Workshop 3

Hydrogen Peroxide Determination

by Redox Titration

Background

Redox titrations can be used for analytes that are oxidizable or reducible. A variety of applications are possible with this method, ranging from the determination of the SO_2 in wine to hydrogen peroxide content in disinfectant solutions. In manganometric redox titrations the powerful oxidizing effect of potassium permanganate is used to oxidize the analyte. Due to its strong color no indicator has to be used to detect the equivalence point visually.

Reactions

1. Titer determination:

$$5\ Na_2C_2O_4 + 16\ H^+ + 2\ KMnO_4 \rightleftharpoons 10\ CO_2 + 10\ Na^+ + 2\ Mn^{2+} + 8\ H_2O + 2\ K^+$$

std. substance	titrant	reaction products
134.01 g/mol	158.03 g/mol	

2. Hydrogen peroxide content determination:

$$5\ H_2O_2 + 6\ H^+ + 2\ KMnO_4 \rightleftharpoons 5\ O_2 + 2\ Mn^{2+} + 8\ H_2O + 2\ K^+$$

analyte	titrant	reaction products
34.02 g/mol	158.03 g/mol	

Safety

Always take the necessary safety precautions when working in the laboratory: work carefully; wear a lab coat, protective gloves and safety goggles. Hydrogen peroxide is corrosive and harmful to your health. Potassium permanganate is also harmful to your health and sulphuric acid is corrosive.

Tasks

1. Titer determination:

Use pure di-sodium oxalate (M = 134.01 g/mol, z = 2) to determine the titer of the titrant $KMnO_4$ $c(1/5\ KMnO_4)$ = 0.1 mol/L. Prepare the sample solution by weighing 25 – 40 mg of di-sodium oxalate accurately into a glass titration beaker on an analytical balance. Dilute the standard substance with 50 mL of 5 % sulphuric acid solution and heat this solution in a water bath to around 70 °C as the titration reaction is too slow at room temperature. Titrate with a platinum ring electrode at this temperature until the equivalence point, which will be recognized by the automated titrator, is reached. When performing a manual titration, the equivalence point is reached as soon as the color of the sample solution turns permanently light pink in the presence of excess of $KMnO_4$.

Calculate the titer and perform this analysis at least three times. Calculate the mean value, standard deviation (*s*) and relative standard deviation (*srel*) for this titer determination.

2. Hydrogen peroxide content determination:

Determine the hydrogen peroxide in the sample of disinfectant. Use the same sample preparation and titration procedure as for the titer determination but don't heat up the sample solution. Use a sample size of about 0.3 g.

Determine the hydrogen peroxide content (in %) at least three times and calculate mean value, standard deviation (*s*) and relative standard deviation (*srel*).

Waste disposal:

Neutralize (pH 7) the aqueous solutions and dispose of it as special waste.

Teacher Information

Hydrogen Peroxide Determination

by Redox Titration

Equipment

Manual titration:

- 1x Analytical balance
- 1x Manual burette (10 mL)
- 6x Titration beakers (glass beakers, e.g. 100 mL)
- 1x Magnetic stirrer
- 3x Magnetic stirrer bars
- 1x Heatable water bath

Automatic titration:

- 1x Analytical balance
- 1x Mettler-Toledo Easy Ox or Easy Pro titrator with 10 mL burette and tubing
- 1x EG40-BNC platinum ring sensor
- 6x Titration beakers
- 3x Magnetic stirrer bars
- 1x Heatable water bath

Chemicals

The quantities below were roughly estimated for 5 titer determinations and 5 acetic acid determinations.

- 1 L deionized water (mainly for manual titration and rinsing)
- 200 mL potassium permanganate solution c = 0.02 mol/L, c(1/5 $KMnO_4$) = 0.1 mol/L (3.16 g solid potassium permanganate in 1 L solution)
- 700 mL of 5 % sulphuric acid solution (50 g of sulphuric acid in 1 L solution)
- 0.5 g di-sodium oxalate of high purity (titration standard)
- 2 g of disinfectant solution (diluted hydrogen peroxide solution with a H_2O_2 content of about 3 %, available in pharmacies) as sample

Preparation

- Prepare the titrant and sulphuric acid solution.
- Rinse the burette of the automatic titrator with titrant at least twice to dispel any air bubbles trapped in the burette and tubing.

Comments

- This method may be slightly adapted depending on the disinfectant used and its hydrogen peroxide content.

Solution

1. Titer determination:

Calculation:

$$t = \frac{m}{VEQ \cdot c \cdot C}$$

$$C = \frac{M}{10 \cdot p \cdot z}$$

t: Titer of the titrant (no unit)
m: Weight of standard substance used for the determination (in g, here: $Na_2C_2O_4$)
VEQ: Titrant consumption at the equivalence point (in mL)
c: Nominal (equivalence) concentration of the titrant (in mol/L, here: $KMnO_4$ $c(1/5\ KMnO_4) = 0.1$ mol/L)
C: Constant (in g/mmol, see equation above)
M: Molar mass of the standard substance (in g/mol, here: $Na_2C_2O_4$, M = 134.01 g/mol)
10: Factor for mg to g and % conversion (in mg/(g·%))
p: purity of the standard substance (in %)
z: equivalent number (no unit, here: 2)

Expected result:

The titer should be around 1 for a fresh standard solution.

2. Hydrogen peroxide content determination:

Calculation:

$$R = \frac{VEQ \cdot c \cdot t \cdot C}{m}$$

$$C = \frac{M}{10 \cdot z}$$

R: Result, content (in %, here: acetic acid content)
VEQ: Titrant consumption at the equivalence point (in mL)
c: Nominal (equivalence) concentration of the titrant (in mol/L, here: $KMnO_4$ $c(1/5\ KMnO_4) = 0.1$ mol/L)
t: Titer of the titrant, as determined before (no unit)
C: Constant (in g·%/mmol, see equation above)
m: Sample weight (in g)
M: Molar mass of the analyte (in g/mol, here: hydrogen peroxide, M = 34.02 g/mol)
10: Factor for mg to g and % conversion (in mg/(g·%))
z: equivalence number (no unit, here: 2)

Expected result:

Depending on the sample the hydrogen peroxide content should be around 3 %.

Example

1. Titer determination:

Di-sodium oxalate with a purity of 99.5 % was used to perform three titer determinations. In the following table the sample size (*m*), titration consumption (*VEQ*) and the calculated titer (*t*) are shown:

Nr.	*m*	*VEQ*	*t*
1	0.031 g	4.625 mL	0.9953
2	0.037 g	5.543 mL	0.9912
3	0.029 g	4.335 mL	0.9934

The calculation of the the first sample is shown below:

$$C = \frac{M}{10 \cdot p \cdot z} = \frac{134.01\ \frac{\text{g}}{\text{mol}}}{10\ \frac{\text{mg}}{\text{g}\cdot\%} \cdot 99.5\ \% \cdot 2} = 0.06734\ \frac{\text{g}}{\text{mmol}}$$

$$t = \frac{m}{VEQ \cdot c \cdot C} = \frac{0.031\ \text{g}}{4.625\ \text{mL} \cdot 0.1\ \frac{\text{mol}}{\text{L}} \cdot 0.06734\ \frac{\text{g}}{\text{mmol}}} = 0.9953$$

The mean value, standard deviation (*s*) and relative standard deviation (*srel*) were calculated from the results of the three titer determinations:

Mean: 0.9933
s: 0.0021
srel: 0.21 %

2. Hydrogen peroxide content determination:

For the hydrogen peroxide content determination three sample solutions were prepared and titrated. The sample size (*m*), the titrant consumption (*VEQ*) and the calculated hydrogen peroxide (*R*) contents for these three measurements are listed in the following table:

Nr.	*m*	*VEQ*	*R*
1	0.334 g	5.338 mL	2.700 %
2	0.376 g	5.998 mL	2.695 %
3	0.359 g	5.763 mL	2.712 %

The calculation for the first measurement is shown in detail:

$$C = \frac{M}{10 \cdot z} = \frac{34.02\ \frac{\text{g}}{\text{mol}}}{10\ \frac{\text{mg}}{\text{g}\cdot\%} \cdot 2} = 1.701\ \frac{\text{g}\cdot\%}{\text{mmol}}$$

$$R = \frac{VEQ \cdot c \cdot f \cdot C}{m} = \frac{5.338\ \text{mL} \cdot 0.1\ \frac{\text{mol}}{\text{L}} \cdot 0.9933 \cdot 1.701\ \frac{\text{g}\cdot\%}{\text{mmol}}}{0.334} = 2.700\ \%$$

As for the titer determination, the mean, *s* and *srel* was calculated:

Mean:	2.702 %
s:	0.009 %
srel:	0.33 %