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## SEPARATION OF METALS ON ION-EXCHANGE RESINS BY MEANS OF $\alpha$ -HYDROXYISOBUTYRONITRILE AS COMPLEXING AGENT

LÁSZLÓ LÉGRÁDI

26 Sagarju Street, 8184 Füzfőgyártelep (Hungary)

### SUMMARY

$\alpha$ -Hydroxyisobutyronitrile (acetone cyanohydrin, ACH) reacts with metals in ammoniacal medium and yields cyano complexes of negative charge. On this basis,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Fe}^{2+}$  can be separated on a strongly basic anion exchanger in the chloride form as cyano complexes from  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ . The structures of complexes were examined on a strongly basic anion exchanger in the  $\text{Cl}^-$  form and on a strongly acidic cation exchanger in the  $\text{H}^+$  form. In slightly ammoniacal medium,  $\text{Cu}(\text{CN})_4$ ,  $\text{Co}(\text{CN})_{3.6}$  and  $\text{Ni}(\text{CN})_{3.2}$  were found. The complex adsorbs on the anion exchanger in the  $\text{Cl}^-$  form as a divalent  $[\text{NH}_4\text{Cu}(\text{CN})_4]^{2-}$  or a monovalent  $[\text{NH}_4\text{Zn}(\text{CN})_4]^-$  complex ion.

### INTRODUCTION

In an earlier paper<sup>1</sup>,  $\alpha$ -hydroxyisobutyronitrile (acetone cyanohydrin, ACH) was recommended as a masking agent to replace potassium cyanide in complexometric analysis.  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  can be masked with ACH in complexometric titrations. With 1 mole of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$  complex 4 moles of ACH react to give a colourless  $\text{Cu}(\text{CN})_4^{3-}$  complex. On this basis, ACH can be determined by titrating  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$  solution with ACH solution until the blue colour disappears. The disadvantage of the use of ACH as a masking agent in comparison with potassium cyanide is that fewer metals can be masked. This difficulty can be overcome by the use of an anion exchanger in the  $\text{Cl}^-$  form.

### EXPERIMENTAL

#### *Stock solutions*

*Preparation of alkaline copper cyano complex solution.* Dissolve 2.4968 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 100 ml of water, add 3.4 g of ACH and ammonia until the precipitate formed re-dissolves and the blue colour of the solution disappears (pH = 9).

*Preparation of neutral copper cyano complex solution.* The preparation is the same as above. Add 4–5 ml of strongly acidic cation-exchange resin in the  $\text{H}^+$  form to the solution to adsorb the excess of ammonia. Filter the solution and dilute to 1 l (pH = 7).

*Preparation of zinc cyano complex solution.* Dissolve 1.363 g of  $ZnCl_2$  and 3.4 g of ACH in 50 ml of water and add ammonia until the precipitate formed re-dissolves, then proceed as in the previous section. The solution can be neutralized only to pH 8 because of the precipitation of zinc hydroxide. The solution does not contain free zinc ions according to the complexometric determination. The excess of ACH can be detected by a colour reaction described below.

#### *Determination of ACH*

*Titrimetric.* Prepare 0.1 M copper tetra-amino complex solution as follows. Dissolve 2.4968 g of  $CuSO_4 \cdot 5H_2O$  in 70 ml of water, add 10 ml of 25% ammonia solution, filter and dilute to 100 ml. To 10 ml of this solution, add 100 ml of water and 3 drops of ammonia solution and titrate with 0.4 M aqueous ACH (3.4 g per 100 ml) solution until the blue colour disappears; 10 ml of copper tetra-amino complex solution is equivalent to 10 ml of 0.4 M ACH solution.

*Complexometric.* To 10 ml of 0.01 M copper tetra-amino complex solution add 4–10 mg of ACH in aqueous solution, 2 ml of ammoniacal buffer and titrate the copper with 0.01 M EDTA using murexide as indicator.

*In the presence of cyano complex.* First prepare diazotized *p*-nitroaniline as follows. Dissolve 0.54 g of *p*-nitroaniline in 5 ml of 65%  $H_2SO_4$  and dilute to 100 ml. Filter off the insoluble matter. To 5 ml of the *p*-nitroaniline solution add 1 ml of 17%  $H_2SO_4$  and 4 ml of  $NaNO_2$  solution (0.34 g per 100 ml). To 10 ml of the solution to be analyzed add 0.5 ml of diazonium salt solution and 0.8 ml of 2 N sodium hydroxide. In the presence of ACH an orange colour appears, and in its absence a yellow colour. The range for measurements is 0.2–6 mg of ACH.

#### *Determination of copper and zinc cyano complexes*

To 10–30 ml of a 0.01 M solution of the complex to be analyzed add 0.5–1.0 ml of 1 N  $H_2SO_4$  and 0.2–0.3 g of ammonium peroxydisulphate and heat until the solution becomes clear. In the case of the zinc cyano complex the solution must be boiled for at least 5 min. Neutralize the solution with ammonia and titrate the metal content with 0.01 M EDTA.

#### *Ion-exchange columns*

In all experiments the same type of column of 6 mm I.D. was used. The height of the resin bed was 8 cm. The strongly basic resin used was Varion AD and the strongly acidic resin was Varion KS (Nitrokémia, Hungary) of the polystyrene-divinylbenzene type with a grain size of 20–50 mesh. The capacity of the anion-exchange columns was determined by the usual method and was found to be 3.2 mequiv.

#### *Determination of $Mg^{2+}$ in the presence of $Ni^{2+}$ , $Cu^{2+}$ , $Hg^{2+}$ , $Zn^{2+}$ , $Cd^{2+}$ and $Fe^{2+}$ on ion-exchange resin*

To a solution containing about 10 ml of 0.01 M of interfering metals add 2 drops of 25% ammonia solution and 4 drops of ACH and allow the mixture to flow through the  $Cl^-$ -form column. To the effluent add 3 ml of ammoniacal buffer and titrate with EDTA using Eriochrome Black T as indicator.

*Investigation of formation of cyano complexes on the anion exchanger*

Allow 10 ml of 0.01 *M* metal salt solution to flow through 10 ml of Cl<sup>-</sup>-form resin and titrate the metal content in the effluent complexometrically. Repeat the operation in the presence of 2 drops of 25% ammonia solution and 4 drops of ACH.

*Investigation of formation of cyano complexes on the cation exchanger*

Allow 10 ml of 0.01 *M* metal salt solution to flow through 10 ml of H<sup>+</sup>-form resin and titrate the effluent with 0.1 *N* sodium hydroxide using methyl orange as indicator. Repeat the operation in the presence of 2 drops of 25% ammonia solution and 4 drops of ACH.

*Determination of breakthrough capacity*

Allow a solution of 0.01 *M* metal cyano complex to flow through Cl<sup>-</sup>-form resin of 3.2 mequiv. Collect the effluent in 50-ml fractions for analysis. On the basis of the obtained data construct the breakthrough curves. The concentrations found by analysis in the fractions are plotted against the volume of the effluent.

## RESULTS

*Investigation of complex formation on the anion-exchange resin*

On the basis of the experiments carried out by Inczédy and Frankow<sup>2</sup>, it was found that considerable adsorption of cyanide and also of metal complex cyanide ions took place on the hydroxide- and chloride-form resin beds only. As hydroxide-form resin cannot be employed because of the precipitation of metal hydroxide on the resin, a strongly basic resin in the chloride form was used. In the presence of ACH, metals will be adsorbed partly or completely as complex anions on the resin, depending on the affinity between the metals and ACH. If a metal does not react with ACH, it will not be held on the resin. According to our investigation, Zn<sup>2+</sup>, Ag<sup>+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Fe<sup>2+</sup> can be adsorbed quantitatively on the resin as complex anions. The binding of Co<sup>2+</sup> is not complete in the presence of other metals. Pb<sup>2+</sup>, Mn<sup>2+</sup>, Sr<sup>2+</sup>, Al<sup>3+</sup> and Bi<sup>3+</sup> react only partly with ACH. In the case of the last two metal ions, total binding can be obtained on the resin but mostly in the hydroxide form. Ca<sup>2+</sup>, Ba<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup> do not react with ACH on the resin. ACH itself can be adsorbed on the resin to the extent of only about 25%.

*Investigation of complex formation on the cation-exchange resin*

The metal salt solution passes through the column of H<sup>+</sup>-form resin and the acid content of the effluent is titrated with sodium hydroxide. In the presence of ammonia, the metal reacts with ACH and a cyano complex is formed:



Ammonia is adsorbed by the H<sup>+</sup>-form resin and a complex acid is formed. Consequently, the amount of sodium hydroxide consumed is increased by the reaction with ACH. If the metal does not react with ACH, then the amount of titrant consumed does not change. From the increase in the amount of sodium hydroxide consumed one can propose a structure for the complex. When a tetracyano complex is formed,

the amount of titrant consumed will be double in the case of a divalent metal as a consequence of the reaction of the metal with ACH. When the increase in the amount of titrant consumed is less, the formation of the tetracyano complex is incomplete. For example, if a tricyano complex is formed, the amount of sodium hydroxide consumed increases only by 50% according to the following equation:



On the basis of our investigation, the amount of titrant consumed did not increase in the case of  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  and alkali metals, indicating that these metals did not react with ACH. On the same basis, it appeared that  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Pb}^{2+}$  react only slightly with ACH. This result agrees with those obtained on anion-exchange resins. In addition, in the case of  $\text{Co}^{2+}$  we found the structure to be  $\text{Co}(\text{CN})_{3.6}$  and for  $\text{Ni}^{2+}$  the structure is  $\text{Ni}(\text{CN})_{3.25}$ . This means that the formation of the tetracyano complexes is not complete for these metals. In the case of other metals, interference effects appeared. With  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ , metal cyanide precipitates were formed on the resin owing to the acidic medium. In the case of  $\text{Fe}^{2+}$ , a blue solution occurred because of oxidation of hexacyanoferrate(II) to hexacyanoferrate(III).

#### *Adsorption of complex cyanide on the anion-exchange resin*

Neutral and alkaline copper and alkaline zinc cyano complex solutions were adsorbed on the  $\text{Cl}^-$ -form resin. These complex ions break through the columns quickly, especially in alkaline solution. The cyano complex ions appeared in the effluent at 85, 10 and 40 ml, respectively (Figs. 1 and 2). At the breakthrough points, the capacity of the column was utilized to the extents of only 18, 2 and 8%, respectively. At the end of the saturation process the extents of utilization were found to be 98, 85 and 86%, respectively. According to our analysis, 157 ml of 0.01 M copper cyano complex in neutral medium and 137 ml in alkaline solution, and 275.2 ml of

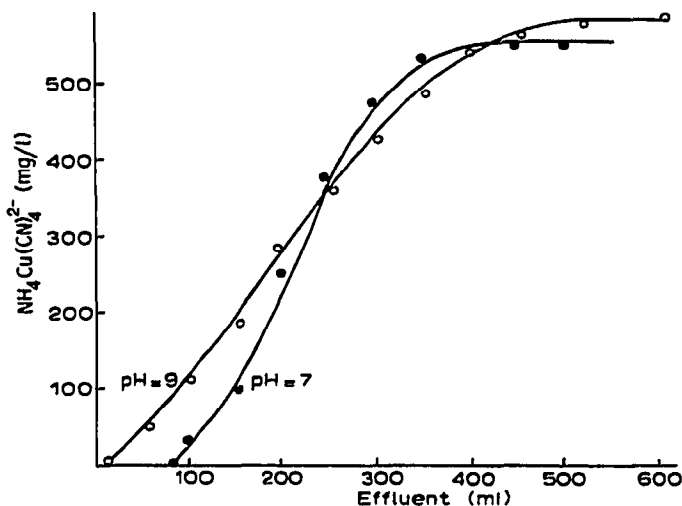


Fig. 1. Breakthrough curves of  $\text{NH}_4\text{Cu}(\text{CN})_4^{2-}$  on anion-exchange resin in the chloride form.

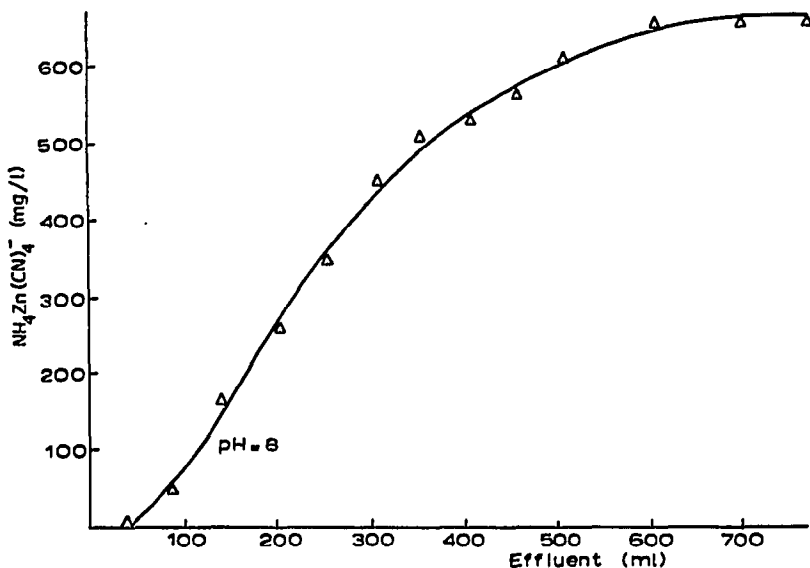


Fig. 2. Breakthrough curve of  $\text{NH}_4\text{Zn}(\text{CN})_4^-$  on anion-exchange resin in the chloride form.

0.01 M zinc cyano complex, respectively, were bound to the columns. Considering the total capacity of the resin columns (3.2 mequiv.) and the amounts of the two species adsorbed, one must assume that a divalent copper and a monovalent zinc cyano complex were adsorbed with the compositions  $\text{Cu}(\text{CN})_3^{2-}$  or  $\text{NH}_4\text{Cu}(\text{CN})_4^{2-}$  and  $\text{Zn}(\text{CN})_3^-$  or  $\text{NH}_4\text{Zn}(\text{CN})_4^-$ . The latter structure is the more probable in each case, as decomposition was not observed. On the basis of the results one can establish the order of adsorbability of metal cyano complexes: copper in neutral solution > copper in alkaline solution > zinc in alkaline solution.

## DISCUSSION

The interaction between metals and ACH studied by means of anion and cation exchangers yielding tetracyano complexes occurs quantitatively in slightly ammoniacal medium only with copper. This is proved by the fact that ACH can be determined complexometrically with the aid of copper. To ACH is added  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ , the excess of which is measured. This determination of ACH is not possible with other metals. On the other hand, if ammonia is employed in large excess, then the reaction proceeds quantitatively with other metals also. For example, in the case of  $\text{Zn}^{2+}$ , the process takes place only to the extent of 25% in the complexometric determination, while in presence of a large excess of ammonia the tetracyano complex is formed quantitatively. In this case, the excess of ACH can be determined by a colour reaction with diazotized *p*-nitroaniline. On this basis, copper is the only metal suitable for the complexometric determination of ACH.

ACH can be used not only more satisfactorily than potassium cyanide for the masking of metals, but also for the preparation of cyano complexes and for the separation of metals on anion exchangers.

## REFERENCES

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