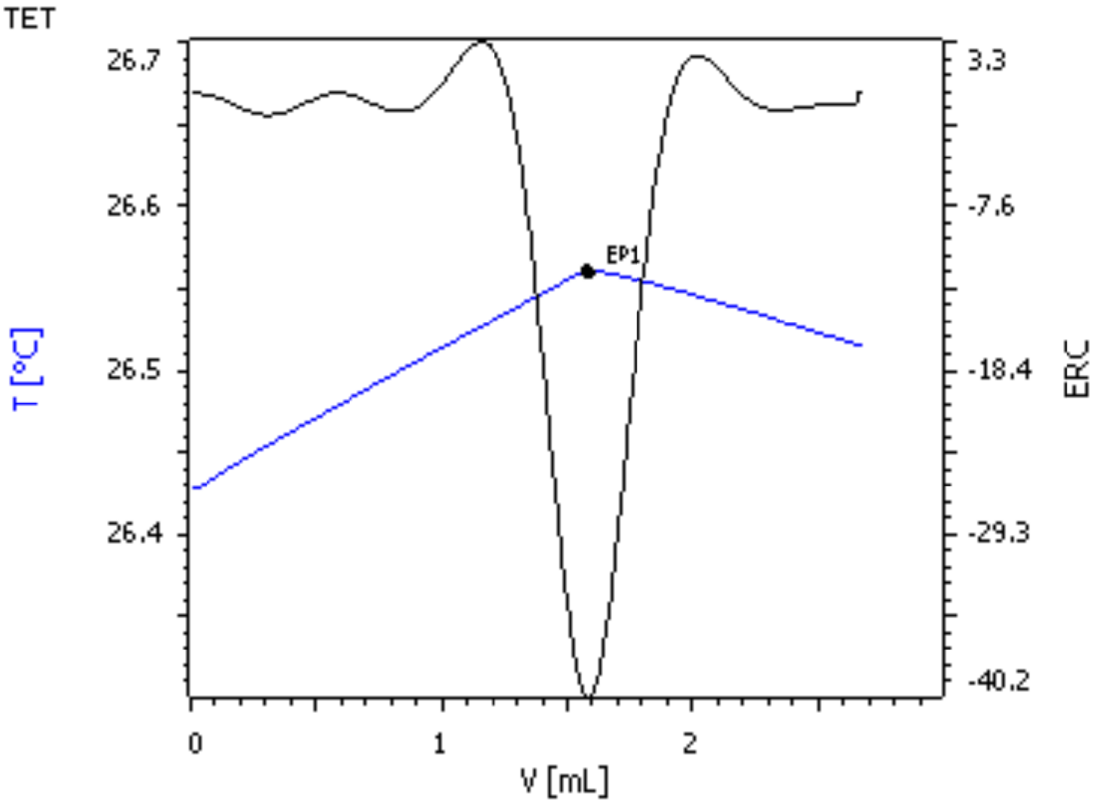
Titration Application Note H–121

Determination of ferrous ion in acidic solutions with ceric solution



This Application Note looks at the determination of ferrous ion in acidic solutions from approximately 0.25 g/L by thermometric titration with ceric titrant. The exothermic oxidation reaction shows a sharp endpoint that is detected using the Thermoprobe as a sensitive temperature sensor.

Metrohm

Method description

Principle

Ceric ion in strongly acidic solution is a suitable titrant for the direct determination of ferrous ion.

$Ce^{4+} + e^- \rightarrow Ce^{3+}$
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$

Thus, one mole Ce^{4+} corresponds to one mole Fe^{2+}. The reaction is exothermic. Although solution temperature rises are not as large as with $Cr_2O_7^{2-}$ or MnO_4^-, endpoints are sharp. Ce^{4+} solutions have the advantage over MnO_4^- solutions in that they are indefinitely stable, and only require standardization on preparation. If desired, perchloric acid may be substituted for sulfuric acid to enhance the redox potential.

E° volts in 1 mol/L acid solutions:
in H_2SO_4: 1.44
in $HClO_4$: 1.70

Samples

«Test solution»

Sample preparation

No sample preparation required

Configuration

Basic equipment list for automated titration

814 USB Sample Processor	2.814.0030
859 Titrotherm	2.859.0010
Sample rack 24 × 75 mL	6.2041.340
Thermoprobe, fluoride resistant	6.9011.040
Sample beaker 75 mL	6.1459.400
802 Rod Stirrer	2.802.0010
Stirring propeller 104 mm	6.1909.020
1 × 800 Dosino	2.800.0010
1 × Dosing unit 10 mL	6.3032.210
tiamo™	6.6056.222

Solutions

Titrant	$c(Ce^{4+})$ = 0.25 mol/L ammonium ceric nitrate, $(NH_4)_2Ce(NO_3)_6$ in 1 mol/L H_2SO_4 or $HClO_4$ solution
Acid	10% (w/v) H_2SO_4 solution, or 20% (w/v) $HClO_4$ solution
Standard solution	$c(Fe^{2+})$ = 0.3 mol/L ferrous ammonium sulfate (FAS), $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, prepared in 0.1 mol/L H_2SO_4 solution. Prepare freshly for each batch of Ce^{4+} solution to be standardized. Calculate amount of FAS to be weighed, taking into account the stated purity of the reagent.
Note: FAS is not a primary standard, but is suitable for standardizing Ce^{4+} solutions used for routine analysis. It is advised that Ce^{4+} solutions should be prepared in large quantities (10 to 25 L) to avoid the necessity of frequent standardizations.	
«Test solution»	A test solution of approx. ~1 g/L Fe^{2+} was prepared from FAS to simulate a customer solution containing a low Fe^{2+} concentration. This was prepared by weighing approximately 1.77 g FAS into a 250 mL volumetric flask containing 10 mL 10% (w/v) H_2SO_4 and making to volume with dist. water.

Analysis

Basic method (for approx. 1 g/L Fe^{2+} solution)
Pipette a 20 mL aliquot of test solution into a titration vessel, add 10 mL 10% (w/v) H_2SO_4, and titrate with $c(Ce^{4+})$ = 0.25 mol/L solution to an exothermic endpoint.

Standardization
Using a specially-constructed *tiamo*™ program, aliquots from 0.5 to 5.0 mL were dispensed in 0.5 mL increments from a Dosino into titration vessels containing 10 mL of 10% (w/v) H_2SO_4 and volumes of dist. water to give a total volume of approx. 30 mL at the start of titration. The *tiamo*™ program performs the regression analysis and automatically calculates the molarity, titration blank, and correlation coefficient of the regression line.

Metrohm

Method description

Parameters

Titrant dose rate (mL/min)	4
ERC EP1 (exothermic)	–15
Data smoothing («filter factor»)	45
Stirring speed (802 Rod Stirrer)	14
Evaluation start (mL)	0.5
Damping until (mL)	0.5

Calculations

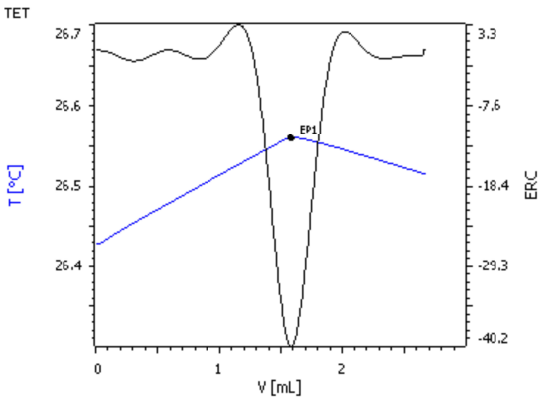
$g/L\ Fe^{2+} = ((EP1 - blank) \times C01 \times C02)/C00$

EP1 = titrant consumption in mL
C00 = sample weight in mL
C01 = concentration of cer titrant in mol/L
C02 = molecular weight of Fe (55.847 g/mol)

Results

«test solution» Fe^{2+}	1.03 ± 0.005 g/L (theoretical = 1.006 g/L)
Standardization:	$c(Ce^{4+})$ = 0.2389 mol/L blank = 0.029 mL coefficient of determination, R^2 = 1.0000

Titration plot



Titration plot, Fe^{2+} with Ce^{4+}

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