Analytical Method for Peracetic acids

Determination of hydrogen peroxide and peracetic acid content by titration

GENERAL INFORMATION ABOUT THE METHOD

The determination of hydrogen peroxide and peracetic acid content by titration is preferably used for products with a peracetic acid content > 1% (e.g. PERACLEAN® 5 and PERACLEAN® 15).

The method is based on two redox titrations, both carried out in turn in one sample. First, the hydrogen peroxide present in the sample is titrated with cerium(IV) sulfate solution (equation 1). Then an excess of potassium iodide is added to the sample, which forms with the present peracetic acid an equivalent amount of free iodine (equation 2). Finally, the free iodine is titrated with sodium thiosulfate (equation 3). The peracetic acid content can be calculated from the consumption of sodium thiosulfate.

1. $H_2O_2 + 2\ Ce(SO_4)_2 \rightarrow Ce_2(SO_4)_3 + H_2SO_4 + O_2$

2. $2\ KI + H_2SO_4 \rightarrow 2\ HI + K_2SO_4$

   $CH_3COOOH + 2HI \rightarrow I_2 + CH_3COOH + H_2O$

3. $I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

The method is preferably carried out manually. The end points are detected visually by the use of redox indicators.

Alternatively, the end points of the two titrations can be determined potentiometrically by using electronic titration equipment. In this case, the titration parameters required must carefully be worked out first.

EQUIPMENT

- analytical balance
- 250 ml beakers (titration beakers) or 300 ml Erlenmeyer flasks
- 1 ml single-use syringes
- dispenser or measuring cylinders for sulfuric acid, potassium iodide solution and starch solution

TITRATION EQUIPMENT

For manual titrations:

- 2 dosing devices or 2 dark glass burettes (50 ml and 20 ml)
- dosing unit with a 50 ml dark glass cylinder including a supply bottle for the cerium(IV) sulfate solution
- dosing unit with a 20 ml dark glass cylinder including a supply bottle for the sodium thiosulfate solution
- magnetic stirrer

Additionally for potentiometric titrations:

- electronic titration equipment, provided with appropriate methods for potentiometric titration of hydrogen peroxide and peracetic acid
- platine-redox electrode

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REAGENTS

- peracetic acid solution (testing material)
- cerium(IV) sulfate solution c ($Ce(SO_4)_2$ * 4 H_2O) = 0.1 mol/l (Titer 1.000 ± 0.002)
- sodium thiosulfate solution c ($Na_2S_2O_3$ * 5 H_2O) = 0.1 mol/l (Titer 1.000 ± 0.002)
- sulfuric acid p.a. c (H_2SO_4) ~ 2.5 mol/l
- potassium iodide solution p.a. 20%
- ferroin solution c (1,10-phenanthroline iron(II) sulfate) = 0.025 mol/l
- starch solution 1% (or ready-to-use zinc iodide starch solution p.a.)
- high purity water (osmosis and ion exchange treated drinking water)
- crushed ice

SPECIAL SAFETY INSTRUCTIONS

All reagents and chemicals must be handled according to the health and safety regulations. Refer to the safety data sheets.

SPECIAL PROCEDURE INSTRUCTIONS

Danger of decomposition by contact with incompatible materials, contaminants, metals, alkalis, reducing agents.

PROCEDURE

In this instruction only the manual method is described. All end points are detected visually by the use of redox indicators.

Put about 25 g of crushed ice, 2 ml of sulfuric acid and 3 drops of ferroin indicator solution in a titration beaker or in an Erlenmeyer flask. Fill a 1 ml single-use-syringe with the sample material, place the syringe on the analytical balance and tare the balance to zero. Then take the syringe and add some drops of sample material into the prepared beaker. Place the syringe back on the balance pan and record the weight (precision 0.0001 g).

Now titrate the orange colored sample solution rapidly and with stirring with cerium(IV) sulfate to a pure blue color. It is important to ensure that the sample is not over-titrated! Record the consumption (V1) of cerium(IV) sulfate solution. With this titration the content of the hydrogen peroxide present in the sample is determined.

To determine the peracetic acid content immediately afterwards, add 5 ml of potassium iodide to the blue sample solution and dilute with 100 – 150 ml high purity water. The sample turns dark brown caused by the free iodide. Now titrate with the sodium thiosulfate solution until the color becomes slowly paler, then add a few drops of starch solution (or 2 ml of the zinc iodide starch solution), the color turns dark again. Now continue to titrate slowly with the sodium thiosulfate solution until the color finally changes to bright orange. After the titration the solution should be clear. Record the consumption of sodium thiosulfate (V2).

Further instructions:

Choose an appropriate peracetic acid amount taking into account the volumes of the dosing cylinders for cerium(IV) sulfate and sodium thiosulfate. Repeated filling of the cylinders during a titration should be avoided.

Following sample amounts can be recommended for the PERACLEAN® products listed below:

PERACLEAN® 5	approx. 0.3 g
PERACLEAN® 15	approx. 0.2 g

The titers (factors) of both titration solutions (cerium(IV) sulfate and sodium thiosulfate) must be known exactly (observe manufacturer's certificates!). If the titers are unknown, titer-determinations with appropriate primary standards must be carried out before. The factors (f) must be taken into account in the calculation.

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CALCULATIONS

1. Calculation of the hydrogen peroxide content in percent by weight (mass fraction):

   ► Hydrogen peroxide [wt%] = $\frac{\mathbf{V1\ [ml]\ Cerium(IV)\ sulfate} * \mathbf{f} * \mathbf{0.17007}\ [\frac{g}{100\ ml}]}{\mathbf{E\ [g]}}$

   V1 = volume of cerium(IV) sulfate solution which was consumed for the titration [ml]

   f = titer (factor) of cerium(IV) sulfate solution

   E = sample amount [g]

2. Calculation of the peracetic acid content in percent by weight (mass fraction):

   ► Peracetic acid [wt%] = $\frac{\mathbf{V2\ [ml]\ sodium\ thiosulfate} * \mathbf{f} * \mathbf{0.38026}\ [\frac{g}{100\ ml}]}{\mathbf{E\ [g]}}$

   V2 = volume of sodium thiosulfate solution which was consumed for the titration [ml]

   f = titer (Factor) of sodium thiosulfate solution

   E = sample amount [g]

3. Calculation of the acetic acid content in percent by weight (mass fraction):

   ► Residual Acetic Acid [wt%] = Initial Acetic Acid [wt%] – 0,79 * Peracetic Acid formed [wt%]

4. Calculation of the peracetic acid content in milligrams per liter (mg/l)

   This calculation is required, for example, for the preparation of a calibration solution in the photometric determination of low concentrations of peracetic acids with ABTS.

   ► Peracetic acid [mg/l] = $\frac{\mathbf{V2\ [ml]\ sodium\ thiosulfate} * \mathbf{f} * \mathbf{0{,}38026}\ [\frac{g}{100\ ml}] * \mathbf{10000}}{\mathbf{E\ [ml]}}$

   V2 = volume of sodium thiosulfate solution which was consumed for the titration [ml]

   f = titer (Factor) of sodium thiosulfate solution

   E = Sample volume [ml] (e.g., 10 ml for titration of the pre-dilution in the photometric determination with ABTS)

Annotation to titer:

$f = \frac{c(Titrant)_{actuel}}{c(Titrant)_{target}}$ $\boldsymbol{e.g.} = \frac{\mathbf{0{,}1010}\ [\frac{mol}{l}]}{\mathbf{0{,}1000}[\frac{mol}{l}]} = \mathbf{1{,}010}$

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ENVIRONMENT/DISPOSAL OF CHEMICALS

The disposal of laboratory quantities of peracetic acid must be in accordance with local regulations.

LITERATURE

- Product information "Peracetic Acids", e.g. PERACLEAN® 15
- Photometric determination of low concentrated peracetic acids with ABTS

  (Analytical Method for Peracetic acids)
- Manufacturers equipment descriptions

REMARKS

The method is based on the internal analytical methods PA-84 [609/PM10] and [609/PM11].

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