

# ION EXCHANGE CHROMATOGRAPHY OF IRON, MOLYBDENUM AND TITANIUM

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A method has been worked out for the rapid separation of iron, molybdenum and titanium. The mixture of these cations in 0.1M hydrochloric acid is added to an anion exchanger and eluted with the same acid to remove iron and titanium. Finally, molybdenum is eluted with 1M hydrochloric acid. The mixture of the two cations ( $\text{Fe}^{\text{II}}$ ,  $\text{Ti}^{\text{IV}}$ ) in 5.5M hydrochloric acid is then adsorbed in an exchanger and eluted with the same acid to remove titanium and iron is finally eluted with water.

## Introduction

One of the most powerful ways to use ion exchange in inorganic analysis is ion exchange in hydrochloric acid solution.<sup>1</sup> Most metals form chloride complexes and these differ greatly in stability and their ability to be adsorbed by polystyrene-type anion exchange resins.<sup>2</sup> Ion exchange separation of titanium from iron, molybdenum and many other metals has been studied.<sup>3,5</sup> A liquid-liquid extraction of ferric chloride or more correctly chloroferric acid, by ethyl ether or isopropyl ether was made from 1:1 hydrochloric acid.<sup>6</sup> Sandell<sup>7</sup> reported it as a good method for the removal of most of the iron in solution. In the present investigations, titanium(IV) chloride was found to be very weakly adsorbed on an anion exchanger at all concentrations of hydrochloric acid and readily eluted, whereas Kraus, Nelson and Smith<sup>4</sup> have, however, reported considerable adsorption of  $\text{Ti}^{\text{IV}}$  on such resin at certain concentrations but no detailed experimental conditions have been given. During the course of investigations, it was also found that the separation of molybdenum can also be achieved from iron and titanium under the conditions employed by previous workers<sup>8,9</sup> for the separation from other cations. The ion exchange separation of molybdenum from iron has also been made by Crouthmel and Johnson,<sup>10</sup> using ammonium thiocyanate as eluting agent. From the difference in absorbilities of the chloro complexes of molybdenum, iron and titanium in different concentrations of hydrochloric acid, on the column of anion exchanger, it appeared that these cations can be separated from each other. The investigations were carried out to this end, and the results obtained are reported below.

## Experimental and Results

**Apparatus and Reagents.**—A borosilicate glass column 1.8 cm in diameter, 40 cm high, provided with a sintered glass plate of coarse porosity was filled up with the resin up to a height of 10 cm.

Hilger Absorptiometer H810.301 (Filter photometer).

**Ion Exchange Resin.**—Amberlite CG 400( $\text{Cl}^-$ ) 100 to 200 B. Sieve Mesh, anion exchanger in the chloride form. The column of the resin was prepared from 10 g of the resin by repeatedly mixing the dry form with water and treating with 100 ml of 2M HCl to reactivate the exchangeable  $\text{Cl}^-$  ions. The resin is then transferred to the column and further washed with 100 ml HCl and finally several times with water.

**Standard Solution of Iron.**—Approximately 20 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in a few ml HCl and the volume made up to 1 l. with 1M HCl and standardized volumetrically by dichromate method. 1 ml of the solution = 3.9088 mg of  $\text{Fe}^{\text{III}}$ .

**Standard Solution of Molybdenum.**—1.5 g pure  $\text{MoO}_3$  was dissolved in a few ml dilute NaOH, made slightly acidic with HCl and diluted with 0.1M HCl to 1 l. 1 ml of the solution = 1 mg.

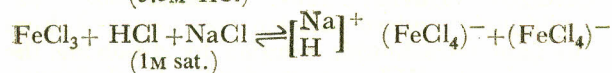
**Standard Solution of Titanium.**—1 g pure metal supplied by B.D.H. was dissolved in sulphuric acid and the solution made up to 1 l. with dilute sulphuric acid so that the acid concentration of the solution was 6N  $\text{H}_2\text{SO}_4$ . The solution was standardized gravimetrically. 1 ml = 1 mg. An additional standard solution was prepared from titanium tetrachloride solution by dissolving the latter in 2M HCl and standardized colorimetrically.

Other reagents used were KCNS,  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , amyl alcohol, stannous chloride and hydrogen peroxide.

**Column Experiments with Titanium.**—From the preliminary experiments on the distribution coefficient of titanium, it was indicated that  $\text{Ti}^{\text{IV}}$  has a very low distribution coefficient at all HCl concentrations. Only traces of titaniums are found to have been adsorbed on the resin phase

when the aqueous phase containing Ti(IV) in varying concentrations of hydrochloric acid was brought into contact with the resinous phase by shaking for 2 min. This was found to be contradictory to the findings of Kraus, Nelson and Smith<sup>4</sup> who reported considerable adsorption of Ti(IV) at higher concentrations of HCl. Further experiments were therefore continued on column by passing a known concentration of Ti(IV) contained in varying concentrations of HCl solution at a flow rate of 5 ml/min. The effluent was found to be free from titanium, but was found to be readily eluted when a small volume of the same acid concentration was passed through the column. This suggests that initially titanium is adsorbed on the column when no trace of it is found in the effluent, but its ready elution with a fraction of the volume of the same acid concentration as of influent indicates that titanium is not strongly adsorbed on the column as a chloro complex anion in 1–11.3M HCl.

*Column Experiments with Iron in HCl Solution.*—Iron solutions of different concentrations in varying concentrations of HCl were passed through the column. Iron was found to be quantitatively adsorbed when contained in an acid concentration of not less than 5M HCl and is not eluted from the column by 5–12M HCl. The same can, however, be successfully eluted with water. Below an acid concentration of 5M HCl, iron is partially adsorbed by the column, and at 1M HCl, it passes through the column completely unadsorbed. Further, it was found that iron is quantitatively adsorbed on the column if it is contained in 1M HCl which has been previously saturated with NaCl and is not eluted from the column by a large volume of the same solution, i.e. 1M HCl previously saturated with NaCl. In presence of NaCl in dilute HCl, additional Cl ions are furnished by the salt which are necessary for the formation of chloroferric acid or sodium chloroferrate as shown below:



The results obtained on column experiments are shown in Table 1.

*Column Experiments with Molybdenum (VI).*—In the first few experiments, Mo(VI) solution contained in 1M HCl solution was passed through the column. The effluent was free from traces of Mo(VI), indicating the quantitative adsorption of the metal on the column. But washing of the column with 1M HCl eluted molybdenum very slowly which shows initially weak adsorption of the metal like Ti(IV) on the column with the

difference that Ti (IV) or titanium was most readily eluted whereas Mo(VI) is eluted slowly. It was, however, noted that Mo(VI) is also quantitatively adsorbed when passed through the column in an acid concentration of 0.1M HCl and is not eluted by washing with a large volume of the same acid. Finally, it was eluted successfully with 300 ml 1M HCl, collecting a fraction of 50 ml each. The results obtained are shown in Table 2.

TABLE 1.—EFFECT OF HCL AND NaCl ON ADSORPTION OF IRON ON AMBERLITE CG-400 (Cl').

HCl M	Iron taken mg/10 ml	Iron adsorbed mg	% adsorption
1	39.088	Nil	Nil
2		7.654	10.94
3		21.543	53.84
4		35.567	91.02
5		39.015	99.81
6		39.088	100.00
8			100.00
11.3			100.00
1M HCl saturated with NaCl (30% w/v).			00.00
—	19.0544	19.0544	100.00
—	39.088	39.088	100.00

TABLE 2.

HCl M	Mo (VI) taken (mg/10 ml)	Mo (VI)(mg) eluted in successive 50 ml fractions of 1M HCl
1	10.00	0.250
		4.000
		5.000
		0.730
0.1	5.00	1.300
		1.700
		0.900
		0.600
		0.425
0.1	5.00	4.075
		4.075
		4.075
		4.075
		4.075
0.1	5.00	1.200
		2.300
		0.800
		0.350
		0.225
		0.150

*Column Experiments with Fe(III) and Ti(IV).*—After studying the ion exchange properties of these three elements separately, it was indicated that the separation of titanium can easily be achieved both from iron and molybdenum, singly or in presence of each other. Their separation was first studied in a pair of iron and titanium and then when all the three cations were present in solution.

*Separation of Iron(III) and Titanium(IV).*—Several mixtures of iron and titanium in different proportions were taken in 5.5 to 6.5M HCl and transferred to the column and washed with three separate 10 ml portions of the same acid. Iron was quantitatively adsorbed on the column, while titanium passes into the effluent and washings. Finally, iron was eluted with 100 ml water. The presence of moderate amount of sulphuric acid in the medium or influent does not affect the adsorption of iron and clear-cut separation is achieved provided the hydrochloric acid concentration of the medium (influent) before passing through the column is not less than 5.5M. Similarly, quantitative separation of both metals is achieved when they are contained in a medium of 1M HCl saturated with NaCl, which would greatly reduce the consumption of HCl when the chlorides of the two metals are separated through the column of anion exchanger.

*Separation of Iron(III), Titanium(IV) and Molybdenum(VI).*—The solution containing known amounts of Fe(III), Ti(IV) and Mo(VI) was taken in 0.1M HCl, transferred to the column of the anion exchanger and washed with three separate portions of 10 ml 0.1M HCl. The influent also contained moderate amount of sulphuric acid, since sulphuric acid up to a concentration of 3-4N has no effect on the adsorptions of molybdenum. The washings were combined with the effluent and reserved for the determination of iron and molybdenum.

*Elution of Molybdenum.*—Molybdenum was eluted from the resin with approximately 300 ml 1M HCl at a flow rate of  $5 \pm 1$  ml/min. The eluates were collected in 50-ml fractions in volumetric flasks. Molybdenum was determined colorimetrically.<sup>11</sup>

*Adsorption of Iron in the Effluent from Mo(VI) Separation.*—After the separation of molybdenum, the remaining cations, Fe(III) and Ti(IV) were received in a flask and an equal volume of concentrated HCl added to raise the concentration to above 5M HCl, transferred to the column at a flow rate of 5ml/min and washed with two or three separate 10 ml portions of 1:1 HCl (5.5-6.3M) till the washings were free from traces of titanium.

The effluent and washings were combined and reserved for the determination of titanium.

*Elution of Iron.*—Iron was eluted from the resin with approximately 100 ml of distilled water and finally with 10 ml of 2M HCl to remove the last trace of iron which might have been retained as cation in between the pores of the resin. The eluate was collected in a conical flask and the amount of iron was determined volumetrically by titration with potassium dichromate.

TABLE 3.—SEPARATION OF KNOWN AMOUNTS OF MOLYBDENUM.

Mo(VI) taken (mg)	Mo(VI) found (mg)	Difference
10.00	10.08	+ .08
20.00	20.03	+ .03
20.00	20.00	Nil
30.00	29.96	- .04
30.00	29.88	- .12

TABLE 4.—SEPARATION OF KNOWN SOLUTION OF IRON.

Iron taken (mg)	Iron found (mg)	Difference (mg)
19.544	19.540	- .004
19.544	19.546	+ .002
39.088	39.100	+ .012
39.088	39.000	- .088
39.088	39.080	- .008

TABLE 5.—SEPARATION OF KNOWN SOLUTIONS OF TITANIUM.

Ti taken (mg)	Ti found (mg)	Difference (mg)
20.00	20.08	+ .08
20.00	20.00	Nil
30.00	29.96	- .04
30.00	30.05	+ .05
40.00	40.05	+ .05

*Determination of Titanium in the Effluent.*—The effluent combined with washings received after the adsorption of iron on the column was transferred to a 250-ml volumetric flask and diluted with water to make up the volume. The amount of titanium was found colorimetrically. The results are shown in Table 5.

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#### References

1. K. A. Kraus and F. Nelson, *Proc. First United Nations Conf. on Peaceful Uses of Atomic Energy*, **7**, 113 (1955).
2. H. F. Walton, *J. Chem. Education*, **2**, 109 (1965).
3. W. E. Brown and W. Reiman, *J. Amer. Chem. Soc.*, **74**, 1278 (1952).
4. K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).
5. J. L. Hagne, E. D. Brown and H. A. Bright; *J. Research National Bur. Standards*, **53**, 261 (1954).
6. J. C. J. Ovenston, C. A. Parker and C. G. Hatchard, *Anal. Chim. Acta*, **6**, 7 (1952).
7. E. B. Sandell, *Colorimetric Metal Analysis* (Interscience Publishers, New York), 3rd ed., p. 869.
8. K. A. Kraus and G. E. Moore, *J. Amer. Chem. Soc.*, **77**, 3974 (1955).
9. Nabi Bux and Akram Khattak, *Pakistan J. Sci. Ind. Research*, **6**, 23 (1962).
10. C. E. Crouthmel and Johnson, *Anal. Chem.*, **26**, 1284 (1954).
11. For reference, see ref. 7, pp. 643, 649.