The Selective Elution of Metals Adsorbed on Cation-exchange Resins by Organic Solvents. Part I.

By N. F. KEMBER, PATRICIA J. MACDONALD, and R. A. WELLS.

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The use of organic solvents in admixture with mineral acids for the selective elution of cations adsorbed on the ion-exchange resin Zeo Karb 225 is investigated. By suitable control of water and acid added to the solvent, selective elution is obtained by using either ketones or alcohols. A procedure for the complete separation of copper and nickel using acetone containing 4% (v/v) of hydrochloric acid (*d* 1·18) and 10% (v/v) of water as eluting agent is described.

IN some cases a mixture of cations adsorbed on an ion-exchange resin can be selectively eluted by a procedure which utilises only the difference in affinity of the resin for each component of the mixture. More usually, however, an eluting agent capable of forming complexes with some or all of the adsorbed cations is used. The complexing agent is so chosen that the most strongly adsorbed metals are those which form the least stable complexes with the eluting agent. The differences in affinity are thus effectively enhanced and better separations result. Eluting agents of this type have usually been aqueous solutions to which complex-forming agents have been added, the best-known example being the use of buffered ammonium citrate solutions for the separation of the rare earths.

Burstall, Forrest, Kember, and Wells (*Ind. Eng. Chem.*, 1953, **45**, 1648) have shown that complex metal cyanides adsorbed on an anion exchanger can be effectively eluted with organic solvents containing mineral acids and that it is possible by suitable choice of solvent and mineral acid to obtain selective extraction of the metals. The present work explores further the possibility of using organic solvents containing mineral acids and water as complex-forming eluting agents for the separation of metals adsorbed on cation-exchange resins. Eluting agents of this type have been used extensively in partition chromatography on cellulose. Separations by paper chromatography, however, suffered from a number of limitations. If the mixture of cations to be separated is in a large volume of dilute solution a preliminary concentration is necessary to enable the solution of the mixture to be applied to the cellulose in small volume. The separation is often sensitive to the presence of interfering anions and removal of these may be imperative. Use of cation-exchange resins as adsorbents overcomes these two difficulties but the subsequent selective elution of the metals with aqueous eluting agents is often difficult or impossible.

It was considered that organic solvents containing mineral acids might be effective eluting agents for the removal of cations from ion exchangers for the following reasons: (1) The presence of mineral acid in the solvent would bring about some dissociation of the resin–cation complexes depending upon their relative affinities for the resin. (2) The cations produced by the dissociation would form in some cases complexes with the solvent whose movement down the column would be dependent upon the stability of the complexes with respect to both water and acid. (3) Two metals both forming suitable solvent-soluble complexes might be separated by a partition mechanism. This assumes that, at equilibrium, the concentration of water in the resin phase is greater than in the external solvent solution. It has been stated (Davies and Thomas, *J.*, 1952, 1607) that if acetone containing 30% of water is equilibrated with a 10% divinylbenzene cross-linked polystyrene resin in the hydrogen form, then the liquid in the resin phase has the composition 72% water, 28% acetone, and the outer liquid 75% acetone, 25% water. A similar type of distribution might be expected to occur with the solvents employed in the present work using the resin Zeo Karb 225. The covalent metal complex with the solvent would then be in contact with a predominantly aqueous phase in the resin. In these circumstances part of the complex would be extracted into the aqueous phase in the resin, where it would undergo dissociation to give metal ions capable of ion exchange with the resin.

The present paper is confined almost exclusively to a study of the elution of nickel and copper adsorbed on Zeo Karb 225. These two metals were chosen for study because of the difference in their solubility in organic solvents containing hydrochloric acid and because of the ease with which either could be determined. In further papers the study will be extended to include the separation of other metals and the use of resins other than Zeo Karb 225.

EXPERIMENTAL

(Percentages of acid and water are in terms of v/v, and hydrochloric acid was of *d* 1·18 where no other concentration is specified.)

In preliminary experiments, a study was made of the elution of zinc, cobalt, manganese, and nickel adsorbed on Zeo Karb 225 with acetone containing hydrochloric acid, and the elution of various mixtures of iron, copper, cobalt, manganese, and nickel with ethyl methyl ketone containing hydrochloric acid. Both groups of metals are given in the order in which they were eluted, the first mentioned being the most easily eluted. In both cases the order of elution is the same as that obtained in cellulose chromatography (Burstall, Davies, Linstead, and Wells, *J.*, 1950, 516). In neither case was complete separation obtained, but results were sufficiently promising to encourage further experiments on simpler mixtures. Attention was therefore directed to the separation of nickel and copper and a study was made of the elution of these metals with acetone containing hydrochloric acid and with a number of alcohols containing hydrochloric acid.

The need for conditioning the column became apparent during the preliminary experiments using as solvent ethyl methyl ketone containing hydrochloric acid. While the water content of the solvent was closely controlled, less control had been kept on the water both inside and outside the resin beads before elution was carried out. The interstitial water could be replaced by eluting the resin with a small volume of solvent not containing acid before elution with the acid-bearing solvent. This solvent would also tend to displace water from the resin beads and could therefore be expected to have an effect on the separation. A number of experiments was carried out to ascertain the effect of various conditioning procedures. A series of four pairs of columns 1 cm. in diameter, each containing 5 g. of the resin Zeo Karb 225 in the hydrogen form, was prepared. On to one of each pair were adsorbed 25 mg. of ferric ion and on to the other 25 mg. of cupric ion. Each column was then washed with 50 ml. of water and each pair of columns was subjected to different conditioning procedures. Through each column were passed 50 ml. of a conditioning solvent followed by 150 ml. of ethyl methyl ketone containing 9% of 1·5N-hydrochloric acid, this solvent giving normally a reasonable separation of iron from copper. The acid solvent eluate was collected in 50-ml. fractions and analysed (results in Table 1).

TABLE 1. *Conditioning of column.*

	Metal (%) eluted per 50-ml. fraction of COEtMe containing 9% of 1·5N-HCl							
	Copper fractions				Iron fractions			
Conditioning solvent	1	2	3	Total	1	2	3	Total
H_2O	0·17	0·28	0·36	0·81	83·6	14·0	1·2	98·8
COEtMe	33·2	0·38	0·13	33·7	93·5	2·6	2·8	98·3
COEtMe satd. with H_2O	0·12	0·09	0·05	0·26	66·5	29·2	1·1	96·8
COEtMe + 7·5% (v/v) H_2O	0·25	0·09	0·11	0·45	84·5	8·4	1·6	94·5

When the column was conditioned with dry ethyl methyl ketone the first fraction of eluting solvent contained a large amount of copper, but further fractions only small quantities. It appeared that the resin was first dehydrated by the passage of the dry ketone and that, when acid-bearing solvent was run down the column, water was extracted from the solvent by the resin. This resulted in the first part of the elution being carried out with a solvent of high acid but low water content which extracted copper. Once the resin attained equilibrium with the solvent the copper elution fell off rapidly. If the column was conditioned with water-saturated solvent, which in this case contained almost the same amount of water as the eluting solvent, only a small amount of copper was removed. Conditioning solvent containing slightly less water led to a small increase in the amount of copper eluted. Conditioning with water alone resulted in a steadily increasing quantity of copper appearing in the volume of solvent required for the elution of iron. In view of these results, in all further experiments the columns were conditioned by the passage of 25 ml. of the solvent identical with the eluting solvent except that the acid was replaced by an equal volume of water.

A standardised technique was developed for evaluating each solvent mixture. Columns about 15 cm. long and 1 cm. in diameter containing the equivalent of 5 g. of dry Zeo Karb 225 resin in the hydrogen form were used in all cases. The adsorption stage was carried out by passing through a column 50 ml. of a chloride solution of the metal under test containing about 8·5 mequiv. of the metal. The metal ion was adsorbed usually as a brightly coloured band on the top third of the column, which was then washed with 50 ml. of water. The column was treated with 25 ml. of conditioning solvent followed by 100 ml. of eluting solvent flowing at 50 ml. per hour. After elution the solvent was removed by evaporation and the metals determined. Copper was determined by electrolysis or colorimetrically with sodium diethyldithiocarbamate, and nickel by precipitation by dimethylglyoxime or colorimetrically with the same reagent. The columns were regenerated for re-use by elution with at least 200 ml. of 4N-hydrochloric acid and subsequently washing them with water until free from acid. The solvents were standardised by titration against N/10-sodium hydroxide. For the determination of trace quantities of nickel in eluates containing copper, a paper-chromatographic technique was used. The eluate was evaporated to dryness and the residue was redissolved in a small, measured volume of dilute hydrochloric acid. A 0·01-ml. aliquot part of the acid solution was applied to a strip of Whatman's No. 1 filter paper (CRL/1 pattern) and the chromatogram developed with acetone containing 5% of hydrochloric acid. The nickel was detected by spraying the strip with an alcoholic solution of rubeanic acid and estimated by comparison with a series of standard strips. It was possible to detect as little as 0·1 μg. of nickel in the presence of several mg. of copper.

Elution of Copper and Nickel with Acetone Solvents.—The first series of experiments were designed to determine the effect of variation in the hydrochloric acid and water content of the acetone eluting solvent on the extraction of copper and nickel. Aqueous solutions of nickel chloride containing approximately 5 g. of Ni/l. and of cupric chloride containing approximately 5·4 g. of Cu/l. were prepared. Portions of 50 ml. of these solutions contained approximately 8·5 mequiv. of the metal; thus the resin column was loaded to about one-third of its total capacity. This degree of loading was arbitrarily chosen. Later experiments on the effect of loading indicated that a 25% loading was the maximum for optimum separations. The eluting solvent was prepared by mixing together measured volumes of acetone, hydrochloric acid, and water and ignoring changes in volume. The results of a series of experiments carried out with three eluting solvents containing different acid concentrations are shown in Fig. 1 and Table 2. (A dash in all tables of results indicates that no determination was carried out at this level.)

TABLE 2. *Elution of nickel and copper with acetone*–HCl–H_2O *mixtures.*

		Metal (%) eluted in 100 ml.						
		Water (%) added to eluting solvent						
HCl (%) in eluting solvent	Metal	0	5	10	25	50	75	No ketone
3	Ni	Nil	—	—	Nil	Nil	0·1	1·3
	Cu	89·0	96·5	92·0	0·1	Nil	0·2	0·4
4	Ni	0·2	0·1	Nil	Nil	Nil	0·4	6·8
	Cu	90·4	99·0	98·9	20·2	0·1	1·2	13·6
5	Ni	0·9	—	—	Nil	0·2	7·7	34·0
	Cu	95·1	—	96·4	28·8	6·2	19·0	35·0

When the eluting solution consisted largely of acetone and acid, little or no nickel was eluted, but the amount of copper eluted was at a considerably higher level. Furthermore, this amount of copper is higher than would normally be eluted with an aqueous solution containing the same proportion of acid. The small amount of nickel eluted when the solvent consisted solely of acetone and concentrated hydrochloric acid was largely held back by addition of a small amount of water (up to 10% v/v) to the solvent. Furthermore, when this was done the rate of copper elution increased slightly. The quantity of both nickel and copper eluted was very small when roughly equal proportions of acetone and water were present in the eluting solvent. The mechanism of the extraction was emphasised by the colour changes which occurred. On adsorption, copper formed a dark blue band and nickel a dark green band at the top of the column. On elution with an acid acetone solvent containing little water, copper was extracted and formed a characteristic orange-brown coloured complex in the ketonic solvent. When it was eluted with a solvent in which the acetone was partially replaced by water, the intensity of the orange colour tended to fade, until, on elution with aqueous hydrochloric acid, the eluted copper solution had the characteristic green colour of aqueous copper chloride solutions. No comparable colour changes occurred with the nickel which, when eluted at all, was obtained in a solution having the normal green colour of aqueous nickel chloride solutions.

(a) *Complete elution of copper.* The results in Fig. 1 and Table 2 were all based on collecting 100 ml. of eluting solution. From previous experience it would be necessary to use a considerably larger volume of solvent to remove the last traces of the mobile metal from the columns. Further experiments were therefore carried out on selected solvents to ascertain the volume of solvent necessary to obtain 100% extraction of copper.

Elution with acetone containing 2—3% of hydrochloric acid showed that 800 ml. were necessary to remove all the copper from the column. From a study of the curves in Fig. 1 it appeared that acetone containing 4% of HCl and 10% of H_2O might be a more efficient eluting agent for copper, while at the same time nickel would remain adsorbed on the resin. Results obtained with this solvent are shown in Table 3 and indicate that only 400 ml. were required for complete elution of copper.

TABLE 3. *Elution of copper and nickel with acetone* + 4% *of* HCl + 10% *of* H_2O.

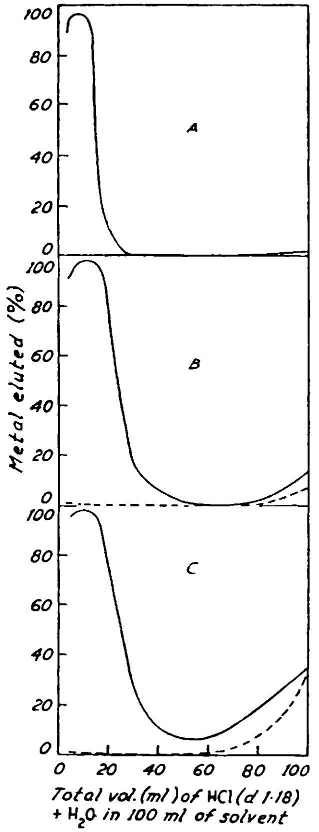
Solvent fraction (each of 50 ml.)	Copper eluted * Wt. (mg.)	Copper eluted * %	Nickel eluted * Wt. (mg.)	Nickel eluted * %
1	163·1	61·09	0·004	0·002
2	98·6	36·93	0·005	0·002
3	5·1	1·91	0·009	0·004
4	0·165	0·062	0·023	0·009
5	0·092	0·035	0·065	0·027
6	0·021	0·008	0·124	0·051
7	0·031	0·012	0·28	0·116
8	0·016	0·006	0·46	0·19
		Total 100·05		Total 0·401

* Solvents 0·494N (for Cu) and 0·488N (for Ni) with respect to acid.

About 99·9% of the copper was extracted in the first 150 ml. of the solvent; the remainder trailed very badly. Under similar conditions a small amount of nickel was eluted. The amount of nickel was possibly dependent on the total loading of the column and further experiments were carried out to ascertain the maximum loading at which a separation of copper and nickel adsorbed on the same column could be achieved.

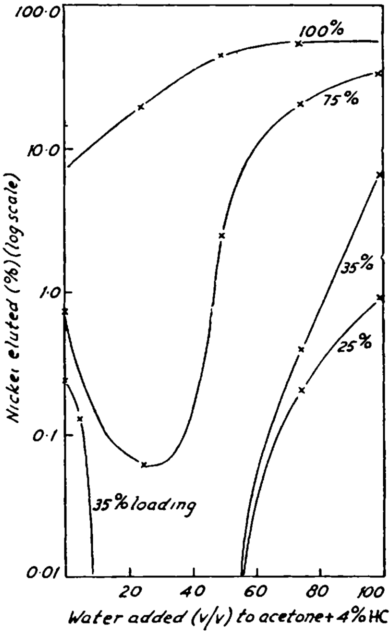
(b) *Effect of column loading on elution of nickel and copper.* In an initial experiment the capacity of the Zeo Karb 225 resin for nickel was found to be 4·82 mequiv./g. of dry resin. A series of experiments was then carried out in which 5-g. columns of resin were loaded to 25, 35, 50, 75, and 100% of their total capacity with nickel. The columns were eluted at each degree of loading with 100 ml. of acetone containing 4% of hydrochloric acid containing varying amounts of water. The results shown graphically in Fig. 2 indicate that the nickel eluted was negligible with a loading of 25% or less of the total capacity with the acetone containing 4% HCl solvent, providing the water added to the solvent was between 0 and 50%. In a check experiment in which 0·1938 g. of nickel was adsorbed on a 5-g. column of resin (equivalent to 27·4% loading) only 0·00001 g. of nickel was eluted with 400 ml. of acetone containing 4% of HCl and 10% of H_2O, and in a further similar experiment with a column loading of 25·1% no nickel was eluted with 400 ml. of solvent.

FIG. 1. *Elutions with acetone* + HCl + H_2O.



A, 3% HCl; *B*, 4% HCl; *C*, 5% HCl.
- - - - Ni; —— Cu.

FIG. 2. *Effect of loading on elution.* (% refer to loading.)



(c) *Separation of copper and nickel.* All elutions had so far been carried out with columns on which only one metal was adsorbed. Further experiments were carried out in which a mixture of nickel and copper was adsorbed on the resin. In all cases the total quantity of copper and nickel adsorbed on a column was equivalent to less than 35% of the total capacity of the resin and in all cases satisfactory recovery of copper was obtained by using 400 ml. of acetone containing 4% of hydrochloric acid and 10% of water (Table 4). When the amount of nickel present on the resin was greater than the amount of copper present, the separation was not quite complete if the total loading of the resin exceeded 25% of its capacity. When copper was in excess of nickel, a quantitative separation was achieved with resin loadings up to 35% of the total possible.

This was probably due to two causes: first, to the smaller quantity of nickel present, and secondly, to some reduction in the effective hydrochloric acid concentration in the solvent brought about by the use of hydrochloric acid to form the ketone-soluble copper chloride complex. The high copper figure obtained in the second experiment recorded in Table 4 was due to interference, by the trace of eluted nickel, in the colorimetric determination of the copper.

TABLE 4. *Separation of copper and nickel.*

Ni on resin (mg.)	Cu on resin (mg.)	Total column loading (%)	Nickel eluted: In 1st 200 ml. (mg.)	Nickel eluted: In 2nd 200 ml. (mg.)	Nickel eluted: Total (%)	Copper eluted: In 1st 200 ml. (mg.)	Copper eluted: In 2nd 200 ml. (mg.)	Copper eluted: Total (%)
242·3	Nil	34·3	0·04	0·93	0·40	—	—	—
242·3	0·245	34·3	0·06	0·62	0·28	0·30	trace	124·5
218·1	26·7	34·3	Nil	0·07	0·03	26·37	0·20	99·5
193·8	53·4	34·4	,,	0·01	0·005	53·1	0·34	100·1
193·8	Nil	27·4	,,	0·01	0·005	—	—	—
165·8	0·320	25·1 •	,,	Nil	Nil	0·318	0·026	107·5
121·2	133·5	34·5	,,	,,	,,	131·5	2·0	100·0
48·5	213·6	34·8	,,	,,	,,	212·9	0·17	99·8
24·2	240·3	34·8	,,	,,	,,	239·8	0·56	100·0
0·28	267·0	34·9	,,	,,	,,	266·4	0·60	100·0
Nil	267·0	34·9	,,	,,	,,	266·8	0·23	100·0

• Fresh batch of resin used with capacity of 4·50 mequiv./g.

TABLE 5. *Elution of nickel and copper with mixtures of alcohols with hydrochloric acid and water.*

Alcohol used	Vol. of HCl (ml.) added to prepare 100 ml. of eluting agent	Metal	Metal eluted (%): Vol. (ml.) of H_2O added to prepare 100 ml. of eluting agent: 0	5	10	25	50	75	No alcohol
MeOH	1	Ni	Nil	—	—	Nil	Nil	Nil	Nil
		Cu	11·5	—	—	,,	,,	,,	,,
	2	Ni	Nil	—	—	,,	,,	,,	,,
		Cu	58·6	—	—	,,	,,	,,	,,
	3	Ni	0·3	—	—	,,	,,	,,	1·3
		Cu	71·6	—	—	,,	,,	,,	0·4
	4	Ni	1·6	Nil	—	,,	,,	0·6	6·8
		Cu	82·9	40·0	—	,,	,,	0·6	13·6
	5	Ni	4·6	0·01	<0·01	,,	<0·01	6·3	29·2
		Cu	90·2	58·7	20·0	2·5	1·1	14·2	29·6
Pr^{i}OH	4	Ni	Nil	—	—	—	—	—	6·8
		Cu	18·9	—	—	—	—	—	13·6
	6	Ni	Nil	—	—	—	—	—	—
		Cu	34·6	—	—	—	—	—	—
	8	Ni	0·05	—	—	—	—	—	—
		Cu	48·1	—	—	—	—	—	—
	10	Ni	0·3	0·03	Nil	0·8	18·6	58·7	83·9
		Cu	52·2	66·9	69·4	47·3	55·3	81·7	90·2
Pr^{n}OH	10	Ni	1·8	—	—	—	—	—	83·9
		Cu	69·4	—	—	—	—	—	90·2
$C_5H_{11}OH$ ("AnalaR")	10	Ni	0·4	—	—	—	—	—	83·9
		Cu	85·5	—	—	—	—	—	90·2

(d) *Behaviour of other elements.* The behaviour of a number of other elements under the conditions used for the separation of copper and nickel was investigated. In each case 8·5 mequiv. of the metal in chloride solution were adsorbed on a 5-g. column of resin. The elution was carried out with 250 ml. of acetone containing 4% of HCl and 10% of H_2O. As is shown in Fig. 3, manganese was eluted very slowly and only 7% of the manganese present was removed with 250 ml. of solvent. Cobalt was eluted more rapidly but the total eluted was only 64%. The elution of iron was similar to that of copper initially but the tendency to trail was more marked; 99·6% of the iron was removed in 250 ml. of solvent.

Elution of Copper and Nickel with Alcohols.—The technique used was the same as that employed with the acetone solvent mixtures. It was noted in all experiments with alcohols that the eluted copper solution was a bright yellowish-green as opposed to the orange-brown solution obtained with ketones.

(a) *Elutions with methanol.* In a series of experiments a study was made of the effect of the concentration of hydrochloric acid and water added to the methanol. Results (Table 5) were similar to those obtained with acetone in that the rate of elution of copper and nickel increased as the acidity of the solvent increased but decreased sharply as water was added to the solvent. Unlike the results with acetone, no initial rise in the rate of elution of copper was obtained when up to 10% of water was added to the system. This tendency for the copper to be more efficiently eluted as the water concentration in the system was lowered, was further confirmed by an elution carried out with methanol containing dry hydrogen chloride in proportion equivalent to 2% of hydrochloric acid. This solvent eluted 71·7% of the copper compared with 58·6% eluted with methanol containing 2% of the acid. Results with the dry solvent for nickel elution were similar, and no nickel was eluted with methanol containing 1% or 2% of acid; 9·8% of the nickel was eluted with the methanol–dry hydrogen chloride mixture.

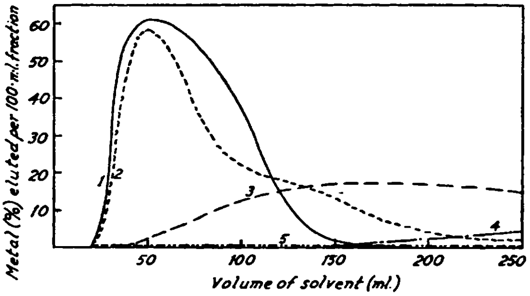


FIG. 3. *Elutions with acetone containing* 4% *of* HCl *and* 10% *of* H_2O.
—— Cu. - - - - Fe. — — Co. —·— Mn.
—··— Ni.

From these experiments it appeared that methanol containing 4% of hydrochloric acid and 5% of water would be a suitable solvent for the separation of copper and nickel, but attempts to use this solvent for the complete elution of copper proved impracticable. While 40% of the copper was removed in the first 100 ml. of solvent, the rate of elution subsequently fell off sharply and after the passage of 500 ml. only 75% of the copper was extracted (Fig. 5).

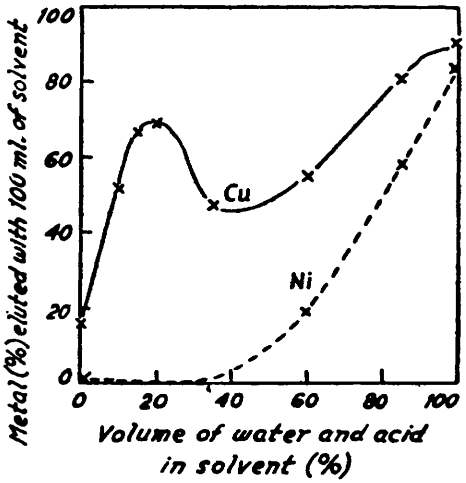
(b) *Elutions with* isopropanol. In elutions with *iso*propanol–hydrochloric acid the quantity of acid necessary for reasonable elution was, as expected, considerably greater than for acetone and methanol elutions (Table 5). *iso*Propanol behaved more like acetone than methanol in that the addition of small amounts of water increased the eluting power of the solvent, which subsequently decreased as further water was added. Results obtained with *iso*propanol containing 10% of acid and 10% of water are shown in Fig. 4. Unlike previous cases, the percentage of copper and nickel eluted in solvents in which most of the alcohol had been replaced by water, was higher than those in which the alcohol predominated, this effect being due to the larger quantity of hydrochloric acid present in the system. The tendency for the elution of copper to decrease as the water content of the solvent was reduced below 10% was confirmed by an elution carried out with *iso*propanol containing dry hydrogen equivalent to 10% of the acid, the elution of copper decreasing from 52·2% to 16·2%. In a similar experiment with nickel the quantity of eluted metal increased from 0·3% to 0·7%. It will be noted that the use of methanol or *iso*propanol containing dry hydrogen chloride led to an increase in the rate of elution of nickel. On the other hand, the rate of elution of copper was respectively increased and decreased with methanol and *iso*propanol each containing dry hydrogen chloride.

An attempt to use *iso*propanol containing 10% of acid and 10% of water for the complete elution of copper gave severe trailing, somewhat similar to that obtained when using methanol containing 4% of acid and 5% of water (Fig. 5). The total quantity of copper extracted was greater with the higher alcohol but trailing of the copper was sufficient to make use of this solvent impracticable.

(c) *Elutions with other alcohols.* Preliminary experiments were carried out on two other alcoholic solvents, *viz.*, *n*-propanol and pentyl alcohol, each containing 10% of acid. Results (included in Table 5) showed that the propanol solvent eluted copper more efficiently than did the *iso*propanol mixture containing the same amount of hydrochloric acid, but it also extracted a larger proportion of nickel. When compared with the *iso*propanol solvent, amyl alcohol containing 10% of acid eluted copper with a surprising efficiency, while causing only a small rise in the rate of nickel elution. This reversed the tendency shown with the lower alcohols for the rate of copper elution to decrease as the homologous series was ascended but this point requires further investigation since the pentyl alcohol used was " AnalaR " containing a mixture of *iso*- and active pentyl alcohols.

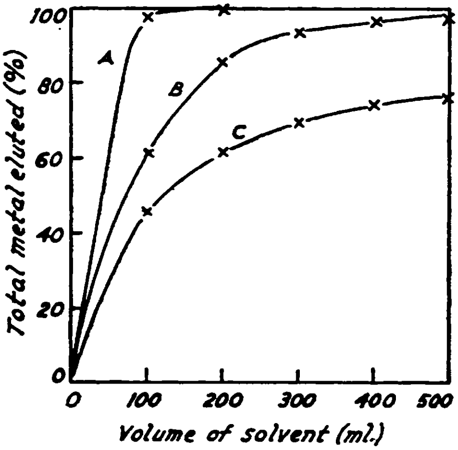
Discussion.—It has been shown that organic solvents containing water and mineral acid can be used for the selective elution of metals adsorbed on cation-exchange resins. Results obtained for the elution of copper and nickel adsorbed on the resin Zeo Karb 225 indicated that the use of acetone containing 4% of hydrochloric acid and 10% of water would provide the basis for an analytical separation of these metals. The large volume of solvent (400 ml. for a 5-g. column) required for the complete elution of copper would be a disadvantage, and the cause, together with means of preventing this trailing elution of copper, requires further investigation. It is suggested that the use of other resins, particularly those with a lower degree of cross-linking, might result in a decrease in the consumption of solvent. Although only the elution of nickel and copper has been studied in detail, preliminary experiments with other metals indicate that by suitable choice of solvent and control of added water and acid other separations would be possible.

FIG. 4. *Elutions with propan-2-ol containing 10% of* HCl *and* 10% *of* H_2O.



—— Cu. - - - - Ni.

FIG. 5. *Elution of copper with various solvents.*



A, Acetone containing 4% of HCl and 10% of H_2O.
B, Propan-2-ol ,, 10% ,, 10% ,,
C, Methanol ,, 4% ,, 5% ,,

The effect of variation in the acid and water content of the eluting solvent on the removal of copper and nickel was, in general, as expected. An increase in acid concentration in the solvent led invariably to a more rapid elution of both metals. The sharp decrease in the eluting powers of both the ketones and alcohols studied, when their water content was raised to more than 20%, was in agreement with the known instability of the solvent-soluble complexes of these metals to water. As the water content of the solvent approached 100%, the eluting powers of the mixture began to increase again as a result of the increased polarity of the solvent mixture. A point of special interest was the temporary increase in the rate of copper elution with acetone containing hydrochloric acid when the amount of added water was increased from zero to about 5%. A similar effect obtained with *iso*propanol indicated that with these solvents some water was necessary for the formation of the solvent-soluble complex. This was further emphasised by the very sharp decrease in the elution of copper when a mixture of *iso*propanol with dry hydrogen chloride gas was used as eluting agent. A similar effect was not observed with methanol; this is possibly due to the higher polarity of the solvent, with the possibility of methanol replacing water in the solvent-soluble complex.

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