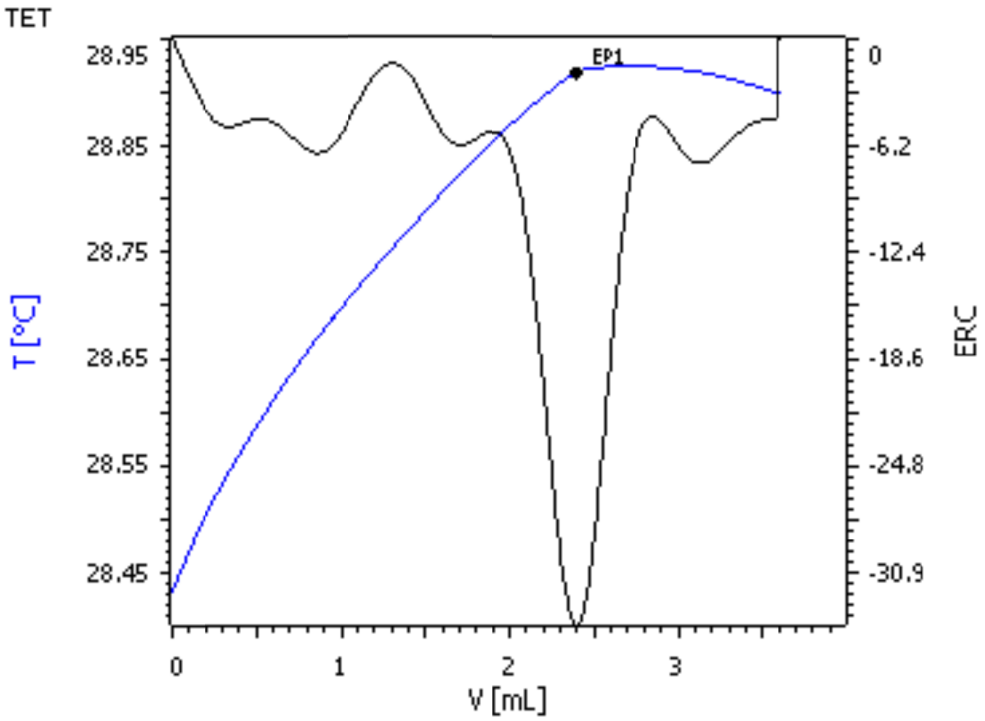
Titration Application Note H–120

Determination of aluminum ion in acidic solutions containing ferric and ferrous ions



This Application Note describes the determination of aluminum ion down to approximately 0.5 g/L in acidic solutions containing ferric, ferrous, and other ions whose hydroxides do not dissolve in strongly basic solutions.

Metrohm

Method description

Principle

Use is made of the amphoteric property of aluminum hydroxide to permit a physical separation from other metal ions whose hydroxides are not soluble in strongly basic media. For example, when NaOH or KOH is added to mixed solutions of Al^{3+} and Fe^{3+}, the Al first precipitates as $Al(OH)_3$, then redissolves to form $[Al(OH)_4]^-$. In contrast, Fe^{3+} precipitates as «ferrihydrite», a poorly-ordered hydrated Fe(III) oxide with a stoichiometry corresponding to $Fe(OH)_3$, and which is not soluble in strongly basic solutions.
The Al may then be quantitatively separated from the Fe by filtration and an aliquot taken for titration. The aliquot is strongly acidified with HCl to return the Al to the Al^{3+} state, then titrated with standard NaF solution in the presence of a pH 4.5 potassium acetate/sodium acetate/acetic acid buffer solution.

$Al^{3+} + Na^+ + 2\ K^+ + 6\ F^- \leftrightarrow\ NaK_2AlF_6$
Thus 1 mol Al^{3+} corresponds to 6 mol F^-

Samples

Nominal concentration of «sample solutions»:

	HCl g/L	Fe^{3+} g/L	Al^{3+} g/L
Sample A	36.4**	76.0***	*
Sample B	30.6**	114.9***	*
Sample C	27.1**	78.3***	*

* Results reported below
** Experimental details reported in **AN H-118**
*** Experimental details reported in **AN H-119**

Sample preparation

See under section «Analysis»

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(NaF) = 1 mol/L NaF solution
	Concentrated HCl solution, ~35% (w/v)
	c(NaOH) = ~5 mol/L sodium hydroxide
Acetate buffer:	pH 4.5 mixed buffer solution: Make 130.9 g anhydrous potassium acetate, 54.7 g anhydrous sodium acetate, and 115 mL of glacial acetic acid to 1000 mL with dist. water. The molar equivalents of the hydrated salts of potassium and sodium acetate may be used if more convenient.

Analysis

Sample preparation and titration
It is necessary to add a sufficient excess of strong base to firstly precipitate all metal ions and then redissolve the Al as$[Al(OH)_4]^-$. In the examples used here, 2 mol/L NaOH was used as it was to hand, but 5 mol/L NaOH could be more convenient. Different sample treatments were used according to the nominal Al contents of the solutions.

Sample A
A 10 mL aliquot of 1:4 diluted sample was pipetted into a 200 mL volumetric flask, and approx. 50 mL dist. water added and mixed by swirling. 75 mL of 2 mol/L NaOH was added while swirling, with the flask made to volume with dist. water. A small precipitated $Al(OH)_3$ had been dissolved and extracted from the metal hydroxide matrix.
The slurry was then filtered through double fast-filtering papers (Whatman #4 or Advantex #1) and 20 mL of filtrate pipetted into a titration vessel. 2 mL of concentrated HCl was added to ensure that all Al was present as Al^{3+}. 10 mL of buffer solution was added and the solution titrated with 1 mol/L NaF solution.

Sample B
A 50 mL aliquot of 1:4 diluted sample was pipetted into a 250 mL volumetric flask and approx. 50 mL dist. water added and mixed by swirling. 50 mL of 2 mol/L NaOH was added while swirling, with the flask made to volume with dist. water. A small magnetic stirrer was added, and the contents were stirred for 5 minutes to ensure that all precipitated $Al(OH)_3$ had been dissolved and extracted from the metal hydroxide matrix.

Method description

The slurry was then filtered through double fast-filtering papers (Whatman #4 or Advantex #1) and 30 mL of clear filtrate pipetted into a titration vessel. 3 mL of concentrated HCl was added to ensure that all Al was present as Al^{3+}. 10 mL of buffer solution was added and the solution titrated with 1 mol/L NaF solution.

Sample C

A 20 mL aliquot of 1:4 diluted sample was pipetted into a 200 mL volumetric flask, and 150 mL of 2 mol/L NaOH was added while swirling, with the flask made to volume with dist. water. A small magnetic stirrer was added, and the contents were stirred for 5 minutes to ensure that all precipitated $Al(OH)_3$ had been dissolved and extracted from the metal hydroxide matrix.
The slurry was then filtered through double fast-filtering papers (Whatman #4 or Advantex #1) and 10 mL of filtrate pipetted into a titration vessel. 3 mL of concentrated HCl was added to ensure that all Al was present as Al^{3+}. 10 mL of buffer solution was added and the solution titrated with 1 mol/L NaF solution.

Blank determination

10, 15, and 20 mL of final filtrate from sample A were acidified, buffered, and titrated with 1 mol/L NaF solution. Aliquot volumes in mL (x-axis) were plotted against EP volumes (y-axis) and the blank determined from the y-axis intercept of the regression line.

Parameters

Basic experimental parameters

Titrant dose rate (mL/min)	4
ERC EP1 (exothermic)	–20
Data smooting ("filter factor")	45
Stirring speed (802 Rod Stirrer)	14
Evaluation start (mL)	0.5
Damping until (mL)	0.5

Note that for Sample B, which had only approx. 0.5 g/L Al, it was necessary to employ the following parameters, as the EP volume was only approx. 0.2 mL:

Titrant dose rate (mL/min)	4
ERC EP1 (exothermic)	–20
Data smooting ("filter factor")	25
Stirring speed (802 Rod Stirrer)	14
Evaluation start (mL)	0.1
Damping until (mL)	0

Calculations

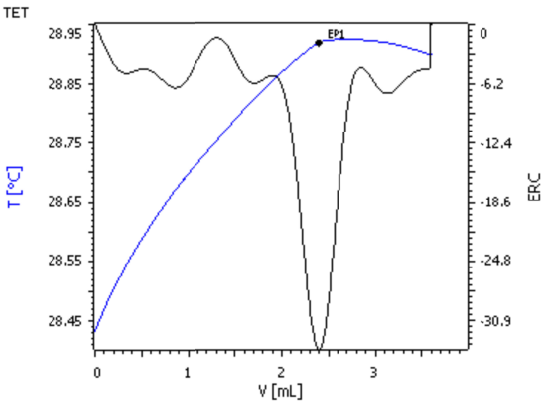
$$g/L\ Al = ((EP1 - blank) \times C01 \times C02)/(C00 \times 6)$$

EP1 = endpoint in mL
C00 = sample weight in mL
C01 = concentration of titrant in mol/L
C02 = molecular weight of Al (26.98154 g/mol)

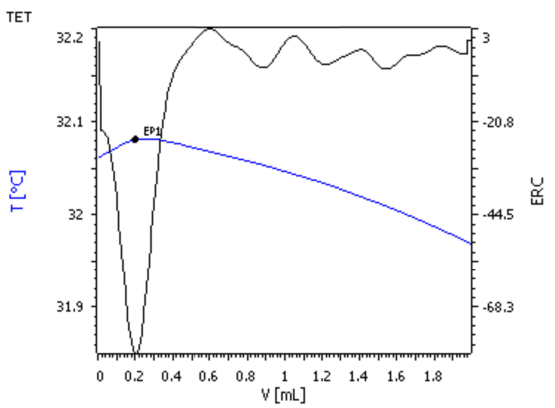
Results

	Al^{3+} g/L
Sample A	56.9 ± 0.07
Sample B	0.54 ± 0.02
Sample C	56.6 ± 0.20

Titration Plots



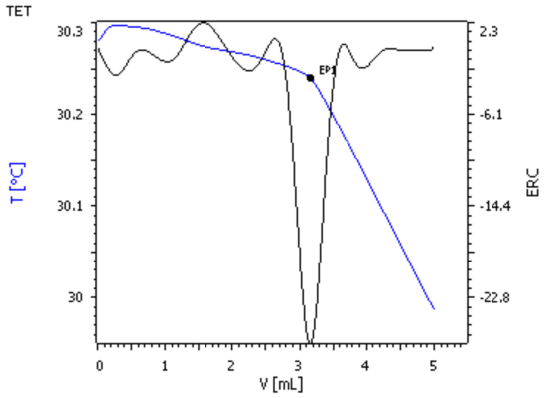
Sample A, Al titration plot.



Sample B, Al titration plot

Metrohm

Method description



Sample C, Al titration plot