Institut für Pharmazeutische Chemie der Philipps-Universität, Marburg, Germany

Determination of iodine values using 1,3-dibromo-5,5-dimethylhydantoin (DBH) and ethyl acetate as solvent

Analytical methods with DBH in respect to environmental and economical concern, part 18*

M. HILP

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Dr. Manfred Hilp, private address: Haselhecke 42, D-35041 Marburg, Germany
manfred@hilp.de

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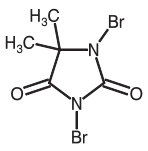
Iodine values (iodine numbers) of several fixed oils and lard can be determined in ethyl acetate, an easily biodegredable solvent, instead of chloroform according to PH. EUR. 2002. Iodine monobromide has been replaced by 1,3-dibromo-5,5-dimethylhydantoin (DBH) and potassium iodide (KI) and the reaction time was reduced to 5 min only. However, cod-liver oil and linseed oil require a reaction time of 30 min and a smaller weight of sample. Longer reaction times are also necessary for soya oil and wheat germ oil. Iodine values of linseed oil determined according to method A of PH. EUR. 2002, are dependent on the amount of sample, even in the range prescribed by the pharmacopoeia.

1. Introduction

The iodine value (iodine number) is characteristic for the content of unsaturated fatty acids in fats, fixed oils, emulsifiers and solubilizers (Hartke et al. 1999). Halogen (Hilp 2002a; Imming and Germershaus 2002) is added to the double bonds. After the addition of potassium iodide the excess of the halogenating reagent reacts to iodine, which has to be titrated with thiosulfate. The determination of the iodine value is of significance for pharmaceutics, food chemistry, cosmetics and others. The iodine monobromide reagent according to Hanuš (Hanuš 1901) applied for PH. EUR. 2002 and USP 2000, can be more simply produced using DBH and potassium iodide (DBH/KI) or DBH and iodine (DBH/I_2), as has been published recently (Hilp 2002a). DBH in contrast to iodine monobromide is a stable and easy to handle crystalline compound (Hilp 2002a).



DBH [77-48-5]

Some nonionogenic emulsifiers can be analysed in aqueous solution with a reaction time of only 5 min, whereas PH. EUR. 2002 applies hepatoxic and environmentally hazardous chloroform and a reaction time of 30 min (Hilp 2002b). In the cases of samples slightly soluble in water the addition of ethyl acetate was necessary. Also fixed oils have been determined in an o/w emulsion using nonionogenic emulsifiers and ethyl acetate. With regard to these results it was interesting to analyse iodine values of fixed oils and fats using only ethyl acetate instead of chloroform and without the employment of nonionogenic emulsifiers.

2. Investigations, results, and discussion

As shown in the Table chloroform can be replaced by ethyl acetate analysing fixed oils, and lard. The results correspond with those of PH. EUR as well with visual

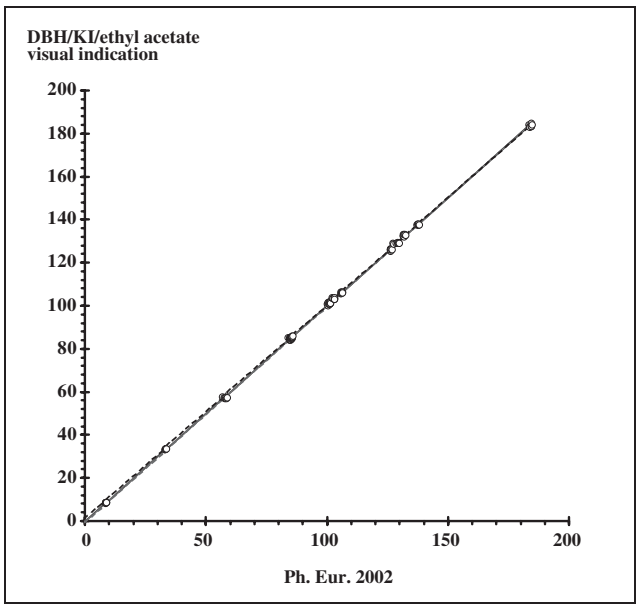


Fig. 1: Method comparison according to Passing-Bablok (Passing, Bablok 1983 1984, Haeckel 1984) of the iodine value determination using DBH/KI in ethyl acetate and visual indication by comparison to PH. EUR. 2002 (95% confidence)

Table 1: Determination of iodine values of fixed oils and fats using DBH and ethyl acetate in comparison to PH. EUR. 2002

Material	Expected Iodine value	Weight of sample mg	Waiting time (min)	DBH/KI							PH. EUR. 2002, Method A				
				n	visual			potentiometric			n	visual		potentiometric	
					Mean (%)	Bias[a]	RSD (%)	Mean (%)	Bias[a]	RSD (%)		Mean (%)	RSD (%)	Mean (%)	RSD (%)
Almond oil	USP/NF 2000 95–105	154–162	5	7	101.3	0.06	0.36	101.1	0.14	0.38	7	101.2	0.31	100.9	0.28
Arachis oil, peanut oil	USP/NF 2000 84–100	194–217	5	7	100.9	0.27	0.44	100.9	0.44	0.35	6	100.6	0.26	100.5	0.30
Avocado oil	DAC 1986 80–90	160–179	5	7	85.5	−0.18	0.27	85.3	−0.23	0.26	7	85.7	0.21	85.5	0.20
Castor oil	PH. EUR. 2002 82–90	156–179	5	7	84.5	−0.36	0.42	84.0	−0.41	0.39	7	84.8	0.49	84.4	0.48
Coconut oil	8–9.5[b]	1012–1199	5	7	8.5	−2.15	1.6	8.5	−2.15	1.5	7	8.7	0.92	8.7	1.0
Cocoa butter	DAB 2000 33–42	294–315	5	6	33.4	0.03	0.58	33.4	0.23	0.51	7	33.4	0.39	33.3	0.35
Cod-liver oil	PH. EUR. 2002	100–116	5	7	138.7	−12.5	0.37	138.4	−12.6	0.31	7	158.6	0.29	158.2	0.19
	suppl. 4.4.	43–58	30	7	152.5	−1.01	0.22	152.1	−1.08	0.39	7	154.0	0.34	153.8	0.29
	150–180	26–38	30	7	155.7	1.47	0.86	155.4	1.67	1.08	7	153.4	0.30	153.0	0.26
Cottonseed oil	USP/NF 2000 109–120	102–106	5	7	103.3	0.47	0.40	103.1	0.40	0.26	7	102.8	0.48	102.7	0.45
Lard[c]	DAB 2000 46–60	336–406	5	7	57.2	−1.31	0.55	57.1	0.94	0.54	7	58.0	1.08	57.6	1.04
Linseed oil	PH. EUR.	100–114[d]	5	7	170.3	−8.0	4.90	170.2	−8.1	4.87	7	185.2	0.32	185.1	0.31
	suppl. 4.4/2003 160–200	52–58	30	7	183.7	−0.28	0.34	184.0	0.14	0.31	7	184.2	0.29	183.7	0.24
Olive oil	USP/NF 2000	154–162	5	7	85.0	0.12	0.33	84.9	0.16	0.39	7	85.1	0.39	84.7	0.33
	79–88	155–170	30	7	85.8	0.43	0.45	85.6	0.51	0.49	7	85.5	0.32	85.2	0.31
Safflower oil	140–150[e]	111–115	5	7	137.6	−0.10	0.12	137.2	−0.20	0.13	7	137.7	0.24	137.4	0.18
Sesame oil	USP/NF 2000 103–116	149–191	5	7	106.0	−0.02	0.23	105.6	−0.39	0.23	7	106.1	0.21	106.0	0.25
Soya oil	USP/NF 2000	102–106	5	3	125.0	−1.11		124.5	−1.43		7	126.4	0.19	126.3	0.17
	126–140		10	3	126.3	−0.08		125.6	−0.55						
			15	3	126.3	−0.08		125.7	−0.48						
			30	7	126.1	−0.27		125.7	−0.44	0.24					
Sunflower oil	DAC 1986 120–140	95–113	5	7	132.7	0.62	0.31	132.5	0.83	0.26	7	131.9	0.32	131.4	0.32
Wheat germ oil	115–129[f]	107–108	5	2	123.4	−4.2		124.8	2.8		7	128.8	0.75	128.4	0.76
		107–114	30	7	129.0	0.19	0.17	128.5	0.06	0.20	7	128.8	0.75	128.4	0.76
					DBH/I_2						PH. EUR. 2002, Method A				
Arachis oil	USP/NF 2000 84–100	191–211	5	7	101.7	0.10	0.68	101.5	0.23	0.69	7	101.6	0.50	101.2	0.43

[a] in comparison to PH. EUR. 2002, method A
[b] O'Neil M. J et al. 2001, p. 430, no. 2486
[c] the sample is dissolved with 5 ml of Miglyol® by heating, cooling to room temperature and addition of 20 ml of ethyl acetate.
[d] a small amount of a white, solid precipitate is formed when the titration is performed
[e] O'Neil M. J et al. 2001, p. 1493, no. 8392
[f] O'Neil M. J et al. 2001, p. 1791, no. 10100

(see Fig. 1) or potentiometric indication (see Fig. 2.). In most cases the reaction time can be reduced from 30 to 5 min.

If ethyl acetate is present, starch solutions do not yield the characteristic blue colour with iodine. Nevertheless, the change from yellow to white at the end point can be recognized clearly. Using potentiometric titration a definite potential jump (Hilp 2002b) can be seen and allows automatisation.

However, cod-liver oil and linseed oil require a reaction time of 30 min and a smaller weight of sample. Longer reaction times are also demanded for soya oil and wheat germ oil.

These results show that the required reaction time and the amount of sample weight is not only dependent on the value of the iodine number, but also on the composition of the fixed oil. Safflower with an iodine number of 138 affords only a reaction time of 5 min. Also olive oil did not give a significant difference between 5 min and 30 min waiting time.

The iodine value determination of linseed oil is problematic (Hilp 2002b). For the determination PH. EUR. 2002 (method A) prescribes a quantity of sample between 0.1 to 0.15 g for a presumed iodine value of more than 100. Fig. 3 demonstrates that the results of the iodine value determination of linseed oil depend on the amount of sample weight in the range of the PH. EUR. 2002. Reproducible results are only obtained if the amounts of sample are nearly equal.

The determination of iodine values using ethyl acetate is furthermore advantageous, because DBH/KI as halogenating reagent can be applied. DBH/KI cannot be applied in the presence of nonionogenic emulsifiers (Hilp 2002b) and can be prepared more simple in contrast to DBH/I_2 (Hilp 2002a).

3. Experimental

3.1. Instrumentation, materials, solutions, and statistical methods

see Hilp (2002a and 2000b)

3.2. Assays

Samples are put into a cut off micro test tube of about 1 cm in length and about 0.6 cm in diameter or directly into the iodine flasks. Therefore, a tared pipette with the sample is used and weighed back after pipetting into the flask.

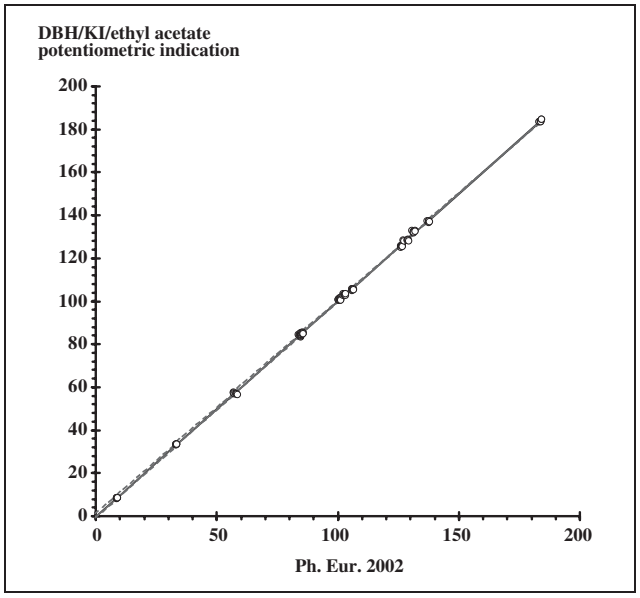


Fig. 2: Method comparison according to Passing-Bablok (Passing, Bablok 1983 1984, Haeckel 1984) of the iodine value determination using DBH/KI in ethyl acetate and potentiometric indication by comparison to PH. EUR. 2002 (95% confidence)

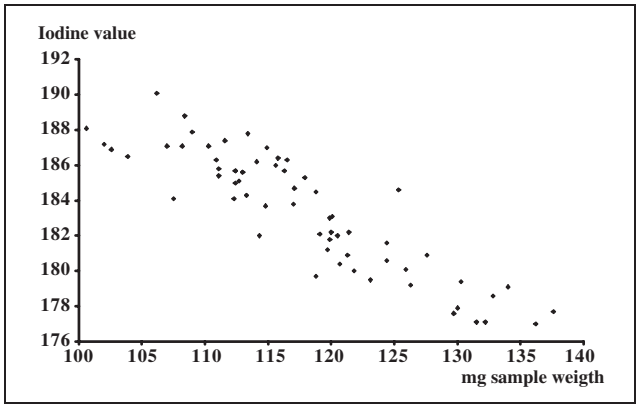


Fig. 3: Determination of iodine values of linseed oil according to method A of PH. EUR. 2002 with various sample weights (n = 69)

Dissolve the amount of sample to be analysed (see Table) in 20 ml of ethyl acetate. Add 20 ml of DBH/KI and stir under light protection as long as described in the Table. Put 10 ml of 0.5 M KI into the flask, titrate with 0.1 M $Na_2S_2O_3$ and visual (yellow to colourless) or with potentiometric indication.

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*Part 17: Hilp (2002 b)

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