Application Note

№TIN-01050

Iron and Steel

Ferrous Salt in Etching Solution

Redox titration by
Automatic Potentiometric Titrator

Standard

1.Abstract

Here we demonstrate measurement of concentration of ferrous salt in etching solution according to the method from technical literatures as referred below.

When a sample does not contain chlorine ion, dissolve it in sulfuric solution, and titrate with 0.01mol/L potassium permanganate.

$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

If it contains chlorine ion, add manganese sulfate to void side reaction. If it contains too much hydrochloric acid, use vacuum evaporative condenser to dispel it.

2.Reference

1) Experiment and Calculation in Quantitative Analysis - Vol.2 - Kyoritsu Publication

3.Cautions in measurement

1) When ferrous salt in hydrochloric acid solution is titrated with potassium permanganate, the potassium permanganate is consumed as per below formula, generating chlorine or hypochlorous acid, which causes measurement error. It is assumed the generation of chlorine is due to hydrochloric acid strongly oxidized by manganese ions which exist temporarily during chemical reaction.

   $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

   Chlorine is generated even in dilute hydrochloric acid if ferric ion coexists. This is supposedly by concurrent reaction of ferric ions. However, if manganese ion coexists, chlorine is not generated. It is assumed that highly oxidizing manganese ions oxidize ions II to III and IV, then ferric ions, and returns to original manganese ions before oxidizing hydrochloric acid and that manganese ion II reduces redox potential of potassium permanganates. It is practiced in the analysis of irons ore to titrate with potassium permanganate by intentionally adding manganese ions II while maintaining hydrochloric acidity. In this test, the sample in etching solution contains chlorine ions, and manganese sulfate is added in order to avoid side reaction.
2) For manual analysis, titrate with potassium permanganate until it shows reddish color. Dense sample may show yellowish color due to ferrous ions generated in titration, however, it turns to colorless when phosphoric acid is added, thus generating complex ion of $Fe(PO4)_3^{6-}$.

4.Post-measurement care

Rinse the electrode with water, and keep it dipped in pure water to avoid drying up.

5.Test equipment

Main unit : Automatic potentiometric titrator (Standard preamplifier: STD－)
Electrode : Option Combination Pt. electrode

6.Reagent

Reagent : 0.01mol/L(0.05N) Potassium permanganate solution
Additive : Manganese sulfate (Crystalline manganese sulfate, Phosphoric acid, Sulfuric acid)

7.Measurement procedure

—Preparation—

1) Add 200mL pure water to 90g crystalline manganese sulfate ($MnSO_4 \cdot 4H_2O$) to dissolve, and add 175mL phosphorous acid (SG:1.7), then add 175mL SO_4 (SG:1.84) gradually, and cool it. Add water to make it total 1L, and leave it for 3 days. The above is how the manganese sulfate was prepared.

—Measurement—

1) Weigh 0.5g sample and put it in a 200mL beaker.
2) Add 40mL manganese sulfate and 50mL pure water.
3) Titrate with 0.01mol/L potassium permanganate to obtain concentration of ferrous salt ($FeCl_2$).
4) Perform a blank test under the same conditions to correct titration volume.

8.Formula

Concentration of ferrous salt (%) = (EPl － BLl) × TF × C1× K1 / SIZE

EPl : Titration volume (mL)
BLl : Blank level (0.0108mL)
TF : Factor of reagent (1.008)
Cl : Concentration conversion coefficient (6.3377mg/mL)
($FeCl_2$ equivalent to 1mL of 0.01mol/L $KMnO_4$)
Kl : Unit conversion coefficient (0.1)
SIZE : Sample size (g)

9.Example of measurement

－Ambient condition－

Room temperature : 23 ℃	Humidity : 45 %	Weather : Fair

-Titration parameters-

Model : AT-510
Method No. : 17
Titr.mode : Auto Intermit
Titr.form : EP Stop

[Titration parameter]

Form	:	EP Stop
APB No.	:	1
Unit No.	:	1
Detector No.	:	1
Unit	:	mV
Max.Volume	:	20.0mL
Wait Time	:	0s
Direction	:	Auto

[Control parameter]

End Point No.	:	1
End Sense	:	Auto
End Point Area	:	Off
Separation	:	Off
Over Titr.Vol.	:	0mL
Gain	:	1
Data samp.Pot.	:	4.0mV
Data samp.Vol.	:	0.5mL
Stability	:	0.5mV/s
Delay Time	:	1s
Limit Time	:	30s

[Result parameter]

<Calculation>
Calc.Type : Sample
Conc.1 : Set
CO1=
(EP1-BL1)*TF*C1*K1/SIZE

Unit : %
EP No. : 1
Temp.Comp. : Off

<Constant>
C1 : 6.3377
K1 : 0.1

<Titr. Constant>
Factor : 1.008

<Blank>
Blank1 : 0.0108

-Titration curve-

*** R e s u l t ***

Sample No. : 03-01
Date : 2001/06/04 16:27
Sample ID :

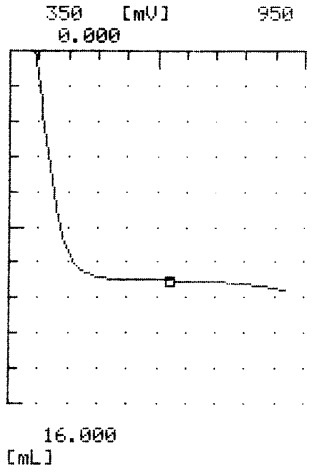
Method No. : 17
<Auto Intermit>
Method Name :

Titr.time : 00:11:19

Size : 0.5163g

Conc-1 : 13.108%

End point-1
Volume : 10.6041mL
Potential : 680.0mV



(The above printout data were obtained from titration by AT-510 unit.)

≪Titration parameter≫
Form: of formula / APB No. the burette used in titration / Unit No. APB Unit File number
Detector No. the detector used in titration/ Unit: potential unit in EP detection/ Max Volume: of titration
Wait Time: before titration starts / Direction: of titration
≪Control parameter≫
End Point No.: number of EPs / End sense: of endpoint / End Point Area: detection area / Separation: of potential
Over Titr.Vol.: over-titration/Gain: sensitivity of detection signal/Data samp.Pot.: potential changes of sampling signal
Data samp.Vol. titration volume for sampling detection signal / Control Speed: of dosing /Stability: of EP sense
Delay Time: before stability check / Limit Time: for stability check
≪Result parameter≫
Calc.Type of formula/Conc.1: formula 1/Unit: of result/EP No. of calculation/Temp.Comp.: temperature compensation
C1: concentration coefficient/ K1: unit conversion coefficient / Factor: of reagent / Blank1: blank level 1

－Measurement results－

N	Sample (g)	Titration (mL)	$FeCl_2$ (%)
1	0.5163	10.6041	13.108
2	0.5199	10.4438	12.820
3	0.5096	10.5516	13.214

Concentration of $FeCl_2$	
Mean	13.047 %
SD	0.2039 %
RSD	1.5627 %

＊ The above results were obtained by 3 tests of the same sample.

＊ Red underline shows the data from page 3/4.

10.Summary

The sample measurement shows favorable results of a good repeatability with 1.5% relative standard deviation.

Precise and reliable measurement is assured by the automated potentiometry.

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