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# DETERMINATION OF TOTAL IRON CONTENT IN IRON ORE AND DRI: TITRIMETRIC METHOD VERSUS ICP-OES ANALYSIS

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## Abstract

The determination of reduction degree in a DR process is sensitive to the total iron in the ore and DRI. An accurate and high throughput analysis method for total iron has been developed. Titration of the solution after tin(II) chloride reduction of ferric ion is a widely used method for iron analysis. However, it is a multistep method that requires many chemical reagents and much time. In this work, an ICP-OES analysis method with higher or equivalent accuracy compared with the titrimetric method was developed. This method has much higher throughput and demands fewer chemical reagents compared with the titrimetric method. In this paper, a comparison of the two methods is presented.

## Introduction

As part of developing a novel flash ironmaking process at the University of Utah [1-10], analysis of a massive number of iron samples is carried out on a regular basis to determine the total iron content. One of the most widely used methods for iron content analysis is the titrimetric method, especially the method involving the reduction of ferric ion by tin(II) chloride (International Standard ISO 2597-1). This method is a multistep procedure requiring the preparation of an overwhelming number of chemical reagents, consuming much time, and challenging in detection of the end point. Regardless of the efforts to develop simpler titrimetric methods for the determination of total iron, titration-based methods still suffer from low throughput [11]. In this laboratory, a method that uses inductively coupled plasma-optical emission spectroscopy (ICP-OES) was developed to determine the total iron content in iron ores and reduced samples. Moreover, HF required in the titrimetric analysis of samples containing a significant content of silica reacts severely with the glassware. Replacing glassware with HF-resistant materials such as plastics is very challenging due to the difficulty in detecting the endpoint due to their opacity. A method that circumvents this problem is to convert silica into soluble salts, which is a very time consuming procedure requiring additional chemicals reagents and high temperature treatment of the samples. Bypassing the use of HF in the titrimetric method introduces significant errors in total iron determination as will be shown subsequently. In this work, an ICP-based method developed in this laboratory was compared with the ISO standard titrimetric method involving tin(II) chloride reduction. A brief description of both methods is presented and the results of the methods are compared.

Compared with the titrimetric method (ISO 2597-1), the ICP-based method requires a significantly fewer steps and chemical reagents, obviates the difficult and error-prone visual detection of the end points, allows high throughput rates, and provides equivalent or better accuracy and precision compared with the titrimetric method.

## Experimental Work

Table I shows the various iron-containing samples and their total iron content used for analysis in this study. Certified reference material (CRM #690) of a Canadian iron ore concentrate was obtained from the National Institute of Standards and Technology (NIST) in Boulder, Colorado, USA. Hematite (99.945%) and magnetite (99.99%) reference materials supplied by Alfa Aesar (Ward Hill, MA, USA) and Sigma Aldrich (St Louis, MO, USA). In addition, hematite concentrate ore from the Yuanjiacun Range, Shanxi Province, China and the flash reduced samples produced from it in a high temperature drop tube reactor [9, 10]. Flash reduced samples of magnetite concentrate from the Mesabi Range (U.S.) were also analyzed by both methods. The particle sizes of all samples were < 50 μm. All the samples were well mixed using a mechanical mixer for about 10 minutes in order to ensure the homogeneity of the samples before sampling for analysis. The accuracy of the analytical balance was ± 0.5 mg. All samples were analyzed at least three times with both methods.

**Table I.** Chemical analysis (in mass fraction) of the samples used in the analysis.

| Samples | Code | Total Iron | $SiO_2$ | $Al_2O_3$ | $P_2O_5$ |
|---|---|---|---|---|---|
| Certified Reference Sample | CRM | 0.6685 | 0.0371 | 0.018 | 0.025 |
| Pure $Fe_2O_3$ Reference Sample | RM 1 | 0.699 | - | - | - |
| Pure $Fe_3O_4$ Reference Sample | RM 2 | 0.724 | - | - | - |
| $Fe_2O_3$ Chinese Ore | H | 0.657 | <0.05 | <0.008 | <0.0007 |
| Flash Reduced Magnetite with High Reduction Degree | FRMH | 0.90 | <0.03 | <0.01 | |
| Flash Reduced Magnetite with Low Reduction Degree | FRML | 0.75 | <0.03 | <0.01 | |
| Flash Reduced Hematite with High Reduction Degree | FRHH | 0.90 | <0.05 | <0.008 | <0.0007 |
| Flash Reduced Hematite with Low Reduction Degree | FRHL1 | 0.72 | <0.05 | <0.008 | <0.0007 |
| Flash Reduced Hematite with Low Reduction Degree | FRHL2 | 0.67 | <0.05 | <0.008 | <0.0007 |

### Sample Analysis by Titrimetric Method after Tin(II) Chloride Reduction (ISO 2597-1)

We summarize here major steps of the titrimetric method to facilitate the comparison with the ICP method developed in this work. In the titrimetric method, iron oxide samples were digested in hydrochloric acid and reduced to $Fe^{2+}$ by $SnCl_2$. Then, $Fe^{2+}$ is titrated with a potassium dichromate solution of known concentration as shown by Eqs. [1] and [2]. When all $Fe^{2+}$ is consumed by potassium dichromate, violet color indicates the endpoint in the presence of sodium diphenylaminesulfonate (indicator):

$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+} \quad [1]$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^{+} = 6Fe^{3+} + 2Cr^{3+} + 7H_2O \quad [2]$$

Chemical solutions used in the titration process were prepared according to the ISO standard method (International Standard ISO 2597-1), which are as follows

1. Hydrochloric acid, HCl, ($\rho$ = 1.19 g/mL at 25 °C): Dilute 1:10 with deionized water (DI).
2. Sulfuric + phosphoric acid, $H_2SO_4$+$H_3PO_4$, mixture ($H_2SO_4$, ρ=1.84 g/mL, 150 mL; $H_3PO_4$, ρ=1.7 g/mL, 150 mL): 150 mL of $H_2SO_4$ are cautiously poured into about 300 mL of water while stirring, cooled in a water bath, then 150 mL of $H_3PO_4$ are added and diluted to 1 L with water.
3. Tin(II) chloride, $SnCl_2$, 100g/L solution: 100 g of $SnCl_2 \cdot H_2O$ are dissolved in 200 mL of HCl (ρ=1.16~1.19g/mL) by heating the solution in a water bath. The solution is cooled and diluted to 1 L with water. Then the solution is stored in a brown glass bottle.
4. Mercury (II) chloride, $HgCl_2$, 50g/L solution: 50 g of $HgCl_2$ are dissolved in 1 L deionized water.
5. Iron standard solution, 0.1 mol/L: 5.58 g of pure iron are weighed into a conical flask and a small filter funnel is placed in the neck. 75 mL of HCl (ρ=1.16~1.19g/mL, diluted 1:1) are added and heated until the iron is dissolved. The solution is cooled and oxidized with 5 mL of $H_2O_2$ (30% by volume), then heated to a boil, transferred to a 1000 mL volumetric flask, and diluted to volume with water.
6. Potassium dichromate, $K_2Cr_2O_7$, 0.01667 mol/L solution: $K_2Cr_2O_7$ powder is dried in an air bath at 140~150 °C for 2 h and cooled to room temperature in a desiccator. 4.904 g of this dried $K_2Cr_2O_7$ is dissolved in water and then the solution is diluted to exactly 1000 mL. Temperature is recorded ($T_1$) at which this dilution is made.
7. Sodium diphenylaminesulfonate**,** $C_6H_5NHC_6H_4SO_3Na$, 2 g/L; It is stored in a brown glass bottle.

The samples were carefully dried to avoid further iron oxidation. In the ISO standard, it was specified that the mass of the samples should be within the range 0.20-0.25 g. In this work, a sample mass in the range of 0.10-0.15 g was determined to be the optimum level. The samples were digested in 30 mL HCl (Reagent 1) in a conical flask covered with a watch glass on a heating plate. The temperature was kept at ~80 °C for about 1 h until the ore was substantially digested. The glass cover was then washed by warm DI water to ensure all the condensate from the decomposed solution vapor was recovered back into the conical flask. Then the solution was diluted to 50 mL with warm DI water and heated to just below the boiling. The solution color now was clear yellow with some precipitated undigested silicates.

Hot HCl (Reagent 2) was used to wash the glass cover and the inside wall of conical flask then $SnCl_2$ solution (Reagent 4) was immediately added drop by drop into the decomposed solution until the yellow color disappeared. An additional drop of $SnCl_2$ solution (Reagent 4) was added to make sure that all the $Fe^{3+}$ iron was reduced to $Fe^{2+}$.

After the solution was cooled in a water bath, 8 mL $HgCl_2$ (Reagent 5) was added to oxidize the excess $SnCl_2$ solution (Reagent 4) and mixed gently for 5 minutes. Then 30 mL $H_2SO_4$+$H_3PO_4$ mixtures (Reagent 3) was added to the solution after it was diluted to 150 mL with cold DI water. Five drops of $C_6H_5NHC_6H_4SO_3Na$ (Reagent 8) was added to the solution as an indicator and then titration with $K_2Cr_2O_7$ solution (Reagent 7) was conducted. The endpoint was obtained when the color of the solution changed to dark green and then to a violet color with one more drop of the titrant. The temperature at which the $K_2Cr_2O_7$ solution was used ($T_2$) and its volume used ($V_1$) were recorded to be used in subsequent calculations.

All the analyses were carried out at least three times at different times of the day on different days on randomly selected samples to minimize operator's systematic errors associated with the timing of the analysis or the level of skills.

In additions to the samples listed in Table I, one blank test was carried with each day's analysis under the same conditions. As $C_6H_5NHC_6H_4SO_3Na$ (Reagent 8) does not react with $K_2Cr_2O_7$ solution (Reagent 7) in the absence of iron, 1 mL iron standard solution (Reagent 6) was added in the blank solution with a 3-mL disposable pipette immediately before the addition of $SnCl_2$ solution (Reagent 4), which would promote indicator response in the blank solution and thus allow a suitable correction for the blank.

The blank test value was determined using the same amounts of all reagents and following all the steps of the procedure. The volume of $K_2Cr_2O_7$ solution (Reagent 7) used in the blank test was recorded as $V_0$. A volume of 1 mL of standard iron solution (Reagent 6) is equivalent to 1 mL of $K_2Cr_2O_7$ solution (Reagent 7) according to their concentration as prepared earlier, Eq. [2]. Thus, the blank test value of this titration ($V_2$) is calculated using the relationship $V_2 = V_0 - 1.00$.

At the end, the total iron content was calculated using the following relationship:

$$wFe = \frac{(V_1 - V_2)[1-(T_2 - T_1)\times 0.0002]}{m} \times 0.0055847 \times 100 \times K \qquad [3]$$

$$K = \frac{100}{100 - A} \qquad [4]$$

where

$wFe$: mass fraction of Fe in sample,

$T_1$: temperature when $K_2Cr_2O_7$ was prepared, ºC,

$T_2$: temperature when $K_2Cr_2O_7$ was used, ºC,

$V_1$: volume of $K_2Cr_2O_7$ consumed in sample titration, mL,

$V_2$: volume of $K_2Cr_2O_7$ consumed in blank titration, mL,

$m$: mass of sample, g,

$A$: moisture content, as a percentage by mass, determined in accordance with ISO 2596, and

$K$: conversion factor which is 1.00 for pre-dried test samples according to Eq. [4].

The above procedure is validated using analytical grade dry iron powder to an accuracy of 0.02 %.

Determination of Iron Fraction Using ICP-OES

Samples were prepared by accurately weighing around 0.2 g of each material in polypropylene disposable centrifuge tube. The weight of the empty tube and the sample were recorded. Under the fume hood, 15 mL of HCl ($\rho$ = 1.19 g/mL) were added into each tube using digital micro pipette to digest the sample. For high silica content samples, 2 mL of HF ($\rho$ = 1.15 g/mL) were added. The tubes were left open for about 20 minutes under the fume hood to release the produced gases in order not to pressurize the tubes when closed. Tubes were then closed and placed in a hot water bath until a solution with a clear yellowish solution with precipitates was observed. The solutions were left to cool down and then well mixed by a mechanical mixer for 10 minutes to ensure solution homogeneity. The solutions were then diluted to about 150 times using HCl (5% by volume). The HCl solution was prepared using HCl acid ($\rho$ = 1.19 g/mL) and DI water which were stirred for at least 2 hours before use.

Using 3-mL disposable transfer pipettes, around 0.2 g of the digested sample solution were added to a new polypropylene disposable centrifuge tube and then diluted by the 5% HCl solution till the overall solution weight was approximately 30. g. The weight of the transferred solution and the final diluted solution were recorded to calculate the actual dilution factor.

To calibrate the ICP machine, four calibration solutions were prepared with concentrations 0, 50, 80 and 100 ppm Fe in 5% HCl solution. In order to prepare these solutions, 500 ppm Fe standard solution in 5% HCl solution supplied by Inorganic Ventures (Christiansburg, VA, USA) was further diluted using the 5% HCl. All the diluted samples were well mixed by mechanical mixer for at least 10 minutes. Using the calibration solutions, the machine was calibrated and the calibration curve ($R^2$) value for the calibration linear curves should be at least 0.99999.

Drift sample and reference sample were analyzed every 5 samples to detect drift or error for the human operator or the machine.

The result obtained by the machine is the concentration of iron in the diluted solution in ppm. In order to calculate the iron fraction, the following equations were used:

$$wFe = C \times 10^6 \times m_{dil} \times F_{dil} \qquad [5]$$

$$F_{dil} = \frac{weight\ of\ diluted\ solution}{weight\ of\ the\ digested\ solution\ sample} \qquad [6]$$

$$\omega_{Fe} = \frac{wFe}{m_s} \qquad [7]$$

where

$wFe$: weight of iron in the diluted solution,

$C$: concentration of iron in the diluted solution in ppm,

$m_{dil}$: weight of the diluted solution,

$F_{dil}$: dilution factor,

$m_s$: weight of the powder sample, and

$\omega_{Fe}$: iron fraction in the sample.

Both analysis methods yield the total iron fraction of the samples. The calculated iron fractions of the samples were compared to the actual iron fraction. The samples standard deviation *SD* and relative standard deviation *RSD* (%) were calculated according to the following equations:

$$SD = \sqrt{\frac{\Sigma\,(X - \bar{X})^2}{N - 1}} \qquad [8]$$

$$\bar{X} = \frac{\Sigma\ X}{N} \qquad [9]$$

$$RSD\% = \frac{SD}{\bar{X}} \boxtimes 100 \qquad [10]$$

where

$SD$: standard deviation,

$X$: iron fraction,

$\bar{X}$: arithmetic mean of *X*,

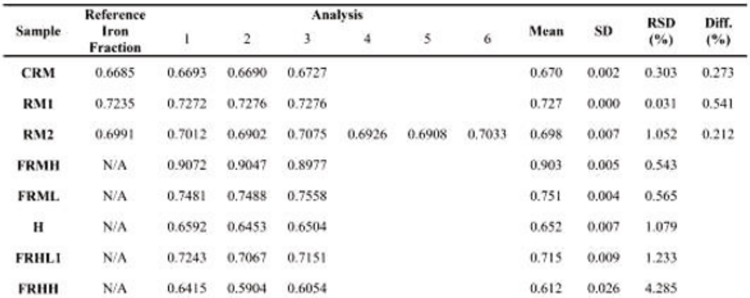
$N$: total number of repeated runs, and

$RSD\%$: percent relative standard deviation.

## Results

Tables II and III shows the results of both analysis methods with the calculated *SD* and %*RSD*. Comparison of the %*RSD* values from the two methods indicates that the methods have similar precision for samples with no or extremely low silica contents, as shown in Figure 1(a). For samples with high silica contents (> 5 mass %), the ICP method gave results with much greater precision than the titrimetric method, as shown in Figure 1(b). The two methods were found to be of similar accuracy, as Figure 2 shows. It is worth noting that a skilled operator can analyze at most 6-10 samples in an 8-hour period using the titrimetric method, whereas 30 – 50 samples can be analyzed using the ICP method in the same amount of time.

**Table II.** Analysis results of the titration method



| Sample | Reference Iron Fraction | Analysis | | | | | | Mean | SD | RSD (%) | Diff. (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | | | | |
| **CRM** | 0.6685 | 0.6693 | 0.6690 | 0.6727 | | | | 0.670 | 0.002 | 0.303 | 0.273 |
| **RM1** | 0.7235 | 0.7272 | 0.7276 | 0.7276 | | | | 0.727 | 0.000 | 0.031 | 0.541 |
| **RM2** | 0.6991 | 0.7012 | 0.6902 | 0.7075 | 0.6926 | 0.6908 | 0.7033 | 0.698 | 0.007 | 1.052 | 0.212 |
| **FRMH** | N/A | 0.9072 | 0.9047 | 0.8977 | | | | 0.903 | 0.005 | 0.543 | |
| **FRML** | N/A | 0.7481 | 0.7488 | 0.7558 | | | | 0.751 | 0.004 | 0.565 | |
| **H** | N/A | 0.6592 | 0.6453 | 0.6504 | | | | 0.652 | 0.007 | 1.079 | |
| **FRHL1** | N/A | 0.7243 | 0.7067 | 0.7151 | | | | 0.715 | 0.009 | 1.233 | |
| **FRHH** | N/A | 0.6415 | 0.5904 | 0.6054 | | | | 0.612 | 0.026 | 4.285 | |

**Table III.** Analysis results of the ICP method

| Sample | Expected Iron Fraction | Analysis 1 | 2 | 3 | 4 | 5 | 6 | 7 | Mean | SD | RSD (%) | Diff. (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CRM | 0.6685 | 0.6719 | 0.6751 | 0.6693 | 0.6752 | 0.675 | 0.6716 |  | 0.6730 | 0.0025 | 0.3646 | 0.676 |
| RM1 | 0.7235 |  | 0.7196 | 0.7317 | 0.7246 | 0.7245 | 0.7329 | 0.7334 | 0.7278 | 0.0057 | 0.7796 | 0.592 |
| RM2 | 0.6991 | 0.7018 | 0.6969 | 0.7029 | 0.693 | 0.696 | 0.7031 |  | 0.6990 | 0.0042 | 0.6045 | 0.021 |
| FRMH | N/A | 0.9069 | 0.9071 | 0.9047 | 0.9047 | 0.8951 | 0.9048 | 0.9159 | 0.9056 | 0.0061 | 0.6725 |  |
| FRML | N/A | 0.7524 | 0.758 | 0.7596 | 0.758 | 0.7501 | 0.7562 |  | 0.7557 | 0.0037 | 0.4890 |  |
| H | N/A | 0.6513 | 0.6525 | 0.6471 | 0.6546 |  |  |  | 0.6514 | 0.0032 | 0.4851 |  |
| FRHL2 | N/A | 0.6667 | 0.6657 | 0.6719 |  |  |  |  | 0.6681 | 0.0033 | 0.4982 |  |
| FRHH | N/A | 0.89999 | 0.9012 | 0.8962 | 0.9087 |  |  |  | 0.9015 | 0.0052 | 0.5810 |  |

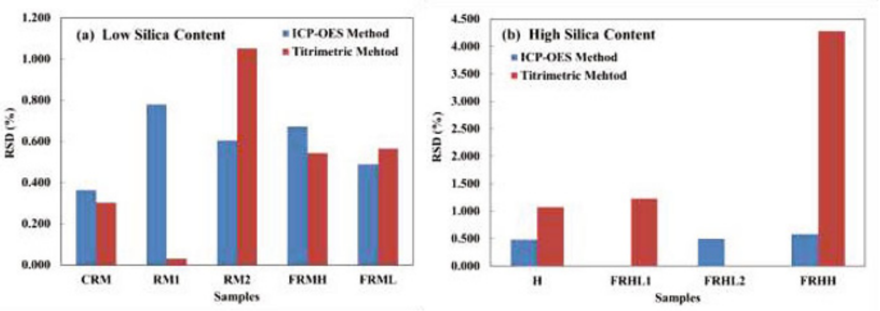


**Figure 1.** RSD values for the ICP-OES and titrimetric methods for samples with (a) low and (b) high silica contents.

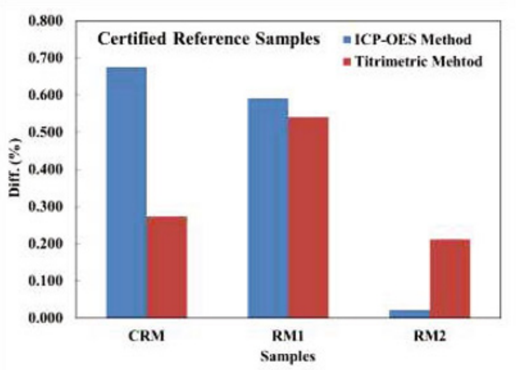


**Figure 2.** Comparison of the accuracy of both methods.

## Conclusions

Titrimetric analysis method was compared to an ICP-OES method developed in this laboratory for determining the total iron fraction in iron ores and DRI samples. The two analysis methods were of similar accuracy and precision. The ICP-OES method is much faster and easier to use than the titrimetric method. The ICP method can be easily used for high or low silica-containing iron samples. Titrimetric method introduces error when analyzing samples with high silica content due to the difficulty in using HF.

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