Metrohm

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Potentiometric and thermometric determination of boric acid

Branch

General analytical chemistry; metals, electroplating; energy, power plants; fertilizers, base materials, explosives

Keywords

Titration; potentiometric titration; thermometric titration; boric acid; primary water reactor; nuclear power; fertilizers; nickel plating bath; Ecotrode Plus; Thermoprobe HF; branch 1; branch 10; branch 11; branch 16; 6.0262.100; 6.9011.040

Summary

Boric acid is used in many primary circuits of nuclear power plants, in nickel plating baths, and in the production of optical glasses. Furthermore, boron compounds are found in washing powders and fertilizers. This bulletin describes the potentiometric and thermometric determination of boric acid. The determination also covers further boron compounds, when acidic digestion is applied.

Boric acid has an acidity constant K_{a1} of $5.75 \cdot 10^{-10}$ (pK_a = 9.24), which means it is a weak acid that is difficult to titrate. The addition of polyalcohols, for example, mannitol, leads to the formation of complexes with a greater acidic strength that behave like a monovalent acid which can be easily titrated with sodium hydroxide solution.

The same titration can be performed thermometrically. In this bulletin, however, the selective determination of boric acid with fluoride is described. This titration is based on the reaction of H_3BO_3 with F^- in the presence of H^+, forming HBF_4 exothermically. The advantage of this method is that boric acid can be determined in the presence of other medium or weak acids or their salts.

Potentiometric determination

Instruments

- Titrator with DET mode
- 20 mL buret
- Stirrer

Electrode

Ecotrode Plus	6.0262.100

Reagents

- Sodium hydroxide, c(NaOH) = 0.1 mol/L volumetric solution
- Potassium hydrogen phthalate (KHP), p.a.
- D-Mannitol, p.a.

Solutions

Titrant	c(NaOH) = 0.1 mol/L
Mannitol solution	Saturated solution of d-mannitol; approximately 200 g d-mannitol are dissolved in 1 L dist. H_2O. This solution should be stored in a refrigerator and prepared freshly every week (e.g. to avoid fungus growth).

Standard

Potassium hydrogen phthalate	Potassium hydrogen phthalate is dried at 120 °C for 2 h and cooled down in a desiccator for at least 1 h.

Sample preparation

No sample preparation is required.

Analysis

Titer

To approximately 180 mg KHP 50 mL mannitol solution are added and the suspension is stirred for about 1 min in order

to dissolve the KHP. The solution is then titrated until the first equivalence point using c(NaOH) = 0.1 mol/L.

Sample

A known volume of a sample solution is allowed to react with 50 mL mannitol solution for 30 s while stirring thoroughly. The solution is then titrated with c(NaOH) = 0.1 mol/L until after the first equivalence point.

Parameters

Titer

Signal drift	50 mV/min
Max. waiting time	10 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	10
EP recognition	greatest

Sample

Signal drift	50 mV/min
Max. waiting time	10 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	greatest

Calculation

Titer

$$f = \frac{m_s}{V_{EP1} \times c_{NaOH} \times M_A} \quad (1)$$

f:	Titer of the selected titrant
m_s:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{NaOH}:	Concentration of the selected titrant in mol/L; here c(NaOH) = 0.1 mol/L
M_A:	Molecular weight of the analyte; here 204.22 g/mol

Sample

$$\text{Content} = \frac{V_{EP1} \times c_{NaOH} \times f \times M_A \times 1000}{V_S} \quad (2)$$

Content:	Content of boric acid in mg/L
f:	Correction factor («titer») without unit
M_A:	Formula mass of boric acid in g/mol; here 61.833 g/mol
1000:	Conversion factor to obtain the result in mg/L
V_S:	Sample volume in mL

Example determination

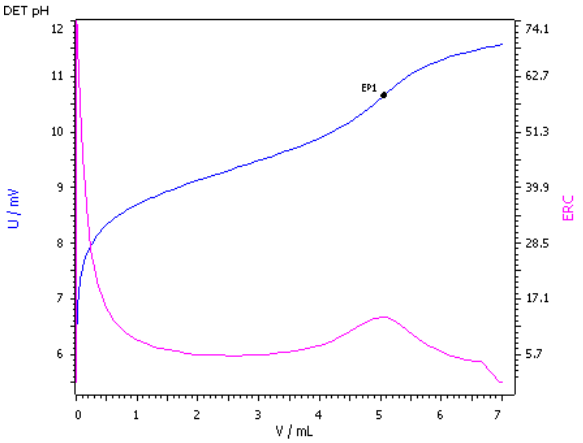

Fig. 1: Potentiometric determination of boric acid without mannitol (blue = titration curve, pink = ERC)

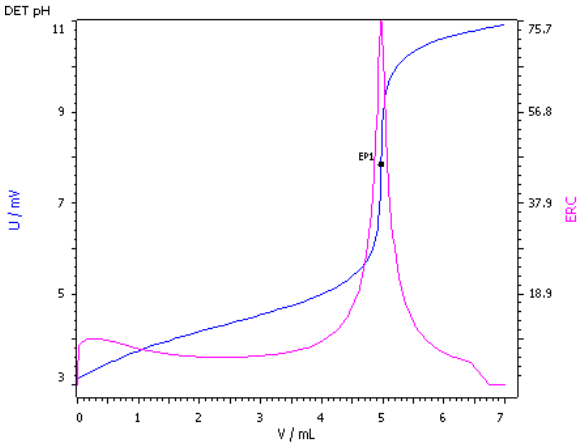

Fig. 2: Potentiometric determination of boric acid with mannitol (blue = titration curve, pink = ERC)

Comments

- In the presence of a strong acid, the solution is titrated until after the second equivalence point and the difference between the two equivalence points is taken to calculate the boric acid content.

- The titration in 50 mL saturated mannitol solution ensures the biggest potential jump.
- Instead of d-mannitol, fructose, dulcitol or sorbitol can be used.
- Medium acids like $H_2PO_4^-$ can interfere with the determination of the boric acid, it is then recommended to use the thermometric determination with potassium fluoride, as the removal of such acids is rather cumbersome.
- It is important to work with CO_2-free chemicals as otherwise a carbonate error can be observed, especially in the lower concentration range.

References

- Jander, G.; Jahr, K.F.: Massanalyse, 15. Auflage, Walter de Gruyter (Berlin 1989)
- Csapo, F.; Bihari, M.; Gilde, M.; Sztanko, E.; Die quantitative Mikrobestimmung von Bor durch pH-Messung von Mannitolborsäure; *Fresen J Anal Chem*; 151; 4; 273-276

Thermometric determination

Instruments

- Thermometric titrator
- 10 mL buret
- Stirrer

Electrode

Thermoprobe HF	6.9011.040

Reagents

- Potassium fluoride, c(KF) = 1 mol/L volumetric solution
- Hydrochloric acid, c(HCl) = 5 mol/L
- Boric acid, H_3BO_3

Solution

Titrant	c(KF) = 1 mol/L

Standard

Boric acid standard c(H_3BO_3) ≈ 0.5 mol/L	Boric acid is dried at 120 °C for 2 h and cooled down in a desiccator for at least 1 h.
	About 6.18 g H_3BO_3 are weighed to the nearest 0.1 mg into a 200 mL volumetric flask, dissolved in deionized water and the flask is filled up to the mark with deionized water.

Sample preparation

No sample preparation is required.

Analysis

Titer

1 to 2.5 mL boric acid standard are pipetted into the titration vessel and 30 mL deionized H_2O are added. 0.5 to 1.25 mL c(HCl) = 5 mol/L (ratio standard: H_2O = 2:1 (v/v)) are added and after a pause of 30 s the solution is titrated until after the first exothermic equivalence point.

Titrate at least 4 different aliquots of the sample in an ascending order.

Blank

5 to 10 mL sample are pipetted into the titration vessel and filled up to a total volume of 30 mL with deionized water. An appropriate amount of c(HCl) = 5 mol/L is added (see equation (3)) and after a pause of 45 s the solution is titrated with c(KF) = 1 mol/L until after the first exothermic equivalence point.

Titrate at least 4 different aliquots of the sample in an ascending order.

Sample

5 to 10 mL sample are pipetted into the titration vessel and filled up to a total volume of 30 mL with deionized water. An appropriate amount of c(HCl) = 5 mol/L is added (see equation (3)) and after a pause of 45 s the solution is titrated with c(KF) = 1 mol/L until after the first exothermic equivalence point.

Amount of acid

$$V_{HCl} = c_{H_3BO_3}(exp) \times V_s \quad (3)$$

V_{HCl}: Volume of c(HCl) = 5 mol/L added to the sample

$c_{H_3BO_3}(exp)$: Expected concentration of the boric acid in mol/L

V_S: Sample volume in mL

Parameters

Titer

Stirring rate	13
Dosing rate	2 mL/min
Filter factor	50
Damping until	0.2 mL
Evaluation start	0.3 mL
Reaction type	exothermic
EP criterion	-4

Blank/Sample

Stirring rate	13
Dosing rate	1 mL/min
Filter factor	50
Damping until	0.2 mL
Evaluation start	0.3 mL
Reaction type	exothermic
EP criterion	-6

Calculation

Titer

A linear regression of the volume (mL) of titrant consumed versus the different volumes of standard in mL is evaluated by ***tiamo***™. The titer is calculated from the slope.

$$f = \frac{4 \times c_{H_3BO_3}}{a \times c_{KF}} \quad (4)$$

f:	Titer of the selected titrant
4:	Stoichiometric factor for the reaction
$c_{H_3BO_3}$:	Exact concentration of standard solution in mol/L
a:	Slope of the linear regression
c_{KF}:	Concentration of titrant in mol/L

Blank

A linear regression of the different sample volumes (mL) against the volume (mL) of titrant consumed is evaluated by ***tiamo***™. The method blank is defined as the intercept of the linear regression line with the y-axis.

Sample

$$\text{Content} = \frac{(V_{EP1} - \text{Blank}) \times c_{KF} \times f \times M_A \times 1000}{V_S \times 4} \quad (5)$$

Content:	Content of boric acid in mg/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
Blank:	Method blank in mL
c_{KF}:	Concentration of titrant in mol/L; here 1 mol/L
f:	Correction factor («titer») without unit
M_A:	Formula mass of boric acid in g/mol; here 61.833 g/mol
1000:	Conversion factor to obtain the result in mg/L
V_S:	Sample volume in mL
4:	Stoichiometric factor for the reaction

Example determination

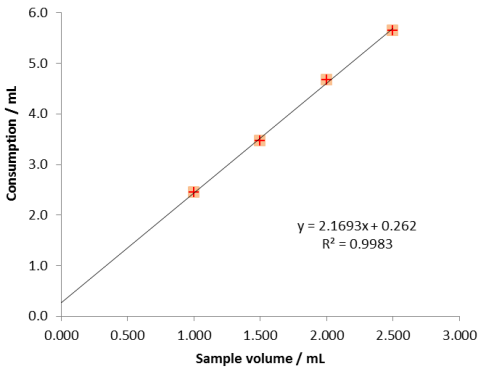

Fig. 3: Linear regression of the titer determination for c(KF) = 1 mol/L

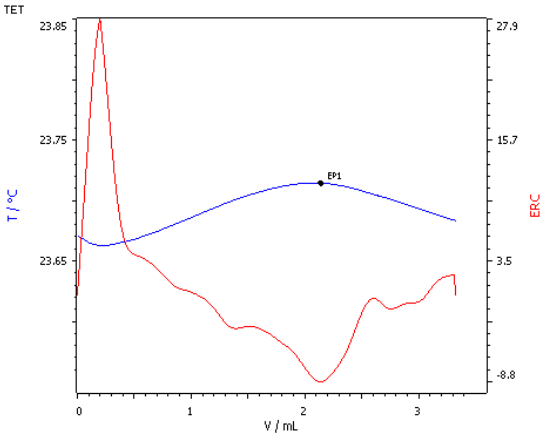

Fig. 4: Thermometric titration curve of the determination of boric acid (blue = titration curve, red = ERC)

Comments

- The determination of boric acid by fluoride is not influenced by metals in the solution, as boric acid decomposes metal-fluoride complexes in order to form HBF_4.
- The shape of the titration curve depends on the added amount of acid. It is therefore necessary to use a fixed ratio of sample size to acid volume.
- The equation (3) is not valid for solid samples. Therefore, the ideal ratio has to be determined for each sample individually.

References

- Miller, F.J.; Thomason, P.F..; Direct thermometric titration of boric acid; *Talanta*; 2; 2; 109–114

Author

Competence Center Titration

Metrohm International Headquarters