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## Note

### Gel filtration of soluble coloured metal hexacyanoferrate(II) compounds

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The use of soluble Prussian blue for measuring the void volume in gel filtration was recently advocated by Saito and Matsumoto<sup>1</sup>, which is of interest in our studies on the gel filtration behaviour of inorganic polymers. Chromium hexacyanoferrate(II) and mixed chromium-iron(III) hexacyanoferrate(II) have also been studied by gel filtration by Matsumoto *et al.*<sup>2</sup>.

We report here results obtained with coloured hexacyanoferrate(II) compounds of  $\text{UO}_2^{2+}$  and  $\text{Cu}^{2+}$ .

#### EXPERIMENTAL AND RESULTS

Soluble hexacyanoferrate(II) compounds were prepared by mixing equal volumes of 0.1 M solutions of potassium hexacyanoferrate(II) [ $\text{K}_4\text{Fe}(\text{CN})_6$ ] and of the metal salts, viz.,  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (violet) and  $\text{UO}_2(\text{NO}_3)_2$ . Precipitates often form if other concentrations are used.

#### Gel filtration

Thin-layer gel filtration was carried out using a Pharmacia TLG chamber and the conditions described previously<sup>3</sup>. Dextran Blue 2000 and  $\text{Co}(\text{en})_3^{3+}$  were used as void volume indicator and small ion reference, respectively.

Fig. 1 shows the movement of the various hexacyanoferrate(II) compounds on Sephadex G-75, G-150 and G-200 gel. Except for chromium(III) hexacyanoferrate(II) all of the soluble compounds are completely excluded on all gels when eluted with distilled water. On some gels, e.g., Sephadex G-150, Dextran Blue 2000 is retarded in comparison with the hexacyanoferrate(II) compounds. This phenomenon is well known in thin-layer gel filtration and seems to be due to the high viscosity of the concentrated Dextran Blue 2000 solutions employed in thin-layer work.

In the presence of electrolytes in the eluent the gel chromatographic behaviour of the soluble hexacyanoferrate(II) compounds is very different, as shown in Fig. 2. Soluble Prussian blue is retarded and can form long comets; copper and uranyl hexacyanoferrate(II) seem to be precipitated at the point of application. None moves with the speed of Dextran Blue 2000. As we were more interested in the polymeric nature of these compounds than in their utility as void volume markers, we tried to characterize the compounds by a variety of techniques.

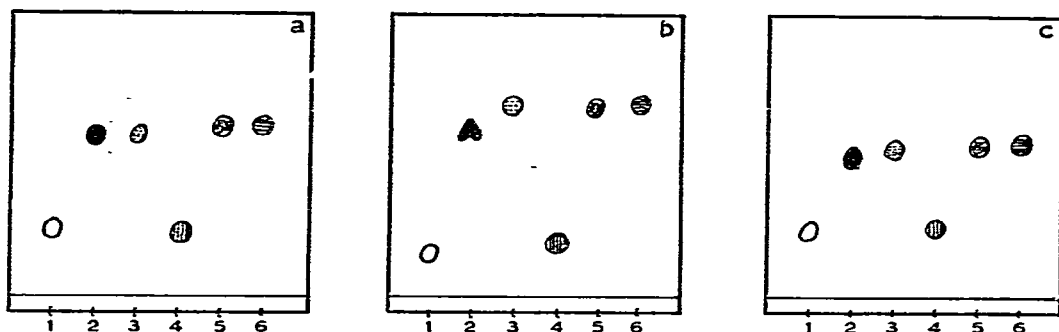


Fig. 1. Thin-layer gel chromatograms of soluble metal hexacyanoferrate(II) compounds. The solutions (chromatographed side-by-side) were as follows: 1 =  $\text{Co}(\text{en})_3\text{Cl}_3$ ; 2 = Dextran Blue 2000; 3 = uranyl hexacyanoferrate(II) prepared by mixing 0.1 *M* solutions of  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ ; 4 = chromium(III) hexacyanoferrate(II) prepared by mixing 0.1 *M* solutions of chromium chloride (violet) and  $\text{K}_4\text{Fe}(\text{CN})_6$ ; 5 = copper hexacyanoferrate(II) prepared by mixing 0.1 *M* solutions of  $\text{CuCl}_2$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ ; 6 = iron(III) hexacyanoferrate(II) (Prussian blue) prepared by mixing 0.1 *M* solutions of iron(III) nitrate and  $\text{K}_4\text{Fe}(\text{CN})_6$ . (a) On Sephadex G-75; (b) on Sephadex G-150; (c) on Sephadex G-200; development with distilled water in each instance. Visible spots were recorded except for that with  $\text{Co}(\text{en})_3^{3+}$ , which was detected by spraying with ammonium sulphide solution, and that of uranyl hexacyanoferrate(II), which was sprayed with  $\text{Na}_3\text{PO}_4$ ,  $\text{CH}_3\text{COONa}$  and  $\text{Zr}(\text{CH}_3\text{COO})_2$  aqueous solutions and viewed under a UV lamp.

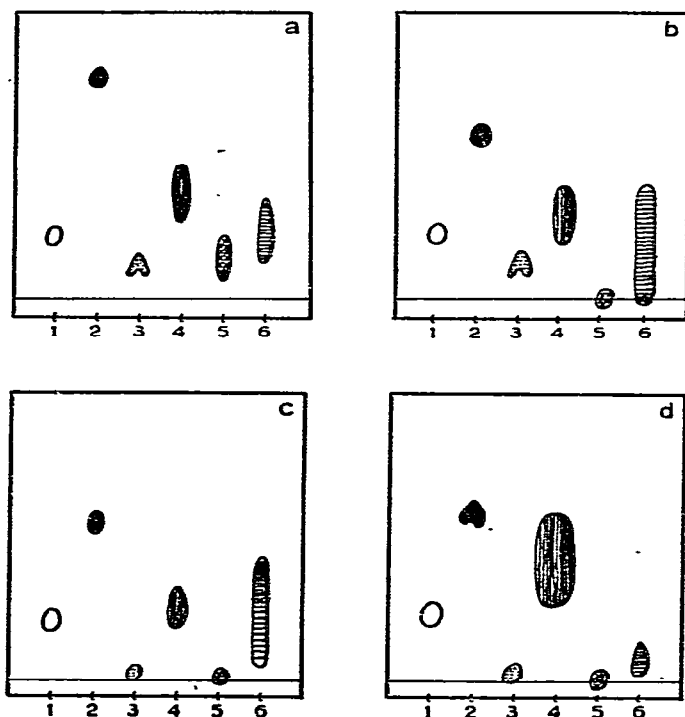


Fig. 2. Thin-layer gel chromatograms of soluble metal hexacyanoferrate(II) compounds obtained using salt solutions as eluents. The solutions chromatographed are the same as in Fig. 1. (a) On Sephadex G-200 developed with 0.1 *M*  $\text{LiCl}$ ; (b) on Sephadex G-75 developed with 0.1 *M*  $\text{NaClO}_4$ ; (c) on Sephadex G-200 developed with 0.1 *M*  $\text{NaClO}_4$ ; (d) on Sephadex G-75 developed with 0.1 *M*  $\text{Na}_2\text{SO}_4$ .

### Chromatography on cellulose paper and thin layers

Chromatograms obtained on acid-washed paper strips and on Polygram Cel 300 layers are shown in Fig. 3. It is remarkable that Prussian blue yields long trails on cellulose whereas it is completely excluded from all Sephadex thin layers when eluted with distilled water. The only compound that seem only slightly adsorbed on cellulose is chromium hexacyanoferrate(II), which is found near the liquid front even in the presence of electrolytes.

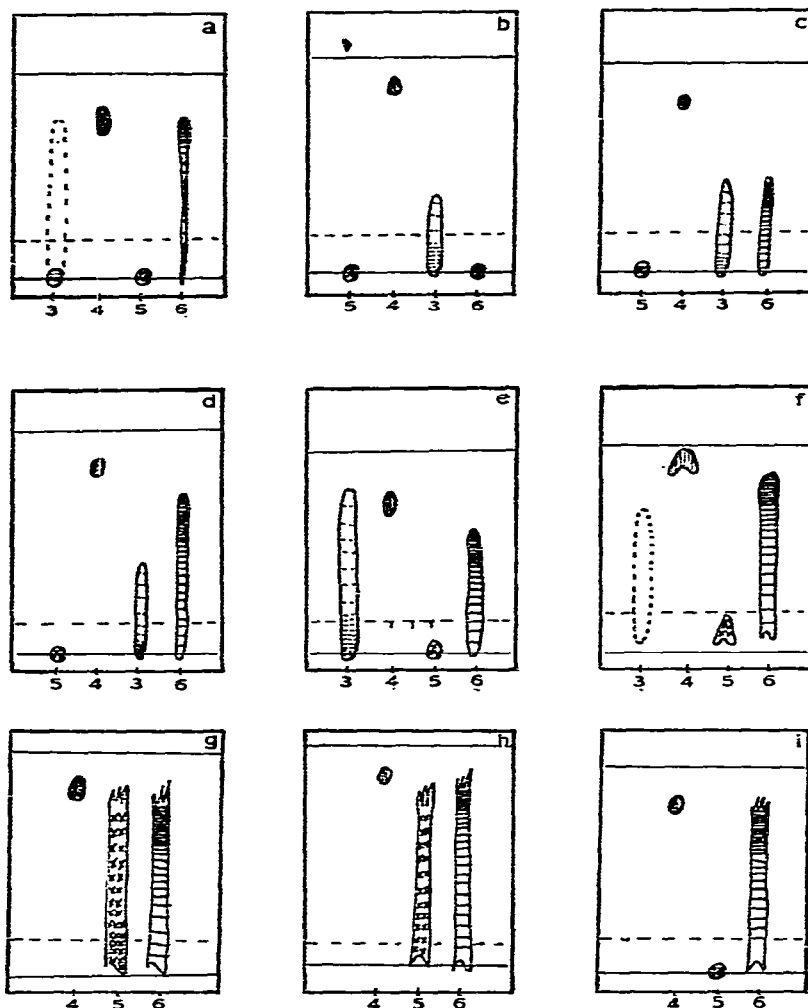


Fig. 3. Chromatograms of soluble hexacyanoferrate(II) compounds on cellulose paper and thin layers. Samples were spotted behind the solvent front (broken line). The solutions chromatographed are numbered as in Fig. 1. (a) Whatman No. 1 paper developed with distilled water; (b) Whatman No. 1 paper developed with 1 *M* acetic acid; (c) Whatman No. 1 paper developed with 0.1 *M* acetic acid; (d) Whatman No. 1 paper developed with 0.005 *M* acetic acid; (e) Whatman No. 1 paper developed with 0.1 *M* LiCl; (f) Polygram Cel 300 developed with distilled water; (g) Polygram Cel 300 developed with 0.1 *M* LiCl; (h) Polygram Cel 300 developed with 0.1 *M* Na<sub>2</sub>SO<sub>4</sub>; (i) Polygram Cel 300 developed with 0.1 *M* NaClO<sub>4</sub>.

*Filtration through Millipore filters*

The solutions of the coloured hexacyanoferrate(II) compounds passed readily through a Millipore membrane with pores between 0.45 and 0.25  $\mu\text{m}$ . However, the membrane became intensely coloured.

## DISCUSSION

It had already been found that Prussian blue<sup>1</sup> and chromium(III) hexacyanoferrate(II)<sup>2</sup> are excluded by Sephadex gels. We have now observed that copper and uranyl hexacyanoferrate(II) are excluded from Sephadex gels when eluted with distilled water but are adsorbed or precipitated when eluted with electrolytes. Copper, uranyl and iron(III) hexacyanoferrate(II) are also adsorbed or precipitated when chromatographed on cellulose paper or thin layers. They pass through Millipore filters with pores between 0.45 and 0.25  $\mu\text{m}$ .

Unfortunately, our experiments do not permit even an approximate estimate of the molecular size of these soluble species, because recently Kirkland<sup>4</sup> has shown that even large colloidal silica sols can be excluded in gel filtration. All we can say is that evidently polymeric species are formed but these may be either true solutions or already in the colloidal range.

## REFERENCES

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