IFRA ANALYTICAL METHOD

DETERMINATION OF THE PEROXIDE VALUE

DEVELOPPED BY THE IFRA ANALYTICAL WORKING GROUP

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IFRA | **THE INTERNATIONAL FRAGRANCE ASSOCIATION**

IFRA Headquarters Rue de la Fontaine 15 | 1204 Geneva | Switzerland
IFRA Operations Avenue des Arts 6 | 1210 Brussels | Belgium

+32 (0)2 214 2059 | ifrafragrance.org

1. Purpose and Scope

This method describes the determination of peroxide values for animal oils and fats, vegetable oils and fats, as well as for flavour and fragrance materials. The peroxide value is a parameter specifying the content of oxygen as peroxide, especially hydroperoxides in a substance. The peroxide value is a measure of the oxidation present.

2. Principle

The sample is treated in solution with a mixture of acetic acid and a suitable organic solvent and then with a solution of potassium iodide. The liberated iodine is titrated with a standard solution of sodium thiosulfate.

Peroxide values are expressed either in milliequivalents of peroxide/kg or in millimoles of peroxide/L.

Reaction Scheme

The general reaction scheme is as follows:

$$O_2^{2-} + 2I^- + 4H^+ \rightarrow I_2 + 2H_2O$$

Reaction (II)

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Reaction (IV)

The specific reaction scheme for hydroperoxides is as follows:

- Generation of hydroperoxides:

$$R - H + O_2 \rightarrow ROOH$$

Reaction (I)

- Generation of iodine:

$$KI + CH_3CO_2H \rightarrow HI + CH_3CO_2^- K^+$$

Reaction (II)

$$ROOH + 2HI \rightarrow ROH + H_2O + I_2 + \text{Starch indicator}$$

Reaction (III)

- Titration Step:

$$I_2(\text{purple}) + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI(\text{colourless})$$

Reaction (IV)

3. Apparatus and Reagents

3.1 Apparatus

Balance, ± 1 mg
Burette
Iodine flask, Erlenmeyer flask, 250 mL with glass stopper
Stop watch

3.2 Reagents

Chloroform, analytical grade
Cyclohexane, analytical grade
Formic acid
Glacial acetic acid, analytical grade
Isooctane, analytical grade
Methanol, reagent grade
Starch, analytical grade
Sodium thiosulfate solution, 0.01 mol/L (0.01 N) or 0.1 mol/L (0.1 N)
Thyodene indicator
Potassium iodide, analytical grade
Distilled water

3.2.1 Saturated potassium iodide solution

Saturated solution of potassium iodide in deionised water, freshly prepared. The solution must remain saturated (undissolved crystals must be present). The solution has to be kept protected from light.

3.2.2 Starch Solution 1 %

Soluble starch, 10 g is dissolved in deionised water, 1000 mL with heating. Formic acid, 3 mL is added to stabilize the solution.

3.2.3 Sodium thiosulfate solution

The solution has to be kept well sealed and in the dark. Determine the titer every week or prepare freshly.
Use 0.1 mol/L sodium thiosulfate solution when the expected peroxide values are over 20 mmol/L.
Use 0.01 mol/L sodium thiosulfate solution when the expected peroxide values are less than 20 mmol/L or unknown.

3.2.4 Solvent Mixture

Solvent mixture might be prepared by measuring volume of glacial acetic acid and organic solvent in separated volumetric flasks prior to be blended. A selection of solvent mixtures is given below.

3.2.4.1 Solvent Mixture I

Glacial acetic acid: chloroform (3:2)

3.2.4.2 Solvent Mixture II

Glacial acetic acid: cyclohexane (3:2)

3.2.4.3 Solvent Mixture III

Glacial acetic acid: isooctane (3:2)

4. Procedure

The sample has to be protected from the air, stored in a cool place and should not be opened before the onset of the determination. Other tests have to be carried out afterwards.
Solid fats may not be melted before the determination.

- Transfer approx. 3 g of the sample, accurately weighed, taken from the centre of the sample (attention must be paid to the fact that no sample is taken from the surface) into a 250 mL Erlenmeyer flask closed immediately with glass stopper.
- Add 50 mL of the appropriate solvent mixture (I, II or III, part 3.2.4)
- Add 1mL of saturated potassium iodide solution, freshly prepared, and allow reacting for 60 seconds ± 1 second while agitating manually but vigorously the solution at least twice.
- Add 100mL of water and shake.
- Titrate with the appropriate sodium thiosulfate solution (0.01 or 0.1 mol/L, part 3.2.3), using 1 mL starch solution or 0.1 g of Thyodene indicator from a purple to a slight yellow or colourless endpoint

The indicator should be added towards the end of the titration but while the pale straw colour is still present. During titration shake until the blue colour disappears.

Carry out a blank titration under the same conditions.
No more than 0.5 mL of sodium thiosulfate solution should be consumed for this purpose. If this volume is exceeded, it is necessary to re-examine the quality of the reagents.

5. Evaluation

5.1 Calculation of the peroxide value in meq/kg

$$\mathrm{POV_1}\ [meq/kg] = \frac{(\mathrm{V_1} - \mathrm{V_0}) * \mathrm{c}\ * 1000\ * \mathrm{T}}{\mathrm{m}}$$

POV_1 = peroxide value expressed in meq/kg
V1 = consumption of sodium thiosulfate solution in the main test, in mL
V0 = consumption of sodium thiosulfate solution in the blank test, in mL
c = molar concentration (molarity) of the sodium thiosulfate solution in mol/L
T = titer of the thiosulfate solution
m = weighed portion of substance in grams

5.2 Conversion of peroxide value unit

5.2.1 Conversion of peroxide value in meq/kg to mmol/L

$$\mathrm{POV_1}\ [meq/kg] = \mathrm{POV_2}\ [mmol/L] \frac{2}{\mathrm{density}\ [kg/L\,]}$$

POV_1 = peroxide value expressed in meq/kg
POV_2 = peroxide value expressed in mmol/L
2 = Correction factor to convert [meq] in [mmol] (valence=2 for O_2)

5.2.2 Conversion of peroxide value in mmol/L to meq/kg

$$\mathrm{POV_2}\ [mmol/L] = \frac{\mathrm{POV_1}}{2} * \ \mathrm{density}\ [kg/L]$$

POV_2 = peroxide value expressed in mmol/L
POV_1 = peroxide value expressed in meq/kg
2 = Correction factor to convert [meq] in [mmol] (valence=2 for O_2)

6. Comments

Accuracy is difficult to evaluate and reproduce, because an adequate standard substance is hard to obtain due to:

- legal restrictions in many countries
- lack of reliable purity information for peroxides
- lack of stability of peroxides.

Peroxides and similar products which oxidize potassium iodide under the conditions of the test will contribute to the peroxide value. After collaborative testing and comparison of data, the FMA Instrumental Analysis and Specifications Committee have concluded that there may be competing reactions inherent in certain materials which may complicate the endpoint and thus can affect the accuracy of the method. It is recommended that replicate analyses be performed.

The determination of peroxide value is highly empirical. Variations in the procedure may affect the results.

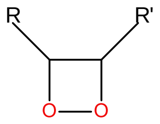
In case of divergent results between two laboratories, the two parts must carry out a second series of analyses strictly applying common critical parameters:

- Test portion

The value obtained depends on the sample mass. Values obtained with the prescribed mass in the present method can be slightly lower than those obtained with a lower sample mass.

- Reaction time

The value obtained depends on the reaction time due to the difference of peroxide reactivity to iodide ions.

The reaction of peroxides of the structures R-O-O-R’ and 

follows an analogous pathway, whilst cyclic peroxides do not react quantitatively under the conditions described here.

- Solvent mixture

The solvent mixture might be carefully chosen to ensure the sample solubility and avoid the underestimation of the peroxide value. Titration with Mixture III might be longer than with Mixture I. Ensure that sufficient time is respected to determine the discoloration of the blend.

For dark coloured products the determination of the peroxide value should be performed by potentiometric titration.

7. Literature/References

ISO-Standard 3960 third edition 2001 AOCS CD 8b-90
European Pharmacopeia
Leatherhead Food RA, second edition
FMA method : Determination_of_Peroxide_content_-__Method_2001.25.01
IFRA method

8. Revision

This document is the second revision of the “IFRA Analytical Method: Determination of Peroxide Value” (October 17th, 2011).
This new version was released in September 2019 after the following modifications, performed by the Analytical Working Group of IFRA:

- Minor modifications of the structure of the present document
- Rewriting of the equations
- Removal of the preparation in volume
- Removal of commercial names
- Removal of the conversion from mmol/L to %
- Addition of remarks on experimental dependence of the method

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