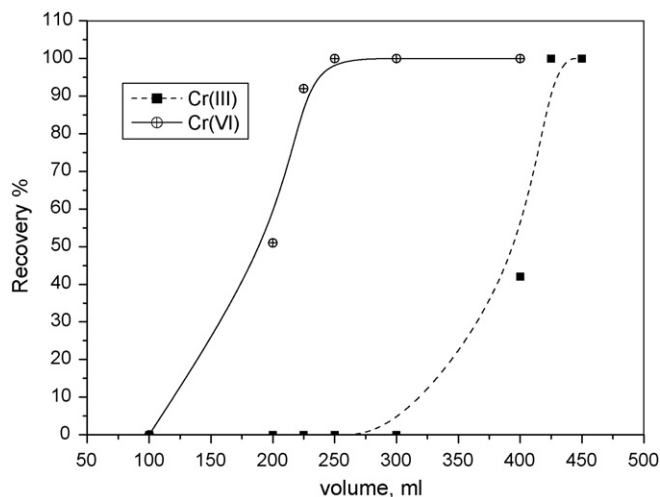


Fig. 5. Breakthrough curves for Cr(III) and Cr(VI) ions with flow rate 2 ml min<sup>-1</sup> at 25 °C and pH 6 for Cr(III) and 2 for Cr(VI).

Table 3

Determination of Cr(III) at pH 2 and Cr(VI) at pH 6 in synthetic mixtures, volume = 100 ml after separation using column technique

Analyte added ( $\mu\text{g ml}^{-1}$ )		Analyte found ( $\mu\text{g ml}^{-1}$ )		Recovery (%) $R \pm ts/n^{1/2a}$	
Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
0.5	0.5	0.49	0.50	98 $\pm$ 1	100 $\pm$ 1
1.0	1.0	1.00	0.99	100 $\pm$ 1	99 $\pm$ 1
1.5	1.5	1.48	1.50	99 $\pm$ 2	100 $\pm$ 1
2.0	1.0	1.89	0.99	99 $\pm$ 2	99 $\pm$ 1

<sup>a</sup> Mean and R.S.D.

ried out by passing the metal solution through the column at the optimum flow rate. The sorbed metal ion is then eluted from the resin with different concentrations of HCl. The procedure was carried out several times and the stability of the column was assessed by monitoring the change in the recoveries of the sorbed metal ions. The results of 50 sorption/desorption cycles indicated that, the recovery decreased by 2–3% for Cr(III) and Cr(VI) ions, which reflect good stability of the modified resin.

### 3.2.4. Effect of volume and preconcentration factor

Aqueous solutions (0.1–1.5 l) containing 10  $\mu\text{g}$  of Cr(III) and Cr(VI) ions were passed through the modified resin bed, eluted with 5 ml of the appropriate concentration of HCl and determined. It was found that, Cr(III) ion could be removed quantitatively from volume up to 750 ml while Cr(VI) ion up to 1000 ml, then the recovery decreased remarkably. Therefore, on using 5 ml of appropriate concentration of HCl as eluent, the preconcentration factor is 150-fold for Cr(III) and 200-fold for Cr(VI).

### 3.2.5. Detection limits of the metal ions

The lowest concentration of metal ion below which its quantitative sorption by the modified resin is not perceptibly seen is called detection limit. It was investigated for Cr(III) and Cr(VI) ions at  $10^{-1}$  to  $10^{-3}$   $\mu\text{g ml}^{-1}$  passed through the resin bed at a suitable flow rate for each metal ion under investigation. The limit of detection (LOD) is 13.3 and 10.0 ppb for Cr(III) and Cr(VI) ions, respectively, showing high sensitivity of the modified resin in preconcentrating trace analyte.

## 3.3. Applications

### 3.3.1. Speciation of Cr(III) and (VI)

Different concentrations of Cr(III) and Cr(VI) were prepared. Sample containing 100 ml of these solutions was precon-

centrated using column technique and determined by the recommended procedure. The experimental data presented in Table 3 gave satisfactory results.

### 3.3.2. Speciation of chromium from water samples

The introduced method was applied to the speciation of Cr(III) and Cr(VI) in tap water sample collected from Mansoura city, Dakahlia. The Cr(III), Cr(VI) and total chromium were determined in spiked and unspiked tap water. For this purpose, different amounts of Cr(VI) and Cr(III) were added to the sample and the proposed method (column) was applied. The obtained results were given in Table 4. As can be seen, the method could be applied successfully for the separation, preconcentration and speciation of trace amount of chromium in tap water samples. The accuracy of the results was quite satisfactory. Relative error is less than 3% for Cr(VI), Cr(III) and the total chromium.

**3.3.2.1. Analyses of the wastewaters containing chromium.** A sample of alum obtained from undesirable materials of company for production of alum was taken. One gram of the sample is dissolved in 100 ml of distilled water. The Cr(III) concentration was estimated as previously described (column). After oxidation of Cr(III) to Cr(VI) with hydrogen peroxide in NaOH, the total amount of Cr(VI) was determined. The solution was found to contain 0.0035 g Cr(III)  $\text{g}^{-1}$  alum. The values were compared with FAAS results.

Another sample is taken from ceramic industry wastewater. The sample was diluted to the appropriate range of concentration with distilled water. The pH of the solution was adjusted to 2.0 with HCl, and the Cr(III) ion was determined applying the recommended procedure. The results of the developed method gave 0.0078 g Cr(III)  $\text{g}^{-1}$  ceramic, reflecting a good tool for separation of chromium from different media.

Table 4

Determination of Cr(VI) and Cr(III) in tap water (water sample + different additives of the analytes), volume = 100 ml after separation using column technique

Analyte added ( $\mu\text{g}$ )			Analyte found ( $\mu\text{g}$ )			Recovery (%) $^aR \pm \text{R.S.D.}$		
Cr(III)	Cr(VI)	Total	Cr(III)	Cr(VI)	Total	Cr(III)	Cr(VI)	Total
–	–	–	1.0	0.5	1.5	–	–	–
10	4	14	10.8	4.4	15.2	98.0 $\pm$ 1	97.5 $\pm$ 2	97.8 $\pm$ 2
4	10	14	4.9	10.3	15.2	97.5 $\pm$ 2	98.0 $\pm$ 1	97.8 $\pm$ 2
10	10	20	10.8	10.4	21.2	98.0 $\pm$ 2	99.0 $\pm$ 1	98.5 $\pm$ 1
3	7	10	4.0	7.3	11.3	100 $\pm$ 1	97.2 $\pm$ 2	98.0 $\pm$ 2

<sup>a</sup> Mean and R.S.D. of five determinations.

#### 4. Conclusion

A new modified resin is introduced for speciation of Cr(III) and Cr(VI). The method evaluated is simple, fast and easily applied for separation and determination of the two cations selectively and individually. Cr(III) is separated at pH 6 and eluted with 5 ml of 0.1 M HCl while Cr(VI) at pH 2 and eluted with 5 ml of 3.0 M HCl using 100 mg of the modified resin with stirring time of 45 and 30 min, respectively. The advantages of the modified resin are: (i) the sorbent is highly stable (ii) it is used for several times with the same sorption capacity (iii) it has higher preconcentration factor and low detection limit and (iv) it is applied successfully for determination of chromium in tap water, synthetic mixtures and real materials using column technique.

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