METHOD

DETERMINATION OF PEROXIDE VALUE

1. SCOPE AND FIELD OF APPLICATION

This Standard describes a method for the determination of the peroxide value of animal and vegetable oils and fats.

2. DEFINITION

The peroxide value is the quantity of those substances in the sample, expressed in terms of milliequivalents of active oxygen per kilogram, which oxidize potassium iodide under the operating conditions described.

3. PRINCIPLE

Treatment of the test portion, in solution in acetic acid and chloroform, by a solution of potassium iodide. Titration of the liberated iodine with standardized sodium thiosulfate solution.

4. APPARATUS

All the equipment used shall be free from reducing or oxidizing substances.

Note1: Do not grease ground surfaces.

4.1. 3 ml glass scoop.

4.2. Flasks, with ground necks and stoppers, of about 250 ml capacity, dried beforehand and filled with a pure, dry inert gas (nitrogen or, preferably, carbon dioxide).

4.3. Burette of 5-ml, 10-ml or 25-ml capacity, graduated in at least 0.05 ml, preferably with automatic zero adjustment, or equivalent automatic burette.

4.4. Analytical balance.

5. REAGENTS

5.1. Chloroform, analytical reagent quality, freed from oxygen by bubbling a current of pure, dry inert gas through it.

5.2. Glacial acetic acid, analytical reagent quality, freed from oxygen by bubbling a current of pure, dry inert gas through it.

5.3. Potassium iodide, saturated aqueous solution, recently prepared, free from iodine and iodates. Dissolve approximately 14 g of potassium iodide in approximately 10 ml of water at room temperature.

5.4. Sodium thiosulfate, 0.01 mol/l (equivalent to 0.01 N) accurately standardized aqueous solution, standardized just before use.

Prepare daily the 0.01 mol/l sodium thiosulfate solution freshly from a 0.1 mol/l sodium thiosulfate standard solution before use, or determine the exact molarity. Experience shows that the stability is limited and depends upon the pH value and the content of free carbon dioxide. Use only freshly boiled water for the dilution, possibly purged with nitrogen.

The following procedure is recommended to determine the exact molarity of the sodium thiosulfate solution:

Weigh, to the nearest 0.001 g, 0.27 g to 0.33 g of potassium iodate (m_{KIO3}) into a volumetric flask (250 ml or 500 ml) and dilute to the mark with freshly boiled water (V_2), cooled down to room temperature. By means of a pipette, transfer 5 ml or 10 ml of this potassium iodate solution (V_1) into a 250 ml Erlenmeyer flask. Add 60 ml of freshly boiled water, 5 ml of 4 mol/l hydrochloric acid, and 25 mg to 50 mg of potassium iodide or 0.5 ml of the saturated potassium iodide solution. Titrate this solution with the sodium thiosulfate solution (V_3) to determine the exact molarity of the sodium thiosulfate solution.

$$T = \frac{m_{KIO3} \times V_1 \times 6 \times 10 \times w_{KIO3}}{M_{KIO3} \times V_2 \times V_3}$$

Where:

m_{KIO3} is the mass of potassium iodate, in grams

V_1 is the volume of the potassium iodate solution, in millilitres (5 ml or 10 ml)

V_2 is the total volume of potassium iodate solution, in millilitres (250 ml or 500 ml)

V_3 is the volume of the sodium thiosulfate solution, in millilitres

w_{KIO3} is the purity of potassium iodate in g/100 g

M_{KIO3} is the molecular mass of potassium iodate (214 g/mol)

T is the exact molarity of the sodium thiosulphate solution (mol/l).

5.5. Starch solution, 10 g/l aqueous dispersion, recently prepared from natural soluble starch. Equivalent reagents may also be used.

6. SAMPLE

Take care that the sample is taken and stored away from the light, kept cold and contained in completely filled glass containers, hermetically sealed with ground-glass or cork stoppers.

7. PROCEDURE

The test shall be carried out in diffuse daylight or in artificial light. Weigh in a glass scoop (4.1) or, failing this, in a flask (4.2), to the nearest 0.001 g, a mass of the sample in accordance with the following table, according to the expected peroxide value:

Expected peroxide value (meqO$_2$/kg)	Weight of test portion (g)
0 to 12	5.0 to 2.0
12 to 20	2.0 to 1.2
20 to 30	1.2 to 0.8
30 to 50	0.8 to 0.5
50 to 90	0.5 to 0.3

Unstopper a flask (4.2) and introduce the glass scoop containing the test portion. Add 10 ml of chloroform (5.1). Dissolve the test portion rapidly by stirring. Add 15 ml of acetic acid (5.2), then 1 ml of potassium iodide solution (5.3). Insert the stopper quickly, shake for one minute, and leave for exactly five minutes away from the light at a temperature from 15 to 25 °C.

Add about 75 ml of distilled water. Titrate the liberated iodine with the sodium thiosulphate solution (5.4) shaking vigorously, using starch solution (5.5) as indicator.

Carry out two determinations on the same test sample.

Carry out simultaneously a blank test. If the result of the blank exceeds 0.05 ml of the 0.01 N Sodium thiosulfate solution (5.4), replace the impure reagents.

8. EXPRESSION OF RESULTS

The peroxide value (PV), expressed in milliequivalents of active oxygen per kilogram, is given by the formula:

$$PV = \frac{V \times T \times 1\,000}{m}$$

Where:

V is the number of ml of the standardized sodium thiosulphate solution (5.4) used for the test, corrected to take into account the blank test

T is the exact molarity of the sodium thiosulphate solution (5.4) used, in mol/l

m is the weight in g, of the test portion.

Take as the result the arithmetic mean of the two determinations carried out.

Report the result of the determination to one decimal place.

PRECISION VALUES FOR PEROXIDE VALUE DETERMINATION

1. ANALYSIS OF THE COLLABORATIVE TEST RESULTS

The precision values of the method are given in the table overleaf.

Twenty-one laboratories took part in the collaborative test arranged by the Executive Secretariat in 2016, some of which used a 0.002 N sodium thiosulfate solution. The laboratories were from seven countries.

The precision data have been calculated using solely the data obtained with sodium thiosulphate at 0.01N because some of the laboratories reported that sodium thiosulphate at 0.002 N was too diluted to permit good evaluation of the change of colour.

The test was performed on five samples:

PA0   70% Lampante Olive Oil + 30% Grape Seed Oil

PA1   90% Lampante Olive Oil + 10% Palm Olein

PA2   Extra Virgin Olive Oil

PA3   Olive Oil

PA4   50 % Extra Virgin Olive Oil + 50 % refined Sunflower Oil

PA5   Extra Virgin Olive Oil (ripe fruitiness)

PA6   Extra Virgin Olive Oil

The results of the collaborative test organised by the IOC Executive Secretariat were statistically processed according to the rules laid down in the international standards ISO 5725 *Accuracy (trueness and precision) of measurement methods and results*. Outliers were examined by applying Cochran's and Grubbs's test to the laboratory results for each determination (replicates *a* and *b*).

The table lists:

n   number of laboratories which participated in the test using sodium thiosulphate at 0.01 N

outliers   number of laboratories with outlying values

mean   mean of the accepted results ($meqO_2$/kg)

S_r repeatability standard deviation ($meqO_2$/kg)

RSD_r (%) repeatability coefficient of variation (S_r x 100 / mean)

r   repeatability limit ($meqO_2$/kg): value below which the absolute difference between two single independent test results obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time may be expected to lie with a probability of 95% results (S_r multiplied by 2.8)

S_R reproducibility standard deviation ($meqO_2$/kg)

RSD_R (%)   reproducibility coefficient of variation (S_R x 100 / mean)

R   reproducibility limit (meqO$_2$/kg): value below which the absolute difference between two single test results obtained with the same method on identical test material in different laboratories with different operators using different equipment may be expected to lie with a probability of 95% (S$_R$ multiplied by 2.8)

	A	B	C	D	E	F	G
n	16	20	15	14	14	19	15
outliers	0	0	0	0	0	0	0
mean	11,7	24	7,8	2,8	4,9	14,3	8,2
r	0,26	1,31	0,41	0,27	0,19	0,52	0,33
S$_r$	0,09	0,47	0,15	0,1	0,07	0,18	0,12
RSD$_r$(%)	0,8	1,9	1,9	3,4	1,4	1,3	1,4
R	1,86	4,00	1,55	1,09	1,19	3,18	2,81
S$_R$	0,66	1,43	0,55	0,39	0,43	1,14	1,0
RSD$_R$(%)	5,7	5,9	7,1	13,8	8,6	8,0	12,3

2. REFERENCES

ISO 5725-1:1994 Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions

ISO 5725-2:1994 Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of the repeatability and reproducibility of a standard measurement method

ISO 5725-5:1998 Accuracy (trueness and precision) of measurement methods and results – Part 5: Alternative methods for the determination of the precision of a standard measurement method

ISO 5725-6:1994 Accuracy (trueness and precision) of measurement methods and results – Part 6: Use in practice of accuracy values

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