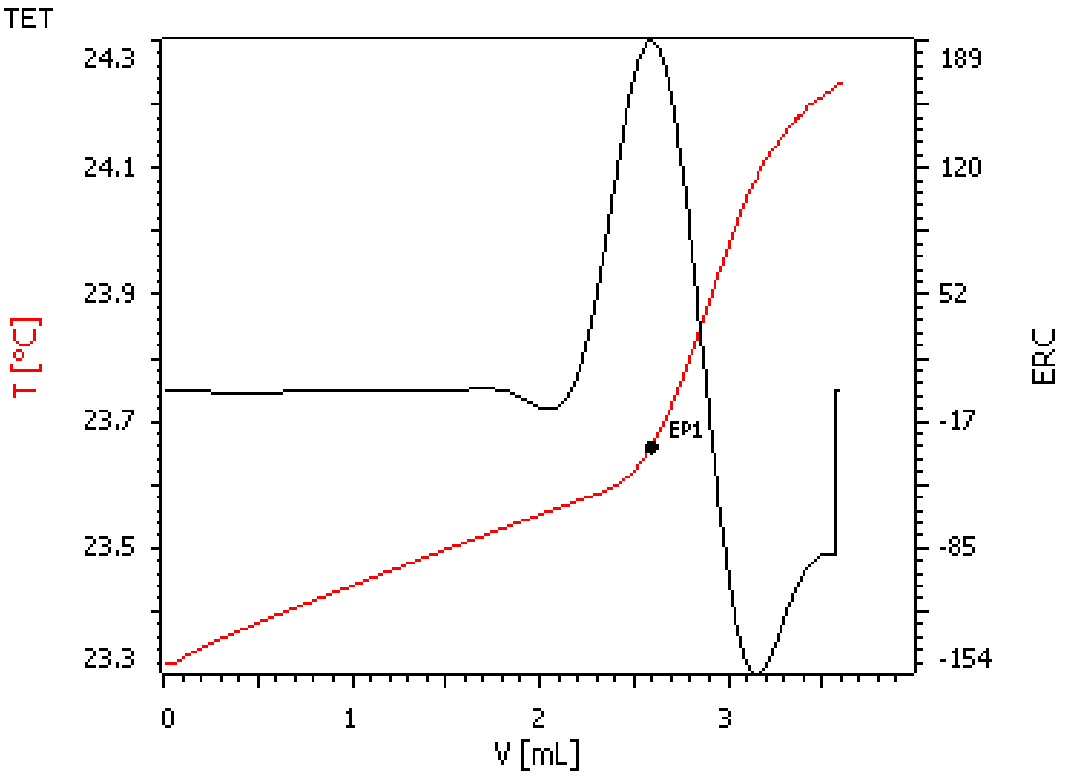
Titration Application Note H–127

Determination of aluminum by EDTA-Cu back-titration



This Application Note covers the determination of aluminum in silica-containing samples with EDTA using thermometric titration. Excess EDTA is titrated with a known concentration of Cu^{2+} ions. First traces of Cu^{2+} cause the H_2O_2 in the solution to decompose very rapidly, which is indicated by a sudden temperature increase.

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Method description

Principle

A thermometric titrimetric complexometric procedure has been adapted to the determination of aluminium in solutions, where the direct titration with fluoride is not practicable because of the interference of silica. For example, from the digestion of clays, zeolites, or other alumino-silicate-containing substances.
The new method involves the use of a thermometric indicator to give a sharp temperature change at the endpoint. When all the excess EDTA has been reacted with the Cu^{2+} titrant, the first trace of free Cu^{2+} ions causes the H_2O_2 in solution to decompose very rapidly, signaled by a sudden increase in the temperature of the solution. The heat of reaction ΔH_f for $H_2O_2 \rightarrow H_2O + [O]$ is approximately -98 kJ/mol, or approximately twice that for the reaction of a strong acid with a strong base or more than 4 times that of EDTA with Cu. This makes the technique quite robust.

Samples

Aluminium salts as test reagents.

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	6.9011.020
Titration Head for Titrotherm	6.9914.159
Sample beaker 75 mL	6.1459.400
802 Stirrer	2.802.0010
Stirring propeller (104 mm)	6.1909.020
4 × 800 Dosino	2.800.0010
4 × Dosing unit 10 mL	6.3032.210
tiamo™	6.6056.222

Solutions

$CuSO_4$ back-titrant	$c(CuSO_4 \cdot 5H_2O) = 0.2$ mol/L
EDTA solution	$c(Na_4EDTA) = 0.2$ mol/L, Na_2H_2EDTA can be used also, with 16 g solid NaOH added per liter of solution prepared to aid dissolution.
H_2O_2 solution	Dilute 35% (w/v) H_2O_2 solution 1:10 with DI water. Stabilize with 2 mL glacial acetic acid per liter of dilute solution.
NH_3/NH_4Cl buffer solution	Dissolve 87.5 g NH_4Cl in 568 mL concentrated ammonia solution and make to 1000 mL with DI water.
Ni solution as standard	$c(Ni^{2+}) = 0.04$ mol/L, other pure metal solutions can be employed as standards

Preparation of the test reagent

Approximately 8 mmol of both $Al_2(SO_4)_3 \cdot 16H_2O$ and $AlK(SO_4)_2 \cdot 12H_2O$ were weighed accurately into 250 mL Erlenmeyer flasks equipped with a magnetic stirrer. 120 mL of 0.2 mol/L Na_4EDTA were accurately dispensed into each flask, and the sides of the flask carefully washed down with DI water. Both flasks were equipped with a short neck funnel to prevent losses by splashing. To each flask, 2 mL concentrated NH_3 solution was added. The flasks were placed on a magnetic hot plate stirrer and brought to and held at a gentle boil for 5 minutes. After cooling, the contents of the flasks were transferred quantitatively to 500 mL volumetric flasks and made to volume with DI water. Aliquots of 25 mL were taken for titration. For the determination of Al in alumina-silicates, a suitable digestion procedure will need to be adopted to bring all Al into the Al^{3+} form before titration.

Analysis

An aliquot of 25 mL is pipetted into a 75 mL titration tube. The titration program automatically adds 2.5 mL NH_3/NH_4Cl buffer solution, with 1 mL 3.5% (w/v) H_2O_2 being injected immediately before the start of the titration. The excess of EDTA is back-titrated with 0.2 mol/L Cu^{2+} solution to the endpoint marked by a strong upward temperature inflection. The aluminium content is calculated both as % Al and % Al_2O_3 (w/w).

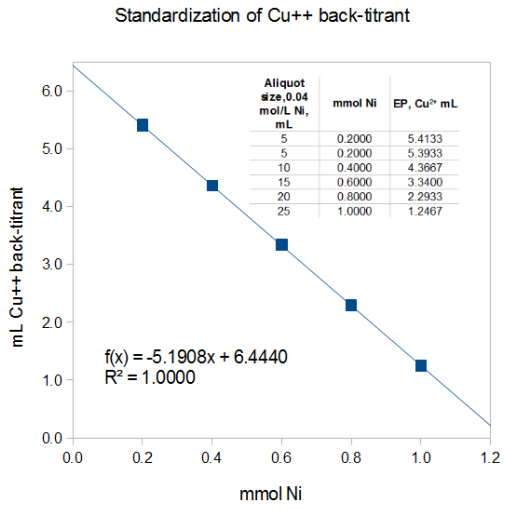
Standardization of $CuSO_4$ back-titrant with Ni^{2+}

Only the Cu^{2+} back-titrant needs to be standardized. Aliquots of 0.04 mol/L Ni^{2+} solution of volume 5, 10, 15, 20, and 25 mL are pipetted by bulb pipette into 75 mL titration tubes. Volumes of the first three aliquots are adjusted to approximately 20 mL with DI water. The titration program automatically and successively adds 6 mL ≈0.2 mol/L Na_4EDTA solution and 2.5 mL NH_3/NH_4Cl buffer solution, with a programmed "wait" of 20 seconds after the Na_4EDTA addition to allow complete reaction of the Ni^{2+} with the EDTA. Immediately before the commencement of the titration, 1 mL of 3.5% (w/v) H_2O_2 solution is injected. The excess of EDTA is back-titrated with 0.2 mol/L Cu^{2+} solution to the endpoint marked by an upward inflection. The

Metrohm

Method description

volume of Na_4EDTA solution predosed was chosen to comfortably accommodate all aliquots of 0.04 mol/L Ni^{2+} solution titrated.
A linear regression analysis is performed, plotting mmol Ni^{2+} on the x-axis against mL Cu^{2+} back-titrant on the y-axis. The molarity of the Cu^{2+} back-titrant is computed from the reciprocal of the gradient, and is stored in *tiamo*™ in Configuration > Titrants/Solutions. The y-intercept is used as the "blank" value (the volume from which back-titration endpoint volumes are subtracted) and stored as a Common Variable (CV) in *tiamo*™.



Regression analysis of standardization of Cu^{2+} back-titrant solution with standard 0.04 mol/L Ni^{2+} solution

Calculation of Cu^{2+} molarity and "blank":

Molarity = 1/gradient = 1/5.1908 = 0.19265 mol/L
The y-intercept from the standardization regression analysis is used for the "blank" (6.444 mL).

Parameters

Main titration parameters for Al determination

Titrant dose rate (mL/min)	4
ERC EP1 (endothermic)	50
Data smoothing ("filter factor")	60
NH_3/NH_4Cl buffer added, mL	2.5
$c(H_2O_2)$ = 3.5% (w/v), mL	1
Stirring speed (802 Stirrer)	10

Main titration parameters for standardization

Titrant dose rate (mL/min)	4
ERC EP1 (endothermic)	50
Data smoothing («filter factor»)	43
c(Na_4EDTA) = 0.2 mol/L predose, mL	6
NH_3/NH_4Cl buffer added, mL	2.5
$c(H_2O_2)$ = 3.5% (w/v), mL	1
Stirring speed (802 Stirrer)	10

Calculations

Sample mass in aliquot = Sample mass weighed × aliquot volume in mL / volumetric flak volume in mL

% Al w/w = ((blank – EP1) × C01 × C02 × 0.1)/C00

% Al_2O_3 w/w = ((blank – EP1) × C01 × C02 × 0.1)/C00 × 2

EP1 = endpoint in mL

C00 = sample mass in aliquot in g

C01 = concentration of titrant in mol/L

C02 = molecular weight of Al (26.981538 g/mol)

0.1 = conversion factor for %

2 = stoichiometry factor

% Al in sample: % Al (w/w) = ((blank, mL – mL Cu^{2+}) × Cu^{2+} mol/L × 26.981538 × 0.1)/sample mass in aliquot, g

% Al_2O_3 in sample: % Al_2O_3 (w/w) = ((blank, mL – mL Cu^{2+}) × Cu^{2+} mol/L × 101.961276 × 0.1)/(sample mass in aliquot, g × 2)

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Method description

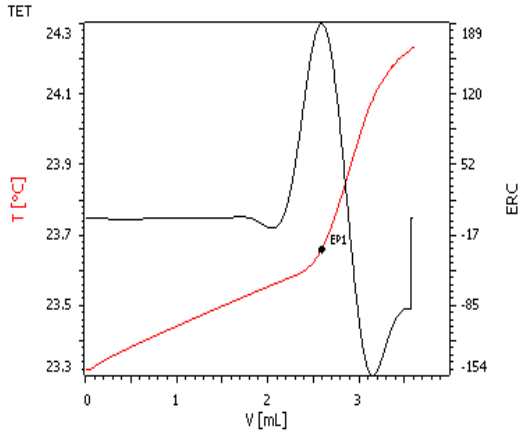
Results and discussion

Results of analysis of aluminium salts

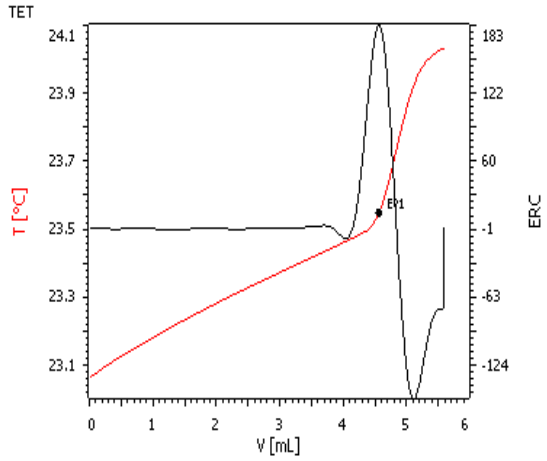
	Al2(SO4)3.16H2O			AlK(SO4)2.12H2O		
no.	mL Cu(II)	% Al	% Al2O3	mL Cu(II)	% Al	% Al2O3
1	2.5733	7.91	14.94	4.5667	5.11	9.65
2	2.6000	7.85	14.83	4.5667	5.11	9.65
3	2.6000	7.85	14.83	4.5667	5.11	9.65
4	2.5867	7.88	14.89	4.5667	5.11	9.65
5	2.5933	7.86	14.86	4.5600	5.12	9.68
6	2.5933	7.86	14.86	4.5600	5.12	9.68
7	2.5867	7.88	14.89	4.5667	5.11	9.65
8	2.5933	7.86	14.86	4.5600	5.12	9.68
9				4.5600	5.12	9.68
10				4.5667	5.11	9.65
average	**2.591**	**7.87**	**14.87**	**4.564**	**5.11**	**9.66**
std dev	**0.01**	**0.02**	**0.04**	**0.00**	**0.01**	**0.02**

The entire automated titration sequence (including rinsing of the titration head) is completed in less than 3 minutes

Titration plots

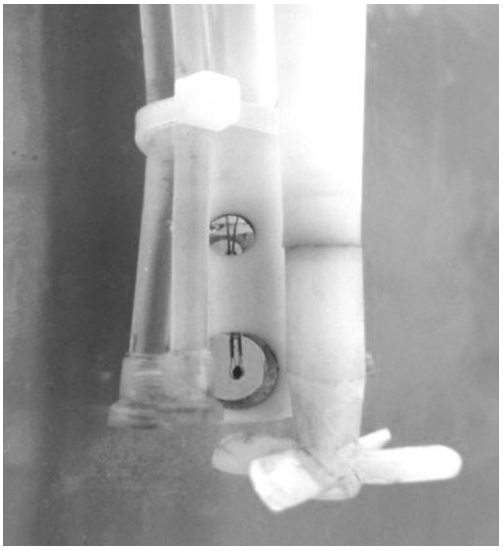


Back-titration of $Al_2(SO_4)_3 \cdot 16H_2O$



Back-titration of $AlK(SO_4)_2 \cdot 12H_2O$

Optimization of the titration arrangement



Optimal arrangement of titration head for use in 75 mL titration tubes. Note titrant delivery tubes are lower than the Thermoprobe.

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