Application Note

Ferrous ion and ferric ion in pickling solution

Industry	:	Iron and steel
Instrument	:	Automatic potentiometric titrator
Measurement method	:	Photometric titration / Chelatometric titration
Standards	:	

1. Scope

Ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}) in pickling solution were measured by chelatometric titration. **Combined method*** enables measurement of Fe^{2+} and Fe^{3+} with one sample.

First, a sample was titrated with 0.1mol/L ethylenediaminetetraacetic acid･2Na (EDTA), using salicylic acid as an indicator. An inflection point on the titration curve was regarded as the end point, and Fe^{3+} concentration was calculated from the volume of EDTA solution consumed to titrate sample to the end point. Then, Fe^{2+} in the solution after titration was oxidized to Fe^{3+} by adding potassium peroxodisulfate, and the solution was titrated with 0.1 mol/L EDTA solution. Total concentration of Fe^{2+} and Fe^{3+} was calculated from the volume of EDTA solution consumed to the end point. Fe^{2+} concentration was calculated by subtracting the Fe^{3+} concentration from the total concentration of Fe^{2+} and Fe^{3+}.

***Combined method**

Combined method is used for perform multiple measurement on one sample. It is possible to connect up to 5 methods.

2. Precautions

1) Adjust pH of a titration solution to 2-3 before measurement.
2) Handle the reagents in a well ventilated room or a draft chamber.

3. Post-measurement procedure

Wash photometric sensor with ethanol and then water.

4. Apparatus

Main unit	:	Automatic potentiometric titrator (preamplifier : PTA)
Electrode	:	Photometric sensor (interference filter : 530 nm)

5. Reagents

Titrant	:	0.1 mol/L EDTA solution
Indicator	:	2% salicylic acid ethanol solution
Addition reagent	:	potassium peroxodisulfate

6. Procedure

-Measurement-

1) Add 5 mL of 10-fold diluted sample into a 200 mL tall beaker.
2) Add 100 mL of pure water and 1 mL of 2% salicylic acid ethanol solution.
3) Titrate with 0.1 mol/L EDTA solution to measure Fe^{3+} concentration.

Method 1 ↑ / Method 2 ↓

4) Add 1 g of potassium peroxodisulfate into the beaker and dissolve it by stirrer during "Wait time" of combined method 2. After dissolving, press [Start] button to skip "Wait time" and start titration.
5) Titrate with 0.1 mol/L EDTA solution to measure total concentration of Fe^{2+} and Fe^{3+}.
6) Calculate Fe^{2+} concentration by subtracting the Fe^{3+} concentration from the total concentration of Fe^{2+} and Fe^{3+}.

7. Calculation

Combined method 1 : Measurement of Fe^{3+}

Fe^{3+} (g/L) = (EP1 - BL1) × TF × C1 × K1 / (R×S)

EP1	:	Titer (mL)
BL1	:	Blank level = 0.0000 mL
TF	:	Factor of titrant = 0.9993
C1	:	Concentration conversion coefficient = 5.585 mg/mL
K1	:	Unit conversion coefficient = 1
R	:	Dilution factor = 0.1
S	:	Quantity of diluted sample (mL)

Combined method 2 : Measurement of Fe^{2+}

Fe^{2+} and Fe^{3+} (g/L) = (EP1 - BL1) × TF × C1 × K1 / (R×S)

EP1	:	Titer (mL)
BL1	:	Blank level = 0.0000 mL
TF	:	Factor of titrant = 0.9993
C1	:	Concentration conversion coefficient = 5.585 mg/mL
K1	:	Unit conversion coefficient = 1
R	:	Dilution factor = 0.1
S	:	Quantity of diluted sample (mL)

Fe^{2+} (g/L) = CO1 - FCO1

CO1	:	Total concentration of Fe^{2+} and Fe^{3+} (g/L)
FCO1	:	Fe^{3+} (g/L)

8. Example

-Titration parameter-

Combined method

＜Titr. Mode＞ : Auto Intermit

＜Titr. Form＞ : EP Stop

＜Titr. Para.＞

Max. Volume	: 20 (mL)
Channel/Unit(Ctrl.)	: Ch3, %T
Channel/Unit(Ref.)	: Off
pH Polarity	: Standard
Titr. Type Check	: No Check
Direction	: Auto
Wait Time	: 0 (s) (Combined method 1) : 600 (s) (Combined method 2)
Dose Mode	: None

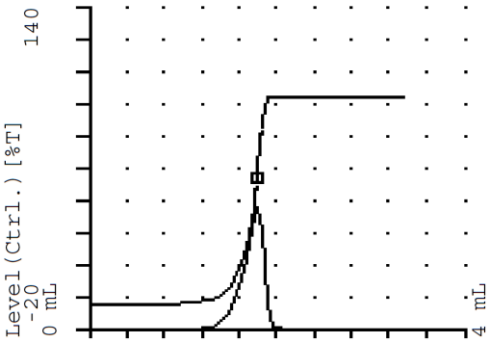
＜Ctrl. Para.＞

Number of EP	: 1
End Sense	: Auto
Gain	: 1
Data Sampling	: Auto
Ctrl. Speed	: Standard
Other Ctrl.	: Standard
Auto Int. Mode	: Standard
Stirrer Speed	: 4

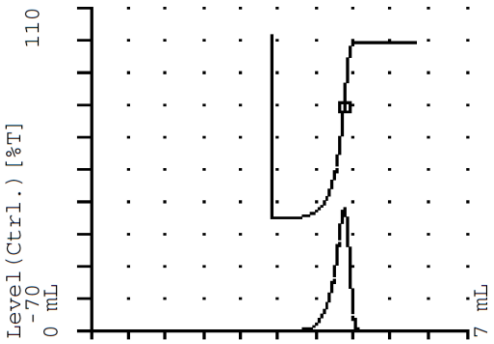
(The measurement parameter and the titration curve are an example of our automatic potentiometric titrator. For other models, parameter item may be different or other parameter item may be added.)

-Results-

-Method1 titration curve-



-Method2 titration curve-



-Measurement results-

	Quantity of diluted sample	Method 1 titer	Fe^{3+}	Method 2 titer	Fe^{2+} and Fe^{3+}	Fe^{2+}
	(mL)	(mL)	(g/L)	(mL)	(g/L)	(g/L)
1	5	1.7639	19.69	4.6807	52.25	32.56
2	5	1.7823	19.89	4.6907	52.36	32.46
3	5	1.7650	19.70	4.6810	52.25	32.55
Mean	-	-	19.76	-	52.29	32.52
SD	-	-	0.11	-	0.06	0.06
RSD (%)	-	-	0.57	-	0.12	0.17

9. Summary

In this measurement, the results showed a good repeatability with below 1% RSD (Relative standard deviation), and continuous titration of Fe^{3+} and total iron ion with “combined method” can be performed. When quantity of Fe^{2+} is less than the quantity equivalent to excess quantity of titrant in “method 1”, continuous titration by “combined method” cannot be performed. In that case, titrate Fe^{3+} and total iron ion separately.

In some samples, verification of the measurement capability is required. In such case, please contact us.

10. References