



Iodine Value of Animal and Vegetable Fats and Oils (EN ISO 3961 (1999) & ISO 3961 1996)

Introduction

The iodine value of animal and vegetable fats and oils measures the amount of -C=C- (double bonds) present in the product. The result is expressed as g of iodine (I₂) per 100 g of sample; the molar weight of I₂ is 253.8 g/mol. Instead of I₂, ISO 3961 and EN ISO 3961 standards use Iodine chloride (I Cl) in acetic acid solution, also known as Wijs solution, for this determination. ISO and EN ISO standards use the reaction of the sample with an excess of Wijs solution followed by determination of excess of Wijs solution using a redox titration with sodium thiosulphate. **As indicated in standard ISO 3961, potentiometric determination of the equivalence point can be used.**

Summary

The iodine value determination involves a three-step operation:

- 1) Reaction of sample with Wijs solution in excess according to $R-C=C-R + I Cl \rightarrow R-Cl-CCI-R$
- 2) Reaction of the excess of Wijs solution with potassium iodide according to $I Cl + I^- \rightarrow I_2 + Cl^-$
- 3) Determination of the amount of released iodine according to $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

According to this three-step operation, the titration is a back titration with a blank. This titration is run according to inflection detection with continuous addition of the titrant with a combined platinum/reference electrode, but it is also possible to work with a pre-set end point titration.

Electrode and reagents

- MC3051Pt combined platinum/ reference electrode (part no. E31M003), CL114 connecting cable (part no. A94L114) or M241Pt2-8 (part no. E32M002) or a M231Pt-2 Metal Electrode (part no. E32M001) with adapter part no. 94P801.
- *Wijs solution 0.1M (see note below)* This solution is commercially available (e.g. part no. 35 071
- from Sigma Aldrich)
- *Titration solvent:* Mix the same volumes of cyclohexane and glacial acetic acid.
- *Potassium iodide solution:* Dissolve 100 g of potassium iodide in 1000 ml of pure water. Store the solution in a brown bottle avoiding oxidation of the iodide ion.
- *Sodium thiosulphate solution 0.1 mol/ (or 0.1N)* Na₂S₂O₃, 5H₂O has a molecular weight corresponding to 248.181 g/mol.

To prepare a 0.1 equivalent/l (or 0.1 mol/l) sodium thiosulphate solution; dissolve 24.8181 g of Na₂S₂O₃, 5H₂O in 500 ml of freshly distilled water (or freshly boiled and cooled deionised water) and 2 or 3 drops of CHCl₃ 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. Look at the solution from time to time and filter/standardise again if necessary. This solution is also commercially available.

Distilled or deionised water

Inflection Detection settings Continuous IP mode

Back titration with blank	
Burette volume:	25 ml or 50 ml (see "burette capacity" below)
Stirring speed:	700 rpm
Working mode:	mV
Start timer:	20 sec
Blank:	YES
Min. ordinate:	200 mV
Max. ordinate:	300 mV
Predose until:	(see "burette capacity" below)
Maximum volume:	25 ml or 50 ml
Stop point:	100 mV
Direction:	decreasing mV
Minimum speed:	0.1 ml/min
Maximum speed:	5.00 ml/min
Smoothing parameter:	5
Back Titration:	Manual (see "back titration" below)
Excess reagent:	Wijs solution
Excess volume:	20 ml
Excess titre:	0.1
Inflection 1:	
Minimum ordinate:	200 mV
Maximum ordinate:	300 mV
Stop at last IP:	YES
Sample unit:	g
Sample amount:	(see "working range" below)
Dilution:	NO
Result:	%
Molar weight:	253.8 g/mol
Excess:	2 Smp + 2 Exc (see "result" below)
Reaction:	1 Exc + 2 Titr

Procedure (see notes)

For blank

For blank determination, prepare a solution in the same way as indicated below but without a sample.



For sample

Weigh the recommended amount of oil (see "working range"). Add the recommended volume of titration solvent (20 or 25 ml). Add 20 ml (10 ml can sometimes be sufficient) of Wijs solution (see "Wijs solution" and "burette capacity"). Mix the solution and stopper the beaker (or the conical flask). Leave the solution in the dark for 1 or 2 hours (refer to local standards) until the first step of the reaction is complete. Remember the reaction time depends on the nature of the sample and excess of Wijs solution if results are to be reproducible. Next add 20 ml of the potassium iodide solution and 100/150 ml of deionised water. If the procedure uses a conical flask with a ground glass stopper, it is possible to pour the solution into a beaker just before the titration, using deionised water to rinse the flask. Titrate the blank followed by the corresponding sample.

Results

As the result is generally expressed in g of I₂ per 100 g of sample; according to the reactions, the Titration Manager calculates the result according to:

$$R = (V_{bl} - V_{smp}) * C_{titr} * 253.8 / 2 * W_{smp} * 10$$

V_{bl} = Titrant volume for blank in ml

V_{smp} = Titrant volume for sample in ml

C_{titr} = Titrant concentration in mol/l

253.8 = Molar weight of I₂

W_{smp} = Sample weight in g

2 = Stoichiometric factor of the reactions (1 mole of I Cl corresponds to 1 mole of I₂ that corresponds to 2 moles of S₂O₃²⁻)

10 = Factor expressing result in %

For determination on old peanut oil

Iodine number: 80 g/100 g

Working range

Depending on the expected iodine value, look at the following table to determine the correct sample amount.

Iodine value in %	Sample amount in g	Solvent in ml	$V_{bl} - V_{smp}$ in ml
<1.5	15	25	17
1.5 - 2.5	10	25	12 - 19
2.5 - 5	3	20	6 - 12
5 - 20	1	20	4 - 16
20 - 50	0.4	20	6.5 - 16
100 - 150	0.13	20	10 - 15
150 - 200	0.1	20	12 - 16

It is important to have a sample amount that corresponds to the volume of the Wijs solution. The quantity of Wijs solution consumed by the sample should be close to 50% of the total amount of Wijs solution added.

Notes

Wijs solution This solution is inflammable and corrosive. Work under a hood. **Never pipette this solution directly with the mouth, always use a pro-pipette.** Always consult the safety data sheet available from the product supplier before handling.

Burette capacity and maximum volume

According to the reaction between I Cl and I⁻ and titration of I₂ with S₂O₃²⁻, if you use 20 ml of I Cl 0.1M, the blank determination theoretically needs 40 ml of S₂O₃²⁻ 0.1M. This should be taken into account when choosing the burette capacity (25 or preferably 50 ml), the maximum volume and the possible predose volume. Use of the predose may be mandatory in continuous IP titration with a 25 ml burette capacity and saves time in end point titration.

Back titration

As it is necessary to wait 1 or 2 hours for a complete reaction, do not use AUTOMATIC back titration.

Procedure

As the titration medium is a two-phase medium, it is advisable to use large diameter beakers and a stirring speed of around 700 rpm in order to obtain efficient mixing of the two phases. *Otherwise, some iodine may stay in the organic phase (becoming light violet coloured) giving a false result.* According to some publications, it is possible to shorten the reaction time by adding 10 ml of 2.5% mercuric acetate [(CH₃COO)₂Hg] solution in water as catalyst after the Wijs solution.

Result

For a back titration, the Titration Manager asks for identical coefficients for Sample and Titrant.

End Point Titration

It is possible to work with a M241Pt-8 Metal Electrode (part no. E32M002) or a M231Pt-2 Metal Electrode (part no. E32M001) with adapter part no. A94P801, using imposed current potentiometry. In this case, the Titration Manager settings should be modified as follows:

Working mode:	mV i>0
Current value:	1 µA
Direction:	Increasing mV
Minimum speed:	0.2 ml/min
Maximum speed:	2.00 ml/min
Number of end points:	1
End point:	200 mV190 mV
Proportional band:	
End point delay:	5 sec

The other settings are similar to those already described.