
DYNAMIC SORPTION OF Cr^{3+} ON STRONGLY ACIDIC CATION EXCHANGERS AND SEPARATION OF Cr(VI) , Cr^{3+} AND CATIONS INTERFERING WITH THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM

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Received January 28th, 1985

The dynamic sorption of Cr^{3+} on two strongly acidic cation exchangers, *viz.* the microreticular Ionenaustauscher I and the macroreticular Amberlyst 15, is studied by measuring the breakthrough curves for the hexaquo chromium(III) ions, products of their partial hydrolysis, and mixtures of Cr^{3+} with Co^{2+} , Cu^{2+} , and Ni^{2+} ions, hence, ions interfering with the spectrophotometric determination of chromium. Analysis of the breakthrough curves made it possible to find the experimental conditions for the quantitative separation of Cr(VI) from Cr^{3+} and for the separation of chromium from the interfering cations. A procedure for the determination of Cr(VI) , Cr^{3+} and total chromium in the presence of the interfering ions is based on the oxidation of Cr^{3+} with hydrogen peroxide, reduction of Cr(VI) with hydroxylammonium chloride, separation of Cr(VI) on a strongly acidic cation exchanger, and spectrophotometric determination of Cr^{3+} with DCTA.

The properties of chromium-containing materials are greatly affected by the trivalent-to-hexavalent chromium ratio; for instance, this ratio has a considerable effect on the sorption properties of whetlerites, industrial sorbents based on activated carbon^{1,2}. The problem of determination of Cr(VI) in the presence of Cr^{3+} is also of importance in clinical analysis and environmental monitoring in view of the different toxicity of the two valency states of chromium, particularly with regard to the recently recognized carcinogenesis of Cr(VI) compounds³.

The majority of methods for the determination of Cr(VI) and Cr^{3+} in their mixtures comprise the determination of total chromium after its reduction or oxidation in an aliquot of sample in combination with the determination of Cr(VI) or Cr^{3+} in another aliquot, which is often associated with the separation of the two oxidation states of chromium⁴.

Cr(VI) can be separated from Cr^{3+} and other cations on ion exchangers, particularly strongly basic anion exchangers^{5,6}. Naranjit and coworkers, however, found⁷ that Cr(VI) does not elute quantitatively from the anion exchanger, nor does Cr^{3+} elute quantitatively from a cation exchanger, and so the authors suggest that both

a cation and an anion exchangers should be used to obtain quantitative data by determining Cr(VI) and Cr^{3+} in the effluents.

It is convenient to make use of separation on strongly acidic cation exchangers for the quantitative determination of Cr(VI) in the presence of Cr^{3+} and other interfering cations. The sorption of Cr^{3+} , however, is affected by the sorbate composition, which varies with pH and time, as was found by Osaki and coworkers⁸ during their investigation of the gel chromatographic behaviour of chromate and hydrolyzed chromium(III) ions.

In this work the breakthrough curves were measured for establishing the optimum conditions for the dynamic sorption of Cr^{3+} ions from aqueous solutions, both alone and in mixtures with other cations; two different strongly acidic cation exchangers were employed under different experimental conditions for this purpose, *viz.*, Ionenaustauscher I and Amberlyst 15. Since cations giving coloured solutions and cations forming coloured complexes with 1,2-diamino-*cis*-cyclohexane-N,N,N',N'-tetraacetic acid (DCTA), particularly Cu^{2+} , Ni^{2+} , and Co^{2+} ions, interfere^{9,10} with the spectrophotometric determination of Cr^{3+} ions with this reagent, recommended for the analysis of Cr(VI) and Cr^{3+} in whetlerites², the dynamic sorption of Cr^{3+} on strongly acidic cation exchangers was also examined in the presence of Co^{2+} , Cu^{2+} , and Ni^{2+} ions with a view to working out a procedure in which the interfering effect of these cations would be eliminated.

EXPERIMENTAL

Apparatus and Chemicals

The spectrophotometric measurements were performed on a Spekol spectral colorimeter (Carl Zeiss, Jena), the pH was measured on an OP 264/1 digital pH-meter (Radelkis, Budapest) with a combined glass indicator and silver chloride reference electrode.

Cr(VI) was separated from cations and the breakthrough curves were measured with a column 10 mm i.d., linked in a closed system with the containers for the solutions measured, eluting agents, and solvent. The flow rate was controlled by adjusting the vertical position of the containers and the nitrogen pressure at the container closures. In this manner the whole system was separated from its environment and the solutions could be displaced rapidly from the column. The column was packed with the microreticular Ionenaustauscher I cation exchanger (Merck, Darmstadt), $d_p = 0.4-0.6$ mm, or with the macroporous Amberlyst 15 cation exchanger (Fluka, Buchs), $d_p = 0.3-1.2$ mm, both in the H^+ -cycle. The two catexes were purified with 7M-HCl, 1.5M-NaOH, and alkaline solution of EDTA (pH \approx 9) by heating on a water bath. The total mass exchange capacity, Q_g , was determined by passing a volume of 0.1M-NaOH through the catex column in the H^+ -cycle. A weighed amount of the pure catex, dried in air, was allowed to swell in deionized water for 24 h before packing the column. The Q_g value per gramme of dry catex, determined from the sodium hydroxide concentration decrease found by titration with 0.1M-HCl, was 5.31 mmol g^{-1} for Ionenaustauscher I and 5.01 mmol g^{-1} for Amberlyst 15. The water content of the catexes was determined by drying to constant weight at 105 °C.

The 10^{-2} M- $K_2Cr_2O_7$ stock solution was prepared from the recrystallized substance dried at $105^\circ C$. The stock solution of Cr^{3+} ions was prepared from $Cr(NO_3)_3 \cdot 9 H_2O$. Chromium was determined chelatometrically by titration of excess EDTA with thorium (IV) nitrate using xylenol orange as the indicator¹¹. Solution of $0.1M-Cu(NO_3)_2$ was prepared from the trihydrate and standardized potentiometrically with EDTA using a Crytur Cu 29-17 ion selective electrode. Solutions of Ni^{2+} and Co^{2+} ions were prepared from $Ni(NO_3)_2 \cdot 6 H_2O$ and $Co(NO_3)_2 \cdot 6 H_2O$, respectively, and their titre was determined chelatometrically using murexide as the indicator¹¹. All the chemicals used were of reagent grade purity and solutions were made up from redistilled water.

Spectrophotometric Determination of Chromium

The procedure for the determination of chromium(III) ions with DCTA and for the simultaneous determination of Cr^{3+} and Cu^{2+} ions has been described². $Cr(VI)$ was reduced for the determination by means of $0.2M-NH_2OH \cdot HCl$ at $pH \approx 4.5$. In cases where the sensitivity of the determination of chromium with DCTA was insufficient, Cr^{3+} ions were determined spectrophotometrically based on their reaction with xylenol orange¹².

Separation of $Cr(VI)$ from Cr^{3+} and Interfering Ions

The procedure for the separation of $Cr(VI)$ from Cr^{3+} on a strongly acidic cation exchanger² was employed for removing the coloured interfering ions (Cu^{2+} , Ni^{2+} , Co^{2+}). For the determination of chromium in the presence of the interferents, Cr^{3+} was oxidized with 5% solution of hydrogen peroxide in $0.5M-NaOH$.

Solution containing the ions to be separated, adjusted to $pH < 3.0$, was passed at a flow rate of $1-2 \text{ ml min}^{-1}$ through the cation exchanger column in the H^+ -cycle (column height 50 to 100 mm). Solution of $Cr(VI)$ was collected for its spectrophotometric determination. The column was recovered by washing it with $4M-HCl$ and $1.5M-NaOH$. The cations retained could be determined in the eluate.

Breakthrough Curve Measurements

A cation exchanger column 50 mm long was used. A weighed portion of pure dry cation exchanger was allowed to swell in deionized water for 24 h before its placing in the column. The cation exchanger in the column was converted to the H^+ -cycle with $2M-HCl$ and then washed with water until no acidic reaction was observed. The stock solutions of $Cr(VI)$, Cr^{3+} and other cations were prepared 24 h before the measurement. The pH of the working solutions was adjusted with HCl and $NaOH$ and recorded before and after the breakthrough measurement. The flow rate was constant at 1.0 ml min^{-1} . The ions followed as well as the pH were determined in 20 ml effluent fractions. The cations retained were eluted successively with 100 ml of $7M-HCl$ and 20 ml of $1.5M-NaOH$ and determined in the eluates collected.

The free column volume was determined, for both cation exchangers, based on the breakthrough of dichromate ions which do not sorb on the cation exchangers in the conditions used. The average values, calculated from the changes in the Cr concentration and also from the amount of dichromate ions retained by the column and displaced by water, were 2.07 ml for Ionenaustauscher I and 2.36 ml for Amberlyst 15.

RESULTS AND DISCUSSION

Sorption of Cr^{3+} and Cu^{2+} Ions on Cation Exchangers in Dynamic Conditions

Data were obtained of the capacity of the two cation exchangers to 5% breakthrough of a cation (M) from the column, $Q_{M(0.05)}$, and of the total capacity, Q_M , expressed in terms of the retained amounts of the cation in question, in mmol, per g of dry cation exchanger. The exchange parameters were compared with the total mass exchange capacity (Q_g), which is slightly higher for the microreticular Ionenaustauscher I than for the macroreticular Amberlyst 15.

TABLE I

Dependence of the total amounts of Cr^{3+} and Cu^{2+} ions retained by Ionenaustauscher I and Amberlyst 15 cation exchangers on pH. Column height 50 mm, initial concentrations of Cr^{3+} and Cu^{2+} ions 10 mmol l^{-1}

Ion	pH	$w_M, \text{mg g}^{-1}$			Recovery %
		breakthrough curve (corrected)	determined analytically	elution with HCl + NaOH	
Ionenaustauscher I					
Cr^{3+}	1.22	88.5	88.4	85.7	96.9
	1.78	89.4	89.4	86.6	96.9
	2.40	91.8	91.7	89.3	97.4
	2.90	97.3	97.5	94.5	96.9
	3.28	100.4	100.4	97.5	97.1
	3.56	106.8	106.9	101.1	94.6
	3.79	125.9	126.3	117.8	93.3
	Cu^{2+}	4.70	162.0	161.9	165.4
Amberlyst 15					
Cr^{3+}	1.29	78.1	77.1	75.2	97.5
	1.67	79.0	79.0	76.4	96.7
	2.22	81.3	81.3	80.1	98.5
	2.70	83.0	83.0	80.2	96.6
	3.06	84.7	84.8	82.6	97.4
	3.41	92.6	92.6	89.3	96.4
	3.87	104.9	105.0	101.4	96.6
	Cu^{2+}	2.51	150.2	150.2	152.6
4.68		154.0	154.2	154.9	100.5

The Q_M values were calculated from the area above the breakthrough curves; the concentrations determined by analysis in the individual volume fractions (ΔV_i) collected during the breakthrough curve measurements were related to the total passed volume V corresponding to the centre of the interval ΔV_i . Alternatively, the Q_M values were calculated from the difference between the analytically determined amount of the cation in the total volume of the influent and the sum of the amounts of the cations in the individual fractions ΔV_i . The amount of the cations sorbed was also determined in the eluate after the elution with 7M-HCl and 1.5M-NaOH. In both procedures of Q_M determination, corrections were made for the free column volume.

The total amounts of retained Cr^{3+} and Cu^{2+} , for various pH, are given in Table I. The Q_{Cr} and Q_{Cu} values determined from the area above the breakthrough curve, after the corrections indicated, agree well with those determined analytically. The amounts of Cr^{3+} ions eluted from the two cation exchangers with HCl and NaOH are invariably lower than those determined from the breakthrough curves, in agreement with the observations of Naranjit and coworkers⁷. The average recovery of Cr^{3+} was $97.0 \pm 0.2\%$ for Ionenaustauscher I at pH 1.22–3.28 and $97.1 \pm 0.8\%$ for Amberlyst 15 at pH 1.29–3.87. For Cu^{2+} ions, the amount determined analytically was slightly higher than Q_{Cu} determined from the breakthrough curves.

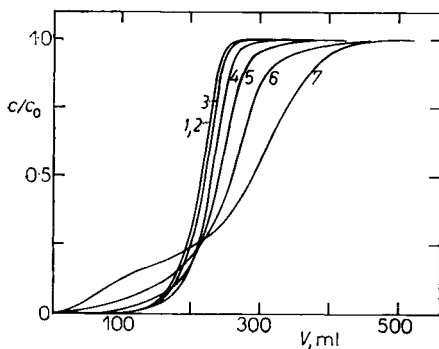


FIG. 1

Breakthrough curves for Cr^{3+} on Ionenaustauscher I cation exchanger. $c_0(\text{Cr}) = 10 \text{ mmol l}^{-1}$, 1.16 g of dry exchanger; pH: 1 1.22, 2 1.78, 3 2.40, 4 2.90, 5 3.28, 6 3.56, 7 3.79

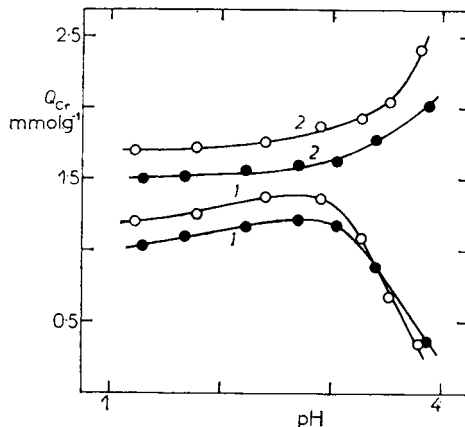


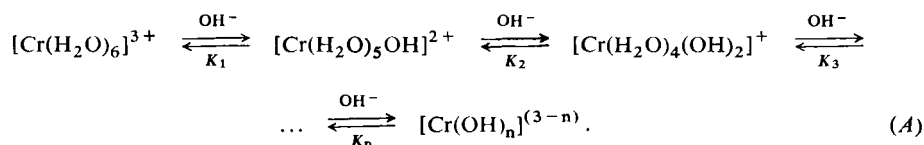
FIG. 2

Effect of pH on the amounts of Cr^{3+} retained to the breakthrough at $c/c_0 = 0.05$ (curves 1) and the total retained amounts of Cr^{3+} on Ionenaustauscher I (\circ) and Amberlyst 15 (\bullet) cation exchangers; $c_0(\text{Cr}) = 10 \text{ mmol l}^{-1}$, cation exchanger column height 50 mm

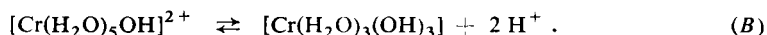
Fig. 1 shows the breakthrough curves for Cr³⁺ ions (10 mmol l⁻¹) on Ionenaustauscher I. The shape of the curves alters if the pH of the influent is changed, and the volume of the solution passed at which the breakthrough of chromium occurs is also affected. The changes with varying pH are similar for Amberlyst 15. The breakthrough curves of equally concentrated solutions of Cu²⁺ ions do not change in shape or position with varying pH over the pH 2.5–4.7 range.

The dependence of Q_{Cr} and $Q_{Cr(0.05)}$ on the pH of the influent are shown in Fig. 2. The rapid drop of the $Q_{Cr(0.05)}$ value is associated with changes in the solution composition, the chromium(III) salt undergoing hydrolysis at pH > 3.

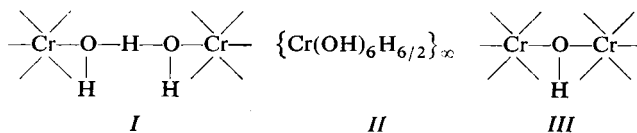
As the pH is increased, hexaquo chromium(III) ions, which exist in chromium(III) salt solutions at pH < 3, become deprotonated. Mononuclear Cr³⁺ hydroxocomplexes should be formed according to the scheme



Actually, however, the deprotonation of hexaquo chromium(III) ions proceeds in the first step only¹³ (Scheme (A)). As additional OH⁻ ions are added, a precipitate of the slightly soluble so-called “active” chromium(III) hydroxide with zero charge appears:

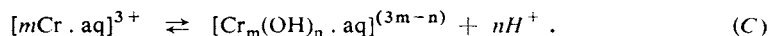


This process occurs rapidly and is associated with the formation of hydrogen bonds always between a coordinated water molecule and an OH⁻ group (formula I). Each chromium ion is linked in this manner with six other chromium ions, so that the crystal structure of the active hydroxide can be written as II (ref.¹³). On ageing, however, active chromium(III) hydroxide transforms into the amorphous, virtually insoluble “latent” species in which the chromium atoms are linked *via* μ -hydroxo bridges (formula III),

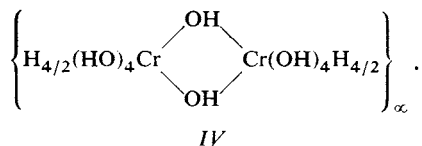


and these OH groups cannot be neutralized with acid, in contrast to those in the active hydroxide which dissolves immediately in acid solutions, giving again the hexaquo chromium(III) ion.

In addition to mononuclear Cr^{3+} complexes, polynuclear complexes are also formed in chromium(III) salt solutions, largely by the pathway



Dimers^{13,14}, trimers¹⁵ and tetramers¹⁶ have been positively identified. Such polynuclear complexes can also give rise to the uncharged "active" chromium hydroxides in which coordinated water molecules are hydrogen-bonded to OH groups, as has been found for the binuclear complex¹³ for which structure *IV* has been suggested.



The breakthrough curves in Fig. 1 give evidence of the formation of species free of positive charge in solutions whose pH established 24 h after the addition of NaOH was higher than 3. The pH decrease during the standing of these solutions indicates that uncharged chromium(III) hydroxide is formed by pathway (B) (Scheme (B)). The highest pH at which the breakthrough curves of Cr^{3+} ions were measured, $\text{pH} \approx 3.8$, established within 24 h in solutions whose initial pH was about 4.6. A slight turbidity was observed if this pH was surpassed. Part of chromium passes the strongly acidic cation exchanger column after delivering the first volume fractions of the influent (curves for pH 3.56 and 3.79 in Fig. 1). It can be assumed that a fraction of the uncharged chromium(III) hydroxide is not protonated according to pathway (B) during its passage through the column. Possibly, the active hydroxide *II*, whose protonation proceeds rapidly¹³ giving rise to cations, has partly transformed into the latent chromium(III) hydroxide *III*. Polynuclear complexes, the formation of which from the aquochromium ions (Scheme (C)) is associated with the liberation of hydrogen ions and which also can give rise to uncharged hydroxides similar to *IV*, may also be present.

The shift of the steep branches of the breakthrough curves measured at $\text{pH} > 3$ to larger volumes (Fig. 1), associated with an increase in the total capacity of the cation exchangers for Cr^{3+} ions in this pH range, is due to the fact that in addition to the hexaquo chromium(III) ions, their hydrolysis products are also present in the influent. The total amount of hydrogen ions (η_{H}) released by the sorbed Cr^{3+} ions also decreases with increasing pH of the influent. The η_{H} values were calculated from the concentrations of H^+ ions found by pH determination in the individual volume fractions ΔV_i during the breakthrough curve measurements. The $\eta_{\text{H}}/Q_{\text{Cr}}$ ratio approaches 3 at $\text{pH} < 3$ (although it decreases slightly with increasing pH), and this

corresponds to the exchange of a $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ cation for three hydrogen ions (Fig. 3). At $\text{pH} > 3$ this ratio drops appreciably, the shape of this dependence being identical for the two cation exchangers within the limits of experimental error. Hence, the Cr^{3+} ion exchange mechanism is not different for the two cation exchangers and it reflects the varying conditions for the dynamic sorption of Cr^{3+} on the strongly acidic cation exchangers.

For assessing the effect of hydrolysis, the sorption of Cr^{3+} was also investigated based on the analysis of the individual volume fractions collected (ΔV). Two pH values of the influent, *viz.* pH 2.40 at which only hexaquo-chromium(III) ions are present, and pH 3.79 at which hydrolysis starts to take place, were used for Ionenaustauscher I. Denote $\eta_{\text{Cr},i}$ the amount of Cr^{3+} sorbed from the i -th volume fraction ΔV_i and $\eta_{\text{H},i}$ the displaced amount of H^+ (determined from the pH of the i -th volume fraction), both in mmol per g of dry cation exchanger. Their sums over all i 's denote $\eta_{\text{Cr,tot}}$ (the amount of chromium(III) ions retained by the cation exchanger from the volume passed, V), and $\eta_{\text{H,tot}}$ (the amount of hydrogen ions that left the column in this volume), *resp.* Fig. 4, which shows the dependences of $\eta_{\text{Cr,tot}}$ and $\eta_{\text{H,tot}}$ on the total amount of Cr^{3+} (n_{Cr}) in the influent volume V , demonstrates the differences in the exchange process for the different pH values. At pH 2.40, the curves both for $\eta_{\text{Cr,tot}}$ and $\eta_{\text{H,tot}}$ show a break at the same $n_{\text{Cr}} \approx Q_g/3$ and then the two quantities remain constant, whereas at pH 3.79 this holds for $\eta_{\text{H,tot}}$ while in the dependence for $\eta_{\text{Cr,tot}}$ this break does not appear any more. At pH 2.40 the $\eta_{\text{H,tot}}/\eta_{\text{Cr,tot}}$ ratio is 3 during the entire breakthrough curve measurement, hence, only the exchange of a hexaquo-chromium(III) ion for three H^+ ions takes place. This is also borne out by the dependences plotted in Fig. 5, where $\eta_{\text{Cr,tot}}^{\text{rel}}$ denotes the number of Cr^{3+} equivalents (1/3 mmol Cr) occupying the surface of 1 g of cation exchanger after collecting the i -th volume fraction, relative to Q_g . At pH 2.4 the $\eta_{\text{Cr},i}$ and $\eta_{\text{H},i}$ curves display plateaus and both end at $\eta_{\text{Cr,tot}}^{\text{rel}} = 1$. Also, the $\eta_{\text{H},i}/\eta_{\text{Cr},i}$ ratio remains constant over the $\eta_{\text{Cr,tot}}^{\text{rel}}$ region from 0 to 1 and corresponds to the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} : \text{H}^+ = 1 : 3$ ratio (Fig. 6). At pH 3.79, the ratio of the slopes in the dependences for $\eta_{\text{H,tot}}$ and $\eta_{\text{Cr,tot}}$ in Fig. 4 is about 2.7 and it remains constant up to $\eta_{\text{Cr,tot}}^{\text{rel}} \approx 0.85$ (Fig. 6). The H^+ ion exchange is practically finished at $\eta_{\text{Cr,tot}}^{\text{rel}} \approx 1$, similarly as at pH 2.40; the sorption of Cr^{3+} , however, continues to proceed (Fig. 5). The total amount of H^+ ions displaced at pH 3.79 is nearly one-fifth lower than at pH 2.40. Hence, the hydrogen ions released by ion exchange are taken up for side processes during the sorption of Cr^{3+} in the region of partial hydrolysis. One of these processes can be the protonation of the $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ complex; the lowering in the $\eta_{\text{H},i}/\eta_{\text{Cr},i}$ ratio from 3 at pH 2.40 to about 2.7 at pH 3.79 roughly corresponds to the amount of H^+ ions required for the complete protonation of $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ in the first step of pathway (A) if the value of $\text{p}K_1 = 4.15$ at 20°C (ref.¹³) is considered. Processes of dissolution of the uncharged active Cr(III) hydroxides, both mononuclear and polynuclear, can also take part; H^+ ions are taken up in these processes as well as in the process of

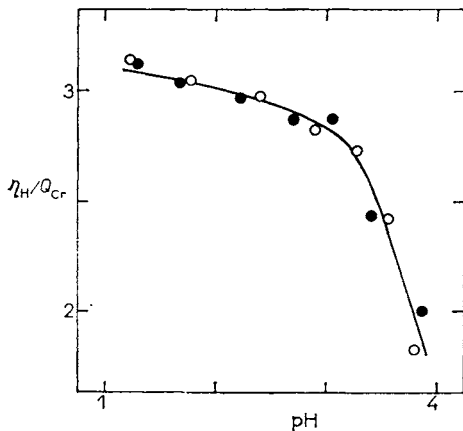


FIG. 3
Effect of pH on the $\eta_{\text{H}}/Q_{\text{Cr}}$ ratio for Ionenaustauscher I and Amberlyst 15. Conditions and labelling as in Fig. 2

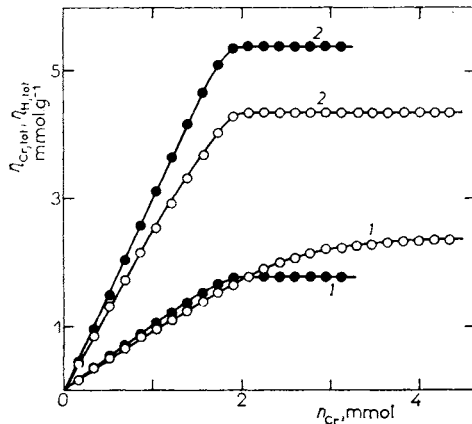


FIG. 4
Course of sorption of Cr^{3+} (curves 1) and desorption of H^+ ions (curves 2) in dependence on the amount of Cr^{3+} passed through the 50 mm column of Ionenaustauscher I at pH 2.40 (●) and pH 3.79 (○); $c_0(\text{Cr}) = 10 \text{ mmol l}^{-1}$

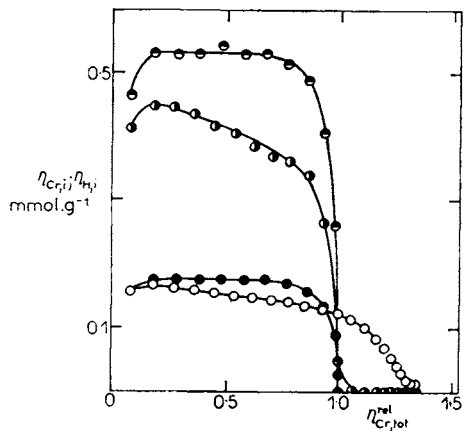


FIG. 5
Changes in the amounts of sorbed Cr^{3+} and released H^+ ions in dependence on the degree of occupation of the active groups of Ionenaustauscher I cation exchanger by trivalent Cr cations. Curves for pH 2.40 (● $\eta_{\text{Cr},i}$, ● $\eta_{\text{H},i}$) and pH 3.79 (○ $\eta_{\text{Cr},i}$, ○ $\eta_{\text{H},i}$)

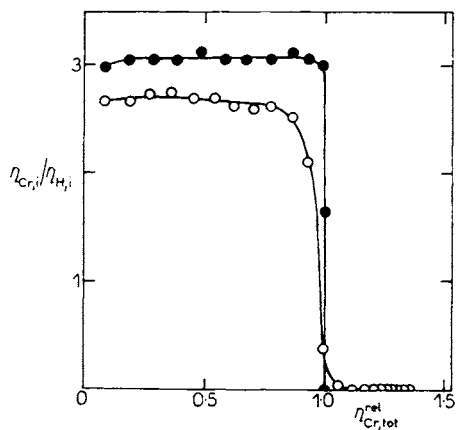


FIG. 6
Changes in the amount-of-substance ratio of retained Cr^{3+} and released H^+ ions in dependence on the degree of occupation of the active groups of Ionenaustauscher I cation exchanger by trivalent Cr cations. Curves for pH 2.40 (●) and 3.79 (○)

decomposition of the polynuclear complexes carrying positive charges. The additional sorption of chromium above $\eta_{\text{Cr},\text{tot}}^{\text{el}} = 1$ probably involves association of additional cations (and possibly also uncharged species) of trivalent chromium *via* hydrogen bridges.

The nature of the ion exchange of Cu^{2+} for H^+ on the two cation exchangers does not change within the pH 2.5–4.7 range, and it is similar to the Cr^{3+} ion exchange mechanism as observed at pH < 3 except that one copper ion is exchanged for two hydrogen ions over the entire pH region.

TABLE II

Elimination of the interfering effect of Cu^{2+} , Ni^{2+} , and Co^{2+} ions on the spectrophotometric determination of Cr^{3+} by separation on Ionenaustauscher I cation exchanger

Cr^{3+} added mg	Cr : M ratio	Separation	Cr^{3+} found ^a , mg		
			M = Cu^{2+}	M = Ni^{2+}	M = Co^{2+}
52.6	1 : 5	—	65.1 (+23.8)	58.7 (+11.6)	59.0 (+12.2)
52.6	1 : 5	±	52.3 (-0.6)	52.0 (-1.1)	52.1 (-1.0)
21.0	1 : 25	+	21.0 (0.0)	20.5 (-2.4)	21.3 (+1.4)

^a Relative error of determination, in %, is given in parentheses. The chromium content was determined with DCTA.

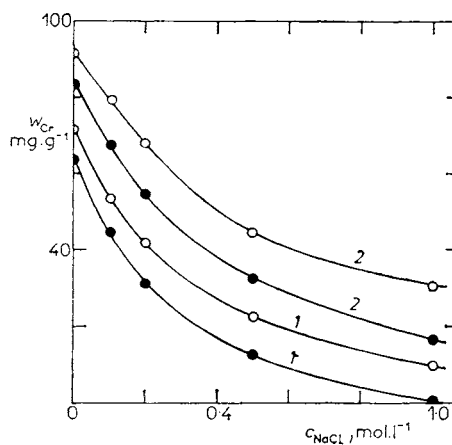


FIG. 7

Effect of concentration of NaCl on the breakthrough of Cr^{3+} at $c/c_0 = 0.05$ (curves 1) and on the total retained amount of Cr^{3+} (curves 2) for Ionenaustauscher I (○) and Amberlyst 15 (●). Conditions as in Fig. 2, pH 2.4

The effect of the concentration of NaCl on the sorption of Cr^{3+} within the region of occurrence of hexaquo chromium(III) ions alone ($\text{pH} \approx 2.4$) was also examined. The total amount of Cr^{3+} ions sorbed and their breakthrough at $c/c_0 = 0.05$ were established by measuring the breakthrough curves at different NaCl concentrations in the influent (Fig. 7). The Q_{Cr} and $Q_{\text{Cr}(0.05)}$ values for the two cation exchangers decrease with increasing concentration of NaCl, the values for Ionenaustauscher I being invariably higher than those for Amberlyst 15; for instance, at $c_{\text{NaCl}} = 1.0 \text{ mol} \cdot \text{l}^{-1}$, 1 g of the former cation exchanger retains approximately two times as much Cr^{3+} as 1 g of the latter.

TABLE III

Testing the analytical procedure for the determination of Cr(VI), Cr^{3+} and total chromium in the presence of interfering cations. Added: 2.644 mg Cr(VI) and 2.667 mg Cr^{3+} ; $c_{\text{M}^{2+}} \approx c_{\text{Cr}^{3+}}$ ($\text{M}^{2+} = \text{Co}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}$)

Species determined	Cr found mg	Relative standard deviation %	Relative error %	Student's t -value ^a
Cr(VI)	2.632	0.65	-0.45	1.729
Cr^{3+}	2.673	1.20	+0.22	0.459
Cr total	5.305	0.64	-0.11	0.432

^a Critical value $t_c = 2.571$ for $\nu = 5$ and $\alpha = 0.05$.

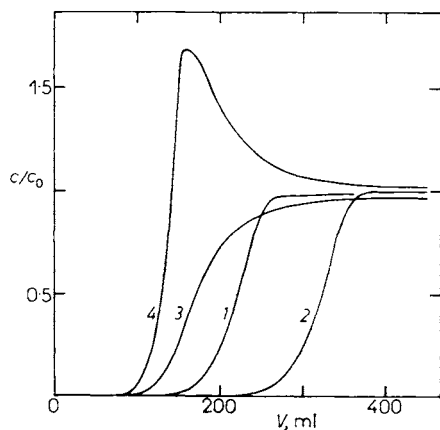


FIG. 8

Comparison of the breakthrough curves of a mixture of Cr^{3+} and Cu^{2+} with those of the individual components on Amberlyst 15 (column height 50 mm). Curves: 1 Cr^{3+} , $\text{pH} 2.22$; 2 Cu^{2+} , $\text{pH} 2.51$; 3 Cr^{3+} in mixture with Cu^{2+} , $\text{pH} 1.94$; 4 Cu^{2+} in mixture with Cr^{3+} , $\text{pH} 1.94$. Concentration of cations invariably 10 mmol l^{-1}

Elimination of the Interfering Effect of Coloured Cations

For eliminating the interfering effect of Co^{2+} , Cu^{2+} , and Ni^{2+} ions on the determination of Cr^{3+} , a procedure was worked out in which the Cr^{3+} ions are oxidized with hydrogen peroxide in alkaline solution, the solution is acidified, and chromium transformed into dichromate is separated on the catex. The results of determination of Cr^{3+} in the presence of Cu^{2+} , Ni^{2+} , and Co^{2+} ions are given in Table II. In case that the cations are not separated from Cr^{3+} , the determined amount of Cr^{3+} is affected appreciably if the interferents (particularly Cu^{2+}) are present in a five-fold excess. Owing to the separation on a catex, the interferences could be eliminated even at the level of a 25-fold excess of the associate ions.

The possibility of determination of Cr(VI) in the presence of Cr^{3+} and Cu^{2+} , Ni^{2+} , and Co^{2+} ions was also examined by the breakthrough curve measurements. In Fig. 8, the breakthrough curves of an equimolar mixture of Cr^{3+} and Cu^{2+} ions are compared with those of solutions of Cr^{3+} and Cu^{2+} alone. Although the total amount-of-substance concentration in the mixed system was double that in the solutions of the sole cations, breakthrough of Cr^{3+} as well as Cu^{2+} took place after the passage of a sufficient volume of the mixed solution. The sorption of mixtures of Cr^{3+} ions with Ni^{2+} and Co^{2+} ions, respectively, was similar to that for the Cr^{3+} - Cu^{2+} mixture.

The accuracy and precision of the method of determination of Cr(VI) and Cr^{3+} with DCTA in the presence of interfering cations were also tested (Table III). The given values represent the average of 6 measurements. The Cr(VI) content was determined after the separation of this species from all the present cations on the Ionenaustauscher I cation exchanger, and the Cr^{3+} content was calculated as the difference between total chromium and Cr(VI), the former being determined after the oxidation of Cr^{3+} with hydrogen peroxide, separation of chromium on the cation exchanger, and reduction with $\text{NH}_2\text{OH} \cdot \text{HCl}$. The data of Table III demonstrate that the method is reasonably precise and accurate for Cr(VI) as well as for Cr^{3+} even in the presence of other cations.

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Translated by P. Adámek.