



Peroxide Number of Edible Oils (NF T 60-220 (1995) and ISO 3960 (2001))

Introduction

The peroxide number is a measurement of the concentration of (-O-O-) groups in edible oils. It is a measurement of the decomposition of the product and in many countries, official standards specify a maximum peroxide number beyond which the oil is unfit for human consumption. The peroxide number is therefore measured by oil manufacturers during production and after storage to check its preservation. International standards use a redox titration in non-aqueous media, results are generally expressed in µg of peroxide (or active oxygen) per gram of product but mmoles/kg or meq of O₂/kg are also used.

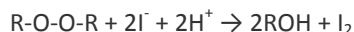
The following two standards use the same titration principle but not the same solvents. NF T 60-220 uses chloroform CHCl₃ ISO 3960 uses isooctane C₈H₁₈.

According to these two standards, the equivalence point of the redox titration is determined using starch as colour indicator, but it is very easy to use potentiometric determination.

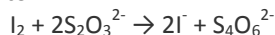
Summary

Peroxide number determination involves a two-step redox reaction:

1) Reaction of peroxide group with an excess of iodide ion according to:



2) Titration of Iodine with Na₂S₂O₃ solution (generally 0.01 or 0.02M) according to:



The titration is run according to inflection detection with continuous addition of the titrant with a combined platinum/reference electrode.

Electrode and reagents

MC3051Pt-9 Metal electrode, combined, platinum (part no. E31M003) with CL114 cable (part no. A94L114).

Glacial acetic acid (CH₃COOH)

Chloroform (CHCl₃) (NF T 60-220)

Isooctane C₈H₁₈ (ISO 3960)

Solvent used for ISO 3960

Acetic acid/isooctane solution by mixing of 3 volumes of glacial acetic acid and 2 volumes of isooctane.

Saturated aqueous solution of potassium iodide (KI). Note that the solubility of KI in water is approximately 150g/100 ml of water. Do not prepare too a large volume of this solution. Store it in the dark.

Distilled water

Sodium thiosulphate solution 0.01M (or 0.02 mol/l) in water (Na₂S₂O₃) To prepare a 0.01 mol/l (or 0.02 mol/l) sodium thiosulphate solution, dissolve 2.4818 g (or 4.9636 g) of Na₂S₂O₃ · 5H₂O in 500 ml of freshly distilled water (or freshly boiled and cooled deionised water). Add 2 or 3 drops of CHCl₃ (or 0.4 g of NaOH), as stabilising agent, and complete to 1000 ml using a volumetric flask. Wait for one day and filter the solution if necessary (precipitation of sulphur can occur). Stock the solution in a brown glass flask. From time to time, look at the solution and filter or standardise again if necessary. Na₂S₂O₃ · 5H₂O has a molecular weight corresponding to 248.181 g/mol. As solutions with a concentration corresponding to 0.01M are not very stable, do not store this solution for more than 1 week. As Sodium thiosulphate solution 0.1M is commercially available, you can prepare the 0.01 or 0.02M solution by dilution.

Check that solvents and reagents do not contain dissolved oxygen. Bubbling nitrogen in the different solutions is one way to do this.

Inflection Detection settings

CONTINUOUS IP MODE	
Titration with blank	
Burette volume	5 ml (see working range)
Max. volume	3.5 ml
Stirring speed	500 rpm
Working mode	mV i=0
Blank	YES
Start timer	10 s
Min. ordinate	150 mV
Max. ordinate	250 mV
Stop point	0 mV
Minimum speed	0.20 ml/min
Maximum speed	3.00 ml/min
Smoothing parameter	4
Titration	Decreasing potential
Inflection number	1
Inflection 1	
Min. ordinate	150 mV
Max. ordinate	280 mV
Stop at last IP	YES



Sample	
Dilution	NO
Sample unit	g
Sample amount	2 (see working range)
Results	
Result 1	
Unit	mg/kg
Reaction	1 sample + 2 Titrant
Molar weight	16 g/mol (see results)
No of equations 2	
Equation 1	
Unit	mmoles O2/kg
Formula	R1/16
Equation 2	
Unit	meq O2/kg
Formula	R1/8

Procedure

According to NF T 60-220

Use a stoppered titration vessel.

First run a blank titration according the following procedure but without sample. Then run a titration.

Accurately weigh the necessary amount of edible oil.

Add 10 ml of chloroform and stir to dissolve.

Add 15 ml of glacial acetic acid and 1 ml of saturated potassium iodide solution.

Stop the titration vessel, stir for 1 minute and wait 5 minutes, keeping away from daylight.

Then add 75 ml of distilled water and titrate with 0.01 (or 0.02 mol/l) thiosulphate solution.

Procedure according to ISO 3960

The general procedure is exactly the same as for NF T 60-220.

Weigh the necessary sample amount.

Dilute with 50 ml of the iso-octane/ acetic acid solution.

Add 0.5 ml of potassium iodide solution and stir for 1 minute then add 30 ml of distilled water.

Results

Expressed as $\mu\text{g/g}$ (or mg/kg) of active oxygen the results corresponds to:

$$R = C_{\text{titr}} * V_{\text{titr}} * 16 * 1000 / 2 * W_{\text{smp}}$$

C_{titr} = Titrant concentration in mol/l

V_{titr} = Necessary titrant volume in ml

1000 = Constant to express the result in μg

16 = molar weight of oxygen

2 = As 2 moles of titrant correspond to 1 mole of sample

W_{smp} = Weighed amount of sample in g

Some other units can be used for result expression.

Result in mmoles/kg corresponds to: R/16

Result in meq of active oxygen/kg corresponds to: R/8

Results

3 determinations on old peanut oil

Mean	192.8 mg/kg (standard deviation: 2.6)
	12.05 mmoles O2/kg (standard deviation: 0.16)
	24.10 meq O2/kg (standard deviation: 0.33)
	(blank determination: 0.107 ml)

Working range

Use the following table which summarises the data in both standards to determine the necessary amount of sample:

Peroxide number $\mu\text{g/g}$ or mg/kg	Peroxide number meq/kg	Sample amount (g)	Titrant volume (ml)
0-100	0-12	5.0-2.0	2.4
100-150	12-18.75	2.0-1.2	2.25
150-250	18.75-31.25	1.2-0.8	2.25-1.5
250-400	31.25-50	0.8-0.5	1.5-2.5
400-700	50-87.5	0.5-0.3	2.5-2.6

(*) Calculated with oleic acid molar weight

(**) For a 0.1M titrant

Procedure Notes

The main difficulty is to obtain reproducible results avoiding the influence of atmospheric oxygen. Note that the saturated solution of potassium iodide is highly oxidisable. It is necessary to check this solution using the thiosulphate 0.01M solution according to the procedure described in the standards. Low values for blanks are recommended (between 0.05 and 0.1 ml according to the standards). After addition of water, the titration medium is a two-phase solution. Check you immerse the measuring electrode in the aqueous phase. Do not use too high a titration speed, because it is necessary to free all the iodine from the solvent layer.

Curve

