

Cation Exchange Separation of Traces of Magnesium and Some Other Metals from High-Purity Aluminium

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A study was made of the conditions for separation of magnesium and cobalt from large amounts of aluminium by cation exchange in hydrofluoric acid solutions. A procedure was developed for separation of small amounts of Co, Cu, Mg, Mn, Ni, Pb, and Zn from 2 g of aluminium using 3 g of resin. The trace elements were eluted as a group and determined by X-ray spectrography or atomic absorption spectrophotometry. The eluate generally contained less than 0.01 mg of Al. Some experiments were also carried out to study the behaviour of iron in similar solutions.

It is well known that aluminium forms strong complexes with fluoride in weakly acidic solutions of hydrofluoric acid. These complexes are only weakly adsorbed on cation exchange resins in H^+ -form.^{1,2} Fritz *et al.*² made use of this to separate some elements from aluminium. They adsorbed aluminium on a cation exchange resin together with the element to be separated (max. 0.5 mmoles in all) from weakly acidic solutions of HNO_3 , HCl, or $HClO_4$. Then aluminium was eluted selectively with 0.1 M HF and the remaining element was stripped from the column with 2–3 M HNO_3 or HCl. This method is not suitable for trace determinations since the ion exchange resin is loaded with the total amount of aluminium. A necessary condition for a successful separation of large amounts of aluminium is evidently that the fluoride complexes are formed before the separation step in the same way as has been used earlier for separation of traces of metals from iron.^{3,4} Preliminary experiments showed, however, that the method developed for iron solutions could not be used directly. In the presence of aluminium the adsorption of the trace elements decreased considerably more than in the presence of equivalent amounts of iron.

EXPERIMENTAL

Experimental details have been given in previous papers.³⁻⁵ The same batch of Dowex 50WX8, 100–200 mesh, was used as before.⁴ The amounts of resin taken refer to dry weights. Columns of acrylic plastic (internal diameters 9.5 and 8.0 mm) with resin supports of plastic wool (Dynel Wool, Union Carbide Corp.) were used.³

All chemicals were of recognized analytical grade. Solutions of Al were prepared from metallic aluminium, 99.99 % Al or purer. In the determination of the trace elements Merck "Suprapur" HF was used. HNO_3 was redistilled in a quartz apparatus and the ion exchange water used was purified by further passage through a small cation exchange column.

The measurements of pH were carried out with a Radiometer pH-meter 22.

Analytical methods. Colorimetric methods were used for Co, Fe, and Al. Co was determined with nitroso-R-salt and Fe with thiocyanate or 1,10-phenanthroline essentially according to Sandell.⁶ Al was mainly determined by a method given by Wilson and Sergeant⁷ which is suitable also in the presence of traces of fluoride.

Magnesium was determined by atomic absorption spectrophotometry using a Perkin-Elmer, Model 303 instrument. Standard conditions laid down by the manufacturer were used. This equipment was kindly put at our disposal by Prof. A. Johansson, Royal Institute of Technology, Stockholm.

The other trace elements were determined by X-ray spectrography in the same way as earlier.⁸ These analyses were made under the supervision of Mr. G. Carlsson.

RESULTS AND DISCUSSION

Dissolution of metallic samples

Hydrofluoric acid seems to be very seldom used for dissolving samples of metallic aluminium for chemical analysis. It was found, however, that samples of pure Al were dissolved more rapidly in dilute solutions of HF than in HCl or H_2SO_4 .

For a successful separation it was essential that the excess of HF was kept low and could be closely controlled. This was achieved in iron solutions by evaporating the solutions to dryness and dissolving the residues in proper amounts of HF of known concentrations. This method was not applicable to solutions of Al since the precipitated aluminium fluoride was not soluble at 1 N or lower concentrations of HF. In this case a simpler and more rapid method was applied. The samples were dissolved in calculated amounts of HF and water to give the proper concentrations of Al and HF (*cf.* Procedure). The solutions obtained contained besides Al and HF, amounts of fluoride equivalent to give AlF_3 . Care was taken to avoid violent reactions and the Teflon beakers used were covered with polyethylene lids. The oxidation needed for some of the trace metals was easily effected by the addition of a few drops of H_2O_2 at the end of the dissolution.

Dissolving a 2 g sample according to the procedure given later takes approximately 30 min. A more rapid dissolution will probably be achieved if a more concentrated solution of HF is used and the proper dilution is made afterwards.

In solutions containing 20 mg Al/ml precipitates of aluminium fluoride may sometimes be formed after a day or two. At 30 mg Al/ml the solutions could not be kept for more than one day.

Adsorption of the trace elements

In previous papers^{3,4} it was shown that trace amounts of Ag, Co, Cu, Mg, Mn, Ni, Pb, and Zn may be separated from at least 10 g of iron using a column (diameter 9.5 mm) with 3 g of Dowex 50WX8, 100–200 mesh. The

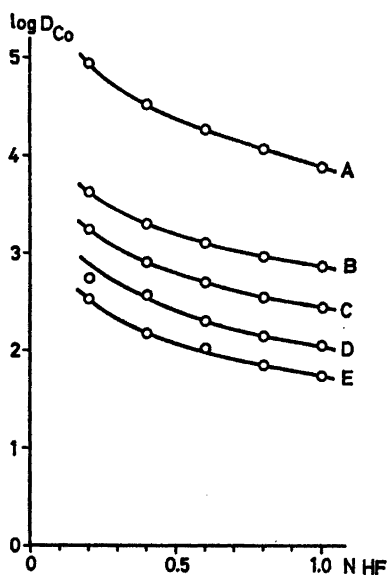


Fig. 1. Adsorption of Co at different concentrations of HF and Al. A: 0 mg Al/ml, B: 4.57, C: 9.15, D: 18.3, and E: 30.8 mg Al/ml. Resin: Dowex 50WX8. Batch method.

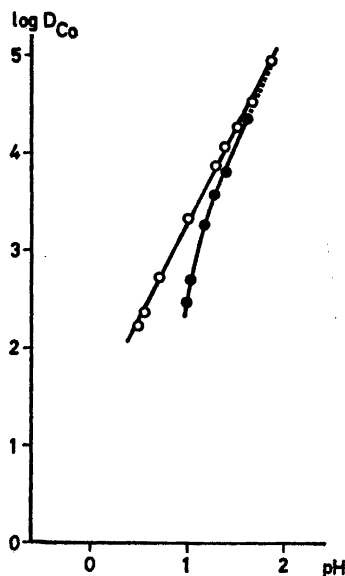


Fig. 2. Adsorption of Co at different values of pH. O solutions of pure HF: 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, and 7.0 N, ● solutions containing 0.2 N HF and 1.0, 2.5, 5.0, 10.0, 20.0, and 30.0 mg Al/ml.

solution contained *ca.* 40 mg Fe(III)/ml and 1 N HF. The weight distribution coefficients, D , were found to be *ca.* 150 for Mg and Ag and more than 400 for the other trace elements. The effect of varying concentrations of Fe(III) and HF was studied using Co as the adsorbable element. In this investigation Co was also used for the same purpose to obtain comparable data.

Fig. 1 shows the adsorption of Co at different concentrations of HF and Al. For comparison a curve for solutions free of Al is included. The batch equilibrium method was used and no corrections were applied for adsorption of Al. Cobalt was separated in the equilibrated solutions by cation exchange and determined by colorimetry. The results for 30.8 mg Al/ml may be less reliable due to the risk of precipitation during the equilibration process. It is obvious that increasing concentrations of Al and HF lead to a decrease in the adsorption of Co. This is in agreement with the results for iron solutions. However, in solutions containing 1 N HF, Co was held about 4 times less strongly in aluminium solutions than in iron solutions of the same molarity. The separation effectiveness thus decreased by a factor 8 since the difference in atomic weights must also be taken into account. At lower concentrations of HF the difference in adsorbability of Co seems to be less, *e.g.* $D_{Co} = 520$ (0.68 M Al, 0.2 N HF) and $D_{Co} = ca. 1100$ (0.67 M Fe(III), 0.2 N HF), but only a few values were available in iron solutions.

One important reason for the decrease in adsorption of the trace elements in solutions containing Al or Fe compared with pure solutions of HF was thought to be an increased acidity. A rough estimation with indicator papers showed a marked decrease in pH in the presence of Al or Fe. In these solutions the excess of HF takes part in the complexation reactions, resulting in a decreased value of pH. Measurements of pH were made in solutions containing 0.2 N HF at different concentrations of Al using the quinhydrone electrode, calibrated with Veibel's solution (0.01 N HCl + 0.09 N KCl, pH = 2.08). In Fig. 2 $\log D_{\text{Co}}$ is plotted against pH for these solutions and also for solutions free of Al. At all concentrations studied a decrease in pH always gave rise to a decrease in adsorption of Co. This was also true if the cause was a raise in the concentration of HF at a fixed concentration of Al. These results are not included in the figure. However, as can be seen in Fig. 2, the values are lower than in pure solutions of HF of the same pH which indicates that other factors are also involved as might be expected.

It was assumed that Mg which was adsorbed considerably more weakly than the other bivalent metals from iron solutions would also set the limit for separation in solutions of Al. (Ag was omitted in this investigation). The adsorption of Mg was therefore studied at different concentrations of HF and Al. The batch method was used except for solutions containing 20 mg Al/ml which were studied by the elution method. The results are shown in Fig. 3. The general picture was the same as for Co. However, the influence of Al was greater: $D_{\text{Co}}/D_{\text{Mg}} = \text{ca. } 7$ (20 mg Al/ml, 0.2 N HF) and $\text{ca. } 14$ (20 mg Al/ml, 1 N HF) compared with $\text{ca. } 3$ (42 mg Fe/ml, 1 N HF).

Evidently, Mg is held so weakly in solutions containing 1 N HF that such solutions could not be used for separation from large amounts of Al. More useful values were obtained in 0.2 N HF and a detailed elution study gave $D = 83$ (20 mg Al/ml, 0.2 N HF). A column (diameter 9.5 mm) with 2 g of Dowex 50WX8, 100–200 mesh, was used. The flow rate was 1.2 ml/min and fractions of 10 ml were collected and analysed after separation of Al. *Ca.* 110 ml passed the column until 1 % of the Mg added was eluted. Thus, passage of 100 ml of a solution containing 20 mg Al/ml, 0.2 N HF (2 g of Al) through a column with 3 g of resin gives a rather large safety margin.

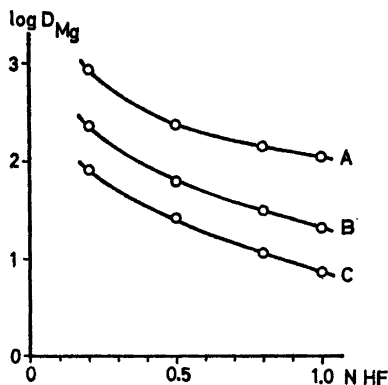


Fig. 3. Adsorption of Mg at different concentrations of HF and Al. A: 5.0, B: 10.0, and C: 20.0 mg Al/ml.

For practical reasons solutions containing 20 mg Al/ml were used in the procedure although a somewhat higher effectiveness was attained at lower concentrations of Al both for Co and Mg (Figs. 1 and 3).

Adsorption and elution of aluminium

Earlier results indicated that Al is more weakly adsorbed than Fe(III) from solutions containing low concentrations of HF.¹ Elution of small amounts of Al was now carried out in solutions of 1.0, 0.8, 0.6, 0.4, and 0.2 N HF using columns (diameter 8 mm) containing 3.0 g of Dowex 50WX8, 100–200 mesh. The values of D calculated from the peak elution volumes increased regularly but rather slightly with decreasing concentrations of HF (1 N HF: $D_{Al} = 0.16$, 0.2 N HF: $D_{Al} = 0.26$). However, at the lowest concentrations of HF a troublesome tailing was observed. A more detailed study of the elution behaviour in solutions of 0.2 N HF revealed a second peak, corresponding to $D = ca. 1.3$. The amounts of Al belonging to the two peaks were almost equal which corresponds to an "apparent" D -value of *ca.* 0.8. Fig. 4 shows the elution curves obtained eluting Al with 1 N HF and 0.2 N HF.

It seemed necessary to use 0.2 N HF for washing out Al because of the low values of D_{Mg} in solutions containing Al at higher concentrations of HF. The adsorption of Al from solutions containing 20 mg Al/ml, 0.2 N HF was studied with the special elution technique used earlier.⁴ The amount of Al adsorbed by 3 g of Dowex 50WX8 was found to be 40.5 mg. This corresponds

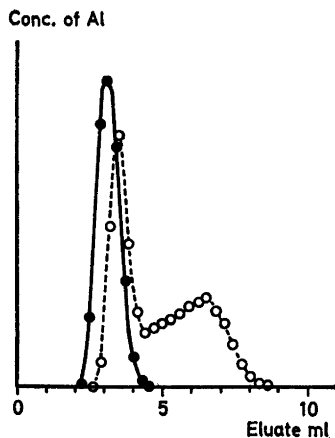


Fig. 4. Elution of Al with two different eluents: O 0.2 N HF, ● 1 N HF. Concentration of Al in arbitrary units. Column diam. 8 mm. Resin: 3 g of Dowex 50WX8, 100–200 mesh.

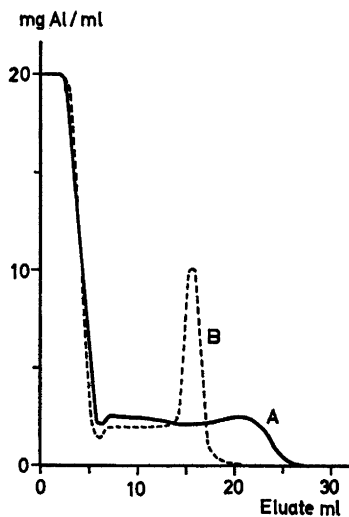


Fig. 5. Study of the washing step. The adsorbed aluminium eluted with 0.2 N HF (curve A —) and with 10 ml of 0.2 N HF followed by 1 N HF (curve B ----). Column diam. 8 mm. Resin: 3 g of Dowex 50WX8, 100–200 mesh.

to $D = 0.7$ and a loading of *ca.* 10 % assuming that the adsorbed ions are univalent.

The efficiency of washing was studied using a column (diameter 8 mm) with 3 g of Dowex 50WX8, 100–200 mesh, equilibrated with a solution containing 20 mg Al/ml, 0.2 N HF. Elution with 0.2 N HF was applied and fractions of 1 ml were collected and analysed. The concentration changes in the effluent can be followed in Fig. 5, curve A. More than 25 ml of 0.2 N HF were obviously needed to elute Al quantitatively. In a second experiment (Fig. 5, curve B) the effect of using 1 N HF to complete the washing out of Al was studied. Elution was performed with 10 ml of 0.2 N HF followed by 15 ml of 1 N HF. In this way a somewhat smaller volume of solution was needed but no special advantages were involved. On the contrary, a local increase in the concentration of Al was observed which might cause a risk of elution of some Mg.

The amount of Al remaining in the column after washing with 25 ml of 0.2 N HF was found to be rather large. With 35 ml, however, the quantities of Al reached a satisfactory level. The remaining amounts of Al washed out afterwards with 1 N HF were in the two cases (3 g of resin, column diameter 8 mm):

25 ml 0.2 N HF: (μg Al) 69, 430, 480, >800, 45, 130.

35 ml 0.2 N HF: (μg Al) 2, 4, 3, 6, 23, 34, 3, 3.

In the recommended procedure 35 ml of 0.2 N HF are used, followed by washing with 15 ml of H_2O and elution of the trace elements with 30 ml of 4 N HNO_3 . The amount of Al accompanying the trace elements under these conditions was determined using 8 mm columns as above and 9.5 mm columns as in most of the separation experiments. The following results were obtained (3 g of resin):

Column 8 mm diam.: (μg Al) 3, 3, 36, 1, 1, 5.

Column 9.5 mm diam.: (μg Al) 3, 5, 6, 2, 3, 1, 1, <1, <1, 1.

These very small amounts of Al will not interfere in the determination of the trace elements using X-ray spectrography. It is known, however, that Al might interfere in the determination of Mg by atomic absorption spectrophotometry. Under the conditions used in this investigation it was found that the presence of 1 ppm of Al (30 μg in 30 ml of 4 N HNO_3) had a negligible effect, whereas 10 ppm of Al decreased the sensitivity of Mg considerably. In some cases when the eluate containing the trace elements is concentrated into a small volume of solution it may be necessary to take this interference into account.

Analysis of high-purity aluminium

Procedure. Weigh accurately 36.1 g of 7.00 N HF into a Teflon beaker and add 65 ml of H_2O . Take a 2.00 g sample of Al and cover the beaker with a polyethylene cover. Warm gently to dissolve avoiding a too violent reaction. At the end oxidize with a few droplets of H_2O_2 (30 %) and boil for a short time. Control that the solution is absolutely clear. A reduction of the volume

of solution of more than a few ml should be corrected for by addition of H₂O before the separation step.

Use a column (diameter 9.5 mm) containing 3 g of Dowex 50WX8, 100–200 mesh, equilibrated with 0.2 N HF. Add the solution, preferably from a plastic reservoir, at the top of the column. Pass the solution through the column at a flow rate of 1–2 ml/min, wash with 35 ml of 0.2 N HF and then with 15 ml of H₂O. Elute the trace metals with 30 ml of 4 N HNO₃ and analyse the solution by X-ray or optical spectrography or by atomic absorption spectrophotometry.

Determination of the trace elements. No samples of Al with known contents were available at a low trace level. Instead, the trace elements were added to samples of metallic Al from solutions prepared from the pure metals involved and in one case as an AlMg-alloy with known content of Mg. Relatively large amounts were generally added to minimize the error in the determination of the separated elements. The pure Al used in most of the tests was analysed using the procedure above (Table 1). In this case the amounts present in 2 g of Al were sometimes too low to allow an accurate determination.

According to earlier experiences⁸ the reagent blanks might be a problem in the case of Mg. Blank values now gave 1.3 ppm Mg (1.3, 1.2, 1.3, 1.4) determined by optical emission spectrography. Since rather dilute HF (*ca.* 2.4 N) is used in the dissolution a simple and effective purification might be achieved by passing the solution of HF through a cation exchange column before use.

Magnesium was studied separately since it could not be determined by X-ray spectrography like the other elements. The precision of the method was studied by analysing a sample with a low unknown content of Mg. In total 14 separate analyses were made. They gave a mean value of 73.0 ppm Mg and a relative standard deviation of 2.3 %.

The results obtained in the determinations of Mg added to metallic Al are given in Table 2. The lowest amount of Mg used was added to a sample of Al of a higher purity (2.2 ppm Mg). The results show that acceptable recoveries were obtained.

The AlMg-alloy used contained 2.69 % Mg determined by titration after separation according to Ginsberg⁹ (2.68) and by atomic absorption spectrophotometry (2.70) using synthetic solutions of Mg containing the same amounts

Table 1. Analysis of a sample of pure Al used in the separation experiments. Determination by X-ray spectrography. (Mg by optical spectrography and atomic absorption spectrophotometry.)

Element	ppm found			
Co	0.4	0.6	0.5	
Cu	15.9	16.9	18.2	
Mg	8.7	8.0	7.8	8.2
Mn	0.5	0.8	0.3	
Ni	1.0	0.9	1.3	
Pb	0.0	0.0	0.1	
Zn	10.0	10.0	9.2	

Table 2. Determination by atomic absorption spectrophotometry of Mg added to 2 g of metallic Al.

Mg added as	ppm calc.		ppm found				Mean recovery %
AlMg-alloy	12.3	13.0	12.9	12.3	12.2	12.4	102.1
synth. solut.	108	107	106	107	107		98.8
AlMg-alloy	195	197	197	195	195	194 190 191 193	99.5
synth. solut.	1008	1000	1000	1015	1010		99.8

of Al for calibration. In some cases small amounts of this alloy were added to 2 g of Al before dissolution but generally an aliquot was taken from a solution prepared by dissolving the AlMg-alloy in HF together with high-purity Al to give 20 mg Al/ml, 0.2 N HF. It was found that precipitates of magnesium fluoride sometimes formed in such solutions at concentrations higher than 0.02 mg Mg/ml. When dissolving the AlMg-alloy in 0.2 N HF without addition of Al precipitates were formed at lower concentrations of Mg.

The other trace elements were determined after separation using X-ray spectrography. All results obtained are given in Table 3. In a single determination the largest relative deviation from the calculated value was 4 %. Generally the results agreed much better and they were considered to be satisfactory. The tests were made using synthetic solutions but there seems to be no reason to believe that difficulties might arise in dissolving metal impurities of these elements present in high-purity Al.

Separation of iron from aluminium and from the trace elements

Small amounts of iron are generally present in pure aluminium. Some experiments were made to study the possibilities of separating Fe from Al as well as from the trace elements in fluoride solutions. Preliminary experiments gave $D_{\text{Fe(III)}} = \text{ca. } 50$ in a solution containing 20 mg Al/ml, 0.2 N HF indicating that Fe(III) was held sufficiently strongly by the resin to allow separation

Table 3. Determination by X-ray spectrography of some elements (100 μg of each) added at the same time to 2 g of metallic Al.

Element	ppm calc.		ppm found				Mean recovery %
Co	50.5	49.9	52.0	51.6	49.9		100.7
Cu	67.0	64.3	68.1	66.5	64.7		98.4
Mn	50.5	49.7	52.0	51.7	52.2		101.8
Ni	51.1	50.0	52.7	52.6	50.4		100.6
Pb	50.0	49.9	50.0	48.6	51.8		100.2
Zn	59.7	60.1	61.1	61.3	60.5		101.8

from Al. However, a necessary condition is also that 35 ml of 0.2 N HF could be passed through the column to wash out Al before the break-through of Fe(III). This was tested in the following way. A column (diameter 8 mm) with 3 g of Dowex 50WX8, 100–200 mesh, was equilibrated with a solution containing 20 mg Al/ml, 0.2 N HF. At the top 1 ml of a similar solution containing 10 mg of Fe(III) was added and 50 ml of the solution of Al used for equilibration (corresponding to 1 g of Al) were passed through. Elution was then performed with 0.2 N HF and fractions of 5 ml collected and analysed. Fe(III) appeared in the fraction 40–45 ml (0.01 mg Fe). Separate experiments showed that Fe(III) was eluted quantitatively with 15 ml of 1 N HF after the elution of Al with 35 ml of 0.2 N HF. Magnesium is held very strongly in pure 1 N HF as well as the other trace elements.

The method was tested with 1 g of Al and rather large amounts of Fe and Mg (0.126 and 1.14 mg, resp.) were added in the form of 40 mg of a commercial AlMg-alloy. The samples were dissolved in HF and oxidized with H_2O_2 to give solutions containing 20 mg Al/ml, 0.2 N HF and iron as Fe(III). In the cation exchange process Al was eluted with 35 ml of 0.2 N HF, Fe(III) with 25 ml of 1 N HF, and Mg with 30 ml of 4 N HNO_3 after passage of 15 ml of H_2O through the column. It can be seen (Table 4) that Fe(III) and Mg were mutually separated. Mg was not detected in the fraction containing Fe(III). The results for Mg are somewhat low. At this concentration of Mg a small precipitate may have formed in some of the solutions.

These results indicate that in the normal procedure (2 g of Al) part of the Fe(III) will be washed out together with the aluminium. Bivalent iron is held more strongly in solutions containing fluoride¹ and it may be possible to separate Fe(II) from 2 g of Al using 3 g of resin but this was not studied.

Concluding remarks

Some differences seem to exist in the applicability of the present method and separation by anion exchange at high concentrations of HCl.^{10,11} In the latter method Cd, Co, Cu, Fe(III), Ga, and Zn may be separated from aluminium and some of the adsorbed metals may also be separated mutually. However, Mg, Ni, and in most cases Mn are not covered and Ag and Pb may be included only if a special separation at a lower concentration of HCl is performed.

Table 4. Separation of Fe and Mg from 1 g of Al (*cf.* text). Added: 0.126 mg Fe and 1.14 mg Mg. Fe(III) eluted with 35 ml of 1 N HF (fraction A), Mg with 30 ml of 4 N HNO_3 (fraction B).

mg Fe	Fraction A mg Al	mg Mg	Fraction B mg Mg
0.128	0.004	0.000	1.12
0.128	0.003	0.000	1.07
0.125	0.006	0.000	1.10
0.133	0.024	0.000	1.12
0.126	0.008	0.000	1.13

In the present investigation separation was effected from 2 g of Al using columns with 3 g of Dowex 50WX8. With larger amounts of resin it should be possible to increase the quantity of Al considerably without changing the principles of separation. Probably, Ag and Cd may also be separated in the same way.

In addition some elements present in the aluminium effluent might be separated on the anion exchange resin Dowex 1. Al is held weakly by this resin at least if small amounts of HNO_3 , H_2SO_4 , or HCl are added to the solution.^{1,12,13} This allows probably separation of Sn, Ti, Zr and several other elements that might be of interest.

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