

Titer determination in potentiometry

Of interest to:
General analytical laboratories
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Summary

This Bulletin provides an overview of the potentiometric titer determination in common volumetric solutions. 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 and accessories

Various instruments or combinations of instruments can be used:

- pH meter und Dosimat for manual titrations
- Titrando, Titrino or Titroprocessor with Dosimats or Dosinos for automatic recording and evaluation of the titration curves and calculation of the results
- Titrators as listed above, combined with a sample changer

The instruments for automatic titrations offer the possibility of transmitting the data to a PC using the VESUV or TiNet Metrodata software.

Titrimetric standard substances

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 and 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:

- Fluka No. 11099, arsenic trioxide
- Merck No. 102400, potassium hydrogen phthalate
- Fluka No. 60357, potassium hydrogen phthalate
- Merck No. 102408, tris(hydroxymethyl)-amino-methane
- Fluka No. 93440, tris(hydroxymethyl)-amino-methane
- Merck No. 102406, sodium chloride
- Fluka No. 71387, sodium chloride
- Merck No. 102407, sodium oxalate

- Fluka No. 71804, sodium oxalate
- Fluka No. 60350, potassium hydrogen diiodate
- Merck No. 102403, potassium dichromate
- Merck No. 102401, benzoic acid
- Fluka No. 21067, calcium carbonate
- Riedel-de Haën No. 34849, HYDRANAL Water Standard
- Riedel-de Haën No. 34803, sodium tartrate dihydrate

Remarks

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.

Literature

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Electrodes and titrimetric standard substances for determining the titer of different titrants

**Table 1: Acid-base titrations (acidimetry, alkalimetry)
 Complexometric/chelatometric titrations**

Titrant	Titrimetric standard	Electrode	Remarks
Aqueous acids HCl, H ₂ SO ₄	Tris(hydroxymethyl)-aminomethane (CH ₂ OH) ₃ CNH ₂ (TRIS) (105 °C)	Combined pH electrode, e.g. 6.0259.100	Solvent: water
Aqueous bases NaOH	Potassium hydrogen phthalate C ₈ H ₅ KO ₄ (105 °C)	Combined pH electrode, e.g. 6.0259.100	Solvent: water
Perchloric acid HClO ₄ in glacial acetic acid	Potassium hydrogen phthalate C ₈ H ₅ KO ₄ or TRIS (105 °C)	6.0229.100 Solvotrode	Solvent: glacial acetic acid Reference electrolyte: c(LiCl) = 2 mol/L in ethanol (6.2312.010)
Trifluoromethane-sulfonic acid CF ₃ SO ₃ H in glacial acetic acid	Potassium hydrogen phthalate C ₈ H ₅ KO ₄ or TRIS (105 °C)	6.0229.100 Solvotrode	Solvent: glacial acetic acid Reference electrolyte: c(LiCl) = 2 mol/L in ethanol (6.2312.010)
Trifluoromethane-sulfonic acid CF ₃ SO ₃ H in isopropanol	Potassium hydrogen phthalate C ₈ H ₅ KO ₄ or TRIS (105 °C)	6.0229.100 Solvotrode	Solvent: glacial acetic acid Reference electrolyte: c(LiCl) = 2 mol/L in ethanol (6.2312.010)
Tetrabutylammonium hydroxide in isopropanol	Benzoic acid C ₆ H ₅ COOH	6.0229.100 Solvotrode	Solvent: isopropanol Reference electrolyte: c(TEABr) = 0.4 mol/L in ethylene glycol (6.2320.000)
Alcoholic KOH	Benzoic acid C ₆ H ₅ COOH	6.0229.100 Solvotrode	Solvent: ethanol Reference electrolyte: c(TEABr) = 0.4 mol/L in ethylene glycol (6.2320.000)
Cyclohexylamine C ₆ H ₁₁ NH ₂ in methanol	Benzoic acid C ₆ H ₅ COOH	6.0229.100 Solvotrode	Solvent: methanol Reference electrolyte: c(TEABr) = 0.4 mol/L in ethylene glycol (6.2320.000)
EDTA (Komplexon III, Titriplex III or Idranal III)	Calcium carbonate CaCO ₃ (105 °C)	6.0504.100 calcium ISE or 6.0502.140 copper ISE; 6.0726.107 reference electrode (filled with c(KCl) = 3 mol/L)	Suspend CaCO ₃ in water, dissolve in HCl and add buffer pH = 10.0 (NH ₃ /NH ₄ OH). For titrations with the Cu ISE, add 1 mL c(Cu-EDTA) = 0.05 mol/L to the sample solution (see also Metrohm AB No. 101).

The indicated electrodes are meant as a suggestion. It is often also possible to use other electrodes or electrode systems.

**Table 2: Precipitation titrations (argentometry)
 Redox titrations (cerimetry, iodometry, permanganometry, ferrometry, Karl Fischer titration)**

Titrant	Titrimetric standard	Electrode	Remarks
Silver nitrate AgNO_3	Sodium chloride NaCl (110 °C)	6.0450.100 combined Ag ring electrode (reference electrolyte: KNO_3 saturated) or 6.0430.100 Ag Titrode	Dissolve NaCl in 40 mL water, then add 2 mL $c(\text{HNO}_3) = 2 \text{ mol/L}$ and possibly 2 mL 0.2% polyvinyl alcohol solution. (Dissolve polyvinyl alcohol (Merck No. 114266) in warm water.)
Lanthanum nitrate $\text{La}(\text{NO}_3)_3$	Sodium fluoride NaF (110 °C)	6.0502.150 fluoride ISE; 6.0726.107 reference electrode (filled with $c(\text{KCl}) = 3 \text{ mol/L}$)	Dissolve NaF in 50 mL water, add 10 mL acetate buffer $\text{pH} = 6.0$ and titrate slowly (see also Metrohm AB No. 82).
Cerium(IV) in H_2SO_4 or HClO_4	Arsenic trioxide As_2O_3 (105 °C)	6.0451.100 combined Pt ring electrode or 6.0431.100 Pt Titrode	Dissolve As_2O_3 in 10 mL $c(\text{NaOH}) = 1 \text{ mol/L}$, then add 6 mL $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$ and 2 g NaHCO_3 (see also Metrohm AB No. 52).
Iodine solution KI_3	Arsenic trioxide As_2O_3 (105 °C)	6.0451.100 combined Pt ring electrode or 6.0431.100 Pt Titrode	Dissolve As_2O_3 in 10 mL $c(\text{NaOH}) = 1 \text{ mol/L}$, then add 6 mL $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$ and 2 g NaHCO_3 .
Potassium permanganate KMnO_4	Sodium oxalate $\text{Na}_2\text{C}_2\text{O}_4$ (105 °C)	6.0451.100 combined Pt ring electrode or 6.0452.100 combined Au ring electrode	Dissolve $\text{Na}_2\text{C}_2\text{O}_4$ in 40 mL water, then add 5 mL concentrated H_2SO_4 and 1 g MnSO_4 .
Sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$	Potassium hydrogen diiodate $\text{KH}(\text{IO}_3)_2$ (100 °C)	6.0451.100 combined Pt ring electrode or 6.0431.100 Pt Titrode	Stock solution: Dissolve $\text{KH}(\text{IO}_3)_2$ in water and make up to 100 mL; use 10 mL of this solution, dilute with 40 mL water, then add 1 g KI and 4 mL $c(\text{HCl}) = 1 \text{ mol/L}$.
Iron(II) solution $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ (105 °C)	6.0452.100 combined Au ring electrode	Dissolve $\text{K}_2\text{Cr}_2\text{O}_7$ in 40 mL water, then add 3 mL concentrated H_2SO_4 .
Sodium nitrite NaNO_2	Sulfanilic acid	6.0452.100 combined Au ring electrode	Dissolve sulfanilic acid in 50 mL water, add 30 mL $w(\text{HBr}) = 20\%$ and titrate immediately using the MET mode (0.10 mL, 25 s).
Karl Fischer reagent	Sodium tartrate dihydrate $\text{C}_4\text{H}_4\text{Na}_2\text{O}_6 \times 2 \text{ H}_2\text{O}$ or water standards in ampoules (Riedel-de Haën)	6.0338.100 polarized double Pt electrode	Fill methanol or KF solvent into the titration vessel and condition. As soon as a steady drift is attained, add the standard and titrate with the KF reagent. The titer is specified in $\text{mg H}_2\text{O} / \text{mL KF reagent}$ (documentation available from Riedel-de Haën or Merck).

The indicated electrodes are meant as a suggestion. It is often also possible to use other electrodes or electrode systems.

Example of a procedure for titer determinations using the 799 GPT Titrino

Summary

Determination of the titer of $c(\text{HCl}) = 0.1 \text{ mol/L}$ using the 799 GPT Titrino.

The titration is carried out in the DET or MET mode. Tris(hydroxymethyl)-aminomethane is used as titrimetric standard substance.

Instruments and accessories

- 799 GPT Titrino
- 2.728.0040 Magnetic Stirrer
- 6.3026.220 Exchange Unit 20 mL
- 6.0259.100 Unitrode (reference electrolyte: $c(\text{KCl}) = 3 \text{ mol/L}$)
- 6.2104.020 electrode cable

Reagents

- Tris(hydroxymethyl)-aminomethane (TRIS) (titrimetric standard substance), Merck No. 102408 or Fluka No. 93440
- Distilled water (free from carbonate)

Analysis

The TRIS is dried in a flat bowl for 2 h at $105 \text{ }^\circ\text{C}$, then allowed to cool down in a desiccator and stored there.

Using an analytical balance, approx. 0.15 g of the dried TRIS is weighed exactly into a 100 mL beaker. After addition of 40 mL carbonate-free water, the solution is stirred until the titrimetric standard substance has dissolved, then titration is performed using the following parameters:

Parameters DET:

Titration parameters

meas.pt.density	4
min.incr.	10.0 μL
signal drift	50 mV/min
start V:	rel.
faktor	50

Stop conditions

stop V:	rel.
stop V	120

Parameters MET:

Titration parameters

V step	0.10 mL
dos.rate	max. mL/min
signal drift	50 mV/min
start V:	rel.
faktor	50

Stop conditions

stop V:	rel.
stop V	120

Calculation

$$\text{Titer} = C00 / (C01 * C02 * EP1)$$

C00 = weight of TRIS in mg

C01 = 121.14 (molar mass of TRIS in g/mol)

C02 = 0.1 (concentration of the titrant in mol/L)

EP1 = titrant consumption in mL

Remarks

The titer determination is carried out five times.

Using the Titrino's statistics function, the mean value as well as the absolute and relative standard deviation can be calculated.

The mean value can be automatically stored as common variable (C3X). This makes it possible to directly use the current titer in other titration methods.