

Spectrophotometric Determination of Monomeric Plus Oligomeric and Polymeric Hydroxy Species of Chromium(III) in Aqueous Solutions

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Abstract

The anion of edta formed complexes with monomeric and oligomeric species of chromium(III), whereas no reaction was observed with polymeric hydroxy forms in aqueous solutions of $\text{Cr}(\text{NO}_3)_3$ and CrCl_3 . A procedure is described to distinguish monomeric plus oligomeric from polymeric forms of chromium(III) in aqueous solutions by determining the Cr^{III} -edta complex spectrophotometrically at 546 nm.

Introduction

Mononuclear and polynuclear forms of aluminium(III) and iron(III) have been distinguished on the basis of rates of reaction with quinolin-8-ol and Ferron.^{1,2} The violet complex formed by the chelation of chromium(III) by edta has been widely used for the spectrophotometric determination of chromium(III). Owing to the stability of different complexes of chromium(III), the rate of formation of the Cr^{III} -edta complex is very slow at room temperature and involves several slow steps.³ However, the lack of reactivity of the hydroxo-bridged chromium(III) polymers with edta allowed the distinction of monomeric plus oligomeric, polymeric and precipitated forms of chromium(III) in aqueous solutions of CrCl_3 and $\text{Cr}(\text{NO}_3)_3$.

Experimental

Solutions

All reagents were of analytical-reagent grade. The edta solution consisted of a 0.1 M solution of the sodium salt of edta in distilled water and had a pH of 4.5.

Procedure

(i) *Total chromium(III)*.—To a 10 ml sample containing 0.05–5 mg of chromium(III) were added 5 ml of 1.0 M HNO_3 (pH of the mixture below 3.0) before heating at 100°C for 1 h. This procedure depolymerized all chromium(III) species. The solution was cooled and then mixed thoroughly with 5 ml of edta solution before heating again at 100°C for 10 min. After cooling, the volume was adjusted to 50 ml with distilled water and the absorbance measured against water at 546 nm in a 1-cm cell.

(ii) *Precipitated form*.—A suitable aliquot containing 0.05–5 mg chromium(III) was filtered through a Millipore prefilter and the filtrate analysed for various forms as below. The difference between the total and soluble forms of chromium(III) gives the precipitated form.

¹ Okura, T., Groto, K., and Yotuyanagi, T., *Anal. Chem.*, 1962, **34**, 581.

² Murphy, P. J., Posner, A. M., and Quirk, J. P., *Aust. J. Soil Res.*, 1975, **13**, 189.

³ Hamm, R. E., *J. Am. Chem. Soc.*, 1953, **75**, 782.

(iii) *Monomeric plus oligomeric forms*.—To a solution containing 0.05–5 mg chromium(III) distilled water was added to make the volume up to 40 ml. The edta solution (5 ml) was added and the solution was maintained at 100°C for 10 min. The solution was cooled and the volume made up to 50 ml. Absorbance was measured as above.

(iv) *Polymeric forms*.—The difference between the total chromium(III) content of the aliquot passed through a Millipore prefilter and the monomeric plus oligomeric forms gives an estimation of polymeric chromium(III) species.

Standard Curves

Standard curves were prepared by procedure (iv); Cr^{III} aliquots of 0.05–5 mg were used for freshly prepared solutions of chromium(III) (pH below 3.5).

Test Samples

Various samples of CrCl₃ and Cr(NO₃)₃ were prepared by diluting suitably the stock solutions. Solutions of various OH/Cr ratios were prepared, with NaOH as base, and aged for periods up to 1 week.

Table 1. Effect of aging on different forms of chromium(III) in aqueous solutions

Solution (0.01 M)	OH/Cr mole ratio ^A	Time of aging	Forms of chromium(III) (%)		
			Precipitated	Monomer + oligomer	Polymer
Cr(NO ₃) ₃ ^B	0	0	0	100.0	0
		2 h	0	100.0	0
		24 h	0	95.0	5.0
		1 week	0	87.5	12.5
	1.0	0	0	100.0	0
		2 h	0	95.0	5.0
		24 h	0	64.3	35.7
		1 week	0	58.2	41.8
	2.0	0	0	100.0	0
		2 h	0	80.5	19.5
		24 h	0	41.3	58.7
		1 week	0	34.4	65.6
CrCl ₃ ^C	2.0	0	0	100.0	0
		2 h	0	84.8	15.2
		24 h	0	50.0	50.0
		1 week	0	39.7	60.3
	2.7	0	24.2	75.8	0
		2 h	20.6	65.2	14.2
	—	—	0	59.4	40.6
		—	0	59.4	40.6

^A This ratio is calculated on the basis of NaOH added.

^B pH 2.4.

^C pH 2.3.

^D Boiled for 6 h.

Results and Discussion

The rate of Cr^{III}–edta complex formation was very slow in solutions with pH values below 3.5 and when the pH was raised above 3.5, by addition of NaOH, colour development was complete after 1 h. The colour development was complete after 10 min boiling of a mixture of chromium(III) and edta solutions. The rapid reaction between chromium(III) and edta, either after adding OH[−] ions or boiling, may be due to the labilization of the coordinating ligands by hydroxy groups^{4,5} formed during

⁴ Postmus, C., and King, E. L., *J. Phys. Chem.*, 1955, **59**, 1216.

⁵ Wilkins, R. G., *Q. Rev., Chem. Soc.*, 1962, **16**, 316.

hydrolysis or due to the formation of reactive oligomers.⁶ The polymeric species could be separated quantitatively by ultrafiltration with a PM10 Diaflo ultrafilter. The separated polymeric chromium(III) species from aged basic solutions of $\text{Cr}(\text{NO}_3)_3$ and CrCl_3 did not complex with edta but were precipitated. This allowed the estimation of the polymeric form as distinguished from the monomers and the reactive oligomers.

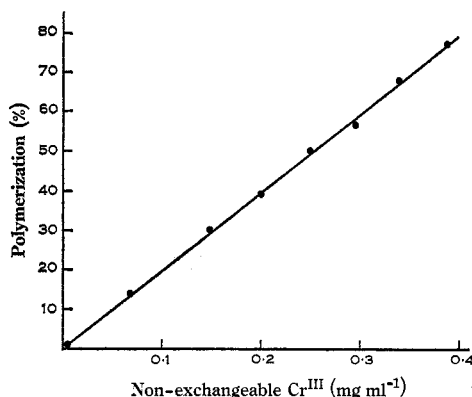


Fig. 1. Relation between non-exchangeable Cr^{III} species and percentage of polymerization.

The percentage of polymeric forms estimated by the suggested procedure was linearly related to the non-exchangeable chromium(III) species found by separation on H^+ -Amberlite resin CG-120 (Fig. 1). The forms of chromium(III) in differentially treated aqueous solutions of CrCl_3 and $\text{Cr}(\text{NO}_3)_3$, determined by the suggested procedure, are given in Table 1. The interference of other ions in complex formation was not investigated here, but has been reported in the case of chromium(III) estimation by edta.⁷ The procedure suggested is simple and highly reproducible.

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⁶ Baes, C. F., and Mesmer, R. E., 'The Hydrolysis of Cations' p. 211 (Wiley-Interscience: New York 1976).

⁷ Beoff, G. den, Jong, W. J. de, Krijn, G. C., and Poppe, H., *Anal. Chim. Acta*, 1960, **23**, 557.