The separation of metals on ion-exchange modified cellulose paper using complexing agents

Whatman ion-exchange modified cellulose paper has been used previously for the chromatographic separation of metals by means of simple eluting agents. It was observed in some later chromatographic experiments that the addition of complexing agents gave evidence of a relationship between the R_F value of the metal ion complex and the gross stability constant of that complex. This subject has now been studied in greater detail.

Experimental

Whatman P. 20 cellulose phosphate, cation-exchange paper and DE.20 diethylaminoethylcellulose, anion-exchange paper was cut into strips of size 20 × 2 cm and small holes punched at each end of the strip. The apparatus was very simple and consisted of test tubes 20 × 3.8 cm, each with two indentations in the upper lip. Bent glass rods supported the strip and weighted the bottom. The test solution (0.02 ml) containing metal(s) equivalent to 1 mg of each per ml was transferred to the strip along a line about 3 cm from one end, by means of a micropipette. The exact position of this band was recorded by means of a thin pencil line. The eluting solution (50 ml) was added to the open tube and the strip hung, so that the lower end containing the test spot was just immersed. Elution by upward displacement was continued until the solvent front was about 5 cm from the upper end of the strip, *i.e.* in about 1 h. The strip was then removed, the position of the elution front marked, and the position of metal or metals detected with the appropriate reagent. R_F values were determined by normal methods and stability constants for comparison were obtained from the literature[1].

Separations on cellulose phosphate. Each 50 ml of the eluting solution consisted of

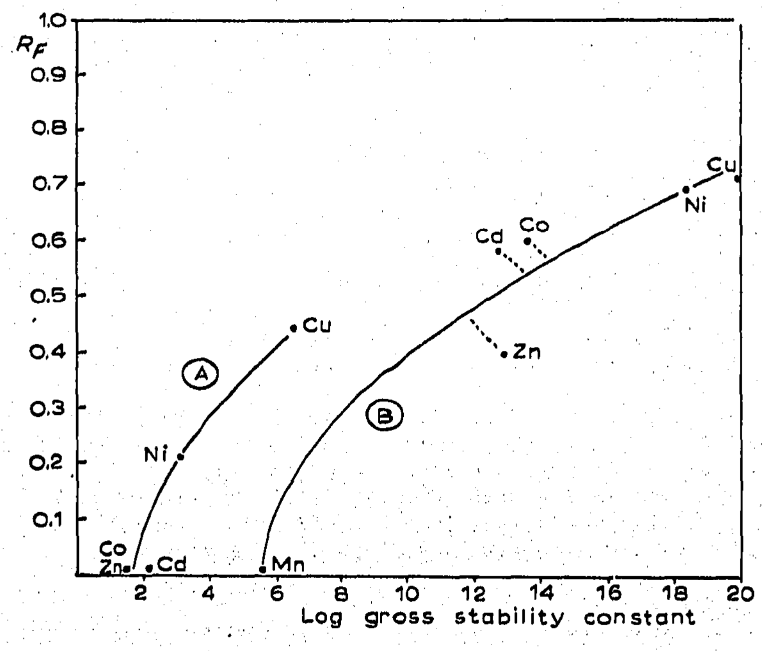

Fig. 1. Elutions with *M* ammonium nitrate containing (A) pyridine; (B) ethylenediamine.

M ammonium nitrate and contained 1.5 ml of the complexing agent. In the first series, simple divalent metals were tested in conjunction with two amines. Results in Fig. 1 show an increase in R_F value with that of the recorded stability constant. Similarly, if any metal was tested in the presence of complexing agents of similar type then the same relationship was shown to apply (see Fig. 2). Similar tests on

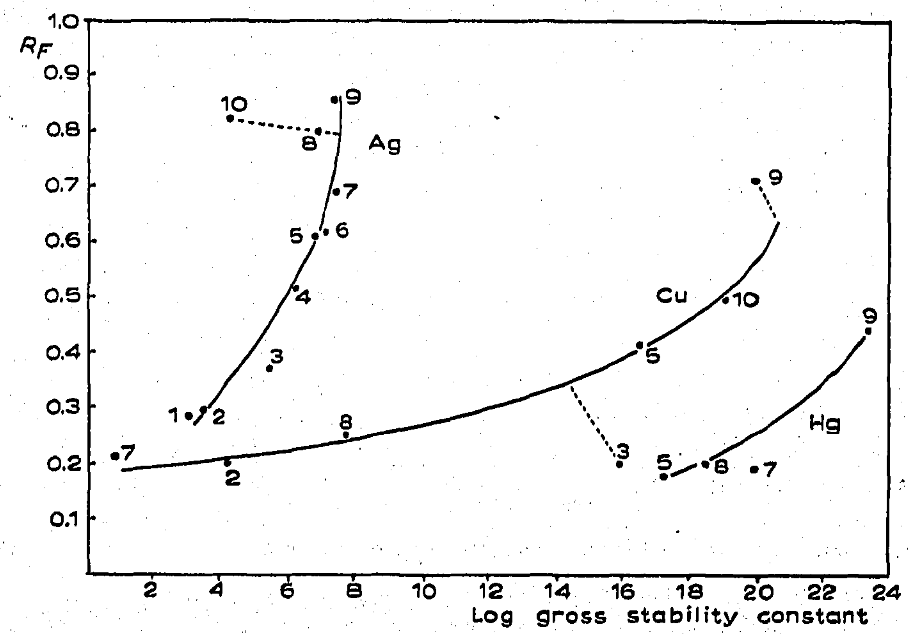

Fig. 2. Elutions with M ammonium nitrate containing (1) trimethylamine; (2) triethanolamine; (3) diethanolamine; (4) diethylamine; (5) monoethanolamine; (6) ethylamine; (7) *n*-butylamine; (8) methylamine; (9) ethylenediamine; (10) pyridine; (11) N-methyl-ethylenediamine.

weaker cation-exchange papers, *e.g.* CM and CT, were not satisfactory as the metals moved together.

Separations on DE paper. Complexing agents were not added as separate components to the eluting solution; instead ammonium salts of acids with known complexing powers were used, *e.g.* ammonium chloride and ammonium thiocyanate solutions. Some results shown in Fig. 3 show a reversed relationship compared to that obtained on cation-exchange papers.

The results obtained bear comparison with many standard techniques used with ion-exchange resins in the presence of complexing agents. The use of ion-exchange paper provides a convenient method for the semi-quantitative study of related complexes of similar metals, though the anomalous behaviour under certain conditions must be taken into account.

As an example of this, certain metals are known to be very strongly absorbed by cellulose phosphate[2] probably because of covalent complex formation. If the stability of this bond is considerably higher than that between the metal and the complexing agent present in the eluting solution, then little or no movement will take place.

The experimental techniques described may be used to effect many convenient and rapid chromatographic separations of metals on ion-exchange cellulose paper. For example, various groups of transition metals may be separated into narrow bands using ammonium nitrate solution and amines. A separation of certain noble metals on DE paper using 2 N HCl has been published[3] and the order of separation is again consistent with the principle. It has been possible to predict the separation

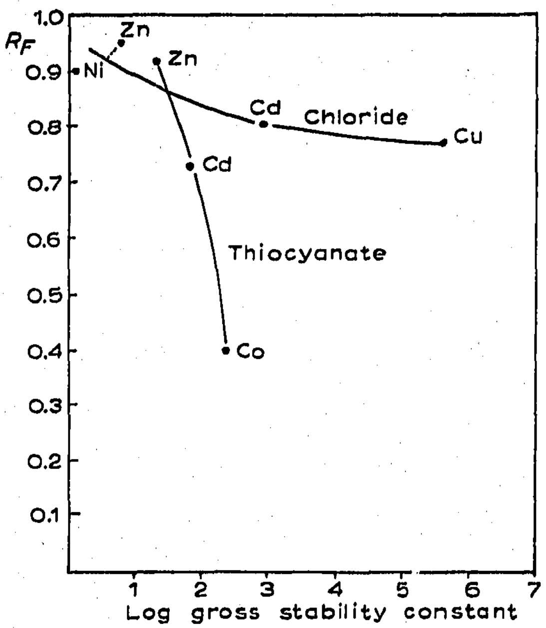

Fig. 3. Elutions with ammonium chloride and thiocyanate (nitrates of metal salts applied to paper).

of certain groups of metals on ion-exchange paper from data published on stability constants of complexes.

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1 *Stability Constants of Metal-ion Complexes*, Special Publications 6 and 7 of the Chemical Society, London, 1957 and 1958.
2 A. J. HEAD, N. F. KEMBER, R. P. MILLER AND R. A. WELLS, *J. Chem. Soc.*, (1958) 3418.
3 N. F. KEMBER AND R. A. WELLS, *Nature*, 175 (1955) 512.

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Papierchromatographie von ätherischen Ölen

Die klassischen Arbeiten, Bestandteile ätherischer Öle durch Dünnschichtchromatographie[1-4] und Gaschromatographie[5,6] aufzutrennen, sind allgemein bekannt und haben in den vergangenen Jahren eine weite Verbreitung gefunden. Nachteilig ist bei der Dünnschichtchromatographie, dass eine quantitative Bestimmung der aufgetrennten Substanzen etwa durch Densitometrie nur äusserst schwer durchführbar ist. Sie wurde bisher nur einmal von HEFENDEHL[7] am Beispiel des Menthofurans im