

## CHROMATOGRAPHIC STUDY OF ANIONIC COMPLEXES

PART IV. SEPARATION OF SOME IONS IN  
THE PRESENCE OF TARTRATE, USING ETHANOL AS SOLVENT

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Complex formation plays an important role in the separation of ions in chromatography, as pointed out by POLLARD and coworkers<sup>1,2</sup>, who observed that for the separation of metal ions on filter paper the formation of complexes is essential. Various workers, including BURSTALL *et al.*<sup>3</sup> and LEDERER<sup>4</sup>, have studied the separation of inorganic ions by paper chromatography, using different solvent mixtures with or without complexing agents. In several earlier papers<sup>5-8</sup> we have described our studies on the diffusion of complex ions formed by the interaction of metal ions with the carboxylic acid groups of oxalic, tartaric and citric acid. In these studies filter paper chromatography was used with aqueous ethanol as solvent. We have also investigated how the  $R_F$  values of the ions formed in mixtures vary according to the proportion of the metal ion and the complexing agent used, with a view to determining the effect of varying concentrations of the complexing agent. In this paper we have extended the work to some mixtures of ions and have attempted to employ complex-formation with tartrate for the separation of ions by filter paper strip chromatography, using aqueous ethanol as solvent.

Mixtures of copper(II), nickel(II), cobalt(II) and cadmium(II) were investigated and the results obtained in a large number of experiments are summarised here.

## EXPERIMENTAL

Solutions of cupric sulphate, nickel sulphate, cobalt sulphate and cadmium chloride were prepared from BDH Analar grade chemicals and standardised as usual. A standard stock solution of sodium tartrate was prepared and diluted as required. All other reagents used were of reagent quality. Strips of Whatman filter paper No. 1 were used for the chromatograms. A simple ascending filter paper strip method, as described by GAGE, DOUGLASS AND WENDER<sup>9</sup>, was employed. Various concentrations of aqueous ethanol were tried and it was found that in most cases 50% ethanol was suitable as solvent. A series of mixtures was prepared in which the concentrations of the metals were the same, but the concentration of tartrate varied, while the total volume of each solution was kept constant. For the metal to tartrate ratio the total concentration of the metals was obtained by addition of the molar concentrations of the metals.

The mixtures were spotted on the filter paper strips and the chromatograms were run at constant temperature in a thermostat-controlled room at 30°; the time allowed was 90 minutes.

#### *Separation of cobalt(II) and cadmium(II)*

The final concentration of each of the metal ions was 0.05 *M*; H<sub>2</sub>S water was used for developing. It was found that cobalt(II) and cadmium(II) are separated at all concentrations of tartrate up to a tartrate:metal ratio of 1:5 to 1:1. With a tartrate:metal ratio of 1 and higher, cadmium(II) does not move and only cobalt(II) diffuses upwards. For practical purposes a 1:1 concentration of tartrate is recommended, since separation is then satisfactory; the metal ions can be detected with the help of H<sub>2</sub>S water.

#### *Separation of cadmium(II) and copper(II)*

The final concentration of each of the metal ions was 0.05 *M*; a freshly prepared mixture of H<sub>2</sub>S water and K<sub>4</sub>Fe(CN)<sub>6</sub> was used for developing. In these systems precipitation is found to occur and redissolution of the precipitate is only complete when 1.7 equivalents of tartrate are added; beyond 0.9 equivalent, however, no separation is possible. It was further found that good separation of the ions from the supernatant liquid is obtained when 0.3 to 0.4 equivalent of tartrate is added, though a portion remains settled as a precipitate.

#### *Separation of cadmium(II) and nickel(II)*

The final concentration of each of the metal ions was 0.05 *M*; a mixture of H<sub>2</sub>S water and dimethyl glyoxime was used for developing. In this case 60% ethanol was more efficient as it gave a better separation. For good separation of the ions 0.7 to 0.8 equivalent of the complexing agent gives the best results; no separation is possible beyond 0.9 equivalent of tartrate because of the spreading and overlapping of the zones.

#### *Separation of copper(II) and nickel(II)*

The final concentration of each of the metal ions was 0.05 *M*; a mixture of K<sub>4</sub>Fe(CN)<sub>6</sub> and dimethyl glyoxime was used for developing. At the beginning precipitation of the tartrates occurs in the systems and when about 0.9 equivalent of tartrate has been added, total redissolution of the precipitate takes place. The separation of the ions is possible when up to 0.9 equivalent of tartrate is added, but with higher concentrations no separation occurs. A good separation is obtained when 0.3 to 0.4 equivalent of the complexing agent is used.

#### *Separation of cobalt(II) and copper(II)*

The final concentration of each of the metal ions was 0.05 *M*; a freshly prepared mixture of H<sub>2</sub>S water and K<sub>4</sub>Fe(CN)<sub>6</sub> was used for developing. In these systems precipitation was found to occur and the total redissolution of the precipitate took

place when 2.2 equivalents of the complexing agent was used. It was also found that the separation of copper(II) and cobalt(II) ions is possible with up to 0.9 equivalent of the complexing agent, but with higher concentrations of the complexing agent separation is not possible. A good separation is obtained with 0.3 to 0.4 equivalent of complexing agent.

#### *Separation of nickel(II) and cobalt(II)*

In the case of these ions no separation is possible because both ions move simultaneously and have nearly the same  $R_F$  values. Both ions can, however, be detected together by spraying with a mixture of dimethyl glyoxime and  $H_2S$  water and finally exposing the chromatograms to vapours of ammonia.

#### *Separation of cobalt(II), cadmium(II) and copper(II)*

The final concentration of each of the metal ions was 0.05  $M$ ; the indicator used was a mixture of  $H_2S$  water and  $K_4Fe(CN)_6$ , freshly prepared. No precipitation occurs when 0.05 to 0.177 equivalent of tartrate is added, but with higher concentrations of the complexing agent precipitation occurs in the system after the solution has been allowed to stand. The separation of copper(II), cobalt(II) and cadmium(II) ions is possible when up to 0.481 equivalent of tartrate is added, but with higher concentrations of the complexing agent separation is not possible under the experimental conditions used.

#### *Separation of copper(II), cadmium(II) and nickel(II)*

The final concentration of each of the metal ions was 0.05  $M$ ; a mixture of  $H_2S$  water,  $K_4Fe(CN)_6$  and dimethyl glyoxime was used as indicator. At the beginning no precipitation occurs in the system and when about 0.177 or more equivalents of the complexing agent are added precipitation occurs after the solution has been allowed to stand for some time. Of a mixture of copper(II), cadmium(II) and nickel(II) ions separation of copper(II) ion is only possible with up to 0.59 equivalent of the complexing agent; with higher concentrations separation is not possible.

#### *Separation of cobalt(II), nickel(II) and copper(II)*

The final concentration of each of the metal ions was 0.05  $M$ ; a mixture of  $K_4Fe(CN)_6$  and dimethyl glyoxime was used as indicator. No precipitation occurs with 0.059 to 0.177 equivalent of the complexing agent, but with higher concentrations precipitation occurs after the solution has been allowed to stand for a long time. Of a mixture of nickel(II), cobalt(II) and copper(II) ions, the separation of copper(II) is only possible with up to 0.59 equivalent of the complexing agent; with higher concentrations of the complexing agent no separation takes place.

#### *Separation of nickel(II), cobalt(II), cadmium(II) and copper(II)*

The final concentration of each of the metal ions was 0.042  $M$ ; a mixture of  $K_4Fe(CN)_6$ ,  $H_2S$  water and dimethyl glyoxime was used for developing. No precipitation occurs

when 0.05 to 0.15 equivalent of tartrate is added, but with higher concentrations precipitation is observed. Only the separation of copper(II) ions from cobalt(II), nickel(II) and cadmium(II) ions is possible with up to 0.65 equivalents of tartrate added. No separation occurs with higher concentrations of tartrate.

#### *Separation of nickel(II), cobalt(II) and cadmium(II)*

No satisfactory separation of nickel(II), cobalt(II) and cadmium(II) ions is possible with ethanol as solvent, due to the spreading and overlapping of the zones.

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#### SUMMARY

In this paper we have summarised the results obtained when an attempt was made to separate copper(II), nickel(II), cadmium(II) and cobalt(II) from mixtures by filter paper strip chromatography, using aqueous ethanol as solvent. The effect of the presence of varying concentrations of tartrate ion as complexing agent was studied. The complexing agent was added to the solution of the metals, and not to the solvent as was usually done by previous workers.

It was observed that, in general, when two metals are present, separation occurs when up to 0.9 equivalents of tartrate ions are added (ratio total metal:tartrate 1:0.9). When the amount of tartrate added is increased to 1.0 equivalent or more, no separation occurs. For good separation in the case of three metals present together, up to 0.6 equivalent of tartrate may be added. Excess of tartrate leads to overlapping of zones.

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