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Note

Gel chromatographic behaviour of trace amounts of chromium(VI) and hydrolysed chromium(III) in aqueous solution

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The existence of appreciable amounts of organically bound trace metals in natural water can be inferred from many papers (reviewed by Florence and Bately[1]). Gel chromatography can be useful for the investigation of metals bound by such organic compounds as humic acid[2,3]. However the gel chromatographic behaviour of inorganic chromium species must be clarified prior to studying the organic species in natural water by gel chromatographic techniques. This paper describes the gel chromatographic behaviour of trace amounts of chromate ions and hydrolysed chromium(III) species in aqueous solution.

EXPERIMENTAL

Reagents and solutions

A Cr(VI) stock solution was prepared by dissolving analytical-reagent grade potassium dichromate in distilled water and was labelled by adding ^{51}Cr as sodium chromate (Daiichi Radioisotope Laboratory; specific activity 191 mCi/mg). A Cr(III) stock solution in 0.1 *M* hydrochloric acid was prepared by mixing the Cr(VI) stock solution, 6 *M* hydrochloric acid and 30% hydrogen peroxide. The excess of hydrogen peroxide was removed by boiling. All other solutions were prepared by dissolving the reagents (analytical-reagent grade) in distilled water. Sample solutions for Cr(VI) were prepared by mixing appropriate volumes of the Cr(VI) stock solution, 0.5 *M* sodium chloride solution and distilled water. Sample solutions for Cr(III) were prepared by mixing appropriate volumes of the Cr(III) stock solution, 0.9 *M* sodium chloride, 0.1 *M* buffer solution (hydrochloric acid–sodium chloride, acetic acid–sodium acetate, ammonium chloride–ammonium hydroxide or sodium chloride–sodium hydroxide) and distilled water, and by adding dropwise 0.1 *M* sodium hydroxide to adjust to accurate pH values. The chromium concentration of the sample solutions was $2 \cdot 10^{-8}$ *M*.

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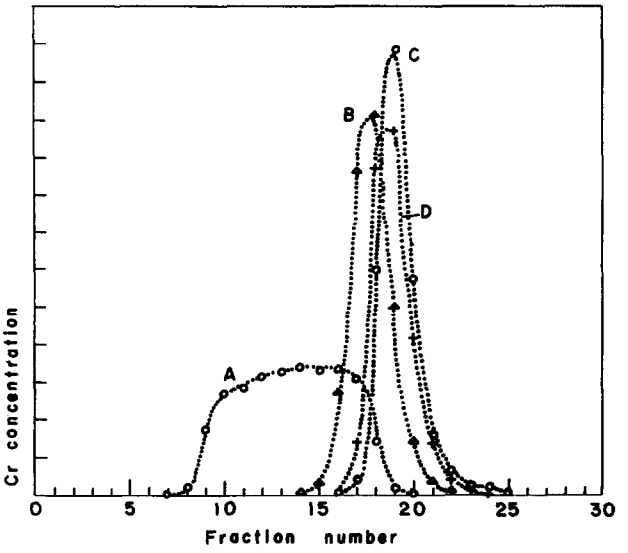

Fig. 1. Chromatograms obtained for Cr(VI) solutions eluted with (A) distilled water, (B) 0.005 *M* sodium chloride, (C) 0.01 *M* sodium chloride and (D) 0.05 *M* sodium chloride.

Sephadex G-50 dry gel (Pharmacia, Uppsala, Sweden; particle size 50–150 μm) was allowed to swell in distilled water for 24 h. A glass column (450 × 19 mm) was packed by continual addition of the slurry. The bed volume was adjusted to 100 ml and then 1 l of 0.1 *M* sodium chloride was passed through the column to settle the gel bed. The column was washed with 200 ml of the eluent used for the following run. Blue Dextran 2000 and chromate ions were used to determine the void and total volumes, which were 41 and 92 ml, respectively.

A 5-ml aliquot of sample solution was transferred to a test tube and the radioactivity was counted by a well-type scintillation counter to give the total counts for the experiment. A 10-ml aliquot of the sample solution was placed on the top of the gel bed. The effluent was collected as 5-ml aliquots with a fraction collector and a flow-rate of 2.1 ml/min. The radioactivity of each aliquot was counted. Another aliquot of the sample solution was stored in a polyethlene bottle and after 1 and 7 days similar procedures were carried out. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

A sharp peak assigned to chromate ions was obtained from gel chromatography of Cr(VI) in 0.01 or 0.05 *M* sodium chloride (pH 7) (Fig. 1). The peak for Cr(VI) in 0.005 *M* sodium chloride was slightly shifted and that for Cr(VI) in distilled water was further shifted and broadened, possibly due to the ion-exchange effect of the gel[4]. For fresh water samples, the supporting electrolyte should be added to avoid such broadening of the peak.

The gel chromatograms obtained from freshly prepared hydrolysed Cr(III) are shown in Fig. 2. The ionic strength of each Cr(III) solution was made up to 0.10 by

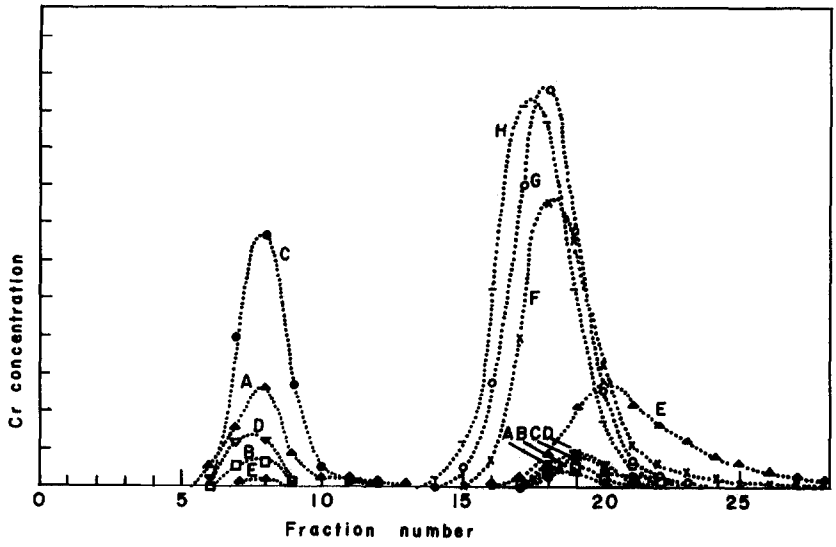

Fig. 2. Chromatograms obtained for freshly prepared hydrolysed Cr(III) solutions of pH (A) 12.67, (B) 10.00, (C) 8.23, (D) 7.30, (E) 5.80, (F) 5.00, (G) 4.0 and (H) 1.42 eluted with 0.01 *M* suitable buffer solutions of 0.09 *M* sodium chloride.

the addition of sodium chloride. Significant quantities of Cr(III) in some of the sample solutions were adsorbed on to the gel. Cr(III) was also partially adsorbed on to the polyethylene bottle, during storage of the sample solution. All the chromium in the sample solutions can be divided into four fractions: the eluted fraction of lower molecular weight (fraction A), the eluted fraction of higher molecular weight (frac-

TABLE I

PERCENTAGE OF Cr IN THE GEL-CHROMATOGRAPHIC FRACTIONS FOR TRACE AMOUNTS OF HYDROLYSED Cr(III) SOLUTIONS

pH	*Storage time 0**			*Storage time 24 h*				*Storage time 7 days*			
	*Fraction***			*Fraction***				*Fraction***			
	A(%)	*B(%)*	*C(%)*	*A(%)*	*B(%)*	*C(%)*	*D(%)*	*A(%)*	*B(%)*	*C(%)*	*D(%)*
1.42	100	0	0	–	–	–	–	–	–	–	–
4.00	93.4	0	6.6	91.5	0	7.2	1.3	87.8	0.8	6.1	5.3
5.00	88.8	0	11.2	71.3	2.9	3.8	22.0	53.2	4.5	1.8	40.5
5.80	67.3	1.1	31.6	40.6	8.6	6.7	44.1	28.0	5.1	1.3	65.6
7.30	10.0	27.4	62.6	–	–	–	–	–	–	–	–
7.53	10.9	20.7	68.4	–	–	–	–	–	–	–	–
7.75	7.9	29.3	62.8	–	–	–	–	–	–	–	–
8.23	9.1	40.4	50.5	8.6	52.3	26.1	13.0	6.4	38.8	23.3	31.5
10.00	6.9	5.1	88.0	8.4	18.9	50.2	22.5	13.0	30.6	26.0	30.4
12.63	10.6	23.6	65.8	9.6	36.7	40.1	13.6	15.6	29.0	26.2	29.2

* The time for preparing the sample solutions is about 10 min.

** A = the eluted fraction of lower molecular weight; B = the eluted fraction of higher molecular weight; C = the fraction adsorbed on the gel; D = the fraction adsorbed on the polyethylene bottle.

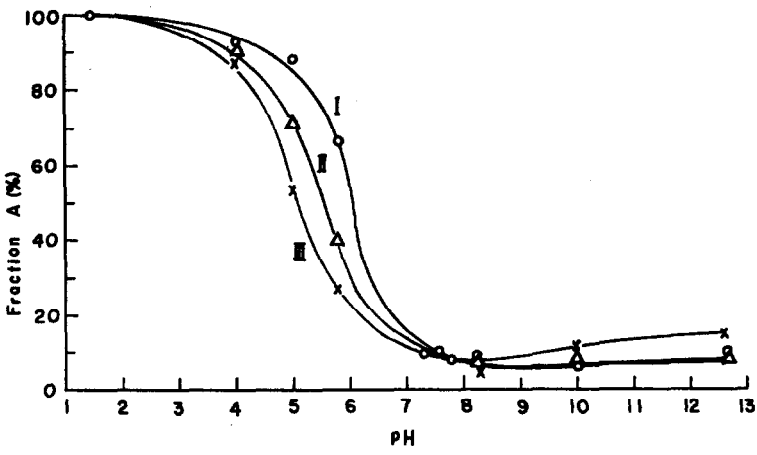

Fig. 3. Influence of pH and storage time on the concentration of Cr in the eluted fraction of lower molecular weight. The storage times are (I) 0 (10 min), (II) 24 h and (III) 7 days.

tion B), the fraction adsorbed on the gel (fraction C) and the fraction adsorbed on the polyethlene bottle (fraction D). The results are listed in Table I.

The deprotonation of Cr(III) aquo ions and the formation of the fresh precipitates (active hydroxide) are extremely fast, and on ageing, the aged precipitates (latent hydroxide) are formed[5].

$$\left[Cr^{3+} \underset{}{\overset{K_1}{\rightleftharpoons}} Cr(OH)^{2+} \overset{K_2}{\rightleftharpoons} Cr(OH)_2^{+} \overset{K_3}{\rightleftharpoons} CrO_2^{-} \right]$$
$$\Downarrow$$
$$\{Cr(OH)_3\}_A \rightarrow \{Cr(OH)_3\}_L$$

The equilibrium constants K_1, K_2 and K_3 are $10^{-4.15}$, $10^{6.5}$ and $10^{17.0}$ at 20°C (refs. 5 and 6), respectively. The solubility product of the active hydroxide $\{Cr(OH)_3\}_A$ is $10^{-30.35}$. Little quantitative information is available on the solubility and the kinetics of the latent hydroxide $\{Cr(OH)_3\}_L$. Since the Cr(III) concentration of the sample solution is very low ($2 \cdot 10^{-8}$ *M*), the active hydroxide is not formed under these experimental conditions. Thus the Cr(III) species in the samples may consist of aquo ions, deprotonated ions and/or the latent hydroxide.

The peaks of fraction A were eluted in the same fraction numbers to the chromate ions. Compared with the peak for Cr^{3+} at pH 1.42, the peaks for the solutions at pH 5 are shifted slightly to higher fraction numbers and have a degree of tailing. The percentages of fraction A for samples of pH 4.00–8.23 decrease with time. In contrast, those for samples of pH 10.00 and 12.63 increase with time (Fig. 3). The equilibria between the dissolved species and latent hydroxide are slow as suggested by Von Meyenburg *et al.*[5] and the rates depend on the pH of the solution. Assuming that the chromium concentrations in fraction A are the same as the total concentrations of the dissolved species, Fig. 3 suggests that the solubility of the latent hydroxide at pH *ca.* 7 is $2 \cdot 10^{-9}$ *M*, which is 2 or 3 orders of magnitude lower than that of the active

hydroxide. The exact values will be obtained from similar experiments run under strictly controlled conditions; however this is out of the range of this study.

The peaks of fraction B were eluted at the void volume of the column. Fraction B may consist of the latent hydroxide. The chromium concentrations of fraction B, C, and D correlate with neither the pH of the sample solutions nor the storage times. The latent hydroxide seems to be irregularly adsorbed on Sephadex gel and the polyethylene bottle.

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