Application Bulletin

Of interest to: General analytical laboratories, Plastics industry   A 1, 3, 6, 11, 14
                    Explosives industry

Potentiometric titration of nitrating acid

Summary

A potentiometric, non aqueous method is described for analysing nitrating acid using cyclohexylamine as titrant. Both sulfuric and nitric acid can be determined quantitatively.

Theory

The non aqueous titration of sulfuric/nitric acid mixtures effects two potential jumps. The first potential jump corresponds to the sum of nitric acid + ½ sulfuric acid. The difference between the first and second jumps corresponds to the remaining half of the sulfuric acid.

pK_a values: HNO_3 = - 1.32 / H_2SO_4 = ca. - 3 (1st jump) and 1.92 (2nd jump)

Various titrating reagents have been proposed in literature (e.g. piperidine, alcoholic KOH, potassium methylate, TBAOH). Apart from piperidine, a reagent unpleasant to use, all the others are affected by atmospheric CO_2, which can cause difficulties with the titrations and lead to serious errors in results. In addition, TBAOH can generate tertiary amines by side reactions which also interfere with the results. These interfering factors can be avoided if cyclohexalamine is used, because it is a stable titrant.

Apparatus and accessories

- Titrino or Titrando with Dosino or Dosimat
- Magnetic Swing-out stirrer
- Exchange unit
- Solvotrode 6.0229.100 with electrode cable 6.2104.020
- Possibly printer with printer cable

Reagents

- Titrant: c(cyclohexylamine) = 0.5 mol/L in methanol
- Solvent: methanol p.a. and demineralized water
- Standard: $c(H_2SO_4)$ = 1.000 mol/L (in H_2O)

Titer determination

Pour 90 mL methanol in a beaker. Add 2.00 mL H_2SO_4 and titrate with cyclohexylamine until passing the second endpoint. Two titers will be determined:

- Titer 1 for reagent consumption up to the 1st EP (C31)
  4.00 / EP1

- Titer 2 for the difference between reagent consumption at the 1st endpoint and the 2nd endpoint (C32)
  4.00 / (EP2-EP1)

Analysis

Pour 20 mL distilled water in a 100 mL calibrated flask. Stopper the flask and weigh it. Add approx. 1 mL of the nitrating acid sample, restopper the flask immediately, mix well and weigh again. (Determination of the sample weight by differential weighing) Now fill up to the mark with methanol at 20 °C and mix thoroughly. Pipet out 10.0 mL of this solution into a glass beaker, add 90 mL methanol and titrate with cyclohexylamine until after the second EP.

Calculations

RS1 (mL cyclohexylamine) = (EP2 - EP1)

RS2 (g/kg HNO_3)   = (EP1 - RS1) * C31 * C01 / C00

RS3 (g/kg H_2SO_4)   = RS1 * C32 * C02 / C00

C00 = Sample weight in g/10 (1/10 original sample)

C01 = Equivalent weight HNO_3 (31.506)

C02 = Equivalent weight H_2SO_4 (49.037)

C31 = Titer 1

C32 = Titer 2

Literature

- Bruttel,P.
  Non-aqueous titration of acids and bases with potentiometric endpoint indication
  Metrohm Monograph 50243-08.1999

Figures

```
'fr
785 DMP Titrino        02287   785.0010
user
date 1999-05-10   time  10:11        10
U(init)       469 mV DET U    ********
EP1         3.965 ml            384 mV
EP2         8.031 ml            164 mV
C31         1.009
C32         0.984
stop V reached
          ============




 'cu
785 DMP Titrino        02287   785.0010
user
date 1999-05-10   time  10:11        10
start V     0.000 ml  DET U   ********
2.0 ml/div       dU=100.0 mV/div


 'BMP-File: C:\DATASCAN\AQ7RS7.bmp
          ============
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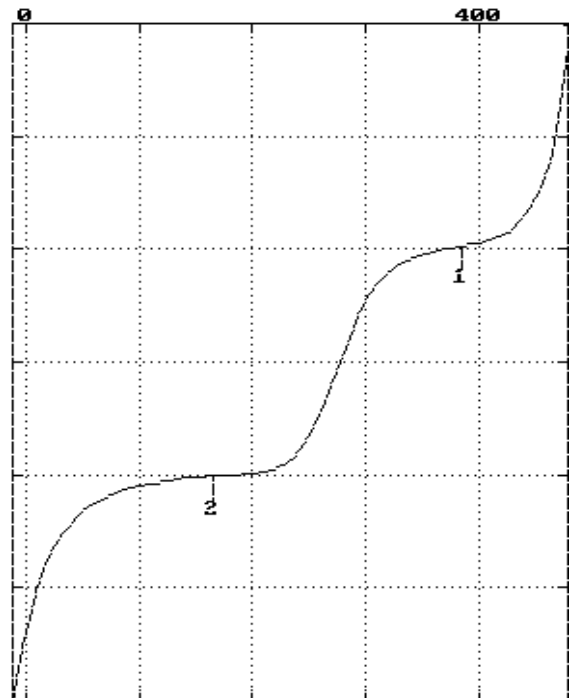
Fig. 1   Titration curve with titer determination (Titrino)

```
 'fr
785 DMP Titrino        02287   785.0010
user
date 1999-05-10   time  11:10        12
U(init)       414 mV DET U    ********
smpl size   0.1898 g
EP1         3.890 ml            337 mV
EP2         5.739 ml            164 mV
C6H13N      1.849ml
g/kgHNO3   341.847 g/kg
g/kgH2SO4   470.07 g/kg
stop V reached
          ============




 'cu
785 DMP Titrino        02287   785.0010
user
date 1999-05-10   time  11:10        12
start V     0.000 ml  DET U   ********
2.0 ml/div       dU=100.0 mV/div


 'BMP-File: C:\DATASCAN\AQ7TCM.bmp
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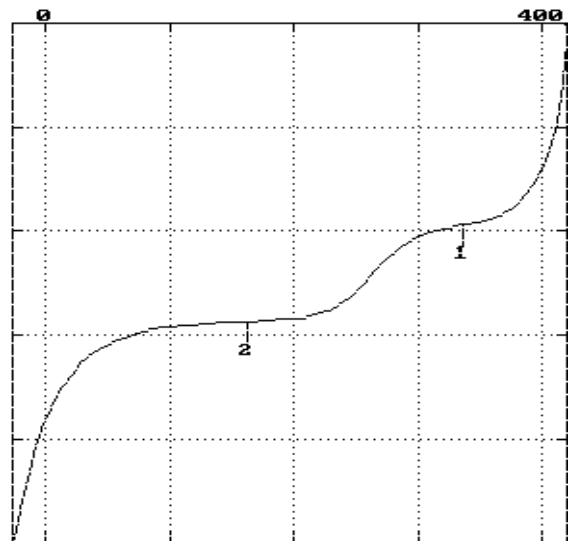
Fig. 2   Results / Titration curve of a sample (Titrino)