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Cation Exchange Separation of Traces of Metals from Iron

I. Study of the Conditions for Separation

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A detailed study was made of the separation of Ag, Co, Cu, Mg, Mn, Ni, Pb, and Zn on the cation exchange resin Dowex 50WX8 from large amounts of iron in dilute solutions of hydrofluoric acid. The influence on the adsorption of factors such as the concentration of iron, presence of ammonium, nitrate, and chloride, and degree of loading was investigated. A special study was made of the dissolution of metallic iron samples. It was possible to separate all the elements mentioned from at least 10 g of iron using only 3 g of the resin. The adsorbed elements were eluted as a group with 4 N HNO_3. The eluate contained less than 0.1 mg of iron.

In an earlier paper [1] it was shown that Fe(III) is only weakly adsorbed by the cation exchange resin Dowex 50WX8 and the anion exchange resin Dowex 1X8 in solutions containing 1 N HF and 0.1 N HNO_3 or H_2SO_4. However, many other elements are strongly adsorbed by one resin or the other. This is of special interest in the analysis of traces of metals in iron and steel, but it might also be useful in the separation of alloying elements in ferrous products.

Similar systems containing 1 N HF have been used for anion exchange separation of some elements from iron and Dixon and Headridge [2] determined low percentages of Mo, Nb, Ti, and W in steel samples using a similar method. The cation exchange separation of traces of several elements from synthetic iron solutions has been reported in a preliminary communication by Danielsson.[3] In this paper the separation step is studied in some detail and some problems associated with analysis of metallic samples are considered.

The elements covered in this investigation are Ag, Co, Cu, Mg, Mn, Ni, Pb, and Zn, which were found to be strongly adsorbed in hydrofluoric acid solutions.[1] In the following these are sometimes referred to as trace elements. Cadmium was also found to be strongly adsorbed but was considered to be of minor importance in steel analysis.

EXPERIMENTAL

Experimental details of the batch and elution methods for determination of weight distribution coefficients, D, have been described earlier.[1,4]

Resins and columns. The cation exchange resin Dowex 50WX8, H^+-form, 100—200 mesh, was used. When not otherwise stated this mesh size was also used in the elution experiments, since one of the main purposes was to study the practical applicability of the method. The capacity for the dry resin was 5.00 mequiv./g.

Acrylic plastic columns [3] (internal diameter 9.5 mm) with a resin support of plastic wool (Dynel Wool, Union Carbide Corp.) were used.

Reagents and solutions. Reagent grade chemicals were used. Plastic ware (polyethylene and Teflon) was used when hydrofluoric acid was present in the solutions.

Some of the solutions of Fe(III) used in the adsorption studies were prepared from $FeF_3 \cdot 2H_2O$ (Hopkin & Williams, code 4856). These solutions were afterwards filtered and purified by cation exchange. Otherwise these solutions were prepared in the following way: $Fe(NO_3)_3 \cdot 9\ H_2O$ (Merck p.a.) was dissolved in dilute nitric acid, the solution evaporated with concentrated HF and taken to dryness. The precipitated ferric fluoride was dissolved in a certain amount of HF of desired concentration. The solution was then purified by cation exchange. In all preparations of ferric fluoride the concentration of Fe(III) was determined by titration or colorimetry, and when necessary nitrate and ammonium were also determined. Small differences in the D-values of adsorbed elements were observed (generally less than 5 %) using different preparations of the iron solutions, but the method was considered to give conditions sufficiently well defined. In the study of a particular separation factor the same preparation was used throughout or different preparations were mixed in advance.

It must be clearly stated that the fluoride solutions mentioned later contain beside Fe(III) and HF an amount of fluoride equivalent to give FeF_3.

RESULTS AND DISCUSSION

Dissolution of metallic iron samples

Certain problems occurred when dissolving large amounts of iron which necessitated some initial experiments. The object was to dissolve up to 10 g of iron or mild steel in a reasonable time and to treat the solutions to obtain reproducible conditions suitable for separation. An insoluble residue, containing elements to be determined, would complicate the procedure and lead to introduction of certain amounts of alkali ions in the fusion step.

The most straightforward method, to dissolve the sample in concentrated HF, is tedious and several grams of iron remain undissolved as a result of some form of passivation. Addition of HNO_3 at intervals or the use of a mixture of HNO_3 and HF was suitable in practice. Complete oxidation to Fe(III) and break-down of the carbides were affected by boiling and generally clear solutions were obtained. It was found, however, that these solutions contained considerable amounts of ammonium formed by reduction of nitric acid by metallic iron. (Table 1, No. 1). It is known that such reduction also takes place in acidic solutions and under special conditions a nearly quantitative reduction of nitric acid by iron may even be possible.[5] In steel analysis the presence of ammonium ions is generally harmless but in the present case the separation was seriously impaired and the eluates also needed special treatment when optical emission spectrography was used.

The results of some of the dissolution experiments are given in Table 1. 10 g portions of a Swedish standard steel JK 2B (Composition: 0.2 % C,

Table 1. Total amounts of NH_4 in the final solutions after dissolving 10 g portions of a carbon steel (JK 2B) in various acids. All solutions were taken to complete dryness afterwards and the residue dissolved in 250 ml of 1 N HF. Concentrated acids were used (for HF 40 %).

Sample No.	10 g of 2B dissolved in	Additions and further treatment before evaporation	NH_4 total mmoles
1	100 ml HF + 25 ml HNO_3	—	6, 11, 13, 15
2	100 ml HF	ox. with 25 ml HNO_3	2.1, 3.3
3	75 ml HNO_3	50 ml HF	0.70 *
4	100 ml HNO_3	50 ml HF	0.4, 0.5
5	75 ml HNO_3 + 75 ml H_2O	50 ml HF	2.6, 2.5
6	75 ml HNO_3 + 100 ml H_2O	50 ml HF	5.7, 5.4
7	75 ml HNO_3 + 3 ml HF	50 ml HF	1.4, 1.4
8	75 ml HNO_3 + 10 ml HF	40 ml HF	1.5, 1.4, 1.2
9	75 ml HNO_3 + 25 ml HF	25 ml HF	2.4, 2.6
10	75 ml HNO_3 + 50 ml HF	—	10.0, 9.2
11	50 ml HNO_3 + 50 ml HF	—	10.2, 10.8
12	75 ml HNO_3	10 ml HCl, boil, 50 ml HF	0.10, 0.04
13	100 ml HNO_3	10 ml HCl, boil, 50 ml HF	0.15, 0.22
14	75 ml HNO_3	10 ml HCl + 50 ml HF	0.15, 0.25
15	100 ml HNO_3	10 ml HCl + 50 ml HF	0.10, 0.06
16	75 ml HNO_3 + 10 ml HCl	50 ml HF	0.10, 0.29

* Mean value of 12 determinations.

0.3 % Si, 0.5 % Mn, 0.004 % P, 0.02 % S, 0.2 % Cu, 0.007 % N) were dissolved in various acids in Teflon beakers. The temperature was kept near the boiling point. All procedures gave clear solutions and with the exception of No. 2 the samples were dissolved rapidly.

As a result nitric acid was preferred to hydrofluoric acid for dissolving the samples. Dilution of HNO_3 with H_2O or HF had a deleterious effect (Nos. 5—6 and 7—11) resulting in an increased amount of NH_4. In many cases, however, it was necessary to add HF before complete solution since some grains of iron were rendered passive in conc. HNO_3. Addition of HCl before evaporation had a positive effect, as was expected (Nos. 12—15). In the HNO_3—HCl mixture (No. 16) about 1 mmole of NH_4 was formed during dissolution and the main effect was due to oxidation of NH_4 during evaporation. Several experiments, not reported here, were carried out with mixtures of HNO_3—HCl and HNO_3—HCl—HF. Rapid dissolution and NH_4 amounts < 0.3 mmoles were obtained, but these procedures often gave reaction products which adhered to the beakers and were difficult to dissolve. Spectrographic analysis showed no enrichment of particular elements in this residue.

One way to avoid complications from the formation of ammonium is, of course, to use an oxidizing agent other than nitric acid. Several experiments were carried out using hydrogen peroxide (30 %) added at intervals during dissolving the samples in HF. They were successful for 1—2 g portions of iron and mild steels, but for larger amounts complete oxidation to Fe(III) was not easily obtained, causing a risk of failure in the separation step. The samples

were dissolved slowly at the end and considerable quantities of H_2O_2 were needed. Because of that the use of HNO_3 afterwards to complete the oxidation to Fe(III) was not studied.

It is essential for a successful separation that as much as possible of the HNO_3 and HCl used is removed during the evaporation to dryness. Analyses of several solutions showed that rather low concentrations in the final solutions of 250 ml of 1 N HF were easily obtained in this way. The concentration of NO_3 was nearly always below 0.01 M, 0.03 M being the highest value obtained. The concentration of Cl never exceeded 0.01 M.

The adsorption step

Generally, only low concentrations of metal ions are involved in adsorption studies and these have a negligible influence on the composition of the solutions studied. It was clearly not possible to maintain a low and fixed concentration of adsorbable ions in the solutions with the large amounts of iron involved in the present work. However, as described in the experimental section, care was taken to ensure uniformity by close control of the preparation of the solutions.

Most experiments were carried out using cobalt as the adsorbable element in the study of factors affecting the adsorption. Cobalt takes an intermediate position in adsorbability and is easily determined even in small amounts by colorimetry using Nitroso-R-salt.

Effect of concentration of HF. The adsorption of the trace elements of interest here increases rapidly when the acid concentration decreases at least as long as no complexation or hydrolysis takes place. It is therefore essential to use a low acidity but, according to earlier results,[1] the concentration of HF must not be allowed to decrease much below 1 N since that would cause adsorption of large amounts of iron ($D_{Fe(III)} = 102$ in 0.1 N HF—0.1 N HNO_3, 5.85 in 0.5 N HF, 1.85 in 1 N HF and 0.7 in 2 N HF).

If the iron concentration is raised to amounts suitable for trace analysis the values of $D_{Fe(III)}$ in 1 N HF decrease regularly with increasing concentration of Fe(III) (Table 2). However, the loading rises to 16 % at 38.7 mg Fe/ml,

Table 2. Values of D_{Fe} in 1 N HF at different concentrations of Fe(III). Resin: Dowex 50WX8, 100—200 mesh. Elution method.

mg Fe/ml	0	9.4	19.8	28.9	38.7
$D_{Fe(III)}$	1.85	1.65	1.42	1.23	1.16

assuming that the adsorbed ions are univalent. A special elution technique was used in this study. The iron solutions were passed through a column containing 2 g of Dowex 50WX8 until equilibrium was reached. The iron content in the resin bed was then eluted with 4 N HNO_3 and determined making allowance for the iron in the interstitial volume. This volume was determined by elution of a small amount of HCl with 1 N HF.

The results were considered entirely satisfactory and at this stage no further experiments were carried out at different concentrations of hydrofluoric acid.

Effect of concentration of Fe(III). It was obvious that the adsorption of the trace elements should be influenced by the high ionic strength of the solutions as well as the presence of adsorbed Fe(III). This was studied at various concentrations of Fe(III) using the batch equilibrium method. Values of D_{Co} were determined in solutions of Fe(III) containing 1 N HF, 0.002 M NO_3, and 0.005 M Co. Cobalt was separated in the equilibrated solutions by cation exchange before determination. The results are shown in Table 3. Allowance was made for the minor concentration changes of Fe(III) that occurred when hydrogen ions were exchanged for Fe(III).

Table 3. Values of D_{Co} in 1 N HF containing different concentrations of Fe(III). Resin: Dowex 50WX8. Batch method.

mg Fe/ml	D_{Co}			D_{Co} Mean value
0	6500	6600	—	6550
9.1	2350	2390	2480	2407
18.2	1165	1165	1158	1163
27.5	720	—	707	714
32.1	—	553	567	560
36.8	468	453	468	463
41.5	407	400	407	405
46.4	353	351	354	353

It can be seen that D_{Co} decreased rapidly from *ca.* 6500 in solutions free of iron to *ca.* 350 at 46.4 mg Fe/ml. However, at all concentrations of Fe(III) studied, separation of Co from large quantities of iron should be easily achieved. A rough estimation of the relative effectiveness at different concentrations of Fe(III) is given by the product: $D_{Co} \times$ conc. of Fe(III). Table 4 shows an

Table 4. Estimation of the volume necessary for elution of 1 % of the amount of Co added at different concentrations of Fe(III), $V_{1\%}$, using 3 g of Dowex 50WX8, 100—200 mesh, and the amount of iron present in that volume. *Cf.* text.

mg Fe/ml	$V_{1\%\,Co}$ ml	g Fe equiv. to $V_{1\%\,Co}$
0	15130	—
9.1	5560	51
18.2	2690	49
27.5	1650	45
32.1	1295	42
36.8	1070	39
41.5	935	39
46.4	815	38

approximate evaluation of the amount of iron that could be passed through a 3 g column of Dowex 50WX8, 100—200 mesh, until 1 % of the total amount of cobalt is eluted. It is based on an estimate that the column has 100 theoretical plates and an ideal elution curve is assumed. In this case the formula $V_{1\%}/V_{max} \approx 1-2.33 \times N^{-\frac{1}{2}}$, cited from Ringbom,[6] where N is the number of theoretical plates, gives $V_{1\%\,Co} \approx 0.77 \times V_{max\,Co}$. According to the results given, separation is possible from as much as 38—51 g of iron. In practice these values are affected by several factors. The necessity to wash out the adsorbed iron leads to a decrease and the fact that the trace element is added continuously to the column leads to an increase.

A somewhat higher effectiveness was evidently attained at lower concentrations of iron but for practical reasons it was decided to use solutions with 35—45 mg Fe/ml. At a low concentration an inconveniently large volume of solution is required for a given amount of iron and in solutions containing *ca.* 50 mg Fe/ml a slight precipitate of ferric fluoride sometimes formed showing this concentration to be near the limit of solubility.

Effect of concentration of NH_4, NO_3, and Cl. The adsorption of Co was studied using the batch method at different concentrations of ammonium, nitrate, and chloride, since these ions might be present after dissolving the samples. Ammonium was added as ammonium fluoride, the other ions as Fe(III) salts to solutions containing 38.8 mg Fe/ml, 0.005 M Co and 1 N HF. Adsorption of Fe(III) reduced the concentration to 36.9 mg Fe/ml at equilibrium. The results are given in Table 5.

Table 5. Effect of NH_4, NO_3, and Cl on the adsorption of Co in 1 N HF containing 36.9 mg Fe/ml. Resin: Dowex 50WX8. Batch method.

M NO_3		D_{Co}			D_{Co} Mean value
0		488	491	485	488
0.050		403	401	402	402
0.100		324	331	329	328
M Cl					
0.050		394	390	390	391
0.100		—	316	314	315
M NH_4					
added	correc.				
0.025	0.011	408	405	412	408
0.050	0.021	385	385	385	385
0.100	0.042	311	314	296	307

In all cases Co was held less strongly with increasing concentration of all the ions. Ammonium had the largest effect as might be expected. Separate elution experiments gave $D_{NH_4} = 29.7$ at 40.5 mg Fe/ml and the results given are corrected for the adsorption of ammonium. Nitrate and chloride are not adsorbed and their influence is probably due to effects on the acidity of the solutions.

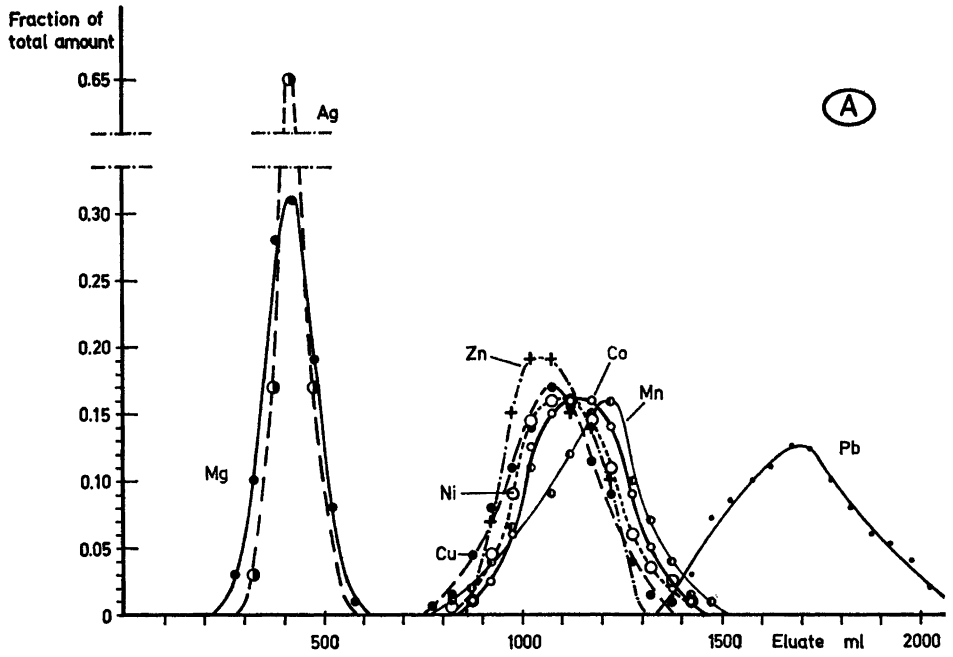


Fig. 1. Elution curves for the trace elements. 0.1 mg each of Ag, Mg, Zn, Cu, Ni, C o, Mn, and Pb eluted from a column (diam. 9.5 mm) of 2.59 g Dowex 50WX8, 100—200 mesh, with two different eluents.

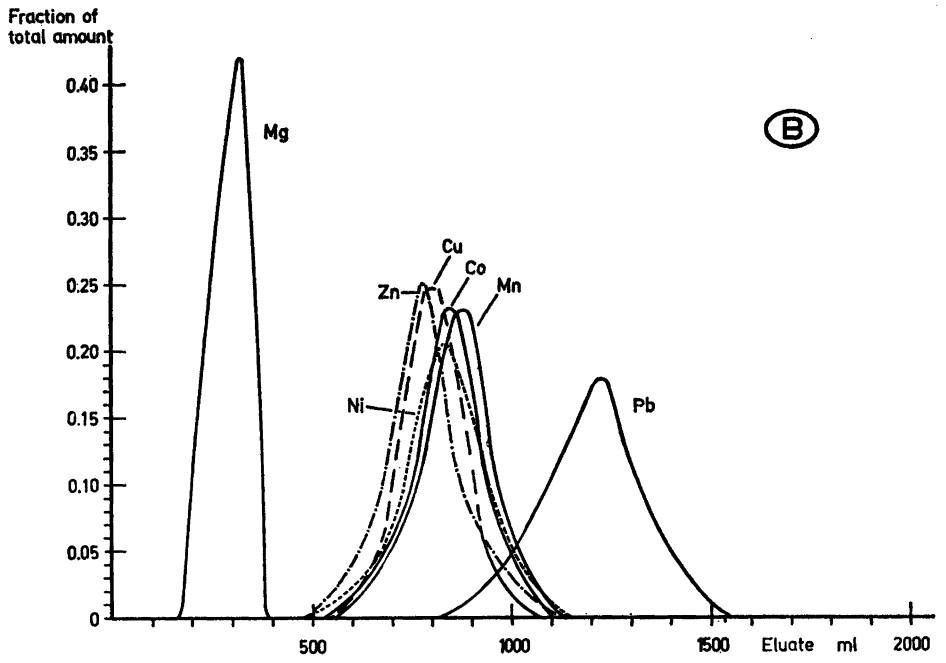
The effect of chloride on the adsorption of Zn was also studied. It was supposed that this effect would be larger due to complexation. At these concentrations, however, such an increased effect was not observed: $D_{Zn} = 452$ (0 M Cl), 387 (0.025 M Cl), 351 (0.050 M Cl), and 285 (0.100 M Cl).

It is obvious that the concentration of these ions must be kept as low as possible. The presence of ammonium causes additional problems. These are considered under the heading Elution.

When steel samples are dissolved under oxidizing conditions certain amounts of sulphuric acid and phosphoric acid are formed. However, the percentages of S and P are generally low and this effect on the separation was not studied.

Effect of loading. It is well known that a certain element is more weakly adsorbed if the loading exceeds *ca.* 1—2 % of the resin capacity, due to intereffects between the adsorbed ions. In this case it might be assumed that the large amounts of iron would cause a more rapid decrease in adsorption with increasing degree of loading.

This was studied in elution experiments using a 1 g column (diameter 9.5 mm). Cobalt was added to the column dissolved in 1 ml of 1 N HF. A solution containing 39 mg Fe/ml, 1 N HF, 0.01 M NO_3, and 0.001 M NH_4 was used as eluting agent and also for pretreatment of the column. The eluate was collected



A: 1 N HF, nil NH_4, nil NO_3, 42.3 mg Fe/ml. Flow rate 1.62 ml/min.
B: 1 N HF, 0.0295 M NH_4, 0.011 M NO_3, 42.2 mg Fe/ml. Flow rate 1.65 ml/min.

in 25 ml fractions and analysed by colorimetry after cation exchange separation. The flow rate was 3 ml/min.

The peak elution volumes, V_{max}, were determined at 0.025—25 % loading. At high loadings the added Co occupied a large amount of the resin and an approximate correction was made for this. An estimation of $V_{1\%\ Co}$ from the elution curves was also made.

Table 6. Adsorption of Co at different degrees of loading. Resin: 1 g of Dowex 50WX8, 100—200 mesh. Column: diameter 9.5 mm. Elution method.

Loading %	$V_{max\ Co}$ ml		$V_{1\%\ Co}$ ml
	observed	corrected	
0.025	435		275
0.25	435		250
2.50	390	395	225
12.5	220	230	125
25.0	120	135	75
0.25 + 2.5 Mn	390	395	225

The results (Table 6) indicate that V_{max} decreased by 10 % at only 2.5 % loading and fell rapidly at higher degrees of loading. An experiment with addition of Mn showed that calculation of the degree of loading must also involve other metals with similar adsorption properties.

Adsorption of the trace elements. Preliminary batch equilibrium experiments showed that all the adsorbable elements were strongly influenced by the presence of iron. To get a clear picture of this an extensive elution study was carried out for eight elements at a fixed concentration of iron.

Ca. 5000 ml of a solution containing 42.3 mg Fe/ml in 1 N HF were prepared from $FeF_3.2\ H_2O$ and purified by cation exchange. One half was used directly as eluting agent in elution A. To the other, used in elution B, a small volume of a similar solution containing NH_4 and NO_3 was added giving 0.0295 M NH_4, 0.011 M NO_3, and 42.2 mg Fe/ml.

The same procedure was applied in the two experiments. The column (diameter 9.5 mm) with 2.59 g Dowex 50WX8, 100—200 mesh, was treated beforehand with *ca.* 50 ml of the eluting agent. At the top of the resin bed 5 ml of a solution (40 mg Fe/ml, 1 N HF) containing 0.1 mg each of Ag, Co, Cu, Mg, Mn, Ni, Pb, and Zn was added and allowed to seep into the resin. The eluting agent was then added carefully to the column and also to a plastic reservoir at the top of the column. The level was kept constant throughout the elution giving constant flow rates (A: 1.62 ml/min, B: 1.65 ml/min). Fractions of 50 ml were collected and analysed by X-ray and optical spectrography after separation of the iron by cation exchange using the method described in this paper.

Elution curves for the elements are shown in Fig. 1. Silver is omitted in Fig. 1B because of some troubles in the quantitative determination but the volume of the elution maximum and $V_{1\%}$ could be established. Correction was needed for Mg present in the 4 N HNO_3 used in the separation procedure of the collected fractions. In Fig. 1B the experimental points are omitted since these would make the curves less clear. These points correspond to the curves in the same way as in Fig 1A.

It can be seen that the adsorption of the elements is descreased in the same way as for Co. However, magnesium, which is adsorbed only a little more weakly than the other bivalent metals in solutions free of iron, is eluted earlier than would be expected and even before silver. If the reason is that more weakly adsorbed fluoride complexes of Mg are formed, it might be possible to find conditions for the elution of Mg after separation from iron as well as from the adsorbed bivalent metals.

The presence of ammonium and nitrate caused a further decrease in adsorption for all the elements but the elution order was not changed. The concentration of NH_4 is equal to 7.0 mmoles in 10 g of iron and might be reached after dissolving a steel sample but is appreciably higher than is necessary if proper precautions are taken (Table 1).

Since the elution curves are almost symmetrical useful distribution coefficients might be calculated from Figs. 1A and 1B (Table 7). At the large fractions collected the values of D could not be determined to better than $\pm$ 10. The volume needed to elute 1 % of an element, $V_{1\%}$, was estimated from the elution curves and is given in Table 7 together with the equivalent amount

Table 7. Values of D and $V_{1\%}$ determined in the elution study (Fig. 1). Column: 9.5 mm diameter. Resin: 2.59 g Dowex 50WX8, 100—200 mesh.

Element	Elution A			Elution B		
	D	$V_{1\%}$ ml	g Fe in $V_{1\%}$ ml	D	$V_{1\%}$ ml	g Fe in $V_{1\%}$ ml
Mg	150	270	11.4	120	185	7.8
Ag	170	320	13.5	140	250	10.6
Zn	410	885	37.4	300	535	22.6
Cu	420	810	34.3	310	600	25.3
Ni	430	880	37.2	320	555	23.4
Co	440	895	37.9	325	585	24.7
Mn	460	835	35.3	340	615	26.0
Pb	650	1380	58.4	470	895	37.8

of iron. It can be seen that most of the elements may be separated from considerable quantities of iron using this very short column. In practical analysis the situation is still more favourable since the metals are dissolved in the eluting agent and thus added continuously to the column. In the case of Mg the values indicate that this column may be too short to allow separation from 10 g of iron even in solutions with low concentrations of NH_4 and NO_3. However, similar separations of Mg were carried out earlier with a 3 g column [3] and some results indicated that the elution curve for Mg was too broad. Thus calculation of the number of theoretical plates gave *ca.* 40 for Mg compared with 85—105 for the other bivalent elements. Calculation was based on the width of the curve in Fig. 1A at the concentration $c = c_{max}/e$. The remarkably low value for Mg may be due to difficulties in applying proper corrections for the blank mentioned earlier.

Some experiments with separation of Mg added to 10 g of iron on a 3 g column showed quantitative adsorption (analysis by optical spectrography).

Mg added:		Mg found:	
0.0200 mg		0.0194 and 0.0198 mg.	
0.100 mg		0.104 and 0.105 mg	
1.00 mg		1.02 and 1.00 mg.	

The washing and elution steps

Washing the column free of iron. Large quantities of iron remained in the resin after the adsorption step. They were washed out with 1 N HF. Fig. 2

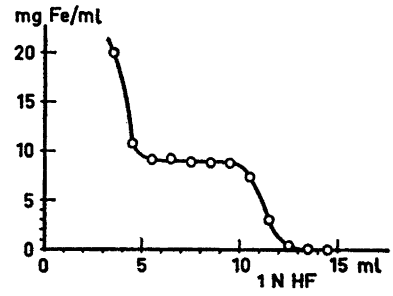


Fig. 2. Control of the washing step. The adsorbed iron eluted from a 9.5 mm column with 1 N HF. Resin: 3 g Dowex 50WX8, 100—200 mesh.

shows the course of the decrease in the concentration of Fe in the effluent from a 3 g column during this operation. After passage of 15 ml of 1 N HF elution with 25 ml of 4 N HNO_3 was applied and a total amount of 0.06 mg of Fe was obtained.

The efficiency of washing was studied further using columns containing 3 g of resin equilibrated with iron solutions (40.4 mg Fe/ml, 1 N HF). The columns were washed with 15—25 ml of 1 N HF and then 15 ml of H_2O were passed through to remove HF. The remaining iron was eluted with 25 ml of 4 N HNO_3 and determined. The results from these experiments are given in Table 8.

Table 8. Total amount of Fe eluted with 25 ml of 4 N HNO_3 after washing with 15, 20, or 25 ml of 1 N HF. Column diameter 9.5 mm. Resin: 3 g of Dowex 50WX8, 100—200 mesh.

1 N HF ml	mg Fe					
15	0.17,	0.20,	0.44,	0.032,	0.062,	0.060
20	0.081,	0.014,	0.080,	0.032.	0.004,	0.055
25	0.036,	0.048,	0.068,	0.017,	0.037,	0.046

It can be seen that 15 ml of 1 N HF is not always sufficient for washing and 20 ml is therefore recommended. The iron present in the eluate of the adsorbed elements from 10 g of iron will then be about 0.05 mg or 0.0005 % of the original amount. This is favourable compared with the best methods used in the solvent extraction of large amounts of iron. It was observed that some iron still remained in the column after elution with 25 ml of 4 N HNO_3. In one case a second elution with 25 ml HNO_3 gave 0.03 mg of iron.

Elution of the adsorbed elements. A mutual separation of the adsorbed elements was not sought. The intention was only to collect the elements in a small volume of solution suitable for analysis. Nitric acid was chosen as eluent since it has been used for a long time at this laboratory for routine spectrographic analysis of solutions. According to published values of D [7-9] proper concentrations of HCl, H_2SO_4 and, but probably less good, $HClO_4$ would also be suitable apart from solubility problems in a few cases. Since too high concentration of nitric acid would attack the resin a 4 N solution was chosen.

Table 9. Values of D in 4 N HNO_3. Elution method. Column: 3 g Dowex 50WX8, 200—400 mesh, diameter 9.5 mm. Flow rate 0.24 ml/min.

Element	D
Ag	2.8
Cd	2.2
Co	2.9
Cu	2.4
Mg	2.6
Mn	3.6
Ni	2.8
Pb	0.45
Zn	2.9

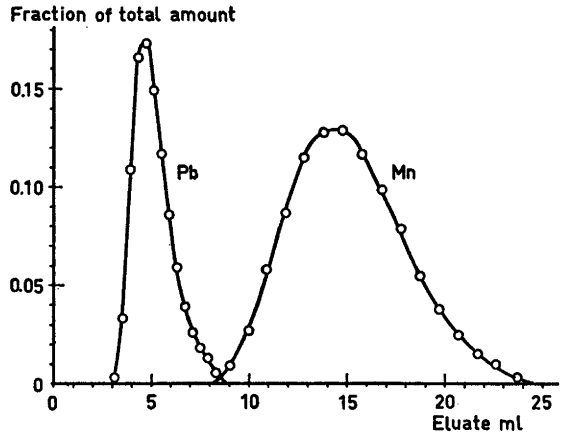


Fig. 3. Elution of Pb and Mn with 4 N HNO_3. Column diam. 9.5 mm. Resin: 3 g Dowex 50WX8, 100—200 mesh. Flow rate *ca.* 2 ml/min.

According to Strelow [8] the *D*-values for the metals of interest here vary from 3.0 (Mn) to 7.3 (Ni) in 4 N HNO_3. It was observed, however, that most of the elements were held less strongly and a determination of *D* was carried out with the elution method using a 3 g column (diameter 9.5 mm) of Dowex 50WX8, 200—400 mesh. The flow rate was 0.24 ml/min (Table 9).

For practical purposes a similar elution was also carried out using a 3 g column of Dowex 50WX8, 100-200 mesh, with a high flow rate (*ca.* 2 ml/min). Curves for the elements showing the weakest and strongest adsorption (Pb and Mn) are given in Fig. 3. Lead is adsorbed so weakly that a separation from the other adsorbed metals should be possible if a column of proper length is used. It can be seen that the 25 ml of 4 N HNO_3 used in most experiments here is a minimum and it is recommended that 30 ml be used.

If ammonium is present after solution of the iron sample a certain quantity is eluted together with the adsorbed elements. It does not seem to be possible to elute NH_4 separately from the short columns used, especially since the trace elements are present all over the column before the washing and elution step.

The quantity of ammonium present in the eluate may be calculated approximately. At $D_{NH_4} = 30$ equilibrium is reached for a 3 g column after less than 100 ml, giving 30 × 3 × molarity of NH_4 mmoles. This was tested after dissolving two 10 g samples as in Table 1 No. 1. The concentrations obtained were 0.053 M (37.7 mg Fe/ml) and 0.069 M (40.4 mg Fe/ml). The columns contained 4.77 mmoles (0.49 mmoles of which were eluted in the washing step) and 5.67 mmoles (0.61 in washing), respectively. Calculation gives 4.8 and 6.2 mmoles. When 10 g samples are dissolved according to the recommended procedure the concentration of NH_4 is generally less than 0.001 M, resulting in less than 0.1 mmoles NH_4 in the eluate.

In a following paper this separation procedure will be applied to analysis of high-purity iron and steel.

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REFERENCES

1. Danielsson, L. *Acta Chem. Scand.* **19** (1965) 1859.
2. Dixon, E. J. and Headridge, J. B. *Analyst* **89** (1964) 185.
3. Danielsson, L. *Jernkontorets Ann.* **149** (1965) 501.
4. Danielsson, L. *Acta Chem. Scand.* **19** (1965) 670.
5. Nydahl, F. *Svensk Kem. Tidskr.* **49** (1937) 158.
6. Ringbom, A. *Complexation in Analytical Chemistry*, Interscience, New York 1963, p.227.
7. Strelow, F. W. E. *Anal. Chem.* **32** (1960) 1185.
8. Strelow, F. W. E., Rethemayer, R. and Bothmaa, C. J. C. *Anal. Chem.* **37** (1965) 106.
9. Nelson, F., Murase, T. and Kraus, K. A. *J. Chromatog.* **13** (1964) 503.

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