# Cation Exchange Separation of Traces of Metals from Iron

## II. Application to the Analysis of High-Purity Iron and Steel

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A method is described for separation and concentration of ppm amounts of Ag, Co, Cu, Mg, Mn, Ni, Pb, and Zn in high-purity iron by cation exchange. The trace elements were determined mainly by spectrography. The proposed procedure was also applied to the analysis of some mild and alloyed steels, including chromium steels. Practical details for shortening the procedure are discussed.

In Part I of this series [1] suitable conditions were developed for the separation by cation exchange of Ag, Co, Cu, Mg, Mn, Ni, Pb, and Zn from large amounts of iron in dilute solutions of hydrofluoric acid. This paper describes a procedure for the analysis of metallic iron samples together with tests performed to confirm its suitability for use with high-purity iron and steel.

## EXPERIMENTAL

Experimental details have been described in a preliminary communication [2] and in Part I of this series.[1] All reagents used were of recognised analytical grade. However, when analysing high-purity iron special precautions were taken.

*Purification of the reagents.* It is essential that high-purity acids are used because of the large quantities necessary to dissolve the samples if minute amounts of metals are to be determined. The normal *p.a.* quality of HF contained *ca.* 10 $\mu$g of Cu and Mn per 100 ml and also easily detectable amounts of Mg and Pb (which were not determined quantitatively), together with Fe and *ca.* 50 $\mu$g of Al/100 ml which was of minor importance. A relatively simple method for obtaining HF of higher purity is to use isothermal distillation of 70 % HF at room temperature.[3] Two polyethylene boxes 95 × 95 × 100 mm, one with 500 ml $H_2O$ and the other with 500 ml 70 % HF were placed in a covered polyethylene box 240 × 160 × 140 mm. After 4—5 days the "water box" contained 640 ml of *ca.* 13 N HF. This solution was boiled before use to remove volatile sulphur compounds. Analysis of 200 ml of this HF by spectrography after evaporation in the presence of some $H_2SO_4$ gave ($\mu$g/100 ml) Al, Ti 0.5, Cu 0.2, Ni 0.1, Mn, Cr, Co, Mo, Ag < 0.1 (not detected), V, Sn, Pb, Zn < 0.5 (not detected). The content of Mg was appreciably lower than in the *p.a.* quality.

This acid was used in some of the separation experiments but later it was found that Merck "Suprapur" HF had about the same purity and most determinations were carried out using this quality.

The other acids were redistilled in a quartz apparatus and the ion exchange water used was purified by further passage through a small cation exchange column.

## RESULTS AND DISCUSSION

### Analysis of high-purity iron

*Procedure.* The principles have been outlined earlier.[1] In the analyses reported here 10 g samples were dissolved in Teflon beakers in 75 ml of conc. $HNO_3$ and 20 ml of HCl (constant boiling) were added to complete the solution. After addition of 50 ml of HF (40 %) the solutions were taken to complete dryness. The precipitates formed were dissolved in 250 ml of 1 N HF at slow boiling. This operation takes some time and care should be taken that the remaining solution is absolutely clear. Repeated treatment may sometimes be useful and, if required, much larger amounts of 1 N HF may be used.

A column (diameter 9.5 mm) containing 3 g (dry weight) of Dowex 50WX8, 100—200 mesh, equilibrated with 1 N HF was used. The solution was added from a plastic reservoir attached at the top of the column. The flow rate was 1—2 ml/min. This operation was often carried out overnight and in this case the resin was allowed to drain. The iron was washed out with 20 ml of 1 N HF and after that 15 ml of $H_2O$ were passed through. The adsorbed elements were eluted with 25—30 ml of 4 N $HNO_3$.

The determinations were made by optical or X-ray spectrography or by colorimetry. As far as possible routine methods used at the Swedish Institute for Metal Research were applied.

When optical spectrography was used the eluate was taken to dryness on a boiling water bath and the residue dissolved in 2 ml of $HNO_3$ containing 200 mg of iron, which was used as an internal standard. If necessary, ammonium was removed beforehand with $HNO_3$- HCl or, when Ag was to be determined, by heating in a platinum crucible. The analysis was then performed according to Carlsson.[4]

The solutions analysed by X-ray spectrography were treated in the same way but the residue was moistened with 5 drops of $HNO_3$ and then dissolved in 2 ml of a slightly acidic solution of strontium nitrate (25 mg Sr/ml). A Philips' automatic instrument PW 1210 with scintillation and flow counters was used.

*Experiments with an increased flow rate.* As in the systematic study,[1] a 9.5 mm column containing Dowex 50WX8, 100—200 mesh, was used. In several experiments different column diameters and various mesh sizes of the resin were tested, mainly in order to study the effect of an increased flow rate. In these experiments the effluent from the tested column was allowed to pass through a 9.5 mm column containing 3 g of Dowex 50WX8, 100 —200 mesh, and the adsorbed elements in both columns were determined. Detailed results will not be given here since these were in agreement with what is already known of simple cation exchange separations.[5]

Columns of diameter 7.0 and 9.5 mm, with resin of mesh sizes 20—50 and 50—100 were not effective for adsorption at high flow rates and large elution volumes had also to be used. The best way to speed up the procedure was apparently to use the 100—200 mesh resin in columns with larger inner diameter. Complete adsorption of Ag from 10 g of iron in 250 ml solution was thus effected using 3 g resin in a column with 18.5 mm inner diameter. The total time for the solution to pass through the column was 20 min. Manganese (1 mg) was separated in the same way in 15 min on 1.5 g of resin from an iron solution (10 g Fe) warmed to near the boiling point. For elution of Mn from this small amount of resin 30 ml of 4 N $HNO_3$ was required. It is recommended that the elution is performed at a lower flow rate in order not to increase the volume of solution more than necessary.

*Verification of the procedure.* Results showing the validity of the separation procedure using synthetic solutions have been given earlier.[2] It was not possible to test the whole procedure at a low trace level using samples with known contents since these were not available. The purest iron at hand was an electrolytic iron and this was analysed using this method. Reagent blanks that were run at the same time gave generally less than 0.2 ppm for the trace elements but the values for Mg were appreciably higher (*ca.* 1.5 ppm) and somewhat irregular.

Various amounts of standard steel samples from National Bureau of Standards were added to 9—10 g of the electrolytic iron to give amounts suitable for analysis. In cases where the actual element was not certified, pure metal samples or especially prepared alloys were added. In order to study traces of Co a purified iron solution was used because of the high cobalt content of the electrolytic iron. This solution was taken to dryness and the procedure described above was followed. The same method was applied for Mg on account of the relatively high and irregular blank values.

The results are given in Table 1. Generally acceptable recoveries were obtained but in a few cases somewhat lower values were found. Since systematically low results for Mn in NBS 125a also were found later (Table 2) Mn in this sample was determined by colorimetry after separation of iron by solvent extraction (methyl isobutyl ketone) and by ion exchange following the procedure given. The results were: 0.048, 0.049, 0.048 % (solvent extraction) and 0.049, 0.049 % (ion exchange).

*Applications.* Considering trace analysis of high-purity iron it must be pointed out that the amounts of the metals investigated here are by no means at the limit of detection but were chosen to allow good control of the procedure. There seems to be no reason why the separation method should fail at considerably lower concentrations of the trace metals. The limit will probably be set either by the blank or by the method of analysis. The amount of iron is of course not restricted to 10 g. This quantity was considered to be the largest of practical interest but in certain cases it might be suitable to use larger amounts. Approximate column dimensions might be calculated using Fig. 1, Ref. 1.

It seems reasonable that the cation exchange method described here could be used in combination with that given by Dixon and Headridge[6] for the metals which are adsorbed on an anion exchange resin. In such a combina-

Table 1. Analysis of a high-purity electrolytic iron and the determination of some elements added, using the procedure described.

| Element | Method | Electrolytic iron ppm found | | Element added as | ppm calc. | ppm found | Recovery % |
|---|---|---|---|---|---|---|---|
| Ag | Opt. | | 0.07, 0.07 | Ag-Fe alloy (0.070 % Ag) | 0.70 | 0.65 | 93 |
| | | | | » | 1.40 | 1.41, 1.44 | 101, 103 |
| Co | X-Ray | 67.6, 67.1, | 67.0 | metallic Co * | 50.0 | 49.6, 49.5 | 99, 99 |
| | Color. | 68.7, 68.7, | 67.8 | » | 10.0 | 9.8, 10.0 | 98, 100 |
| | | | | » | 5.0 | 5.10, 5.07 | 102, 101 |
| Cu | Opt. | 0.9, 0.9, | 1.3, 1.5 | NBS 125a (0.084 % Cu) | 9.3 | 8.9, 8.9 | 96, 96 |
| | | | | NBS 55E (0.065 % Cu) | 7.4 | 7.3, 7.3 | 99, 99 |
| | X-Ray | | | NBS 125a | 84.8 | 83.1, 83.6 | 98, 99 |
| | | | | NBS 55E | 65.8 | 68.7, 67.9 | 104, 103 |
| Mg | Opt. | 1.7, 1.9, | 1.3 | metallic Mg * | 2.0 | 2.1, 2.1 | 105, 105 |
| | | | | » | 10.0 | 9.2, 9.0 | 92, 90 |
| | Titr. EDTA | | | » | 300 | 301, 301 | 100, 100 |
| Mn | Opt. | 1.6, 1.6, | 1.5, 1.5 | NBS 125a (0.052 % Mn) | 6.8 | 5.6, 6.3 | 82, 93 |
| | | | | NBS 55E (0.035 % Mn) | 5.1 | 5.1, 5.3 | 100, 104 |
| | X-Ray | 1.7, 1.8, | 1.8 | NBS 125a | 53.8 | 48.0, 47.9 | 89, 89 |
| | | | | NBS 55E | 36.8 | 35.6, 35.5 | 97, 96 |
| Ni | Opt. | 0.7, 0.9, | 0.9, 0.8 | NBS 125a (0.053 % Ni) | 6.1 | 6.1, 6.1 | 100, 100 |
| | | | | NBS 55E (0.038 % Ni) | 4.6 | 4.9, 4.7 | 107, 102 |
| | X-Ray | | | NBS 125a | 53.8 | 54.2, 54.3 | 101, 101 |
| | | | | NBS 55E | 38.8 | 39.8, 38.3 | 103, 99 |
| Pb | X-Ray | 13.2, 13.2, | 13.1, | NBS 130a (0.23 % Pb) | 35.6 | 36.0, 34.9 | 101, 98 |
| | | 13.3 | | » | 57.9 | 56.4, 58.3 | 97, 101 |
| Zn | X-Ray | 23.6, 23.6, | 23.3, | metallic Zn | 43.5 | 42.5 | 98 |
| | | 23.4 | | » | 53.5 | 52.9 | 99 |

* Mg and Co added to purified solutions; cf. text.

tion it may be advisable to add some HF together with $HNO_3$ when dissolving the samples to avoid hydrolysis. A study must be made, however, to ensure that those metals to be adsorbed on the anion exchange resin are present quantitatively in the iron effluent from the cation exchange step. It would also be necessary to establish the optimum conditions for anion exchange separation from large amounts of iron. It might even be possible to use a mixed resin for absorption of both cationic and anionic metal species, they could then be eluted together using, for example, 4 N $HNO_3$—1 N HF. This would appear to be effective for all metals of interest except tantalum.

## Analysis of steel

Application of the cation exchange process described to the analysis of different steel qualities has not been studied in detail. The main aim has been to point out some possibilities and limitations in the use of the method for this purpose.

The separation method is of course not restricted to traces of metals. In ordinary steel analysis separation from 1—2 g of iron is generally sufficient and using this method separation will also be achieved from many other elements present in steel that might interfere in the chemical determination. However, often one of the adsorbable elements is present at a considerably higher concentration than the rest and that will set the limit, *e.g.* manganese in carbon steels and nickel in stainless steels.

The procedure used for high-purity iron has three time-consuming steps: 1. evaporation of the solution to dryness, 2. dissolving the precipitate in 1 N HF and 3. adsorption on the resin. However, immediate attention is not required during these operations. Using the same method for 1—2 g samples the preparation time will be quite reasonable but for routine analysis a shorter procedure would be of great interest.

*Rapid preparation of the solution.* As pointed out earlier [1] 1—2 g samples of mild steels may be dissolved in HF + $H_2O_2$. If only a slight excess of HF is used steps 1 and 2 will not be necessary and thus the procedure is considerably shortened. Some separations were made (Table 2) using the following method: Portions of 1 g were dissolved in 3 ml HF (40 %) and 10 ml $H_2O$ and oxidized with 10 ml of $H_2O_2$ (30 %) added in small portions. The excess of $H_2O_2$ was

*Table 2.* Determination of Cu, Mn and Ni in two steels from National Bureau of Standards using the shorter procedure. Results in percent.

| Number and type of steel | Cu by cert. | found | Mn by cert. | found | Ni by cert. | found |
|---|---|---|---|---|---|---|
| 55E open-hearth iron | 0.065 | 0.0634 | 0.035 | 0.0315 | 0.038 | 0.0365 |
| | | 0.0642 | | 0.0318 | | 0.0368 |
| 125a silicon steel (3.32 % Si) | 0.084 | 0.0843 | 0.052 | 0.0461 | 0.053 | 0.0537 |
| | | 0.0841 | | 0.0462 | | 0.0535 |

boiled off. Separation and determination were performed as earlier. The results were satisfactory with the exception of Mn in 125a.

Experiments with alloyed steels showed some difficulties in destroying the carbides during solution of the samples in this way. If an excess of $HNO_3$ is used for this purpose evaporation seems inevitable. A possible alternative was to filter off the carbides, ash, and fuse with $NH_4HSO_4$ in a platinum crucible according to Feldman,[7] or with $NH_4F$. The excess of ammonium salt could then be evaporated without losing any of the constituents of the sample. Only small amounts of ammonium and sulphate or fluoride would thus be transferred to the solution after dissolving the melt.

Unfortunately, this procedure was not successful due to difficulties both in breaking down carbides and oxides, especially those of chromium, and also in dissolving the melt. It seemed more suitable to filter off the carbides on a plug of Teflon wool, and break down the carbides on the wool in a Teflon beaker with a small volume of $HNO_3$ and HF. The plug was then removed after washing, the solution taken to dryness and the residue dissolved in a small volume of 1 N HF. However, the practical performance was difficult and little time was saved. In most cases it is therefore recommended that $HNO_3$ be used and that the solution is taken to dryness according to the normal procedure.

*Adsorption at low concentrations of HF.* Adsorption may be performed as described earlier but the time required will be much less because of smaller volumes of solution and smaller amounts of resin necessary for separation. Using the shorter procedure, however, it is more difficult to reach the exact conditions used earlier especially regarding the concentration of HF. Thus some experiments showing the adsorption of Co were performed at different concentrations of HF in the presence of *ca.* 40 mg Fe/ml and 0.01 M $NO_3$. The batch equilibrium method was used. The results are shown in Fig. 1.
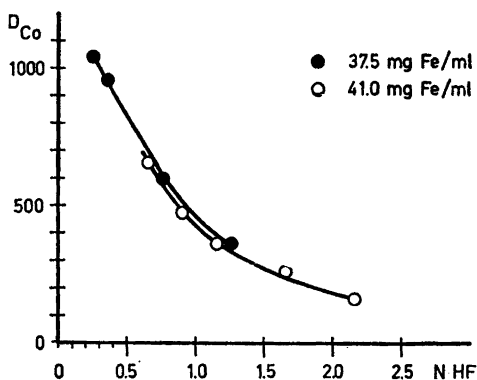


Fig. 1. Adsorption of Co at different concentrations of HF in the presence of Fe(III). Resin: Dowex 50WX8. Batch method.
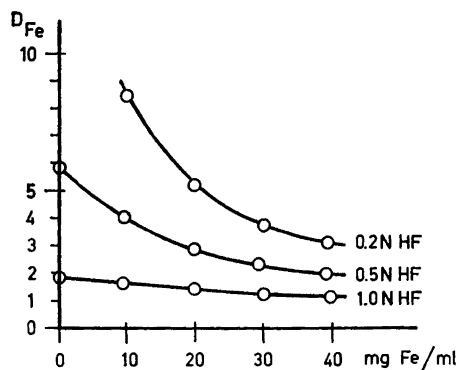
Fig. 2. Adsorption of Fe(III) at different concentrations of HF and Fe(III). Resin: Dowex 50WX8, 100−200 mesh. Elution method.

Since a surprisingly good effect was obtained at the lowest concentrations of HF a study of the adsorption of Fe(III) at different concentrations was also carried out in the same range. The same elution method was used as earlier [1] and the results for 1 N HF are also included in Fig. 2. It can be seen that the values of $D$ for Fe(III) decrease more rapidly with increasing concentration of iron at lower concentrations of HF.

Although much more iron is adsorbed at low concentrations of HF, cobalt is still taken up more strongly. Above 1 N HF the adsorption of Co decreases to relatively low values. It is therefore recommended that a small excess of HF is used when dissolving the sample or that the solution is diluted so that the concentration of HF in the separation step does not exceed 1 N. A reasonable margin should be kept since a lower concentration may even be preferable.

*Table 3.* Amount of Cr(III) in the effluent immediately and after washing with portions of 1 N HF and elution with 4 N $HNO_3$. Solution: 1 g of a chromium steel (12.85 % Cr) in 25 ml of 1 N HF. Column diameter 9.5 mm. Resin: 1 and 3 g of Dowex 50WX8, 100—200 mesh.

| Influent | 3 g column Cr in the effluent | | Influent | 1 g column Cr in the effluent | |
|---|---|---|---|---|---|
| | mg | % | | mg | % |
| 25 ml steel soln. | 88.54 | 68.90 | 25 ml steel soln. | 115.20 | 89.70 |
| 1 N HF ml | | | 1 N HF ml | | |
| 0 — 15 | 21.57 | 16.78 | 0 — 5 | 5.80 | 4.52 |
| 15 — 30 | 4.28 | 3.33 | 5 — 10 | 1.58 | 1.23 |
| 30 — 45 | 3.94 | 3.07 | 10 — 15 | 1.24 | 0.97 |
| 45 — 60 | 3.34 | 2.60 | 15 — 20 | 0.99 | 0.77 |
| 60 — 75 | 2.40 | 1.87 | 20 — 25 | 0.50 | 0.39 |
| 75 — 90 | 0.89 | 0.69 | 25 — 30 | 0.25 | 0.19 |
| 30 ml 4 N $HNO_3$ | 3.55 | 2.76 | 30 ml 4 N $HNO_3$ | 2.86 | 2.23 |
| Total | 128.51 | | | 128.42 | |

*Analysis of alloyed steels.* As reported in a previous paper [8] some problems occur in the elution of Cr(III) with solutions containing 1 N HF. This effect was studied in some experiments with a chromium steel (12.85 % Cr). Samples of 1.00 g were dissolved in HF + $HNO_3$, taken to dryness and the residue taken up in 25 ml of 1 N HF. The solutions were then passed through a 1 g or 3 g column (diameter 9.5 mm). The main fraction of Cr appeared immediately in the effluent and all but 2—3 % was washed out with 1 N HF. Typical examples are given in Table 3. The remainder was adsorbed strongly at the top of the column but was remarkably easily eluted with 4 N $HNO_3$. Chromium was determined by potentiometric titration.

Although addition of Ni and Mn to 1 g of a chromium steel showed 100 % recovery using a 1 g column, analysis of some alloyed steels were done with a 3 g column. Samples of 1 g were taken and washing with 90 ml of 1 N HF applied. The results are given in Table 4.

*Table 4.* Determination of Cu, Mn and Ni in some highly alloyed steels from National Bureau of Standards. Results in percent.

| Number and per cent of alloying elements | Cu by cert. | found | Mn by cert. | found | Ni by cert. | found |
|---|---|---|---|---|---|---|
| 50B (4.1 Cr, 1.0 V, | 0.110 | 0.106 | 0.325 | 0.317 | 0.089 | 0.085 |
| 0.4 Mo, 18.1 W) | | 0.106 | | 0.317 | | 0.085 |
| 132A (4.2 Cr, 1.9 V, | 0.12 | 0.112 | 0.27 | 0.264 | 0.14 | 0.136 |
| 4.5 Mo, 6.2 W) | | 0.112 | | 0.264 | | 0.135 |
| 134 (3.7 Cr, 1.1 V, | 0.114 | 0.109 | 0.155 | 0.153 | 0.077 | 0.076 |
| 8.7 Mo, 1.8 W) | | 0.109 | | 0.153 | | 0.076 |

In the eluates no Mo or W was detected and the content of V was less than 0.005 mg. The amount of chromium was 1.20 mg (50B), 1.20 mg (132A) and 1.12 mg (134) or 2.94, 2.85, and 3.00 %, respectively, of the original chromium content.

The results are in good agreement with the previously reported figures and the overall precision obtained is in this case better than 1 %.

## REFERENCES

1. Danielsson, L. and Ekström, T. *Acta Chem. Scand.* **20** (1966) 2402.
2. Danielsson, L. *Jernkontorets Ann.* **149** (1965) 501.
3. Kwestroo, W. and Visser, J. *Analyst* **90** (1965) 297.
4. Carlsson, C. G. *Jernkontorets Ann.* **129** (1945) 193.
5. Samuelson, O. *Ion Exchange Separations in Analytical Chemistry*, Almkvist & Wiksell, Stockholm 1963, chapters 5 and 9.
6. Dixon, E. J. and Headridge, J. B. *Analyst* **89** (1964) 185.
7. Feldman, C. *Anal. Chem.* **32** (1960) 1727.
8. Danielsson, L. *Acta Chem. Scand.* **19** (1965) 1859.

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