Utilization of Ion Exchangers in Analytical Chemistry. XV

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In previous papers [1-4] the great applicability of cation exchange columns as analytical tools in separating quantitatively the cations of a solution from its anions has been demonstrated. During the last few years many similar applications of this technique have been described [5-18]. Summaries of what has been done so far in the field of ion exchange have been published recently [19-21].

In the present paper some questions of practical importance for this technique will be discussed, namely the influence of the particle size of the resin and the acidity of the solution upon the adsorption process, and the influence of particle size, regenerant concentration and some other factors upon the regeneration process.

Apparatus

The equipment now generally used in the laboratory for analytical purposes is an apparatus similar to that shown in Fig. 1 (A). This type of apparatus is chosen because it is important that air never enter the ion exchanger filter bed, since this would cause channelling, which would result in partial inactivation of the filter.

However, in the experiments presented in this paper another construction of the ion exchange column was used, Fig. 1 (B). The upper glass wool plug must be well packed, so that by means of the capillary forces of the liquid the air is prevented from entering into the filter. The resistance of the plug to the streaming liquid is not great compared to the resistance of the rest of the column. However this construction is possible only for rather short columns. The exit opening must not be more than about 15 cm below the upper glass wool plug.

In order to keep the flow-rate constant and equal from time to time, independent of the different resistances of the filter beds, the solution in question has been dropped into the column by means of a dosage capillary, Fig. 1 (B). The flow-rates have never been so great, that liquid has accumulated in the container of the column.
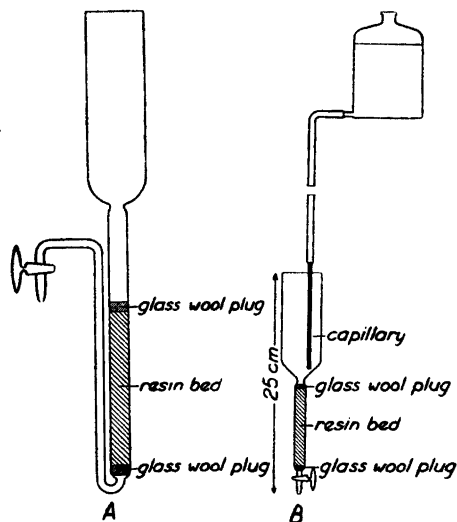
Fig. 1. Ion exchange columns.

Except for a few preparatory experiments the dimensions of the filter beds have been: height 95 mm, inner diameter 12 mm. The free volume of the column (that is the part of the column below the upper glass wool plug which is occupied by the liquid phase) has been 8 ml. The ion exchange resin used throughout this work has been Wofatit KS (except for the preparatory experiments).

ADSORPTION PROCESS

Influence of the particle size

The theory of adsorption of ions in ion exchange columns is similar to the theory of adsorption of gases by gas adsorption filters. If, for example, a solution of KNO_3 of the concentration $C = C_0$ passes through a vertical column of an H^+-charged ion exchanger, and the flow-rate is so slow that equilibrium between the ions of the solution and the ion exchanger is always attained, one might expect a sharp boundary in the solution. Above this boundary the K^+-concentration C should be C_0, and below it C should be $= 0$. The conditions for this ideal case, of course, should be that no channels would occur in the column so that the solution could penetrate uniformly over the whole area, that the static equilibrium in all parts of the filter is obtained, and that the diffusion in the free liquid volume could be neglected [2, 3].

According to this theory the composition of the effluent would suddenly change from $C_{K^+} = 0$ to $C_{K^+} = C_0$, when a certain amount of the solution has passed through the column. However, in practice many factors interfere,
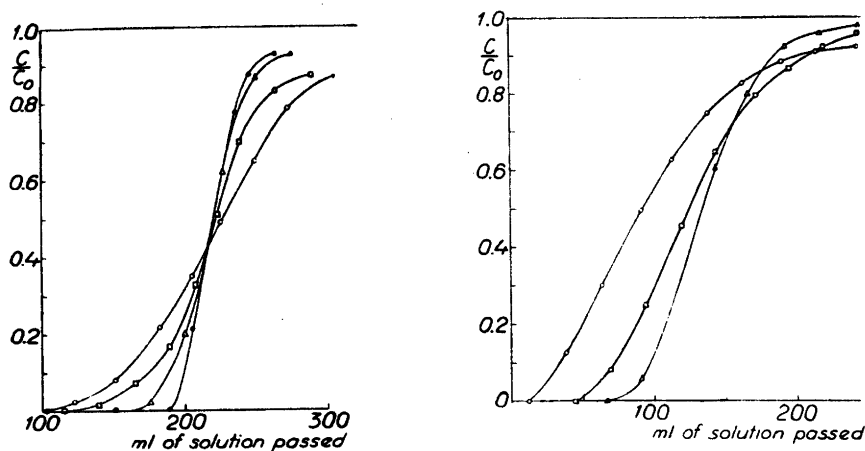
Figs. 2—3. Exchange isoplanes for Wofatit K resp. sulphite waste liquor resin.
Solution: 0.037 M KNO_3.

○   Particle size 2.0—1.0   mm
□   »   »   1.0—0.5   »
△   »   »   0.5—0.25 »
●   »   »   < 0.25   »

so that the results deviate very much from the theoretically expected ones. When the function C/C_0 is plotted against the time or the volume of the effluent, an S-like curve, usually called an exchange isoplane, is always obtained [2, 3]. The reason why the isoplanes are S-like is that the ideal conditions mentioned above are not fulfilled. When commercial ion exchangers are used the chief reason is that the diffusion in the capillaries of the resin is slow [22-24] and therefore the static equilibrium is not attained. The diffusion in the capillaries being rate-determining as equilibrium in ion exchange is approached, the particle size of the resin must have a great importance upon the dynamic equilibrium occurring in a filter bed [4].

In the preparatory experiments presented in this paragraph two different ion exchangers have been investigated, namely Wofatit K and an ion exchanger made by condensing sulphite waste liquor with furfural [25]. The exchange isoplanes were determined for solutions of KNO_3 passing through columns of different particle size. The height of the columns was in this special case 135 mm and the diameter 10 mm. The ion exchanger was first regenerated with hydrochloric acid and washed with water. A 0.037 M solution of KNO_3 was then passed through the filter with a flow-rate of 10 ml/min. The effluent was collected in small fractions and the percent conver-
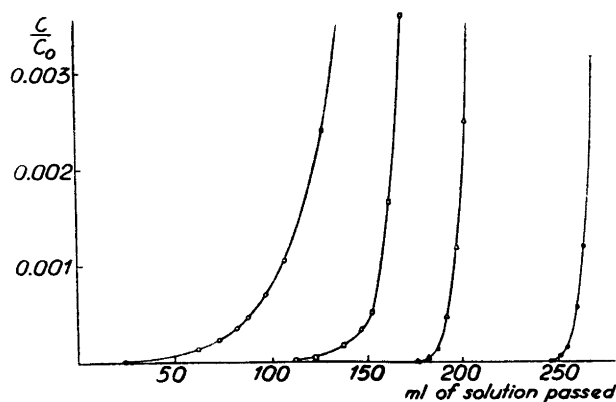
Fig. 4. Exchange isoplanes for Wofatit KS. Solution: 0.03 M FeCl₃.

O   *Particle size 1.0 — 0.6 mm*
□   »   »   0.6 — 0.4   »
△   »   »   0.4 — 0.2   »
●   »   »   0.2 — 0.1   »

sion was determined by titration with NaOH. The results are presented in Figs. 2 and 3, where C/C_0 is plotted against the volume of the solution passed through the filter columns.

For analytical purposes the lowest part of the curves are of the greatest interest. As a complement to the results shown, some determinations of these lower parts have been made with Wofatit KS and $FeCl_3$-solutions. In these experiments (and all the following) the dimensions of the columns were: height 95 mm and diameter 12 mm.

A freshly prepared solution of 0.03 M $FeCl_3$ was passed through the column at a constant flow-rate of 4.5 ml/min. The effluent was collected in fractions and the iron content determined colorimetrically with KSCN. The results are presented in Fig. 4, which shows only the lower parts of the exchange isoplanes. Especially in these experiments the great importance of using finely divided ion exchangers is demonstrated. The "break through capacity" of a column is very much increased as the size of the particles is diminished.

The results show that the greater the particle size, the more the curves deviate from the ideal shape. Where quantitative separation is desired, it is obviously of great importance to use relatively fine particles of the ion exchanger in the column.

When using ion exchangers for analytical purposes a particle size of 0.2 —0.4 mm diameter is the most suitable, as far as the adsorption cycle is con-

cerned. Finer particles should be separated because they diminish the flow-rate too much for most purposes. Even a relatively small amount of finely divided exchanger would considerably raise the resistance of the filter bed to the streaming liquid. In most cases greater particles should be avoided, partly because of their disadvantageous influence on the exchange isoplane, but above all because of their detrimental effect on the regeneration of the filter, even if only a small amount is present (as will be shown below).

In certain cases, where the time of operation does not matter it may be convenient to diminish the particle size, and in other cases, where a high filtering velocity is desirable, it may be suitable to raise the lower limit of the particle size.

Effect of the acidity of the solution

In many cases the solution to be analyzed contains hydrogen ions beside the ions to be removed by the ion exchanger. As examples may be mentioned phosphate analyses where a low pH is necessary in order to prevent precipitation[1 V], or sulphite waste liquor[5]. The presence of hydrogen ions decreases the break through capacity for the other cations. Therefore the higher the acidity the greater is the filter volume needed. For routine analyses it is recommended to find out in every special case the amount of ion exchanger that is necessary to obtain quantitative conversion at the acidity in question.

In order to facilitate the estimation of the amount of ion exchanger needed (or the maximum acidity allowable) in different cases, experiments have been made with solutions of KCl, $CuCl_2$ and $FeCl_3$ containing varying amounts of HCl.

The solutions were 0.05 N with respect to the metal salt (*i. e.* 0.05 M, $\frac{0.05}{2} M$ and $\frac{0.05}{3} M$ resp.) and, besides, 0, 0.05, 0.15 and 0.35 M with respect to HCl. They were filtered through an H^+-charged column of Wofatit KS (0.2—0.4 mm), and the effluents were collected in small fractions that were analyzed. The KCl-solutions were evaporated to complete dryness and the remaining KCl was titrated with $AgNO_3$ according to Mohr. Cu^{2+} was determined iodometrically in a biphthalate buffer solution. Fe^{3+} was determined by titration with $KMnO_4$ after reduction with $SnCl_2$.

The results are shown in Figs. 5—7 which show the adsorption isoplanes. From these diagrams it is seen that a quantitative separation can be performed by filtering even very acid salt solutions through H^+-charged filters. However, the break through capacity of the filter is diminished. In Table 1 the break through capacities are tabulated for different capacities of the salt solutions. The break through capacity is arbitrarily chosen as the point where
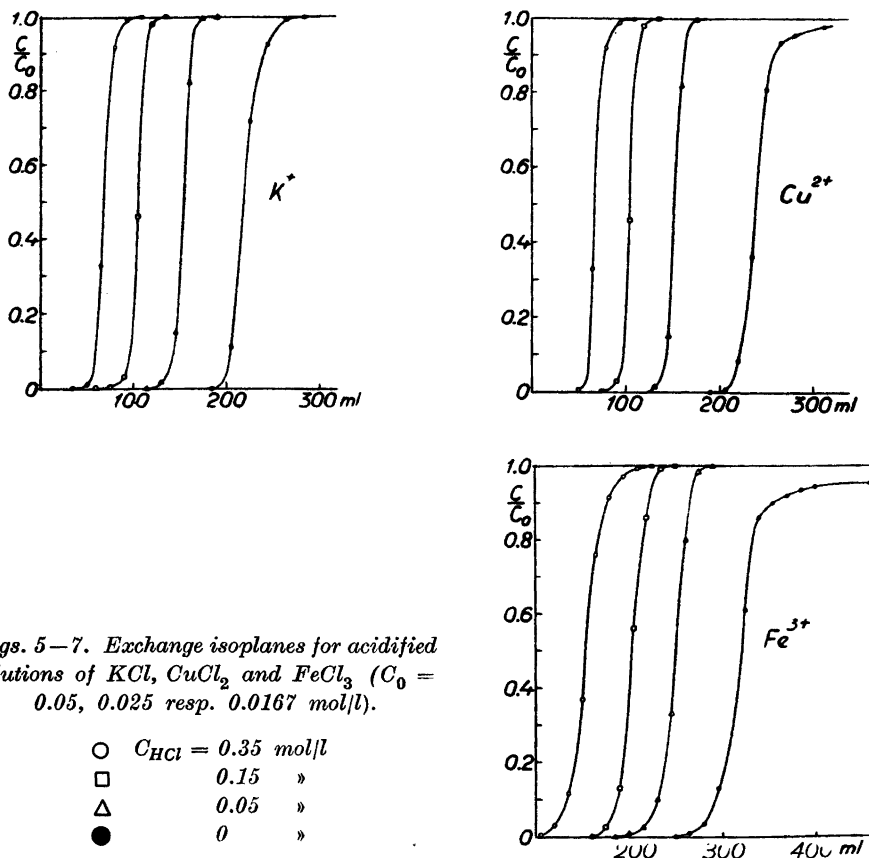
Figs. 5—7. Exchange isoplanes for acidified solutions of KCl, CuCl$_2$ and FeCl$_3$ (C$_0$ = 0.05, 0.025 resp. 0.0167 mol/l).

O	C$_{HCl}$ = 0.35 mol/l	
□	0.15	»
△	0.05	»
●	0	»

$\dfrac{C}{C_0}$ reaches 0.001. Also the capacities for $\dfrac{C}{C_0} = 0.5$ are tabulated in this table. A correction has been made for the free volume of the filter, 8 ml, which has been deducted from the values observed in Figs. 5—7.

In Table 1 the break through capacity is expressed in terms of mval of the the metal cation. As is seen the capacity for the metal cations is considerably decreased when the acidity of the solution is raised. If instead the capacity is expressed in terms of the total amount of cations in the solution, *i. e.* mval cation plus hydrogen ion, the capacities shown in Table 2 are obtained. It is seen that when calculating the capacity in this way it is found to be greater for the acidified solution than for the pure salt solution.

From these experiments the following very crude rule can be formulated: The separation will be quantitative if the amount of metal cations and hydrogen ions together does not exceed the capacity of the filter for a pure salt

Table 1. Capacity of filter column (in terms of mval of cations, H^+ not included).

Concn. of HCl (mol/l)		0	0.05	0.15	0.35
At $\frac{C}{C_0} = 0.50$	KCl	10.5	7.3	4.9	3.0
	CuCl$_2$	11.5	7.2	4.8	2.9
	FeCl$_3$	15.6	12.1	9.8	7.3
"Break through capacity" $\frac{C}{C_0} = 0.001$	KCl	8.8	5.4	2.9	1.6
	CuCl$_2$	9.5	5.3	3.3	1.8
	FeCl$_3$	12.1	9.1	7.6	4.8

solution. This rule may be of interest especially for the analyst not familiar with the ion exchange method. It may fail (Li^+, see below), but mostly it leads to overdimensioned filters.

The results are in accordance with previously published data. H^+ is known to have the least affinity for this kind of ion exchanger of all cations (except for Li^+ [2]). From this observation and from the Donnan equation governing the ion exchange equilibrium, it is also to be expected that the lower the acidity of the solution and the higher the valency of the metal cation, the greater is the total amount of metal cations that may be taken up by the filter without any leakage.

It may also be mentioned here that the amount of ion exchanger that is necessary for complete removal of polyvalent cations in presence of H^+ or other monovalent cations may be decreased (or the break through capacity of a filter may be increased) simply by diluting the solution with water [4].

Table 2. Capacity of filter column (in terms of mval of cations, H^+ included).

Concn. of HCl (mol/l)		0	0.05	0.15	0.35
At $\frac{C}{C_0} = 0.50$	KCl	10.5	14.5	19.6	24.0
	CuCl$_2$	11.5	14.4	19.2	23.2
	FeCl$_3$	15.6	24.2	39.0	58.0
"Break through capacity" $\frac{C}{C_0} = 0.001$	KCl	8.8	10.8	11.6	12.8
	CuCl$_2$	9.5	10.6	13.2	14.4
	FeCl$_3$	12.1	18.2	30.4	38.0

REGENERATION PROCESS

For analytical purposes one generally works with H^+-charged cation exchangers, and the regeneration is made with an acid. Hydrochloric acid is generally chosen as a regenerant, because it has several advantages: it is a strong acid, it is cheap (even in very pure qualities), it is easy to evaporate and does not oxidize the ion exchanger (nitric acid does, even when rather dilute). Ordinarily other regenerants are used only if the system contains ions giving insoluble chlorides.

A systematic work on the regeneration of cation exchange columns for analytical purposes does not seem to have been published as yet. In the following, investigations concerning regeneration of ion exchange columns with hydrochloric acid will be described. The effect of the particle size of the ion exchanger, the concentration of the acid, the flow-rate of the acid and the time between adsorption and regeneration have been studied. As a complement, some experiments concerning the static ion exchange equilibria in the presence of relatively high concentrations of hydrochloric acid have been performed.

E f f e c t   o f   t h e   p a r t i c l e   s i z e

In order to study the effect of the particle size on regeneration the exchanger was partially transformed into the Fe^{3+}-form (Fe^{3+}-charged) by passing 100 ml of a solution of 0.03 M $FeCl_3$ through the previously H^+-charged columns and washing afterwards with water. Then 5 M HCl was passed through the filter, the flow-rate being kept at 4.5 ml/min. The effluent was collected in fractions and evaporated. The iron content was determined by titration with $KMnO_4$ after reduction with $SnCl_2$.

The titrations of different fractions from one experiment have been made in the right order in a big Erlenmeyer flask without pouring out the successively collected liquid from time to time. In this way the accumulated titration errors have been diminished. The fractions corresponding to 95 — 100 % regeneration have been analyzed in a separate series (with smaller titration volumes) because of the greater requirements for accuracy. This method of titration has been used throughout this section (except for the experiments concerning static ion exchange equilibria).

The results are presented in Fig. 8, where the integral per cent regeneration of the columns is plotted against the volume of 5 M HCl used.

The experiments show, that the volume of acid necessary for the regeneration of the column increases very much when the particle size of the ion exchanger is increased. Using a smaller size means a saving of regeneration acid as well as of time. As mentioned in the preceding chapter, however, too small particle sizes should ordinarily be avoided. In all the following experiments we have used Wofatit KS with the particle size 0.2—0.4 mm, which seems to be most suitable for ordinary analytical purposes.

Fig. 8. Regeneration of Fe^{3+}-charged ion exchange column. Regenerant: 5 M HCl.

O   Particle size 0.1—0.2 mm
☐   »   »   0.2—0.4 »
△   »   »   0.4—0.6 »
●   »   »   0.6—1.0 »
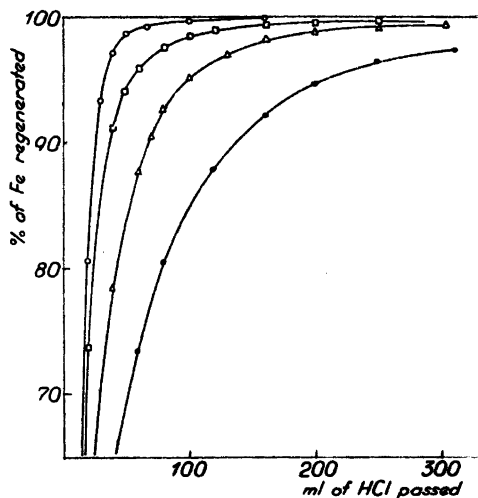
Effect of the concentration of the acid

Experiments have been made with cation exchangers partially transformed into the K^+-, Cu^{2+}-, Al^{3+}- and Fe^{3+}-form resp., which have been regenerated with hydrochloric acid of varying concentration.

100 ml of a 0.09 N salt solution (0.09 M KCl, 0.045 M $CuCl_2$, 0.03 M $AlCl_3$ or 0.03 M $FeCl_3$ respectively) was percolated through the column, and after washing with water the regeneration was started. Hydrochloric acid was passed through the column at a constant flow-rate. The effluent was collected in small fractions (5 or 10 ml, in certain cases, more), and after evaporation to dryness the fractions were analyzed. The experiments have been repeated with varying concentrations of the acid. The analyses were made as earlier described. Al^{3+} was precipitated and weighed as hydroxyquinolate. As a control, the precipitate in certain cases (small amounts) was dissolved and titrated with bromate.

Tables 3—8 contain the percentage of the originally adsorbed ions found in the eluate, tabulated as a function of the eluate volume and the concentration of the hydrochloric acid used. To these tables correspond curves similar to Fig. 8. They are, however, not reproduced here. With the help of these curves, it is easy to determine the volume of a certain regenerant that will be necessary to give a desired efficiency of regeneration. In Figs. 9—12 the volumes thus found are plotted as functions of the hydrochloric acid concentration at 90, 95, 98, 99, 99.5 and 99.8 % regeneration. The results correspond to the flow-rate 4.5 ml/min.

Table 3. Regeneration of K+-charged ion exchange column. The figures express the completeness (in %) of the regeneration as a function of the volume and concentration of the hydrochloric acid used. Flow-rate 4.5 ml/min.

Concn. (mol/1):	1.09	2.17	3.12	4.41	5.47	6.61	7.75	9.88	12.3
Volume (ml)									
10	14.3	36.6	46.2	57.0	58.0	—	64.9	62.1	57.0
15	54.3	76.5	84.8	89.6	90.1	92.0	90.1	82.0	73.0
20	73.0	89.8	95.0	97.0	97.3	97.8	95.7	91.0	83.7
25	83.3	95.3	98.2	99.1	99.3	99.2	98.8	96.7	92.1
30	89.1	97.6	99.3	99.7	99.8	99.7	99.5	98.8	96.3
35	92.8	98.9	—	99.9	100	99.8	99.8	99.5	97.8
40	95.2	99.6	99.8	100		100	99.9	99.8	98.5
50	97.9	99.8	100				100	99.9	99.2
60	99.1	100						100	99.6
80	99.9								99.9
100	100								100

These diagrams show that for the cations studied the regeneration can be performed with a minimum volume of the regenerant if a certain optimum concentration of the acid is chosen. This optimum concentration is about 3 to 4 M HCl, and is about the same for all of the ions examined. The effect is greater at the greater flow-rate and less at the lower flow-rate, and it is most obvious in the case of Fe^{3+}. It is evident, that when using a too strong solu-

Table 4. Regeneration of Cu2+-charged ion exchange column. The figures express the completeness (in %) of the regeneration as a function of the volume and concentration of the hydrochloric acid used. Flow-rate: 4.5 ml/min.

Concn. (mol/1):	1.09	2.17	3.12	4.41	5.47	6.61	9.88	12.3
Volume (ml)								
10	19.0	39.3	—	55.4	57.0	57.0	54.4	49.5
15	45.1	72.3	79.6	81.0	82.5	79.6	—	65.0
20	63.2	85.4	89.5	90.8	90.9	89.2	82.2	73.4
25	74.5	92.0	94.4	95.2	95.4	94.0	—	80.2
30	81.5	95.4	96.9	97.5	97.4	96.5	92.5	84.1
35	87.0	97.4	98.3	98.6	98.5	97.9	—	87.4
40	90.0	98.5	99.0	99.2	99.2	98.7	96.0	99.8
50	94.6	99.4	99.7	99.8	99.7	99.5	98.0	93.2
60	97.0	99.8	99.9	99.9	99.9	99.9	98.9	95.7
80	99.0	100	100	100	100	100	99.8	99.0

Table 5. Regeneration of Al^{3+}-charged ion exchange column. The figures express the completeness (in %) of the regeneration as a function of the volume and concentration of the hydrochloric acid used. Flow-rate: 4.5 ml/min.

Concn. (mol/l):	1.09	2.17	3.12	5.47	7.75	9.88
Volume (ml)						
20	49.2	66.6	73.7	73.8	69.9	65.2
30	—	78.0	84.7	84.7	81.3	76.0
40	70.1	86.8	90.3	90.2	87.5	82.6
60	80.7	93.3	95.4	95.3	93.7	90.0
80	86.7	96.4	97.6	97.6	96.4	93.9
100	90.6	98.0	98.6	98.5	97.8	96.0
150	95.9	99.4	99.5	99.5	99.2	98.2
200	98.1	99.7	99.8	99.7	99.5	99.0

tion of hydrochloric acid it will be practically impossible to elute Fe^{3+} quantitatively. This is a fact, which, if not observed, may cause considerable errors and discredit the use of ion exchange columns for analytical purposes.

A comparison between the results at the two flow-rates shows the influence of the flow-rate upon the regeneration, as will be shown more clearly by the experiments described below.

Table 6. Regeneration of Fe^{3+}-charged ion exchange column. The figures express the completeness (in %) of the regeneration as a function of the volume and concentration of the hydrochloric acid used. Flow-rate: 4.5 ml/min.

Concn. (mol/l):	1.09	2.17	3.12	4.41	5.47	6.61	7.75	9.88	12.3
Volume (ml)									
10	0.9	21.3	40.6	38.6	—	—	—	35.3	29.0
20	23.3	68.2	73.0	76.2	69.6	66.2	54.0	45.0	39.2
30	41.7	82.5	86.0	87.8	83.0	79.4	—	55.5	47.5
40	56.3	90.3	91.8	93.4	89.8	85.9	73.9	62.5	54.0
50	65.0	94.2	95.0	96.4	93.5	89.8	79.4	66.8	59.3
60	71.3	—	97.0	97.5	95.8	92.5	83.4	70.8	63.0
70	76.1	97.3	—	—	—	—	—	—	—
80	80.0	97.9	98.5	98.9	97.6	95.3	87.6	76.6	69.7
100	85.0	98.7	99.2	99.4	98.7	96.8	90.5	80.1	74.5
150	92.0	99.4	99.7	99.8	99.6	98.5	94.4	85.6	81.0
200	95.1	99.5	99.9	99.9	99.8	99.1	96.0 .	89.0	85.7
250							97.1	91.0	

Table 7. Regeneration of Cu^{2+}-charged ion exchange column. The figures express the completeness (in %) of the regeneration as a function of the volume and concentration of the hydrochloric acid used. Flow-rate: 0.8 ml/min.

| Concn. (mol/1):	2.17	3.12	4.41	6.61	7.75	9.88	12.3
Volume (ml)							
10	55.0	71.2	85.5	85.6	85.7	85.0	85.2
15	95.8	99.6	99.7	99.4	99.6	99.3	97.8
20	99.7	100	100	100	100	99.9	99.4
25	100					100	99.8
30							99.9

Table 8. Regeneration of Fe^{3+}-charged ion exchange column. The figures express the completeness (in %) of the regeneration as a function of the volume and concentration of the hydrochloric acid used. Flow-rate: 0.8 ml/min.

Concn. (mol/1):	2.17	3.12	4.41	6.61
Volume (ml)				
10	32.8	48.5	59.1	66.5
15	78.8	88.8	92.5	87.6
20	92.1	96.7	98.0	94.2
25	96.5	98.9	99.3	96.8
30	98.4	99.4	99.7	98.0
40	99.6	99.9	99.8	98.7
50	99.9	100	99.9	99.0
60	100		100	99.4
75				99.7
100				99.8

Effect of the flow-rate

These investigations have been performed with ion exchangers partially transformed into the Cu^{2+}- and Fe^{3+}-form resp., which have been regenerated with 3.3 M HCl at different flow-rates. Fractions were taken at one or two minute intervals, and the time was measured from the moment the acid began to flow out from the dosage capillary into the column. In Figs. 13 and 14 the regeneration efficiency is plotted as a function of the time required for regeneration.

The regeneration curves for the different flow-rates have nearly the same shape. The chief difference is their varying displacement along the time axis. This is due to the free volume of the filter, which was about 8 ml. It takes some
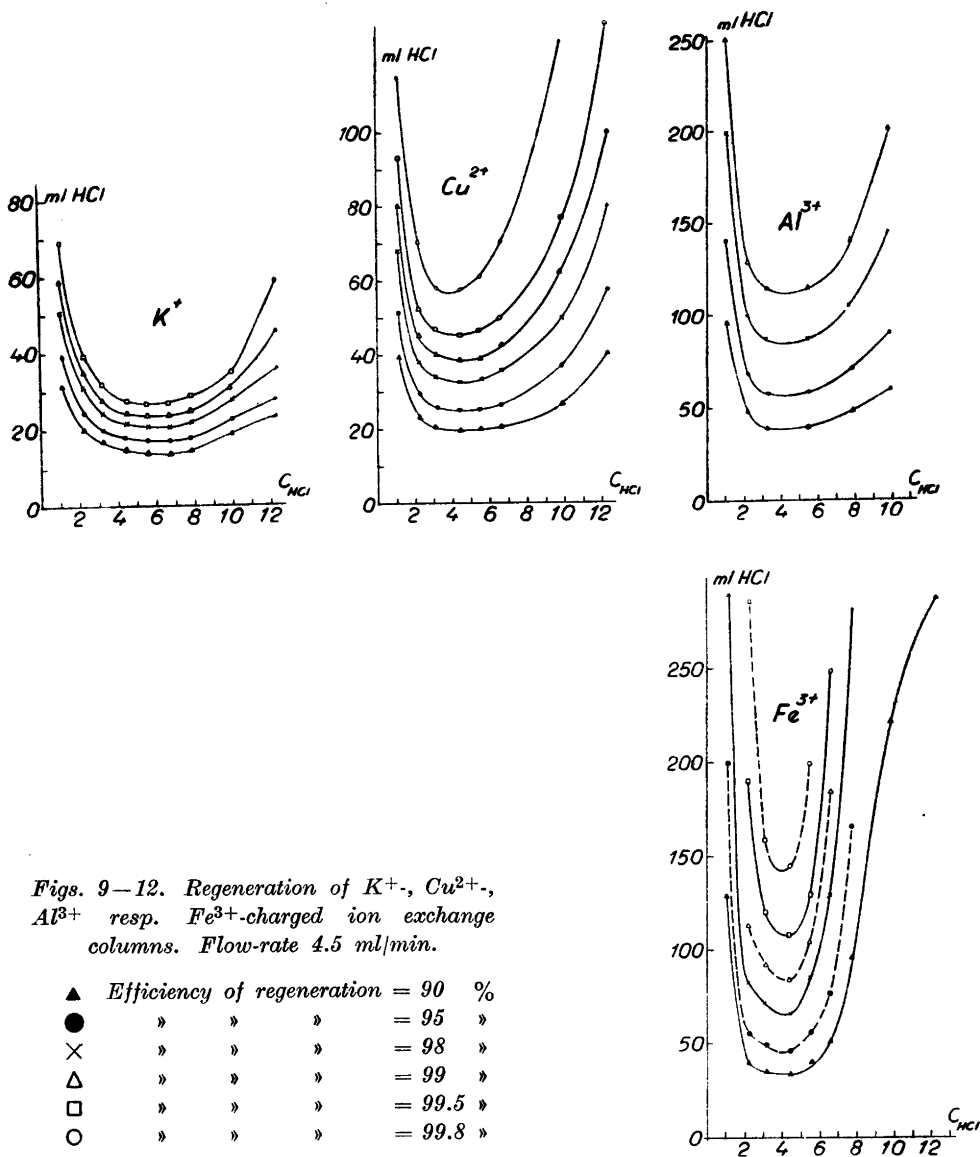
Figs. 9—12. Regeneration of K^+-, Cu^{2+}-, Al^{3+} resp. Fe^{3+}-charged ion exchange columns. Flow-rate 4.5 ml/min.

▲   Efficiency of regeneration = 90   %
●   »   »   »   = 95   »
×   »   »   »   = 98   »
△   »   »   »   = 99   »
□   »   »   »   = 99.5 »
○   »   »   »   = 99.8 »

time before the regenerant has reached all parts of the filter column and the regeneration process is started all over the column, and this start time is different for the different flow-rates. If the curves are corrected with respect to this time they will all very nearly coincide.
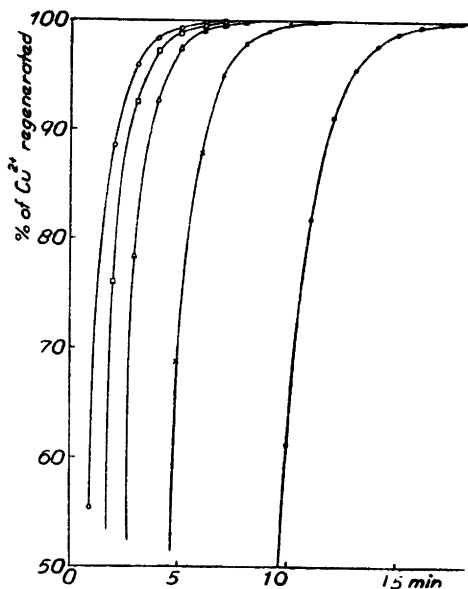
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Fig. 13. Regeneration of Cu^{2+}-charged ion exchange column. Regenerant 3.3 M HCl.

O	*Flow-rate*	*11*	*ml/min*	
□	»	»	*6.6*	»
△	»	»	*4.0*	»
×	»	»	*2.2*	»
●	»	»	*0.95*	»
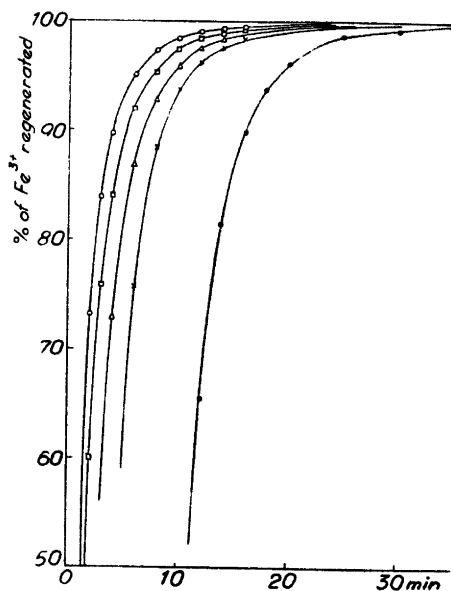
Fig. 14. Regeneration of Fe^{3+}-charged ion exchange column. Regenerant 3.3 M HCl.

O	*Flow-rate*	*13*	*ml/min*	
□	»	»	*7.8*	»
△	»	»	*4.0*	»
×	»	»	*2.2*	»
●	»	»	*0.95*	»

The experiments show that, within wide limits, variation of the flow-rate of the regenerant has very little influence upon the speed of the regeneration. It is the time of the regeneration process that determines the efficiency, not the flow-rate nor the volume of acid used. For example the regeneration of the Fe^{3+}-charged filter takes about 30 minutes, independent of the flow-rate (except for very low flow-rates, of course). It is of no value to try to hasten the regeneration by increasing the flow-rate over a certain value. For example, from Fig. 14 it is seen that if the flow-rate of the regenerant is raised from 2.2 to 13 ml/min, the only effect will be an increase of the volume of the effluent from 70 to 350 ml. The efficiency of the regeneration will not be increased, nor will the result be achieved in a shorter time (except for the difference in start time: 4 min).

It may be mentioned that, for a study of the kinetics of the regeneration process, it would be better to let the regenerant pass through the column from

below. Avoiding convection streaming due to the greater specific gravity of the acid in this way, would make the conditions more ideal [4]. However the purpose of these investigations has been to examine the regeneration process under the conditions ordinarily used in laboratory work. When as small volumes as possible are desirable, back wash regeneration may be used even for analytical purposes.

Effect of time between adsorption and regeneration

In all the preceding experiments the regeneration was started within 15 to 30 minutes after the filter had been charged with the metal ion in question. However it was of interest to determine if the regeneration process would be slower if the filter was allowed to stand charged for a long time before the regeneration. In one experiment the filter was not regenerated until 20 days had passed from the charging with Fe^{3+}-ions. The regenerant was 3.3 M HCl and the flow-rate was 4.0 ml/min. The results are presented in Table 9 (experiment A). This table also contains the values from a corresponding experiment (B), in which the regeneration was started within 15 minutes after charging. As seen from the table the time between the adsorption and regeneration has only a slight influence upon the regeneration process.

Table 9. Regeneration of Fe^{3+}-charged ion exchange column.

Regeneration time (min)	Efficiency of regeneration (in %)	
	A	B
2	17.9	19.0
3	57.9	56.0
4	74.1	72.4
6	87.5	87.0
8	93.3	92.9
10	95.4	96.0
12	97.7	97.5
14	98.5	98.4
16	99.0	99.1
20	99.5	99.4
25	99.7	99.7
30	99.8	99.8

Experiments   concerning   the   static   ion   exchange
equilibria

Earlier investigations with strongly swollen ion exchangers [3] have shown that the Donnan equation can be used for quantitative calculations of ion exchange equilibria. The measurements were carried out in dilute solutions of univalent cations. As the concentrations of the micellar solution were fairly low, it was possible to neglect the activity coefficients in the micellar as well as in the outside solution. Wofatit KS, however, like all slightly swelling ion exchangers now commercially available and used for industrial and analytical purposes, has a very high concentration of the micellar solution, and consequently the activity coefficients cannot be neglected. As no reliable means of calculating them exists, the exchange equilibrium must be studied empirically. A great number of measurements concerning dilute solutions have appeared. As far as the equilibria in concentrated solutions are concerned no systematic measurements have been published.

In order to elucidate the regeneration process, some measurements of static ion exchange equilibria will be described. The experiments were made with solutions of chlorides of K^+, Cu^{2+}, Al^{3+}, Cr^{3+} or Fe^{3+} respectively, and in each case with a large excess of hydrochloric acid. The composition of the solutions obviously corresponds to the conditions of regeneration of an ion exchange column with hydrochloric acid.

The experiments were made as follows:

A large amount of air dry ion exchanger in the hydrogen form was prepared and stored in a bottle with a close-fitting stopper. It had an exchange capacity of 2.39 mval/g as determined in separate experiments through charging until saturation with K^+-, Cu^{2+}- and Al^{3+}-ions and analyzing.

10.00 ml of a solution of KCl (or $CuCl_2$, $AlCl_3$ or $FeCl_3$ resp.), containing 4.78 mval of cations was pipetted out into each of nine 125 ml Erlenmeyer flasks with ground glass stoppers, and the solutions were evaporated to dryness. 2.00 g of air dry H^+-charged ion exchanger were then put into the dry flasks and 50.00 ml of hydrochloric acid in the concentrations shown in Table 10 were added with a pipet. The flasks were then closed and shaken several times a day, and after five days 25.00 ml of the liquid was pipetted out of each flask for analysis, which was made according to the methods previously described. The chromium experiments were made in a somewhat different way (see below). Chromium was determined iodometrically after oxidation to chromate with hot concentrated perchloric acid.

As mentioned above, each series of experiments comprised (as a rule) 9 different concentrations of the acid. Reference measurements have been made, firstly where 10.00 ml of the metal-salt solution in question has been analyzed for the metal directly, and secondly where 10.00 ml has been pipetted out in an Erlenmeyer flask and evaporated; 50.00 ml of hydrochloric acid (of the two concentrations 3 M and 10 M) has been added,

Table 10. Regeneration equilibrium.

Concn. of hydrochloric acid added (mol/l)	1.09	2.17	3.12	4.41	5.47	6.61	7.75	9.88	12.3
K$^+$	82.6	—	91.8	—	95.0	95.8	96.1	96.8	98.0
Cu^{2+}	85.8	97.0	99.2	99.6	99.6	99.8	99.7	99.7	99.6
Fe^{3+}	78.0	95.8	98.8	99.8	100.0	98.8	95.8	89.7	81.5
Al^{3+}	49.2	93.6	96.7	98.4	98.3	98.6	98.7	99.7	—
Cr^{3+}	69.4	89.4	95.6	98.5	100.1	99.7	99.9	100.0	100.1

and so on, completely corresponding to the main determinations except for the absence of the ion exchanger. These two ways of reference measurements have given results that very closely agree.

In the Al^{3+}-series no determinations were made with concentrated hydrochloric acid, because AlCl$_3$ is rather insoluble in it. In the Cr^{3+}-series it was found impossible to dissolve the evaporation residue in cold hydrochloric acid. Therefore these experiments were made so that 40.00 ml of hydrochloric acid of different concentrations and 10.00 ml of a solution of CrCl$_3$ in water (containing 4.78 mval) were added to an Erlenmeyer flask containing 2.00 g of the H$^+$-charged ion exchanger.

A summary of the results is presented in Table 10, where the percentage of metal cation found in the solution at equilibrium is given. As is seen from the measurements, Fe^{3+} deviates in behavior from the other ions and from what might be expected from the Donnan equation. According to this equation a higher concentration of the acid should perform a more complete regeneration, and that is also the case for the ions K$^+$, Cu^{2+}, Al^{3+} and Cr^{3+}.

As far as Fe^{3+} is concerned, the existence of a maximum value of the static regeneration equilibrium at a certain concentration of the acid seems to be difficult to explain from the facts collected here. The tendency of Fe^{3+} to form complexes with chloride ions should favour the regeneration at high acid concentration. Further experiments are needed in order to explain this anomaly.

It might seem preferable in these experiments to analyze the ion exchanger instead of the solution. This is not possible, however, as was shown in orientating experiments (not presented here). After separation of the ion exchanger from the bulk of the solution by means of a small glass filter funnel, the adhering solution must be washed away with distilled water. The very short period during which the concentration of ions in the acid solution around the ion exchanger is thus sinking towards zero is long enough to make possible a considerable rearrangement of ions.

Orientating experiments have also shown that the volume of water that is taken up by the ion exchanger in the swelling process has only a negligible influence upon the measurements. For 1 M acid the correction volume is found to be 0.50 ml, but at the higher concentrations which are of more interest in this connection the corrections are practically immeasurable. Other measurements have shown that the position of the equilibrium was exactly the same after 1 day as after 5 days and that the same results were obtained even when the equilibrium was approached from different sides (*i. e.* from H^+-charged and from Fe^{3+}-charged ion exchanger).

DISCUSSION

The experiments presented in this paper confirm the earlier known fact that the rate of adsorption of ions is mainly determined by the rate of diffusion in the capillaries of the particles of the ion exchanger. It is also evident that this diffusion process is the rate determining factor in the regeneration process. This will explain the great influence of the particle size upon the speed of adsorption and regeneration as well as it explains the fact that within wide limits it is the time of regeneration that is essential for efficiency and not the amount of acid used.

The experiments with varying concentrations of the acid in regenerating filter columns gave the somewhat unexpected result that the use of a moderately concentrated acid (3 to 4 M HCl) gave a maximum speed of regeneration. When using more concentrated acid the regeneration is slower, as is also the case when more dilute acid is used.

Earlier works on the swelling of ion exchangers, containing sulphonic acid groups [3] have shown that the swelling is greatest in pure water, and that the higher the concentration of the electrolytes in the solution, the more the ion exchangers shrink. The optimum effect now obtained in the regeneration experiments may be explained by the shrinkage of the ion exchanger due to the increasing concentration of the acid. This shrinkage is accompanied by a diminished diffusion velocity of the ions in the capillaries of the ion exchanger. The increasing viscosity of the more concentrated acids has an influence in the same direction. At a certain point these effects predominate over the favourable effects of increasing acid concentration which are observed at lower concentrations and which are generally due to a displacement of the ion exchange equilibrium. As far as Fe^{3+} is concerned, the static regeneration equilibrium explains the extremely pronounced optimum found in the dynamic regeneration curves.

One would perhaps believe that ions that have been kept adsorbed for a very long time would be difficult to elute from the resin because they would have had time to diffuse deep into very narrow and unapproachable capil-

laries. However any effect in this direction has not been observed for the resin examined.

From the present investigations it is possible to draw the following conclusions of how to regenerate an ion exchange column. The particle size should ordinarily be 0.2—0.4 mm. Greater and smaller particles should be removed. As regenerant should be used 3 to 4 M HCl. The regeneration may start by passing acid through the column at a fairly high flow-rate so that the acid will penetrate the whole filter column. Then the flow-rate is preferably diminished to low values — with the filter dimensions here used 1 to 2ml/min — until the regeneration is complete, which will take 5 to 30 minutes, depending upon the cation in question.

The flow-rates are more conveniently expressed in terms of ml per minute per ml of ion exchanger, this being applicable to filters of different dimensions. The recommended values of regeneration conditions then are: Start flow-rate about 1 ml per minute per ml of ion exchanger, followed by a flow-rate of about 0.1 to 0.2 ml per minute per ml of ion exchanger.

SUMMARY

Some questions of practical importance for the ion exchange technique described in earlier papers have been investigated. The effect of the particle size is shown, and an optimal size is recommended. The ion exchange is shown to be quantitative even for rather acid solutions. The conditions for regeneration of the ion exchange column with hydrochloric acid have been studied. A maximum speed of regeneration is obtained for a regenerant concentration of 3 to 4 mol/l and it is shown that the time of regeneration is ordinarily a more important factor than the amount of regenerant used. It is further shown to be especially important in the case of Fe^{3+} to follow the directions of regeneration given.

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