Metrohm

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Titer determination in potentiometry

Branch

General analytical chemistry

Keywords

Titration; potentiometric titration; titer; branch 1

Summary

This Bulletin provides an overview of the potentiometric titer determination in common volumetric solutions which are recommended by Metrohm AG. Many publications only describe methods with color indicators. However, the titration conditions chosen for the titer determination should resemble those used for the actual analysis as closely as possible.

The tables below contain suitable titrimetric standard substances and electrodes for selected titrants as well as additional information. Following this, a procedure for titer determinations is described.

Instruments

- Titrator
- 10 or 20 mL buret
- Stirrer
- Optional: sample changer

Standards

Titrimetric standard substances have the following characteristic features:

- Their content remains virtually unchanged
- They have a defined, high degree of purity
- They can be dried
- They can be directly traced back to standard reference materials (e.g. from NIST = National Institute of Standards and Technology, USA)

Some examples of such recommended titrimetric standard substances or secondary standards are:

- Potassium hydrogen phthalate, KHP
- Tris(hydroxymethyl)-amino-methane, TRIS
- Sodium chloride, NaCl
- Sodium oxalate, NaC_2O_4
- Potassium hydrogen diiodate, $KH(IO_3)_2$
- Benzoic acid, C_6H_6COOH
- Calcium carbonate, $CaCO_3$
- Sodium thiosulfat pentahydrate, $Na_2S_2O_3 \cdot 5\ H_2O$
- Hydranal water standard
- Sodium tartrate dehydrate, $Na_2C_4H_4O_6 \cdot 2\ H_2O$

Standard solutions

Of these standard substances standard solutions of a defined concentration can be made.

Comments

- The weight of titrimetric standard substance depends on the concentration of the titrant and the buret volume used.
- For accuracy reasons, the sample weight must not be too small. A sample weight >100 mg normally yields good analytical results. However, the minimum weight varies considerably, depending on the substance, the balance used and the required accuracy.
- In order to increase the measuring accuracy, it may be a good idea to prepare a stock solution instead of weighing the titrimetric standard substance directly into the titration vessel.
- The indicated electrodes below are meant as a suggestion. It is often also possible to use other electrodes or electrode systems.
- Instead of indicators electrodes can be used as well. If color indicators must be used the Optrode is a good way to monitor the color change objectively. But it has to be taken care of that no precipitation is present during analysis.

References

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Author

Competence Center Titration

Metrohm International Headquarters

Procedures recommended by Metrohm AG

Acid-base titrations, complexometric/chelatometric titrations

Titrant	Titrimetric standard Drying temperature &	Electrode	Remarks
Aqueous acids HCl, H_2SO_4	TRIS, 105 °C	Combined pH electrode e.g. 6.0259.100	TRIS is dissolved in approx. 60 mL deion. water and titrated to after the first equivalence point.
Aqueous bases NaOH	KHP, 105 °C	Combined pH electrode e.g. 6.0259.100	KHP is dissolved in approx. 60 mL deion. water and titrated to after the first equivalence point.
Perchloric acid $HClO_4$ in glacial acetic acid	TRIS or KHP 105 °C*	Solvotrode easyClean 6.0229.010	TRIS or KHP is dissolved in glacial acetic acid and titrated to after the first equivalence point. Reference electrolyte: c(LiCl) = 2 mol/L in ethanol
Trifluoromethanesulfonic acid, CF_3SO_3H in glacial acetic acid	TRIS or KHP 105 °C*	Solvotrode easyClean 6.0229.010	TRIS or KHP is dissolved in glacial acetic acid and titrated to after the first equivalence point. Reference electrolyte: c(LiCl) = 2 mol/L in ethanol
Trifluoromethanesulfonic acid, CF_3SO_3H in isopropanol	TRIS or KHP 105 °C*	Solvotrode easyClean 6.0229.010	TRIS or KHP is dissolved in glacial acetic acid and titrated to after the first equivalence point. Reference electrolyte: c(LiCl) = 2 mol/L in ethanol
Tetrabutyl ammonium hydroxide in isopropanol	Benzoic acid or KHP*	Solvotrode easyClean 6.0229.010	Benzoic acid is dissolved in isopropanol and titrated with TBAOH to after the first equivalence point. Reference electrolyte: c(TEABr) = 0.4 mol/L in ethylene glycol
Alcoholic KOH	Benzoic acid or KHP*	Solvotrode easyClean 6.0229.010	Benzoic acid is dissolved in approx. 50 mL ethanol and titrated to after the first equivalence point. Reference electrolyte: c(TEABr) = 0.4 mol/L in ethylene glycol
Cyclohexylamine $C_6H_{11}NH_2$ in methanol	Sulfamic acid	Solvotrode easyClean 6.0229.010	Sulfamic acid is dissolved in approx. 50 mL methanol and titrated to after the first equivalence point. Reference electrolyte: c(TEABr) = 0.4 mol/L in ethylene glycol

* If the titration is carried out under anhydrous conditions, benzoic acid or TRIS should be used as standard substances, respectively. On the other side KHP should be used if the titration is carried out under semi-aqueous conditions.

EDTA, Komplexon III, Titriplex III, Idranal III	Calcium carbonate, 105 °C	Combined Ca ISE 6.0510.100	Calcium carbonate is suspended in approx. 20 mL deion. water and dissolved with as little c(HCl) = 5 mol/L as possible. After the addition of 30 mL deion. water, 5 mL buffer pH = 10.0 (NH_3/NH_4OH) and the solution is titrated with sodium EDTA to after the first equivalence point.

Precipitation titrations, Redox titrations

Titrant	Titrimetric standard Drying temperature	Electrode	Remarks
Silver nitrate $AgNO_3$	NaCl, 110 °C	combined Ag ring electrode (reference electrolyte: KNO_3 sat.) 6.0450.100 or Ag Titrode 6.0430.100	NaCl is dissolved in 40 mL water, then add 2 mL $c(HNO_3)$ = 2 mol/L and possibly 2 mL 0.2% polyvinyl alcohol solution. The solution is titrated with silver nitrate to after the first equivalence point.
Cerium(IV) in H_2SO_4 or $HClO_4$	$Na_2C_2O_4$, 105 °C	combined Pt ring electrode 6.0451.100 or Pt Titrode 6.0431.100	Sodium oxalate is dissolved in 50 mL deion. water. 10 mL $c(H_2SO_4)$ = 1 mol/L is added and the solution is heated up to 60 °C. The titration is carried out at 60°C with cerium(IV) to after the first equivalence point.
Iodine solution, KI_3	$Na_2S_2O_3$, 105 °C	combined Pt ring electrode 6.0451.100 or Pt Titrode 6.0431.100	Anhydrous sodium thiosulfate is dissolved in 50 mL deion. water and titrated with iodine solution to after the first equivalence point.
Potassium permanganate $KMnO_4$	$Na_2C_2O_4$, 105 °C	combined Pt ring electrode 6.0451.100 or combined Au ring electrode 6.0452.100	Sodium oxalate is dissolved in approx. 40 mL deion. water and 5 mL sulfuric acid conc. is added. Two options for the further procedure is available: The first one contains heating to 70 °C and titrating hot with potassium permanganate. In the second procedure 2 g $MnSO_4$ is added as catalyst. So the titration can be carried out at room temperature.
Sodium thiosulfate $Na_2S_2O_3$	KIO_3, 180 °C	combined Pt ring electrode 6.0451.100 or Pt Titrode 6.0431.100	Potassium iodate is dissolved in approx. 100 mL deion. water. Afterwards 1 g KI and 10 mL $w(H_2SO_4)$ = 25% are added and the titration is carried out to after the first equivalence point.
Sodium nitrite $NaNO_2$	Sulfanilic acid	combined Au ring electrode 6.0452.100	Sulfanilic acid is dissolved in 50 mL deion. water and 30 mL w(HBr) = 20% is added. The solution is cooled to 15 °C and titrated immediately using the MET mode (0.10 mL, min. waiting time 5 s).