MICRO-DETERMINATION OF HYDROGENATION-IODINE-NUMBER OF VEGETABLE OILS[1]

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Unsaturation in oils and fats have generally been estimated by the determination of *iodine value* (I.V.) by any of the established methods among which Hubl's and Wijs' methods are prominent.[2] Halogenation as a means of determining unsaturation has the defect that substitution also may possibly occur during the process.[2] Further, in compounds containing hydroxyl groups or conjugated double bonds, *iodine value* does not indicate the correct unsaturation.[3] With tung oil which contains triene conjugated eleostearic acid, varying iodine values have been obtained.[4]

Fokin[5] first used *hydrogen value* as a means of determining unsaturation of organic compounds in a manner similar to *iodine value*. He defined *hydrogen value* as the number of ml. of hydrogen at N.T.P. absorbed by one gram of the compound. The amount of hydrogen absorbed by the compound when expressed in *iodine value units* gives a quantitative measure of total unsaturation and has been designated as *hydrogen-iodine value* by Waterman *et al.*[4, 6] Kaufman and Baltes[3] have named this constant as *hydrogenation-iodine-number*, *Hydrierjodzahl* (*HJZ*). Although the catalytic hydrogenation method has none of the defects of the halogenation process, only sporadic efforts[3, 4, 6–13] have been made to employ the method as it requires special type of apparatus.

In the present study on the application of this method in the field of oils and fats, the *hydrogenation-iodine-number* (*H.I.N.*) of ten vegetable oils as well as of maleic acid, monomethyl fumarate and methyl oleate, have been determined using "Towers" micro-hydrogenation apparatus.

The amount of hydrogen absorbed at room temperature and atmospheric pressure, by a known weight of the oil under investigation, is converted into volume in ml. at standard conditions of temperature and pressure and H.I.N. calculated by means of the following equation.

$$\text{H.I.N.} = \frac{v \times 253 \cdot 84 \times 100}{22412 \times w}$$

v = Volume of hydrogen absorbed, in ml. at N.T.P.

253·84 = Weight of two atoms of iodine.

22412 = Volume in ml. of one molecule of hydrogen at N.T.P.

w = Weight of sample in grams.

The *hydrogenation-iodine-numbers* thus obtained have been compared with the *iodine values* determined by Hubl's and Wijs' methods and are recorded in the table below.

TABLE

Comparison of I.V. with H.I.N.

No.	Material	Iodine value (I.V.)		Hydrogenation iodine number (H.I.N.)
		Hubl	Wijs	
1	Groundnut oil	85·13	89·39	91·38
2	Cocoanut oil	9·06	9·07	9·30
3	"Venthenna" (Oil from cocoanut milk)	9·06	9·10	9·13
4	Neem oil	71·50	73·08	75·01
5	Castor oil	85·42	85·28	88·28
6	Tung oil	89·52	97·25	226·25
7	Olive oil	75·36	78·54	80·96
8	Sesame oil	112·10	117·00	123·20
9	Soyabean oil	103·60	105·20	107·10
10	Groundnut oil (Hydrogenated) ..	58·67	59·38	59·51
11	Methyl oleate		84·34	86·63 (85·63)
12	Monomethyl fumarate		..	193·55 (194·50)
13	Maleic acid		..	220·00 (218·83)

Figures enclosed in brackets indicate calculated *iodine value*.

Each value in the table is the average of at least two experiments. It is significant that in the case of tung oil only low iodine values could be obtained although the estimation has been repeated more than a dozen times.

The reliability of this method with respect to completion of the hydrogenation has been checked by the *iodine value* (Wijs') determination made on the catalyst-free residue following a determination of *hydrogenation-iodine-number*, when no iodine absorption occurred.

The simplicity and reliability coupled with the possibility of working with micro quantities should warrant wide use of this method for the determination of unsaturation in oils and fats.

Experimental

"Towers" micro-hydrogenation apparatus designed by A. R. Gilson, consists essentially of a gas burette, two reaction flasks, manometer, shaking arrangement and water-bath. Adams Pt-oxide has been prepared as per details given in *Organic Synthesis*.[14] A.R. glacial acetic acid has been used in all the experiments. Hydrogen from the cylinder has been used after drying (sulphuric acid). A typical experiment is described below:—

H.I.N. of groundnut oil.—Adams Pt-oxide catalyst (10 mg.) is suspended in glacial acetic acid (5 ml.) in one of the two reaction flasks having the side arm, the second flask serving to conduct the blank experiment with the solvent only. Groundnut oil (19·9 mg.) is weighed in a small tube and held in the side arm of the reaction flask out of contact with the solvent and catalyst inside. After the catalyst is saturated with hydrogen, the substance is dropped into the flask and the hydrogenation is carried out at room temperature until no more hydrogen is absorbed.* H.I.N. of the oil is calculated as under.

Volume of hydrogen absorbed is 1·94 ml. at 25° C. and 685 mm. pressure.

$$\text{Volume } (v) \text{ of hydrogen absorbed in ml. at N.T.P.} = \frac{1\cdot94\times685\times273}{298\times760}$$

$$= 1\cdot61$$

$$\text{H.I.N.} = \frac{1\cdot61\times253\cdot84\times100}{22412\times0\cdot0199} = 91\cdot48$$

* In the case of tung oil, hydrogenation has been conducted at 50 to 60° C.

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