# VOLUMETRIC ESTIMATION OF IRON USING ALUMINIUM*

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Abstract

Ferric iron has been estimated after reducing it to ferrous state in sulphuric and hydrochloric acid media using fine Laminal aluminium powder. Difficulties experienced previously in hydrochloric acid medium, due to air oxidation have been overcome, using Bunsen valve. The various parameters influencing reduction such as aluminium powder concentration, acid concentration, etc. have been studied and suitable conditions for reduction have been arrived at. This method has been used to estimate iron in ferric salts, iron ore etc. Results obtained have been found to be $\pm$ 0.1% of those obtained by other standard methods.

## Introduction

The volumetric estimation of iron is usually done by reducing the ferric iron with suitable reductants to the ferrous state and is subsequently titrated with a standard soluion of an oxidant. Several methods are available for the reduction such as Jones reductor[1], Silver reductor[2], Stannous Chloride method, liquid amalgams, zinc and sulphuric acid etc.

Very little has been reported on the use of aluminium as a reducing agent. Mention has been made in the literature on the use of aluminium in the form of foil, wire[3] and Spirals[4]. E.R. Riegel[5] et al are the first to use aluminium powder for reducing ferric iron. They fail to get satisfactory results in hydrochloric acid solution due to air oxidation, when its concentration exceeds 1M.

In this paper an attempt has been made to estimate ferric iron volumetrically in sulphuric acid and hydrochloric acid solutions after reducing it with aluminium. The reaction between aluminium and ferric iron has been mentioned by Keith et al[6].

## Experimental

### Estimation of iron in sulphuric acid solution

A soluble salt of the ferric iron, i.e. A.R. ferric ammonium sulphate is used as the source of ferric iron. Very fine Laminal aluminium powder is used for the reduction. The excess of aluminium dissolves quickly enough to make its removal unnecessary. The aluminium powder is found to contain only 0.69% of iron. However, since the quantity of powder used in the analysis is very small, blank for the iron content is found to be negligible. Bunsen[7] valve is used to prevent air oxidation. The percentage of iron in the solution is first determined with the freshly prepared Jones reductor. It is calculated to be 11.71% and the theoretical content being 11.61%.

A suitable quantity of iron solution is pipetted out into a conical flask and 200 cc of dilute sulphuric acid of required concentration is added, followed by calculated amount of aluminium powder. The flask is closed with a cork fitted with Bunsen valve and the solution is boiled until the reaction is completed (till the solution becomes colourless). It takes normally 10-15 minutes. The cooled solution is titrated against 0.1N potassium permanganate solution. The iron content is found to be 11.71% which agrees well with the value found from the Jones reductor.

Table I (a) shows the effect of aluminium powder concentration. From the Table, it is clear that 1.55 Meq. of aluminium is not enough for reducing 1 Meq. of ferric iron, 3.11 Meq. of aluminium is seen to be enough for complete reduction and when higher amounts of powder are used, the acid concentration should be increased to 1.8772M to effect complete dissolution of the powder.

But when 3.11 Meq. of aluminium is used, the acid concentration as seen from Table II(a) should be below 0.9386M $H_2SO_4$ and this is quite understandable. On the other hand, 4.66 Meq. of aluminium is found to be effective at higher acid concentration too, i.e. 2.8 (See Table III (a). Thus, 1 Meq. of iron requires 4.66 Meq. of Aluminium in 0.5-3M $H_2SO_4$ for complete reduction. 3.11 Meq. of aluminum is enough if the acid concentration is below 1 M.

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When aluminium is used in the form of spiral, experiment can be carried out with ease. In order to see how far it compares with aluminium powder, super-purity aluminium wire wound in the form of spiral (Fig. 1) is used for the reduction of iron.

As seen from Table IV (a) in aluminium wire 6.64 Meq. of aluminium only brings complete reduction instead of 3.11 Meq. with aluminium powder. This is evidently due to the large surface area of the powder. Atomized aluminium powder is found to give similar results. Smaller the size of the particle greater the rate of dissolution and the efficiency of reduction.

Small amounts of iron can be easily determined by this method choosing proper metal and acid concentration. Table V (a) shows the estimation of different amounts of iron. As seen from the Table that at lower iron concentration, the amount of aluminium required is slightly higher than at higher concentration. For example, the aluminium powder required for reducing 0.2497 Meq. of iron should be 0.7766 Meq. But it requires 1.17 Meq. of aluminium powder. Because the chemical dissolution of aluminium powder is significant at the lower concentration than at higher concentration of iron, the amount of aluminium powder required to effect complete reduction is greater. The other reducible materials such as nitrate will interfere in the determination of iron in this method as in other methods, as it gets reduced to nitrous acid or hydroxylamine which react with the oxidizing agents. For this A.R. ferrous sulphate is oxidized by concentrated nitric acid to ferric sulphate and the nitrate is removed by heating the sample to the evolution of sulphur trioxide fumes and then the iron is estimated as described above. The iron content determined both by Jones reductor and aluminium method is 20.35% while the theoretical content being 20.1%.

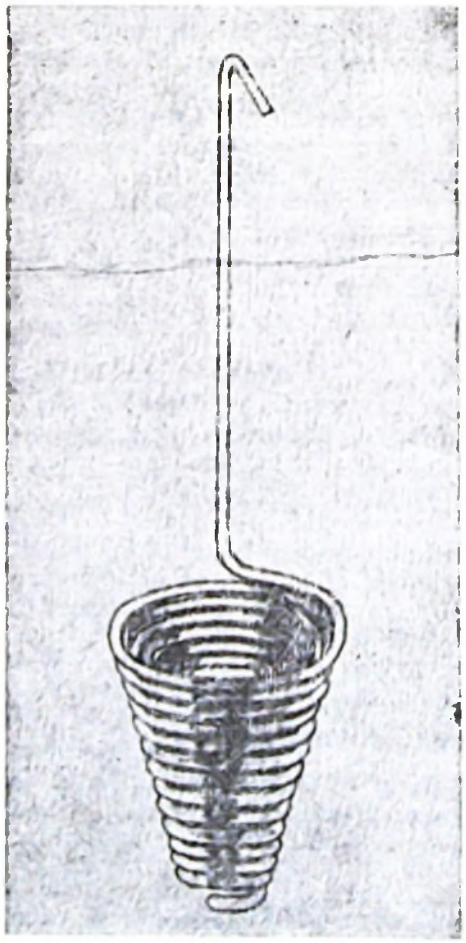


FIGURE 1

**Estimation of iron in HCl solution**

The estimation of iron in hydrochloric acid medium is difficult as the chloride iron accelerates the air oxidation of ferrous iron by forming complex with ferric iron. Hence, it is necessary to boil the solution in an inert atmosphere like that of carbon dioxide, nitrogen etc. But we are able to overcome the difficulty by using the Bunsen valve.

Ferric chloride is used as the source of iron and the same Laminal aluminium powder is used here too. The percentage of iron in the solution is estimated with freshly prepared silver reductor. It is calculated to be 20.25% and the theoretical value is 20.64%.

The experiment is carried out in the same way as described above except that ferric chloride and hydrochloric acid are used in the place of ferric ammonium sulphate and sulphuric acid. Unlike the sulphuric acid solution, the reduction is completed soon. Then the cooled solution is titrated against 0.1N potassium dichromate using diphenylamine as the indicator. The iron content is found to be 20.25% which coincides well with the value obtained from the silver reductor method.

Table 1(b) shows the effect of aluminium powder concentration. As seen from the Table, 6.22 Meq. of aluminium powder is necessary for complete reduction of 1 Meq. of iron unlike in sulphuric acid solution. From Table II (b) it is clear that 6.22 Meq. of aluminium can be used from 0.16M-3.9M hydrochloric acid. Above this acid concentration, complete reduction is not there (The solution remains

TABLE I (a)

EFFECT OF ALUMINIUM POWDER CONCENTRATION

| NO | AMOUNT OF Al POWDER IN Meq | VOL. IN ml | IRON(III) IN Moles/l | $H_2SO_4$ Moles/l | % OF IRON |
|---|---|---|---|---|---|
| 1. | 1·55 | 10 | 0·04992 | 0·4693 | 7·771 |
| 2 | 3·11 | 10 | 0·04992 | 0·4693 | 11·71 |
| 3 | 4·66 | 10 | 0·04992 | 0·4693 | 11·71 |
| 4 | 6·22 | 10 | 0·04992 | 0·4693 | 11·71 |
| 5 | 9·44 | 10 | 0·04992 | 1·8772 | 11·71 |
| 6. | 11·11 | 10 | 0·04992 | 1·8772 | 11·71 |

TABLE I (b)

EFFECT OF ALUMINIUM POWDER CONCENTRATION.

| NO | AMOUNT OF Al POWDER IN Meq | VOL IN ml | IRON(III) IN Moles/l | Hcl IN Moles/l | % OF IRON |
|---|---|---|---|---|---|
| 1 | 3·89 | 10 | 0·09961 | 1·5628 | 17·36 |
| 2 | 4·66 | 10 | 0·09961 | 1·5628 | 19·42 |
| 3 | 6·23 | 10 | 0·09961 | 1·5628 | 20·25 |
| 4. | 7·78 | 10 | 0·09961 | 1·5628 | 20·25 |
| 5 | 9·44 | 10 | 0·09961 | 1·5628 | 20·25 |
| 6 | 11·11 | 10 | 0·09961 | 1·5628 | 20·25 |

TABLE II (a)

INFLUENCE OF ACID CONCENTRATION
(WITH 3·11 Meq Al. POWDER)

| No. | $H_2SO_4$ IN Moles/l. | VOL. IN ml. | IRON III Moles/l | % OF IRON |
|---|---|---|---|---|
| 1. | 0·09389 | 10 | 0·04992 | 11·71 |
| 2. | 0·2347 | 10 | 0·04992 | 11·71 |
| 3. | 0·4693 | 10 | 0·04992 | 11·71 |
| 4. | 0·9386 | 10 | 0·04992 | 11·60 |
| 5. | 1·4079 | 10 | 0·04992 | 11·48 |
| 6. | 2·8158 | 10 | 0·04992 | 11·26 |

TABLE – II(b)

INFLUENCE OF ACID CONCENTRATION

| No. | Hcl IN Moles/l | VOL. IN ml. | IRON III IN moles/l | % OF IRON |
|---|---|---|---|---|
| 1. | 0·1563 | 10 | 0·09961 | 20·35 |
| 2. | 0·3907 | 10 | 0·09961 | 20·35 |
| 3. | 0·7814 | 10 | 0·09961 | 20·35 |
| 4. | 1·172 | 10 | 0·09961 | 20·35 |
| 5. | 1·5628 | 10 | 0·09961 | 20·25 |
| 6. | 2·3442 | 10 | 0·09961 | 20·35 |
| 7. | 3·1256 | 10 | 0·09961 | 20·25 |
| 8. | 3·9070 | 10 | 0·09961 | 20·25 |
| 9. | 4·6884 | 10 | 0·09961 | 20·04 |

TABLE III (a)

INFLUENCE OF ACID CONCENTRATION
with 4·66 Meq. Aluminium)

| No. | $H_2SO_4$ IN Moles/l | VOL. IN ml. | IRON III Moles/l | % OF IRON |
|---|---|---|---|---|
| 1 | 0·09389 | 10 | 0·04992 | 11·71 |
| 2 | 0·2347 | 10 | 0·04992 | 11·71 |
| 3 | 0·4693 | 10 | 0·04992 | 11·71 |
| 4 | 0·9386 | 10 | 0·04992 | 11·71 |
| 5 | 1·4079 | 10 | 0·04992 | 11·71 |
| 6 | 1·8772 | 10 | 0·04992 | 11·71 |
| 7 | 2·8158 | 10 | 0·04992 | 11·71 |

TABLE III (b)

| No. | TYPE OF Al | VOL IN ml | Iron moles/l | Meq of Al | % OF IRON |
|---|---|---|---|---|---|
| 1 | Al. Wire | 10 | 0·09961 | 10·44 | 20·25 |
| 2 | Al. Wire | 10 | 0·09961 | 11·7 | 20·25 |
| 3 | Al. Powder | 10 | 0·09961 | 6·22 | 20·25 |
| 4 | Al. Powder | 10 | 0·09961 | 7·78 | 20·25 |

TABLE IV (a)

| No | TYPE OF Al. | VOL. IN ml. | IRON(III) Moles/l. | Meq. OF Al. | % OF IRON |
|---|---|---|---|---|---|
| 1. | ALUMINIUM WIRE | 10 | 0·04992 | 4·13 | 11·02 |
| 2. | ,, | 10 | 0·04992 | 6·64 | 11·71 |
| 3. | ,, | 10 | 0·04992 | 5·38 | 11·54 |
| 4. | ALUMINIUM POWDER | 10 | 0·04992 | 3·11 | 11·71 |
| 5. | ,, | 10 | 0·04992 | 4·66 | 11·71 |

TABLE IV (b)

| NO | Method of Heating | HCl IN moles/l | Meq of Al | % OF IRON |
|---|---|---|---|---|
| 1 | With B valve | 1·5628 | 6·22 | 20·25 |
| 2 | | 2 3442 | 6·22 | 20·25 |
| 3 | " " | 3·1256 | 6·22 | 20·25 |
| 4 | Without B. valve | 1·5628 | 6·22 | 20·25 |
| 5 | " " | 3·1256 | 6·22 | 19.04 |

TABLE V (a)

ESTIMATION OF DIFFERENT AMOUNTS OF IRON

| No. | Meq. of Iron Taken | $H_2SO_4$ in Moles/l | Meq. of Aluminium used | % OF IRON |
|---|---|---|---|---|
| 1 | 0·2497 | 0·09389 | 1·17 | 11·8 |
| 2 | 0·4994 | 0·1878 | 2·33 | 11·8 |
| | 0·9988 | 0·4693 | 3·11 | 11·71 |
| | 1·9976 | 0·4693 | 6·22 | 11·66 |

TABLE V (b)

ESTIMATION OF DIFFERENT AMOUNTS OF IRON

| No | MEQ. OF IRON TAKEN | HCl IN Moles/l | MEQ OF Al. USED. | % OF IRON |
|---|---|---|---|---|
| 1 | 0·2491 | 0·1563 | 2·22 | 20·36 |
| 2 | 0·4982 | 0·3907 | 3·11 | 20·36 |
| 3 | 0·9964 | 1·5628 | 6·22 | 20·25 |
| 4 | 1·9928 | 3·1256 | 12·44 | 20·25 |

TABLE VI(b)

| No | HCl IN Moles/l | MEQ. OF Al | % OF IRON |
|---|---|---|---|
| 1 | 0·3907 | 1·55 | 18·51 |
| 2 | 0·1563 | 1·55 | 19·34 |
| 3 | 0·1563 | 1·89 | 19·74 |
| 4 | 0·1563 | 2·22 | 20·36 |
| 5 | 0·1563 | 2·22 | 20·36 |

TABLE VII(b)

| No | SAMPLE | THEORETICAL | Percentage of Iron | |
|---|---|---|---|---|
| | | | Al. Method | Ag. Reductor |
| 1 | Iron oxide ($Fe_2O_3$) | 69·9 | 69·65<br>69·65 | 69·65 |
| | Iron ore (Laterite) | | 25·03<br>25·03 | 25·03 |

TABLE VIII

| NO | SAMPLE | THEORETICAL | % OF IRON JONES REDUCTOR | SILVER REDUCTOR | ALUMINIUM METHOD |
|---|---|---|---|---|---|
| 1 | FERRIC AMMONIUM SULPHATE | 11·61 | 11·71 | – | 11·71<br>11·71 |
| 2 | FERRIC CHLORIDE | 20·64 | – | 20·25 | 20·25<br>20·35 |

yellow in colour). When the amount of aluminium powder is increased to 11.11 Meq. in 4.68M HCl complete reduction is effected. Since the dissolution of aluminium in hydrochloric acid is greater than in sulphuric acid at higher acid concentration more than the required amount of aluminium should be added for complete reduction and for the same reason, higer amount of aluminium powder is required for reducing 1 Meq. of iron in HCl solution.

As in sulphuric acid solution here also the quantity of aluminium required when wire is used is used is double (See Table III (b), Thus, only 10. 44-11.0 Maq. of aluminium completely reduces 1 Meq. of iron. Sulphuric acid solution can be heated even at higher acid concentration without air oxidation of ferrous solution unlike the hydrochloric acid solution. Table IV(b) shows how the Bunsen valve helps to prevent air oxidation especially at higher acid concentration. Thus, with Bunsen valve even 3.1 M hydrochloric acid solution can be boiled without air oxidation. If Bunsen valve is used, there is no need for removing HCL by evaporation until its concentration is reduced to 1M as mentioned by Riegel.[5] There is no need for maintaining a carbon dioxide atmosphere as used by Keith Light[6] for estimating the metallic aluminium in aluminium pigments and pastes.

To estimate small amounts of iron in hydrochloric acid solution care should be taken to maintain the acid concentratien and the quantity of aluminium. Thus, 0.2491 Meq. of (Table VI (b), iron should be reduced by 1.55 Meq. of aluminium. But it requires 2.22 Meq. of aluminium in 0.1563 HCl. This can be again attributed to the greater dissoluion of aluminium in hydrochloric acid than in sulphuric acid. Table V(b) shows the estimation of different amounts of iron and the appropriate amounts of acid and powder concentration. Iron in an iron ore is usually estimated after leaching it with hydrochloric acid and reducing it with stannous chloride or silver reductor and then titrated against standard dichromate or ceric sulphate. This method is applied for the estimation of iron in iron oxide ($Fe_2O_3$) and iron ore. As seen from Table VII(b) the values got by the aluminium method agree well with that obtained from the silver reductor.

## Conclusion

This method is applicable to any type of sample for which the Jones reductor and silver reducter methods are applicable. Table VIII shows the results obtained by different methods for comparison.

The results are confimed further by EDTA method using variamine blue B as indicator, ceric sulphate with n-phenylan-thranilic acid as indicator and by potentiometric tiration. Aluminium powder method for iron reduction is more effective than zinc powder.

Aluminium is baser than zinc ($Al^{+++}/Al = -1.66$ $Zn^{++}/Zn = -.763$) ; hence serves an effective reducing agent than zinc. As the equivalent weight of aluminium is only one fourth of that of Zinc (eq. wt. of Zn = 32.69, eq. wt. of aluminium = 8.99), the consumption for reduction is very small.

This study reveals the advantages in using aluminium over that of zinc. The difficulties confronted by earlier workers in using alumnium in presence of hydrochloric acid have been eliminated. Compared to other reduction methods, this method is cheap and convenient.

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