Elution of copper and neodymium from a cation-exchange resin with ammonia-ethylenediaminetetraacetic acid solutions

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ELUTION OF COPPER AND NEODYMIUM FROM A CATION-EXCHANGE RESIN WITH AMMONIA-ETHYLENEDIAMINETETRAACETIC ACID SOLUTIONS

By
Lyle K. Matson
F. H. Spedding

December 1957
Ames Laboratory
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Ames, Iowa

Technical Information Service Extension, Oak Ridge, Tenn.
F. H. Spedding, Director, Ames Laboratory.

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Elution of Copper and Neodymium from a Cation-Exchange Resin with Ammonia-Ethylenediaminetetraacetic Acid Solutions*

Lyle K. Matson and F. H. Spedding

ABSTRACT

Several experiments were performed eluting neodymium bands behind copper bands with dilute ammonia-EDTA solutions. A few other experiments were performed eluting only copper bands. If there were a certain amount of ammonium and hydrogen mixed homogeneously with the copper in the resin, very flat elution curves were obtained. Thus, the concentrations of the ions in solution were constant throughout the band, and the composition of the resin changed very little during the elution.

The charge balance equations, the material balance equations, and a number of mass action equilibria were written for both the copper band and the neodymium band. Equations were also indicated for the material balance at the boundary of an ideal system and this system was compared with the actual experimental results. Two experiments were found to deviate only slightly from this ideal system.

The experiments described in this report establish the groundwork which was necessary to design an ideal elution system. If conditions can be established so that the retaining bed is completely compatible with the eluant and flat top elution curves can be obtained by the choice of suitable boundary conditions, then a powerful tool is available for determining the equilibrium constants of complex ions in

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solution. Having established this system, one has \( n \) equations and \( n \) unknowns and can calculate a constant for each variable determined experimentally. By determining the mass action constants for various ionic strengths and equivalent fractions on the resin, the activity coefficient ratios for various pairs of ions can be determined as a function of these variables.

It should be noted that the ideal elution system is not the system which is most suitable for separating pure materials. In the ideal system the bands seem to be diluted with other ions which are not involved in the separation. For a fixed retaining bed, equilibrium does not have to be established between the retaining bed and the eluate as long as the drift toward equilibrium is slow. The retaining bed can be kept nearly constant by regularly inserting retaining beds of a fixed composition. With a retaining bed of a fixed composition, the band behind it can be maintained constant if the boundary conditions are suitable. In the commercial separation of rare earths, the retaining bed contains only copper. The copper bed tends to pick up hydrogen and ammonium, but before it picks up much of these ions new beds are inserted. Pure copper retaining beds keep the rare-earth bands compact and give more efficient separations.
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INTRODUCTION

The group of elements with atomic numbers 39 and 57 through 71 are commonly known as the rare earths. At present the greatest demand for pure rare-earth elements, other than lanthanum, cerium, and perhaps neodymium, is for fundamental scientific research. Since the atoms of each of the respective rare-earth elements differ from each other essentially only by the number of electrons contained in the shielded 4f subshell and the number of protons in the nucleus, their unique physical and chemical properties, such as ionic size, make them valuable tools for testing many of the theories that have been proposed in chemistry and physics.

Their similar chemical properties make it extremely difficult to isolate rare earths individually in pure form by classical physical chemical methods such as fractional crystallization and precipitation. In recent years, however, ion-exchange techniques have been applied with great success to this separation problem and all of the rare earths are now available in kilogram quantities with a purity of 99.99 per cent or greater.

The ion-exchange methods which have proven most successful involve the use of an organic chelating agent in the eluant. The successful separation of the rare-earth elements by such a method depends for the most part upon the differences in the stabilities of the complexes formed between
individual rare-earth elements and the chelating agent present in a given mixture.

The chelating agent which gives the most economical and best separation of most of the rare earths is ethylenediaminetetraacetic acid (EDTA). The retaining ion which works the best with EDTA is the cupric ion. Even though the approximate conditions have been worked out for the best separation of the rare earths, more knowledge was desired concerning the elution of the rare earths behind a copper bed with an eluant composed of EDTA and ammonia in order to determine precisely the best conditions for separation. It is hoped that better conditions for the separation will be an outcome of a greater knowledge of the elution process. This report will describe one type of retaining bed which gave some degree of a true equilibrium. A number of retaining beds will be described which failed for some reason or another to give any indication that satisfactory results could be obtained.
PRESENT STATUS OF THE THEORIES OF ION EXCHANGE

Ion exchange was discovered by Spence in the middle of the 19th century (1), but much of the development of ion exchange has been in the past decade. Some of the better scientific papers have been written by Gregor, Glueckauf, Davidson, Argersinger, Bonner, Ekedahl, Högfeldt, and Sillen (2, 3, 4, 5, 6, 7, 8). These papers give a good qualitative picture of what happens in an ion-exchange resin. However, the present knowledge does not allow one to predict even semi-quantitatively the variation in an ion-exchange constant as the mole fraction on the resin changes. Except for a solution phase of less than about 0.1 ionic strength, the ion-exchange constant, and thus the activity coefficients of the components in the resin phase, vary unpredictably with changes in the ionic strength of the solution phase. Davidson finds that the activity coefficients for the resin phase are mainly a function of the mole fraction of the components on the resin and not a function of the ionic strength of the solution phase for sodium and hydrogen.

One problem in which ion exchange has been very useful is the separation of the rare earths. An early method of separating the rare earths by means of ion exchange was developed at Ames (9, 10, 11, 12, 13) and elsewhere (14, 15, 16, 17, 18, 19, 20, 21). This method consisted of eluting the rare earths down an ion-exchange column which was initially in
the hydrogen cycle with an approximately 5 per cent citric acid-ammonium citrate solution. The elution curve of each individual rare earth was "bell shaped". The different rare earths moved down the column at different rates so that they gradually separated from each other. However, to separate macro quantities of the rare earths the bands had to travel a great distance and a considerable fraction of the bands overlapped. This method was particularly successful for separating radioactive tracers where adsorbed bands were very short.

Spedding and his co-workers performed numerous experiments in which a rare-earth band was eluted down a resin bed with a 0.1 per cent citric acid solution, adjusted to a pH between 5.0 and 8.0 with ammonium hydroxide (22, 23, 24, 25, 26, 27). A resin bed in the hydrogen form was used to retain the rare-earth band. Under these conditions, the rare-earth band lengthens initially as it moves down a resin bed until it reaches an equilibrium value. The equilibrium band has very sharp front and rear edges and the elution curve is rectangular in shape. The concentrations of the total rare earth, the ammonium ion, and the hydrogen ion in contact with any part of this band are constant. The ratio of the total rare-earth concentration to the ammonium concentration to the hydrogen-ion concentration in solution is the same as the ratio of the total rare earth to the total ammonium to the
total hydrogen on the resin in the rare-earth band. This correspondence of the solution and the resin is due to the fact that everything is picked up at the rear edge and laid down at the front edge of the fully developed rare-earth band.

Since the ammonium ion does not move past the rare-earth band, only a pure hydrogen-form resin is found ahead of the adsorbed band and an essentially pure ammonium-form resin is found behind the rare-earth band. If several individual rare-earth species are present in the originally adsorbed band, they tend to separate into individual bands which follow one another 'head to tail' as the total band is eluted down the column. The boundaries between the individual species are fairly sharp once an equilibrium state has been reached, and the bands do not pull apart from one another. The sharpness of individual rare-earth band fronts is a result of the equilibria set up between the various rare-earth species and the smallness of the theoretical plates that can be obtained in an ion-exchange column.

The sharp front and rear edges of the rare-earth band and the rectangular shaped elution curve are a result of the constraining reactions which take place at the front and rear edges of the band once equilibrium conditions have been established. When the ammonium ions in the eluant reach the rear edge of the rare-earth band, they are partially exchanged for the rare-earth and hydrogen ions on the resin. The ammonium
ions are adsorbed on the resin, the rare-earth ions are chelated by the citrate anions, and the hydrogen ions form weak acids. When the rare-earth complex reaches the front edge of the rare-earth band, the rare earth and the ammonium is readSORBED on the resin in place of hydrogen. The citric acid which is formed flows out the bottom of the column.

Spedding and Powell (28, 29) have proposed a theory which explains the formation of the sharp bands and the elution curves. There are twelve important unknown variables in this system; and it is possible to write twelve independent equations involving only material balances, electrical neutrality, stability constants of the various complexes formed, and the equilibrium conditions. The authors found that, knowing the composition of the eluant, the capacity of the resin bed, and the total amount of rare earth adsorbed on the resin, they could solve the twelve equations and calculate the concentrations of all ionic species in the eluate and on the resin to better than 1 per cent accuracy.

At the present time, EDTA has replaced citrate in the separation of rare earths but knowledge of the separation of the rare earths with EDTA is not as far advanced as the separation of the rare earths with citrate. Several articles have been written by Spedding, Powell, and Wheelwright on the stability of rare earth-EDTA complexes and the separation of rare earths by ion exchange using EDTA (30, 31, 32, 33). A
cation-exchange bed of cupric ion has been found to be best for retaining the rare-earth band. Although copper does not have as stable a complex as the heavier rare earths, the resin has a greater affinity for the rare earths than for copper at the concentrations used. This difference in affinity more than compensates for the difference in the stability of EDTA complexes, and the copper band is laid down ahead of the rare-earth band.
Materials and Apparatus

Materials

The resin used in the following experiments was a sulfonated polystyrene-divinylbenzene type which was purchased from the Dow Chemical Company of Midland, Michigan. It was labeled as Dowex 50-X8 and was a 100-to 200-mesh resin. The neodymium was supplied as the oxide by the rare-earth-separation group at the Ames Laboratory of the Atomic Energy Commission. Its purity was greater than 99.9 per cent.

The diammonium dihydrogen ethylenediaminetetraacetate, which was supplied by the rare-earth-separation group, was purchased from the Geigy Chemical Corporation of New York, New York. In order to remove a slight amount of sodium and the heavy metals that might be in the \((\text{NH}_4)_2\text{H}_2\text{Y}\), the \(\text{H}_4\text{Y}\) was precipitated with hydrochloric acid and washed with deionized water. The \(\text{H}_4\text{Y}\) was converted to a concentrated solution of \((\text{NH}_4)_2\text{H}_2\text{Y}\) by adding deionized water and ammonia. The \((\text{NH}_4)_2\text{H}_2\text{Y}\) was precipitated by adding 95 per cent ethyl alcohol. No chloride or sodium was found in the resulting compound.

Baker and Adamson C. P. reagent hydrochloric acid was used for dissolving the neodymium oxide and making up the solutions, and Baker and Adamson C. P. reagent ammonia was
used in making the eluant. All other chemicals used, such as the ammonium chloride, cupric sulfate, sodium hydroxide, and oxalic acid, were "Baker Analyzed" reagent grade.

The water which was used was the regular laboratory distilled water which had been passed through glass wool filters and a cation and anion exchange deionizer.

Apparatus

A diagram of the apparatus is shown in Figure 1. The container for the eluant was a 10-gallon carboy. The long column was approximately 140 centimeters in length and contained approximately 92 centimeters of resin, and the medium-sized column was about 105 centimeters in length and contained approximately 30 centimeters of resin. The appendages were approximately 14 centimeters in length and contained about 3 centimeters of resin. The exact length of the resin bed depended on the cycle of the resin, the solution with which the resin was in contact, and how well the resin was packed.

A short piece of Tygon tubing with a screw clamp in the middle was attached to the bottom of each column and appendage, and a medicine dropper type tip was inserted into the other end of the Tygon tubing so that the eluate from the column could be either collected in a volumetric flask or passed by means of Tygon tubing to another column or append-
Figure 1. Schematic drawing of apparatus
age. A rubber stopper with a glass tube through the center was inserted in the top of each column and appendage so that the columns and appendages could be attached together by means of Tygon tubing.

Procedure

Methods of analysis

The neodymium analysis consisted of precipitating the neodymium ion from the unknown solution, which was near boiling, with an excess of a saturated solution of oxalic acid. The precipitated sample was allowed to cool and then filtered with Schleicher and Schuell No. 589 White Ribbon filter paper. The precipitate was washed with dilute oxalic acid and transferred to a porcelain crucible which had been brought to constant weight. The sample was then ignited in a muffle furnace overnight at approximately 850°C. The sample was removed from the furnace, cooled for five hours in a desiccator, and weighed. From the difference in weight between the crucible plus sample and the empty crucible, the weight of the neodymium oxide was obtained.

The ammonium ion was determined by the Kjeldahl procedure. The samples were placed in a distillation apparatus and the ammonia was driven off by adding concentrated sodium hydroxide and then boiling. The ammonia was collected in a receiver containing an indicator-boric acid solution, and titrated with
a standard solution of hydrochloric acid. The indicator-boric acid solution was prepared by adding 10 milliliters of the concentrated methyl purple indicator solution, which was supplied by Fleisher Chemical Company, and 30 grams of boric acid crystals to a liter volumetric flask and diluting to volume with water. About 20 milliliters of this solution was added to the flask used to collect the ammonia as it was distilled over.

The total EDTA concentration was determined by titrating a known amount of a standard zinc chloride solution with the unknown solution using Eriochrome Black T as the indicator. The standard zinc chloride solution was buffered with 10 milliliters of an ammonia-ammonium chloride solution. The buffer solution was prepared by diluting 6.75 grams of ammonium chloride and 57 milliliters of concentrated ammonium hydroxide to 100 milliliters.

The copper analysis consisted of plating out pure copper metal on a platinum screen by electrolysis. The weight of copper was determined by the difference between the weight of the screen plus copper and the weight of the screen. This analysis was performed by the analytical group at the Ames Laboratory.

**Preparation of the eluant**

Two liters of a standard \((\text{NH}_4)_2\text{H}_2\text{Y}\) stock solution and
the desired amount of ammonia were added to a 45.90-liter carboy and the carboy was diluted to the mark. This solution was then stirred with a large stirrer for 15 minutes.

The eluant concentrations of the ammonium and the EDTA were determined as indicated in the previous section.

**Determination of resin bed capacity**

An approximately 0.3 molar neodymium chloride solution was prepared by reacting an excess of Nd₂O₃ with concentrated hydrochloric acid, titrating the solution to the equilibrium pH with dilute hydrochloric acid, boiling the solution, and diluting to 40 liters.

The resin was converted to the ammonium cycle by passing ammonium citrate through the column and washing with deionized water. The neodymium chloride solution was passed through each of the columns and appendages to saturate them with neodymium. Five hundred milliliters excess neodymium chloride solution was passed through each of the resin beds. The neodymium chloride in the pores of the resin was washed from the columns and appendages with deionized water. Then the neodymium of each column and appendage was stripped into a volumetric flask with a concentrated ammonia-EDTA solution having a pH of about 8.5. The volumetric flasks were diluted to the mark and an aliquot was taken from each flask and analyzed for the amount of neodymium. From these data, the capacity of each resin bed was calculated.
Preparation of resin beds

The rare-earth band which was to be eluted down the columns was prepared by saturating the first column indicated in Figure 1 with neodymium as described in the previous section. This band expanded slightly as it was driven down the column by the eluant. The expansion was caused by the adsorption of ammonium and hydrogen until it reached an equilibrium length. The equilibrium band could have been attained with less eluant if a predetermined amount of ammonium chloride and hydrochloric acid had been added to the neodymium chloride load solution.

A number of retaining beds were prepared and the rare-earth band was eluted down the column behind each of the retaining beds. These included copper, copper-ammonium, copper-hydrogen, copper-ammonium-hydrogen, and thorium beds.

An appendage was connected in series above the large column shown in Figure 1 and another appendage was connected below the six appendages. A copper-ammonium resin bed is prepared by passing a concentrated solution of cupric sulfate and ammonium chloride through the large column and eight appendages. If this concentrated solution should be washed from the column and the appendages, there would be a non-uniform shift of copper from the solution to the resin. This shift would be due to the dilution of the load solution. Therefore, in order to get a homogeneous copper-ammonium
band, a ten-fold excess of a dilute solution of cupric sulfate and ammonium chloride was then passed through the column and appendages (see lines 1 through 5 in Table 1). At this time the column and appendages were carefully washed by taking the excess solution from the top of the resin and passing deionized water through the columns and appendages separately. During the washing operation, there could only be a very small shift of the copper from the solution to the resin compared with the amount of copper and ammonium already on the resin.

The two appendages that were above and below the large column and six appendages were analyzed for the equivalents of copper per equivalent of resin ($\equiv_{\text{Cu}}$) and the equivalent fraction of ammonium ($\equiv_{\text{NH}_4}$). The cupric and ammonium ions on each of the two appendages were stripped with a four normal sodium chloride solution into separate 500-milliliter volumetric flasks and the solutions in the volumetric flasks were diluted to volume. After thorough mixing, aliquots were taken to determine the equivalent fractions of the ammonium and copper on the resin. If the top and bottom appendages had the same equivalent fractions for the copper and for the ammonium, the column and appendages in between were assumed to be homogeneous and to have these same equivalent fractions.

To prepare a set of homogeneous beds of copper and hydrogen, the large column and the eight appendages were treated in exactly the same manner as in the preparation of
Table 1. Ion exchange data on copper, ammonium, and hydrogen

<table>
<thead>
<tr>
<th>Line no.</th>
<th>Solution data</th>
<th>Molar conc. of HCl</th>
<th>Molar conc. of NH₄Cl</th>
<th>Molar conc. of CuSO₄</th>
<th>Resin data</th>
<th>Mass action equilibria</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≤H</td>
<td>≤NH₄</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>0.284</td>
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<td>0.514</td>
<td>0.486</td>
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<tr>
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<td>0.0402</td>
<td></td>
<td>0.430</td>
<td>0.570</td>
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<td>3</td>
<td></td>
<td>0.178</td>
<td>0.0402</td>
<td></td>
<td>0.394</td>
<td>0.606</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.0182</td>
<td>0.0100</td>
<td></td>
<td>0.1103</td>
<td>0.890</td>
</tr>
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<td>5</td>
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<td>0.0089</td>
<td>0.0100</td>
<td></td>
<td>0.0667</td>
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</tr>
<tr>
<td>6</td>
<td></td>
<td>0.495</td>
<td>0.0402</td>
<td></td>
<td>0.491</td>
<td>0.509</td>
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<tr>
<td>7</td>
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<td>0.0402</td>
<td></td>
<td>0.405</td>
<td>0.595</td>
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<td>8</td>
<td></td>
<td>0.265</td>
<td>0.0756</td>
<td></td>
<td>0.199</td>
<td>0.801</td>
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<tr>
<td>9</td>
<td></td>
<td>0.036</td>
<td>0.218</td>
<td></td>
<td>0.031</td>
<td>0.423</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.057</td>
<td>0.106</td>
<td></td>
<td>0.052</td>
<td>0.258</td>
</tr>
</tbody>
</table>

^aDefined on page 25.
homogeneous copper-ammonium beds except that the large column and the appendages were brought to equilibrium with a solution of hydrochloric acid and cupric sulfate (see lines 6, 7, and 8 in Table 1). The equivalent fraction of hydrogen ($\Xi_H$) on the resin rather than the equivalent fraction of ammonium was determined.

A homogeneous bed of copper, ammonium, and hydrogen was prepared by bringing the bed to equilibrium with a solution of cupric sulfate, ammonium chloride, and hydrochloric acid (see lines 9 and 10 in Table 1). A set of copper beds were prepared by passing a solution of cupric sulfate through the column and the appendages. A set of thorium beds were prepared by passing a solution of thorium nitrate through the column and the six appendages. The excess thorium nitrate or cupric sulfate was washed out with deionized water.

Observation and measurement of the adsorbed neodymium bands

After the columns and the six appendages were connected in series with Tygon tubing as shown in Figure 1, the eluant was started through the series at the rate of 2 milliliters per minute. The eluate was collected in volumetric flasks by means of an automatic bottle changer. The position of the top and bottom of the neodymium band was recorded three times a day at approximately equal time intervals and the amount of the eluate was noted at these times. Since there
is a slight expansion or contraction of the bed when the different ions are adsorbed on the resin, the position of the top of the resin bed was also noted at these times.

**Analysis of the eluate samples**

The pH was taken of all the eluate samples in the volumetric flasks with a Beckman glass electrode pH meter. The pH meter had been standardized against the Beckman pH 4 buffer and checked against the Beckman pH 7 buffer.

The concentration of the ammonium and the copper were determined for a representative number of the samples from the copper band. The concentrations of the ammonium and the neodymium were determined for all of the samples from the neodymium band.

**Analysis of the resin samples**

The top three appendages were taken from the system when there was about 2 centimeters of the copper band left on the large column. The remaining three appendages were put back into the system by connecting the Tygon tube from the large column to the top of these appendages, and the elution was continued until the three appendages were in the middle of the neodymium band. These three appendages were then removed and the large column was connected directly to the bottle changer by means of the Tygon tubing. The elution
was continued until the neodymium band was completely off of the large column.

After the eluate was washed out to the first three appendages with deionized water, they were analyzed to determine the equivalent fraction of the copper and the ammonium in the copper band. The remaining three appendages were washed and analyzed for the equivalent fractions of the neodymium and the ammonium in the neodymium band.

Each operation of preparing the beds, eluting the neodymium band down the complete set of beds, and analyzing the solution and resin samples was called a run. Several of the more important runs are recorded in Table 2.

Results

In several of the earlier runs the copper band had a composition of less than 0.20 equivalents of ammonium per equivalent of resin. When the eluate samples from the neodymium band were plotted (concentration vs. time) in succession, the curves showed a hump in the neodymium concentration and a corresponding dip in the ammonium concentration. Some ammonium was found to leak through the neodymium band into the rear edge of the copper band.

An equivalent fraction of 0.50 ammonium in the copper band proved to be too high for an eluant of 3.50 moles of ammonium per mole of EDTA. However, the concentration curves
Table 2. Column data

<table>
<thead>
<tr>
<th>Run no.</th>
<th>( \bar{Y}_T )</th>
<th>( \bar{NH}_4 )</th>
<th>( \bar{NH}_4/\bar{Y}_T )</th>
<th>Eluate samples from the copper band</th>
<th>Eluate samples from the neodymium band</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>( Cu_T )</td>
<td>( NH_4 )</td>
</tr>
<tr>
<td>16</td>
<td>0.01766</td>
<td>0.06102</td>
<td>3.45</td>
<td>0.0187</td>
<td>0.0232</td>
</tr>
<tr>
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<td>0.02268</td>
<td>0.07808</td>
<td>3.44</td>
<td>0.0241</td>
<td>0.0296</td>
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<tr>
<td>13</td>
<td>0.01658</td>
<td>0.05610</td>
<td>3.38</td>
<td>0.0174\textsuperscript{a}</td>
<td>0.0230\textsuperscript{a}</td>
</tr>
<tr>
<td>12</td>
<td>0.01653</td>
<td>0.05787</td>
<td>3.50</td>
<td>0.01705\textsuperscript{a}</td>
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<tr>
<td>10</td>
<td>0.01731</td>
<td>0.06754</td>
<td>3.90</td>
<td>0.01745</td>
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</table>

\textsuperscript{a}These are the values of the samples taken from near the rear edge of the band.
<table>
<thead>
<tr>
<th>Run no.</th>
<th>Z Cu</th>
<th>Z NH₄</th>
<th>Z H</th>
<th>Z Cu</th>
<th>Z NH₄</th>
<th>Z H</th>
<th>Z Nd</th>
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<td>0.5932</td>
<td>0.3933</td>
<td>0.0136c</td>
<td>0.5832</td>
<td>0.3972</td>
<td>0.0196c</td>
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<tr>
<td>15</td>
<td>0.5960</td>
<td>0.3423</td>
<td>0.0117c</td>
<td>0.5923</td>
<td>0.3990</td>
<td>0.0087c</td>
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<td>0.6097</td>
<td>0.3800</td>
<td>0.0103c</td>
<td>0.7269e</td>
<td>0.2616</td>
<td>0.0115c</td>
</tr>
<tr>
<td>12</td>
<td>0.5699c</td>
<td>0.4301</td>
<td>0.0000</td>
<td>0.5626</td>
<td>0.4258</td>
<td>0.0126c</td>
<td>0.6753e</td>
<td>0.3109</td>
<td>0.0135c</td>
</tr>
<tr>
<td>10</td>
<td>0.512c</td>
<td>0.0000</td>
<td>0.488</td>
<td>0.5132</td>
<td>___</td>
<td>0.4894</td>
<td>0.7577e</td>
<td>0.2322</td>
<td>0.0101c</td>
</tr>
</tbody>
</table>

b $S_1 = 0.0068; \ S_2 = 0.0251$ (These quantities will be explained later.)

c The equivalent fraction of the hydrogen is determined by difference.

d $S_1 = 0.0083; \ S_2 = 0.0268$ (These quantities will be explained later.)

e Initially the equivalent fraction of the neodymium was 1.000.
from the neodymium band were almost completely flat.

When a lower equivalent fraction of ammonium was used, relatively flat copper bands were obtained (see runs 12 and 13 in Table 2 and the definition of the symbols used in Table 2 on pages 24 and 25). However, the concentrations of the copper and ammonium got slightly smaller as more of the eluate was taken from the columns. The reason for the change in the concentrations of the copper and the ammonium is that a small amount of hydrogen was taken from the solution by the resin and replaced by copper and ammonium, as there was no hydrogen on the resin at the beginning of the elution while there was some hydrogen on the resin at the end of the elution.

Since there was not any ammonium or hydrogen in the neodymium band at the beginning of the elution, there are added complications by the adjusting of the neodymium band. The neodymium band got longer at a constant rate and changed length only slightly after coming to a particular length. At the end of the elutions, the pH and the concentrations of the neodymium and ammonium were almost constant, within experimental error, for the eluate samples from runs 12 and 13.

A neodymium band was not used in runs 15 and 16 in order to be able to study the copper band without the complications of the neodymium band. Three long resin beds were used
instead of one. As can be seen in Table 2, a small amount of hydrogen was on the resin at the beginning of the elution. The pH and the concentrations of copper and ammonium were constant for runs 15 and 16. It may be noted that the composition of the resin changed only a small amount from the beginning to near the end of the elution.

When a copper band having an equivalent fraction of hydrogen slightly less than 0.50 and an eluant having slightly less than four moles of ammonium per mole of EDTA were used (run 10), the concentration of neodymium and the ammonium in the eluate was constant for the whole band. However, if one prepares a bed having an equivalent fraction of hydrogen greater than 0.50 or an eluant having much less than four moles of ammonium per mole of EDTA, a precipitate of EDTA will form in the neodymium band adjacent to the copper band. If the equivalent fraction of the hydrogen on the resin is much less than 0.50, a copper band containing ammonium forms between the neodymium band and the copper-hydrogen band.

When thorium was used as the retaining ion instead of copper, the thorium was found to contaminate the whole neodymium band to some extent.
DISCUSSION OF RESULTS

It has been pointed out at the Ames Laboratory (28, 29) that there are \( n \) unknown concentration variables in this system. If the material balance equations and mass action equilibria are written, \( n-1 \) independent equations can be determined for solutions of a known ionic strength and for known equivalent fractions on the resin. Therefore, if boundary conditions can be devised so that an extra equation can be derived, the \( n \) equations can be solved for the \( n \) unknowns.

The column data which have been collected in trying to obtain equilibrium bands in the elution of copper and neodymium with the ammonia-EDTA solutions are compared with the results derived from this theory.

Copper Band

Mass action equilibria

Table 3 gives a list of the equilibrium constants that are thought to be of any consequence. The following symbols will be used in the remainder of this report (\( Y \) represents the EDTA anion):

Knowns (eluant) -

\( Y_T \) = total molar concentration of EDTA
\( NH_4 \) = total molar concentration of the ammonium
Table 3. Mass action equilibria in copper band

<table>
<thead>
<tr>
<th>$K'$</th>
<th>Definition</th>
<th>Ionic strength$^a$</th>
<th>$K'$</th>
<th>$\log K'$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_A'$</td>
<td>$\frac{CuY}{Cu \times Y}$</td>
<td>0.1</td>
<td>18.8</td>
<td>19.3$^b$</td>
<td>(34)</td>
</tr>
<tr>
<td>$K_B'$</td>
<td>$\frac{HCUY}{H \times CuY}$</td>
<td>0.03</td>
<td>3.2$^c$</td>
<td>3.3$^b$</td>
<td>Run 16</td>
</tr>
<tr>
<td>$K_C'$</td>
<td>$\frac{H_2CuY}{H \times HCUY}$</td>
<td>0.01</td>
<td>1.7$^a$</td>
<td>1.65$^b$</td>
<td>Run 10</td>
</tr>
<tr>
<td>$K_1'$</td>
<td>$\frac{H_4Y}{H \times H_3Y}$</td>
<td>0.02</td>
<td>2.43$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_2'$</td>
<td>$\frac{H_3Y}{H \times H_2Y}$</td>
<td>0.02</td>
<td>2.97$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_3'$</td>
<td>$\frac{H_2Y}{H \times HY}$</td>
<td>0.02</td>
<td>6.39$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_4'$</td>
<td>$\frac{HY}{H \times Y}$</td>
<td>0.02</td>
<td>10.52$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_D'$</td>
<td>$\frac{(NH_4)^2 \leq Cu}{Cu \leq^2 NH_4}$</td>
<td>0.04</td>
<td>2.3$^c$</td>
<td></td>
<td>Run 15</td>
</tr>
<tr>
<td>$K_E'$</td>
<td>$\frac{H^2 \leq Cu}{Cu \leq^2 H}$</td>
<td>0.03</td>
<td>1.92$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_F'$</td>
<td>$\frac{H \leq NH_4}{NH_4 \leq H}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$All the constants are reported at 25°C except for $K_A'$ which is reported at 20°C.

$^b$Estimated by the Debye-Hückel Theory.

$^c$Estimated from the data given in Table 2 (pages 20 and 21).

$^d$Unpublished work done by the senior author.
\( \tilde{H}_T = \text{total molar replaceable hydrogen} \)

Variables (copper band) -

- \( H = \text{molar concentration of } H^+ \)
- \( \text{NH}_4 = \text{molar concentration of } \text{NH}_4^+ \)
- \( Y = \text{molar concentration of } Y^- \)
- \( HY = \text{molar concentration of } HY^- \)
- \( H_2Y = \text{molar concentration of } H_2Y^- \)
- \( H_3Y = \text{molar concentration of } H_3Y^- \)
- \( H_4Y = \text{molar concentration of } H_4Y \)
- \( Cu = \text{molar concentration of } Cu^{+2} \)
- \( CuY = \text{molar concentration of } CuY^- \)
- \( HCuY = \text{molar concentration of } HCuY^- \)
- \( H_2CuY = \text{molar concentration of } H_2CuY \)
- \( Cu_T = \text{total molar concentration of the copper} \)
- \( HT = \text{total molar concentration of the replaceable hydrogen} \)
- \( \tilde{H} = \text{equivalents of } H^+ \text{ per equivalent of resin} \)
- \( \tilde{NH}_4 = \text{equivalents of } \text{NH}_4^+ \text{ per equivalent of resin} \)
- \( \tilde{Cu} = \text{equivalents of } Cu^{+2} \text{ per equivalent of resin} \)

The value of \( H \) for an ionic strength between 0.01 and 0.03 can be estimated by means of the following equation:

\[-\log H = pH - 0.05. \quad (1)\]

The concentration of any of the complexes in solution can be expressed in terms of the ionization or formation mass action constants and the concentration of the simple ions, for example \( Cu, H, Y, \) and \( \text{NH}_4 \).
There are three constants $K_D^1$, $K_E^1$, and $K_F^1$ relating the equivalent fractions of the ions on the resin to the concentration of the ions in the solution. Since only two of these are independent, only two variables can be eliminated with these constants. The use of these equilibrium equations presupposes that the resin stream maintains equilibrium with the solution stream. If the two streams are not compatible, a flat top elution band will not be maintained and the two phases will not be in equilibrium. To be compatible, the entering resin stream must be in equilibrium with the exiting eluate. Therefore, the problem concerning the retaining bed is to find the resin bed that will meet the above conditions.

**Material balance equations**

The following material balance equations should be obeyed:

\[
\begin{align*}
\text{Cu}_T &= \text{Cu} + \text{CuY} + \text{HCuY} + \text{H}_2\text{CuY} \\
\tilde{Y}_T &= \text{CuY} + \text{HCuY} + \text{H}_2\text{CuY} + \text{H}_4\text{Y} + \text{H}_3\text{Y} + \text{H}_2\text{Y} \\
\text{H}_T &= \text{H} + \text{HCuY} + 2\text{H}_2\text{CuY} + 4\text{H}_4\text{Y} + 3\text{H}_3\text{Y} + 2\text{H}_2\text{Y}
\end{align*}
\]

The equations (2), (3), and (4) are a statement that the whole is equal to the sum of the parts for the total copper, the total EDTA, and the total replaceable hydrogen in solution. The concentrations of HY and Y have no effect on material balance at the pH encountered in the copper band.
The following equation must be obeyed for the system:
\[ \tilde{\text{NH}_4} + \tilde{\text{H}_T} = 2\text{Cu}_T + \text{NH}_4 + \text{H}_T. \] (5)
The equation is simply a statement that the total number of equivalents of replaceable cations per liter of eluate is the same as the total number of equivalents of replaceable cations in the eluant since the EDTA concentration is the same in the eluant and the copper band eluate.

Charge balance equations

The following equations are simply a statement that the summation of the positive charges is equal to the summation of the negative charges in solution and on the resin:
\[ \tilde{\text{NH}_4} + \tilde{\text{Cu}} + \tilde{\text{H}} = 1 \] (6)
\[ \text{NH}_4 + 2\text{Cu} + \text{H} = 2\text{CuY} + \text{HCuY} + \text{H}_3\text{Y} + 2\text{H}_2\text{Y}. \] (7)

Material balance at the boundary between the copper and the ammonium bands

Equations will be written for the ideal system indicated in Figure 2. The deviation of the runs 15 and 16 from this ideal system will then be discussed.

Since the bed is driven to equilibrium with the eluant, the composition of the solution phase of the ammonium band is assumed to be the same as the composition of the eluant. The composition of the resin phase in the ammonium band, the composition of the resin phase in the copper band, and the
Figure 2. The material balance at the boundary
composition of the solution phase in the copper band are each considered homogeneous and unchanging as the elution progresses since only flat type elution bands are considered. The previous conditions simply state that the net exchange of ions between the solution and the resin is zero except in the boundary region.

The resin phase in Figure 2 can be considered as flowing upward through the boundary between the copper and ammonium bands while the solution phase flows downward through the boundary. The boundary moves through one equivalent of resin as the boundary moves from the top line to the bottom line in Figure 2.

As one equivalent of the mixed copper band is replaced by the ammonium band, \( S_2 \) equivalents of hydrogen and \( S_1 \) equivalents of ammonium are not removed from the resin but flow up in the resin phase to form part of the ammonium band.

There are \( V' \) liters of the eluate produced when \( V \) liters of the eluant replace one equivalent of the mixed copper band with one equivalent of the ammonium band. Figure 2 shows that the copper is uniformly stripped into the \( V' \) liters of the eluate as the eluate is formed at the boundary. The HT is assumed to remain in solution as the solution phase flows past the boundary. The rest of the hydrogen in the resin phase on the copper band, \( \Sigma_H - S_1 \), and the rest of the ammonium, \( \Sigma_{NH_4} - S_2 \), are assumed to be stripped uniformly.
into the \( V' \) liters of the eluate. All of the ammonium in the \( V \) liters of the eluant is assumed to be laid down in the resin phase as the solution flows into the boundary. Since the exchange of water as the resin changes composition is extremely small for dilute solutions, the \( V' \) is set equal to \( V \), and the following equations can be written (see Figure 2):

\[
\begin{align*}
V \cdot 2C_{\nu T} & = \leq Cu \tag{8} \\
V \cdot (H_{\nu} - \tilde{H}_{\nu}) & = \leq H - \delta_{2} \tag{9} \\
V \cdot NH_{4} & = \leq NH_{4} - \delta_{1} \tag{10} \\
V \cdot \tilde{NH}_{4} & = 1 - \delta_{1} - \delta_{2}. \tag{11}
\end{align*}
\]

Solving for \( 1/V \) in each of the above equations, one obtains the following equation:

\[
\frac{1}{V} = \frac{2C_{\nu T}}{\leq Cu} = \frac{H_{\nu} - \tilde{H}_{\nu}}{\leq H - \delta_{2}} = \frac{NH_{4}}{\leq NH_{4} - \delta_{1}} = \frac{\tilde{NH}_{4}}{1 - \delta_{1} - \delta_{2}}. \tag{12}
\]

Equation (12) can be split into the three equations:

\[
\begin{align*}
\leq Cu & = \frac{2C_{\nu T}(1 - \delta_{1} - \delta_{2})}{\tilde{NH}_{4}} \tag{13} \\
\leq H & = \frac{\Delta(1 - \delta_{1} - \delta_{2})}{\tilde{NH}_{4}} + \delta_{2} \tag{14} \\
\leq NH_{4} & = \frac{NH_{4}(1 - \delta_{1} - \delta_{2})}{\tilde{NH}_{4}} + \delta_{1} \tag{15}
\end{align*}
\]

where

\[
\Delta = H_{\nu} - \tilde{H}_{\nu}. \tag{16}
\]

Using the data of the retaining bed at the beginning of the elution and the eluate samples from runs 15 and 16, one
can calculate the values of $S_1$ and $S_2$ from the equations (14) and (15). The values of $S_1$ and $S_2$ are recorded in Table 2 (see page 20). When the values of $S_1$ and $S_2$ are substituted into equation (13), the value of $\leq_{Cu}$ obtained is nearly the same as the experimental value. The difference is probably due to the experimental error.

The $S_1$ equivalents of ammonium ions which move into the ammonium band do not give any trouble. However, the $S_2$ equivalents of hydrogen which go into the ammonium band may cause some difficulty. If the hydrogen is laid down uniformly and is in equilibrium with the eluant, the equations for the ideal system apply. If it is not in equilibrium with the eluant, the hydrogen will be turned back and will not be laid down uniformly. Therefore, the solution phase which flows into the boundary will be changing and the equations will not apply.

The $S_2$ calculated from the equations is several orders of magnitude larger than that calculated to be in equilibrium with the eluant. Therefore, the hydrogen was actually concentrating behind the copper band.

Table 2 shows that the resin changed slightly in composition as the elution progressed for runs 15 and 16. Therefore, these runs deviate from the ideal system in that the different phases are not of constant composition. This was brought about by the fact that the hydrogen-copper and
hydrogen-ammonium ratios of the retaining bed were not quite compatible with the eluant used. The eluate leaving the column was not completely in equilibrium with the resin bed. This is reflected in the fact that the $K_E$'s and $K_F$'s are not good constants. Also, hydrogen was accumulating above the boundary. However, it should be possible to prepare a resin bed for the copper band which will not change in composition as a copper band eluate of constant composition flows over the resin.

The approximate constants can be calculated from the parts of the various runs where equilibrium conditions are approached, or they can be determined experimentally under the concentration conditions found in these experiments. These constants can then be used with the equations to determine what the retaining bed equivalent fractions should be. The equations show the ideal retaining bed is very sensitive to the hydrogen-ion concentration on the bed. In future runs the equivalent fraction of the hydrogen should not be determined by difference but analyzed for directly or made up to a known value.

The copper band eluate seemed to come to equilibrium because the constants calculated from the solution data were reasonably constant when corrected for ionic strength. The composition of the resin changed slowly so that the concentrations in solution were hardly affected. Therefore, nearly
flat type elution curves were obtained in these runs. Equilibrium of the resin bed with the solution was evidently not obtained, particularly in regard to the hydrogen exchange with the other ions on the resin. Since the hydrogen concentration is very low in solution, the mass transfer to change the resin occurred slowly.

The variables which have been proposed are $H_T$, $Cu_T$, $H$, $Cu$, $NH_4$, $CuY$, $HCuY$, $H_2CuY$, $H_4Y$, $H_3Y$, $H_2Y$, $HY$, $Y$, $\leq H$, $\leq Cu$, $\leq NH_4$, and $\Delta$. The equilibrium constants which relate the variables are $K_A^1$, $K_B^1$, $K_C^1$, $K_1^1$, $K_2^1$, $K_3^1$, $K_4^1$, $K_B^1$, and $K_F^1$. The equations (2), (3), (4), (13), (14), (15), and (16) are independent. Thus, there are seventeen variables and seventeen equations. The $S_2$ can be calculated from the eluant data. The $S_1$ is an arbitrary constant in the boundary conditions and can be chosen to be any value which can be made to satisfy the constraints of the independent equations and mass-action equilibria.

Using the equation (16) and the definitions of the respective equilibrium constants $K_A^1$, $K_B^1$, $K_C^1$, $K_1^1$, $K_2^1$, $K_3^1$, and $K_4^1$, one can express the equations (3) and (4) in terms of the unknowns $Cu$, $H$, and $Y$. The elimination of $Y$ between the two equations gives equation (17) for $Cu$.

Eliminating $H_T$, $Cu_T$, and $NH_4$ between equations (2), (5), (7), and (16) and using the definitions of the respective equilibrium constants $K_A^1$, $K_B^1$, $K_C^1$, $K_1^1$, $K_2^1$, $K_3^1$, and $K_4^1$,
\[
C_u = \frac{\overline{Y}_T}{\overline{H}_T + (\Delta - H)} \left[ 2H^2K'_4K'_3 + 3H^3K'_4K'_3K'_2 + 4H^4K'_4K'_3K'_2K'_1 \right] - \left[ H^4K'_4K'_3K'_2K'_1 + H^3K'_4K'_3K'_2 + H^2K'_4K'_3 \right]
\]

(17)
one can obtain an equation in terms of $H$, $Cu$, and $Y$. Using equations (13) and (14) and the definitions of $K_E^I$, $K_A^I$, $K_B^I$, and $K_C^I$, one can express equation (2) in terms of $H$, $Cu$, and $Y$. Eliminating $Y$ between these two equations gives equation (18).

Eliminating $HT$ and $NH_4$ between equations (5), (7), and (16) and using the definitions of the respective equilibrium constants $K_A^I$, $K_B^I$, $K_C^I$, $K_1^I$, $K_2^I$, $K_3^I$, and $K_4^I$, one obtains an equation in terms of $H$, $Cu$, and $Y$. Using equations (3) and (6) and the definitions of $K_D^I$, $K_A^I$, $K_B^I$, and $K_C^I$, one can express equation (2) in terms of $H$, $Cu$, and $Y$. Eliminating $Y$ between these two equations and neglecting the $S_{12}^{2}$ term gives equation (19).

Equation (20) is obtained by setting the right sides of equations (18) and (19) equal to each other and simplifying.

The equations can now be solved by successive approximations. The $H - \Delta$ and $S_{1}$ are known to be small and to a first approximation can be assumed to be zero or approximate values can be substituted from one's knowledge of the system. When $Cu$ versus $H$ is plotted for equations (17) and (19), the solution for $H$ and $Cu$ is obtained as the intersection of these two curves. Almost exactly the same solution is obtained by setting the denominator of equation (17) equal to zero and substituting the resulting value of $H$ into equation (19) in order to obtain $Cu$ since the quantities $H_4Y$, $H_3Y$, $H_2Y$,
\[
\begin{align*}
\text{Cu} &= \frac{(\widetilde{\text{NH}}_{4}+\text{H}-\Delta)(1+\text{HK}_{B}+\text{H}^{2}\text{K}_{B}^{'}\text{K}_{C}^{'})}{2\text{H}^{2}\left[\frac{\Delta^{2}(1-\delta_{1}-\delta_{2})}{\text{NH}_{4}}+2\delta_{2}\Delta+\frac{\text{NH}+\delta_{2}^{2}}{(1-\delta_{1}-\delta_{2})}\right]} - \frac{\text{H}^{2}\text{K}_{4}^{'}\text{K}_{3}^{'}+\text{H}^{3}\text{K}_{4}^{'}\text{K}_{3}^{'}\text{K}_{2}^{'}}{\text{K}_{A}} - 1 \\
\text{Cu} &= \frac{(\widetilde{\text{NH}}_{4}+\text{H}-\Delta)(1+\text{HK}_{B}+\text{H}^{2}\text{K}_{B}^{'}\text{K}_{C}^{'})}{4+3\text{HK}_{B}^{'}+2\text{H}^{2}\text{K}_{B}^{'}\text{K}_{C}^{'} - 2\text{H}^{2}\text{K}_{4}^{'}\text{K}_{3}^{'}\text{K}_{2}^{'}} - \frac{\text{H}^{2}\text{K}_{4}^{'}\text{K}_{3}^{'}+\text{H}^{3}\text{K}_{4}^{'}\text{K}_{3}^{'}\text{K}_{2}^{'}}{\text{K}_{A}} - 1 \\
\frac{K_{E}^{1}}{K_{D}^{1}} &= \frac{\text{H}^{2}\frac{\text{NH}_{4}}{\Delta^{2}(1-\delta_{1}-\delta_{2})} + 2\delta_{2}\Delta + \frac{\text{NH}+\delta_{2}^{2}}{(1-\delta_{1}-\delta_{2})}}{\text{H}^{2}(1-\delta_{1}-\delta_{2})} - \frac{\text{H}^{2}\frac{1-\delta_{1}-\delta_{2}}{\text{NH}_{4}} + 2\delta_{1}}{\text{NH}_{4}-2\text{Y}_{T}-\Delta-2\text{Cu}}
\end{align*}
\]
HY, and Y are found to be so small that they have essentially no effect on the material balance for runs 15 and 16. For the same reason, the total copper concentration is essentially equal to the cupric-ion concentration plus the total EDTA concentration, and the second term in the numerators of equations (18) and (19) is essentially zero. The value of $\Delta$ is estimated using equations (14), (13), and $K^i_F$; and $S_1$ is estimated from equation (20). With the new values of $H - \Delta$ and $S_1$, the calculation is repeated until one gets the desired accuracy. Since the value of $K^i_F$ is not known, this calculation has not been performed.

**Neodymium Band**

The neodymium band can be treated in precisely the same way as the copper band has been treated except that the neodymium in the solution phase is laid down at the front edge of the band and replaces the copper band. In contrast, the solution phase of the copper band flows out the bottom of the column.

**Mass action equilibria**

Table 4 gives the equilibria which are thought to be of any consequence in the neodymium band. The same conventions are used in the neodymium band as were used on pages 24 and 26. For example, $\equiv_{Nd}$ represents the equivalents of neodymium.
Table 4. Mass action equilibria in the neodymium band

<table>
<thead>
<tr>
<th>$K'$</th>
<th>Definition</th>
<th>°C</th>
<th>Ionic strength</th>
<th>Log $K'$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_G'$</td>
<td>$\frac{NdY}{Nd \times Y}$</td>
<td>20</td>
<td>0.1</td>
<td>16.48</td>
<td>(35)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>0.019</td>
<td>17.36$^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.019</td>
<td>17.8$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.022</td>
<td>17.7$^c$</td>
<td></td>
</tr>
<tr>
<td>$K_H'$</td>
<td>$\frac{H \times NdY}{H \times NdY}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_I'$</td>
<td>$\frac{(NH_4)^3 \leq Nd}{Nd \leq 3 NH_4}$</td>
<td>25</td>
<td>0.1</td>
<td>2.374$^d$</td>
<td>(36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.019</td>
<td>2.394$^e$</td>
<td>(36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.022</td>
<td>2.300$^f$</td>
<td></td>
</tr>
<tr>
<td>$K_J'$</td>
<td>$\frac{H^3 \leq Nd}{Nd \leq 3 NH_4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Estimated by the Debye-Hückel Theory.

$^b$For $K_G'$, was calculated from the values of Nd, Y, and NdY which were obtained from the constants $K_1'$, $K_2'$, $K_3'$, $K_4'$, and the material balance equations for run 13.

$^c$For $K_G'$, was calculated from run 12 (see footnote b).

$^d$The equivalent fraction of the neodymium was the same as for run 13 (page 21).

$^e$The equivalent fraction of the neodymium was the same as for run 12 (page 21).

$^f$For $K_I'$, estimated for run 13 from the approach given on page 40.

$^g$For $K_I'$, estimated for run 12 from the approach given on page 40.
per equivalent of resin, and \( \text{Nd}Y \) represents the molar concentration of \( \text{Nd}Y^- \).

Although there are a number of other conventions, one could define the ion-exchange constant, \( K \), of the neodymium-ammonium exchange in the following way:

\[
K = \frac{\gamma_{\text{NH}_4}^3 (\text{NH}_4)^3 \overline{\gamma}_{\text{Nd}}}{\frac{\gamma_{\text{Nd}}}{\gamma_{\text{Nd}}^3} \gamma_{\text{NH}_4}^3} \tag{21}
\]

\[
K = K_1^1 \frac{\gamma_{\text{NH}_4}^3 \gamma_{\text{Nd}}}{\gamma_{\text{Nd}}^3} = K_1^1 \frac{\gamma_{\text{NH}_4 \text{Cl}}^6}{\gamma_{\text{NdCl}_3}^2} \frac{\gamma_{\text{Nd}}^3}{\gamma_{\text{NH}_4}^3} \tag{22}
\]

The \( \gamma \)'s are the activity coefficients of the corresponding symbols.

For low ionic strengths, one would predict by the argument given on page 3 that \( \overline{\gamma}_{\text{Nd}}/\overline{\gamma}_{\text{NH}_4}^3 \) may be mainly a function of the equivalent fraction of the neodymium on the resin, and relatively independent of the ionic strength of the solution phase. Therefore, \( \overline{\gamma}_{\text{Nd}}/\overline{\gamma}_{\text{NH}_4}^3 \) could be evaluated from the knowledge of \( K_1^1 \) as a function of the equivalent fraction of neodymium since \( K \) is a constant and \( \gamma_{\text{NH}_4 \text{Cl}}^6 \) and \( \gamma_{\text{NdCl}_3}^2 \) are mean activity coefficients which can be obtained from the literature (37, 38).

For the low ionic strengths, one might be able to correct an ion-exchange constant by the previous method which has been found to work for hydrogen and sodium but has not been tried for two ions of different charges.
Material balance equations

The equations (23), (24), and (25) are simply a statement that the whole is equal to the sum of the parts:

\[ N_{dT} = N_d + N_dY + HNdY \]  
\[ \tilde{Y}_T = N_dY + HNdY + H_4Y + H_3Y + H_2Y + HY \]  
\[ H_T = H + HNdY + 4H_4Y + 3H_3Y + 2H_2Y + HY. \]

The concentration of Y is so low that it has no effect on the material balance at the pH encountered in the neodymium band.

The concentration of EDTA in the neodymium band is the same as in the eluant; therefore, the number of equivalents of cations accompanying the EDTA is the same for both the neodymium band eluate and the eluant:

\[ NH_4 + 3Nd_T + H_T = \tilde{NH}_4 + \tilde{H}_T. \]

Charge balance equations

Since the net charges in the solution phase and the resin phase must be zero, the summation of the positive charges must equal the summation of the negative charges in both phases:

\[ \xi_{NH_4} + \xi_{Nd} + \xi_H = 1 \]  
\[ NH_4 + 3Nd + H = NdY + H_3Y + 2H_2Y + 3HY \]
Material balance at the boundary between the neodymium and the ammonium bands

One may assume that there is an ideal system for the neodymium band the same as the one for the copper band represented in Figure 2 except that $\xi_{\text{Nd}}$, $3\text{Nd}_T$, $S'_1$ and $S'_2$ are substituted for $\xi_{\text{Cu}}$, $2\text{Cu}_T$, $S_1$, and $S_2$, respectively. The resulting equation is as follows:

$$\frac{\text{NH}_4}{\xi_{\text{NH}_4} - S'_1} = \frac{3\text{Nd}_T}{\xi_{\text{Nd}}} = \frac{\Delta'}{\xi_{\text{H}} - S'_2} = \frac{\text{NH}_4}{1 - S'_1 - S'_2}$$

where $\Delta' = H_T - \text{H}'_T$.

(29)

For a band to maintain the same composition while the elution progresses, the same amount of material must leak into the lower boundary as leaks out of the upper boundary. If $S_1$ equivalents of ammonium leak from the copper bed into the bottom of the neodymium band per equivalent of band movement, then $S_1$ equivalents of ammonium must move out the top of the band or the neodymium band will change in composition. Thus, $S'_1$ must equal $S_1$ and $S'_2$ must equal $S_2$ or the neodymium band will change in composition.

If the equations (23) through (30) and the equilibria in Table 4 are solved in exactly the same manner as were the equations for the copper band, equations (31), (32), (33), (34), and (35) are obtained.

The solutions of $H$ and $\text{Nd}$ can be obtained by plotting $H$ versus $\text{Nd}$ for equations (31) and (33) and assuming that
\[ \text{Nd} = \frac{\frac{Y_T}{H_T} \left[ 4H^4 K_4^1 K_3^1 K_2^1 K_1^1 + 3H^3 K_4^1 K_3^1 K_2^1 + 2H^2 K_4^1 K_3^2 + HK_4 \right]}{K_G^1 + HK_H K_G^1 \left[ 1 - \frac{Y_T}{H_T + \Delta - H} \right]} - \frac{H^4 K_4^1 K_3^1 K_2^1 K_1^1 + H^3 K_4^1 K_3^1 K_2^1 + H^2 K_4^1 K_3^2 + HK_4}{K_G^1 + HK_H K_G^1 \left[ 1 - \frac{Y_T}{H_T + \Delta - H} \right]} \]  

\[ \text{Nd} = \frac{3H^3 (1 - \delta_1 - \delta_2) (1 - HK_H^1) (\bar{N}H_4^2 + H - \Delta^1)}{\Delta^1 3K_J^1 \left[ \frac{\Delta^1 (1 - \delta_1 - \delta_2)}{\bar{N}H_4^2} + \delta_2 \right]^3 - 3H^3 (1 - \delta_1 - \delta_2)} - \frac{H^3 K_4^1 K_3^1 K_2^1 + 2H^2 K_4^1 K_3^2 + 3HK_4}{K_G} \]  

\[ \text{Nd} = \frac{3\bar{N}H_4^2 (1 + HK_H^1) (\bar{N}H_4^2 + H - \Delta^1)}{K_1^1 \left[ 1 + (3\bar{N}H_4^2 - 2)\delta_1 - 2\delta_2 \right] - 3\bar{N}H_4^2} - \frac{H^3 K_4^1 K_3^1 K_2^1 + 2H^2 K_4^1 K_3^2 + HK_4}{K_G} \]  

\[ \text{Nd} = \frac{2 + HK_H^1}{2 + HK_H^1} \]
\[ K_{P2} = \frac{H^3 \left[ 1 + \frac{3NH_4}{NH_4} - 3\delta_1 - 3\delta_2 - 3NH_4(1-\delta_1-\delta_2) \right]}{\Delta'3NH_4 \left[ (\frac{\Delta'(1-\delta_1-\delta_2)}{NH_4} + \delta_2)^3 - 3H^3(1-\delta_1-\delta_2) \right]} \] (34)

The ammonium is related to \( \Delta' \), Nd, and H in the following manner:

\[ NH_4 = \tilde{NH}_4 - \Delta' - 3Nd - \frac{3Nd \left[ k_G' + HK_G'H'_1 \right] Y_T}{Nd \left[ k_G'H'_1 + H^4K_4'K_3'K_2'K_1' + H^3K_4'K_3'K_2'K_1' + H^2K_4'K_3'K_2'H'_1 \right]} \] (35)
$H - \Delta'$ is zero. The solutions for $H$ and Nd are given by the intersection of the two curves. The $\Delta'$ can then be estimated from equations (34) and (35). As in the case of the copper band, these calculations are repeated with the new value of $H - \Delta'$ until the desired accuracy is obtained. The concentrations of all of the ions can be estimated by substituting $H$ and Nd into the appropriate equations.

Since $\delta_1$ is an arbitrary constant in the boundary conditions of the copper band, there are the same number of independent equations as variables. However, it may not be possible for the corresponding $\delta$'s to be the same for the constraints of both the copper and neodymium bands. Thus, the neodymium band may be forced to take on the $\delta_1$ of the copper band.

In contrast to the copper band, the quantities $H_4Y$, $H_3Y$, and $H_2Y$ are big enough to affect the material balance in the neodymium band for runs 12 and 13. For this reason $K_G^1$ can be estimated from a knowledge of $K_1^1$, $K_2^1$, $K_3^1$, $K_4^1$, $K_5^1$, and the column data. This calculation is indicated on page 40. The value obtained for $K_G^1$ is compared with a value of $K_G^1$ determined by another method.


4. Gregor, H. P. ibid., 75, 3539 (1951)


8. Högfeldt, E. Arkiv Kemi, 5, 147 (1952)


26. Spedding, F. H., and Powell, J. E. ibid., 74, 856 (1952)
27. Spedding, F. H., and Powell, J. E. ibid., 74, 857 (1952)
