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ENTHALPIMETRIC DETERMINATION OF THE IODINE VALUE OF SOME EDIBLE OILS AND FATS

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A simple, rapid and accurate direct injection enthalpimetric (DIE) method has been developed for the determination of the iodine value of some commercial edible oils. A significant heat pulse of halogen addition reaction of the double bonds of unsaturated fatty acid esters in the oils is produced by injecting a solution of iodine monochloride into the sample solutions. The method is calibrated against real samples and the standard compounds (oleic, linoleic and linolenic acids) whose iodine values have been determined by a standard method. Once calibrated, the proposed method can be operated routinely by semi-skilled personnel. The method is sensitive and give results as acceptable as those obtained by standard methods. The main advantages of the method are those of time and cost of analysis and the potential of the enthalpimetric method for automation.

The "iodine value" of oils and fats is one of the most valuable and widely used characteristic for the evaluation and differentiation of these substances representing as it does a measure of the degree of unsaturation. For some time the determination of this value has been of universal importance, and there is, at present, a steadily increasing demand for a simple and rapid method which will be adaptable for routine work, will require no special apparatus and be relatively economical in use. In spite of this, no single, rapid and accurate method which will give consistent results on all types of oil has been previously reported.

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A number of methods have been devised for the determination of the iodine value, and it is well known that all the methods do not yield identical results. Although many halogen absorption methods are available, only those using iodine monochloride (Wijs method) [1] and iodine monobromide (Hanus method) [2] are widely. used, even though these methods are time consuming. Catalysts have been used to decrease the long time required for complete absorption and reaction of the halogen. Mercuric acetate has been used in the Wijs procedure [3-5]. Benham and Klee [6] modified the Rosenmund Kuhnhenn method [7] using this reagent. Another reagent, hypochlorous acid was introduced [8] to reduce the time of reaction, and was used [9] for determining the iodine value of oils with conjugate unsaturation, commercial bleaching solutions were later introduced [10] as reagents.

Since the halogen addition reaction generally releases a significant amount of heat, and the reaction could be forced to occur immediately by the use of a large excess of reagent, the Direct Injection Enthalpimetric (DIE) method [11] potentially provides an ideal technique to satisfy the problem of providing a rapid method of analysis. The reported potential uses of iodine monochloride in solution thermal chemistry [12], indicate that it should be useful for the rapid determination of the amount of unsaturation in oils and fats.

Experimental

Apparatus

The basic circuit of the electrical bridge system and the reaction vessel have been previously reported [13, 14].

Reagents

All reagents used were of analytical-reagent grade.

For determining the iodine value by standard Wijs and Hanus methods

Carbon tetrachloride was used to dissolve the samples. Solutions of 0.5 *M* iodine monochloride and of iodine monobromide and of 5% w/v mercuric acetate in glacial acetic acid were used as iodinating agents and catalyst respectively. The unabsorbed iodine was titrated using solutions of 10% w/v potassium iodide and of 0.1 *N* sodium thiosulphate.

The Wijs and Hanus solutions (ICl and IBr) were prepared and used in accordance with standard procedure [15] with a slight modification in the concentration of ICl and IBr used.

For determining the iodine value by the DIE method

It is necessary to dissolve the sample in a solvent which does not give an unacceptable heat of mixing with the solvent used to dissolve the reactant (ICl). Since both the iodine monochloride and the catalyst are dissolved in glacial acetic acid, this must form a significant proportion of the solvent used to dissolve the samples of oils and fats. In the standard Wijs and Hanus method, carbon tetrachloride is used to dissolve the sample.

Various compositions of the solvent to be used were investigated. A range of proportions of components from 0% to 100% v/v carbon tetrachloride and from 100% to 0% v/v glacial acetic acid were used. From the results obtained, it was decided to use a 1:1 (v/v) mixture. This gave optimum results regarding the production of both a mono-phase solution and a thermal response and was used throughout as the solvent for the oils and fats. Solutions of 0.5 *M* iodine monochloride and of mercuric acetate 5% w/v in glacial acetic acide were used as titrant and catalyst respectively.

Procedure

To obtain maximum reproducibility, the disposable reaction vessel (an expanded polystyrene beaker with a nominal capacity of 200 ml) is contained in a Dewar flask fitted with a loosely fitting lid through which passes the temperature sensor (a glass coated thermistor bead) and the shaft of a constant speed stirrer. The reagent is dispensed (in 5 ml aliquots) from a semi-automatic dispenser pipette having a thermostatted 1 litre reservoir. The reaction system (Dewar flask and reagent reservoir) is contained in a water filled thermostat regulated to 25 ±1°.

Comparison of the DIE method and the standard Wijs and Hanus methods for the determination of the I.V. of oils and fats

a) The Wijs and Hanus procedure

The principle of these two methods is similar, the difference is only the reagent used. In the Wijs method iodine monochloride solution is used, whereas iodine monobromide solution is used in the Hanus method. To a known amount of sample in carbon tetrachloride (ca. 20-25 ml), contained in a iodine flask, add an aliquot (5 ml) of iodine monochloride solution. Add an aliquot (2 ml) of mercuric acetate solution to accelerate the reaction. Swirl and keep the mixture in the dark for 5 minutes. Dilute the solution obtained with cool boiled water, until a mono-phase system is obtained. Add KI solution (20 ml of 10% w/v) and then titrate with the standard solution of 0.1 N sodium thiosulphate. Obtain a blank determination in the same manner. Calculate the Iodine Value using the following formula:

$$\text{Iodine Value (I.V)} = [(B - \text{S}) \cdot \text{N} \cdot 12.69] / \text{grams of sample}$$

B is the number of ml of thiosulphate solution required by the blank
S is the number of ml of thiosulphate solution required by the oil/fat solution
N is normality of the thiosulphate solution

The results are presented in Table 1.

Table 1 Iodine value of the oleic, linoleic, linolenic and some commercial oils and fats used in this work and determined by the standard methods

Sample	Amount of sample used, g	Iodine value Wijs*	Hanus*	Theor./Ref.	
Oleic acid	0.201	88.39	87.56	89.85	(a)
Linoleic acid	0.050	180.20	177.66	180.99	(a)
Linolenic acid	0.040	269.12	268.45	273.45	(a)
Corn oil	0.205	124.42	119.92	103–128	[16]
Olive oil	0.199	77.80	75.51	75– 79	[16]
Groundnut oil	0.202	81.93	80.17	80–106	[16]
Grapeseed oil	0.201	132.57	130.47	125–143	[17]
Soya oil	0.200	123.73	123.11	120–143	[17]
Lard	0.500	62.69	60.49	45– 70	[16]
Dripping	0.500	47.37	46.78		(b)
Soft margarine	0.500	67.51	65.39		(b)

(a) = theoretical
(b) = no reference available
* Average of 5 results

b) The proposed (DIE) procedure

Dissolve a known amount of the sample in the solvent, transfer quantitatively to a volumetric flask and dilute to 50 ml with the solvent. Transfer the whole volume to the reaction vessel, allowing the flask to drain for a fixed time (1 minute). Add an aliquot (2 ml) of mercuric acetate solution to accelerate the reaction. Fit the lid, thermistor and stirrer into the top of the

Dewar flask. Switch on the stirrer, electronic bridge and recorder. When the temperature equilibrium has been attained (recorder reading is steady) inject an aliquot (5 ml) of the thermostated iodine monochloride solution. Note the heat pulse recorded.

A calibration curve is obtained from the plot of the iodine value from Wijs determination against the heat pulses using assayed samples. The results are presented in Table 2. Using the previously prepared calibration curve, the iodine value of the sample may be evaluated.

The amount of sample to be used depends on a) the nature of the sample b) the sensitivity of the apparatus (see discussion).

Table 2 Heat pulses (normalised) (mm) of oils and fats in consercutive order of iodine value

Sample	I.V. (Wijs method)	Amount of sample taken, g					
		0.05	0.10	0.15	0.20	0.25	0.30
Dripping	47.37	20	41	59	81	102	122
Lard	62.69	26	53	79	105	131	158
Soft margarine	67.51	30	59	91	119	151	182
Olive oil	77.80	33	65	98	134	165	200
Groundnut oil	81.93	36	73	107	145	178	218
Oleic acid	88.39	38	76	115	152	189	230
Soya oil	123.73	53	106	158	207	130*	160*
Corn oil	124.42	55	109	164	218	137*	164*
Grapeseed oil	132.57	58	115	173	229	146*	173*
Linoleic acid	180.20	75	152	226	151*	186*	228*
Linolenic acid	269.12	112	223	117*	224*	113@	134@

All values except those marked * and @ obtained with a recorder sensitivity of 100 mV FSD.

* = Sensitivity of recorder 200 mV

Sensitivity of recorder 300 mV

Normalised value = (Actual heat pulse – heat pulse of blank)

(In above work the blank value was 10 mm), then

Normalised value = (actual heat pulse – 10) mm.

Statistical parameters of the proposed method

In separate experiments two series of 10 aliquots of two different concentrations of oleic acid were assayed by the proposed method and by the standard Wijs method for the iodine value. The statistical results are presented in Table 3.

Table 3 Statistical results on oleic acid samples

Amount of sample taken, g	DIE			Wijs method		
	Average height pulse	SD	RSD	Average titre	SD	RSD
0.10	76 mm	0.47 mm	0.62%	7.1 ml	0.18 ml	2.54%
0.20	152 mm	0.82 mm	0.54%	14.1 ml	0.27 ml	1.92%

Number of samples: 10 samples per series

Results

Typical results of determining the iodine values of oils and fats presented in the tables are an average value of at least 5 determinations. All of the experiments accomplished by the proposed method were carried out at 20°, with an appropriate recorder sensitivity (100 mV-1 V for FSD), a sensitivity of the bridge of 5.0 (arbitrary units) and the chart speed of 80 mm per minute. The recorder sensitivity was adjusted so that each heat pulse did not exceed 250 mm. For those marked (*) the sensitivity was 200 mV, for (@) the sensitivity was 500 mV and for the others the sensitivity was 100 mV for FSD.

Discussion

The most favourable solvent for an enthalpimetric method is chosen not only for its capability to dissolve the sample, but also on the heat of mixing with the reagent. Thus for an ideal solvent, the samples should be readily soluble in the solvent and the heat of mixing of the solvent and the reagent (the blank value) should be zero. From the studies of the effect of solvent, it is considered that a (1 : 1) mixture of carbon tetrachloride and glacial acetic acid, although giving a blank approximately 10% greater than that obtained with glacial acetic acid, is the best solvent for oils and fats regarding both the production of a mono-phase solution and the thermal response.

Since different methods, used for the determination of the iodine value of oils and fats routinely or in control laboratories in the oil industry, produce results which are not directly comparable because they are obtained by different techniques, it is regarded as being necessary to have a comparison method to evaluate and calibrate any proposed method. The comparison of results obtained by different methods or in different laboratories must be based on a commonly accepted reference method. In the edible oil industry, the reference methods widely adopted are the Wijs and Hanus methods. From a consideration of the stability of the reagents used in these two methods, the Wijs method was chosen to be used to calibrate the proposed method.

Calibration

In the DIE method of analysis, it is usual to have a calibration curve using the pure analyte in the materials being determined. In some cases there is no pure component available for this purpose. In these circumstances, the calibration must be done using samples which have been assayed by standard methods.

Commercial oils and fats are mixtures of triglycerides containing combined unsaturated fatty acids as well as many other substances (see Table 4).

Table 4 Typical composition of lard and pork dripping [16]

Substances	Lard	Pork dripping
Saponification Value (mg KOH/g)	192–203	192–203
Iodine Value (Wijs)	45– 70	45– 70
Unsaponifiable matter (g/kg) (max)	10	12
Acid Value (mg KOH/g) (max)	1/3	2.5
Peroxide Value (mEq/kg) (max)	10	16
Matter volatile at 105°C (% m/m) (max)	0.3	0.3
Iron (mg/kg) (max)	1.5	1.5
Copper (mg/kg) (max)	0.4	0.4
Lead (mg/kg) (max)	0.1	0.1
Arsenic (mg/kg) (max)	0.1	0.1

For the purpose of determining iodine values of these substances by an enthalpimetric method, difficulty is encountered in obtaining standard materials which have similar chemical and physical compositions as those being determined. It is therefore necessary to calibrate the DIE method in a similar manner to that used for most other proposed method i.e via the titrimetric determination utilizing the Wijs procedure.

Figure 1 shows that for each material used, there is a linear relationship between the heat pulse and the amount of sample taken. Aliquots of the various samples were analysed by the standard Wijs method and by the proposed method, and Fig. 2 shows the relationship between the iodine value determined using the Wijs titrimetric method and the heat pulse obtained by the DIE method. This linearity indicates that no other component of the oil/fat samples reacts with the injected ICl to give a thermal response, thus indicating that the ICl reaction is highly selective for the material. This selectivity means that since there exists a strictly linear relationship between the normalised heat pulse, the amount of sample and the iodine value, it is only necessary to determine one sample from a particular batch of natural oil or fat or any particular type of manufactured or processed oil or fat, in order to establish the calibration curve.

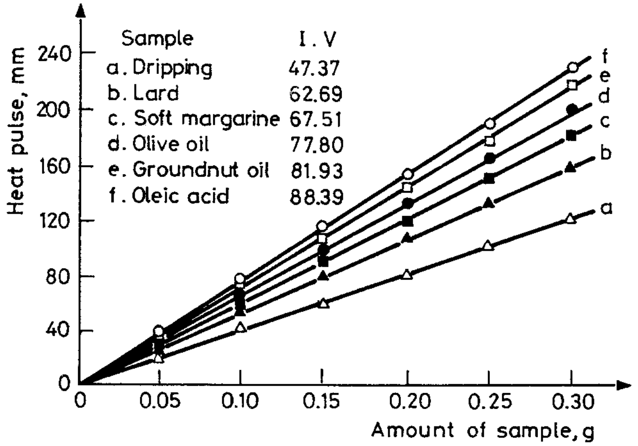

Fig. 1 Relationship between the amounts of sample and the heat pulse

It is considered necessary to use enough sample to give a normalised heat pulse of at least 100 mm (to ensure 1% precision). Since the blank (for the apparatus used in this work) is approximately 10 mm, the following minimum amounts of sample are recommended: For samples with an expected iodine value of less than 100, used 0.20 grams, and those of their iodine value are greater than 100, used 0.10 grams.

It is emphasised that any change in the enthalpimetric system such as reaction temperature, thermal sensor, sensitivity of the bridge or the recorder will necessitate re-calibration.

It is recognised that if frequent recalibration is required, then it would to some extent detract from the advantages of the proposed method when used for routine quality control or quality assurance. In order to ascertain the frequency of calibration required, over a period of two working weeks, a series of approximately 200 samples was determined by the proposed method and every 20th sample was also determined by the Wijs standard method. The results indicate that it is not necessary to calibrate the DIE method more than once per week or whenever the type of sample is altered.

The results outlined in Table 3 indicate that on statistical grounds the enthalpimetric method is at least as acceptable as is the Wijs standard method, moreover the relative standard deviation is lower than that of the standard method.

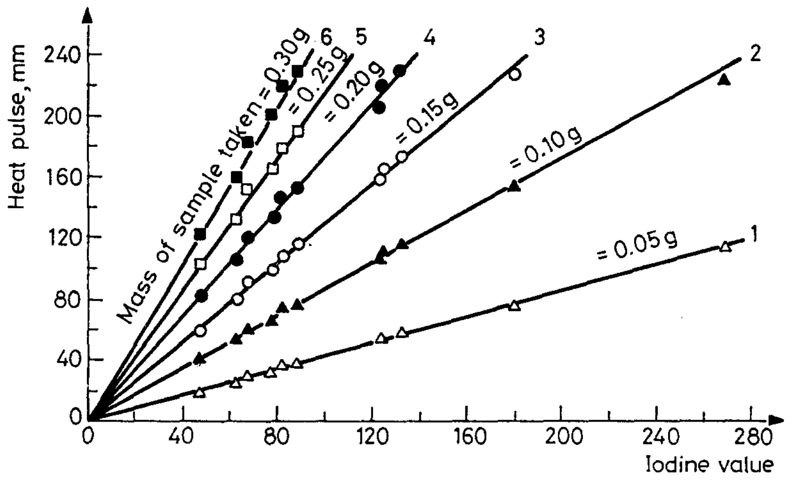

Fig. 2 Relationship between the iodine value obtained by titration and the heat pulse

Most of the methods used for determining iodine values of oils and fats specify relatively long absorption times, 30-60 minutes and even 2 hours. Such times are too long for both rapid control of continuous plant operations and for routine analysis. The proposed method takes less than 10 minutes per sample. The enthalpimetric method has other advantages when considered for routine use in quality control or quality assurance laboratories involved in the iodine value determination. One of the major costs of routine assay is that of labour. Thus any method which allows the use of less skilled labour and less operational time, will overall be less costly. A comparison of costs per sample using the two methods, indicates that the proposed method gives costs approximately 50% of those incurred using the Wijs method. In quality control or quality assurance situations, rapid low cost analysis lowers the overall industrial costs.

Using the proposed procedure, with a disposable polystyrene reaction vessel, having samples determined in triplicate with a blank determination every 10 samples and standardisation once per working week, 20-25 samples can be determined per working day by a single operator. The time between receiving the sample and the calculation of the results is approximatley 10-15 minutes, if two sets of apparatus are used the time may be decreased to 5 to 10 minutes. Most of this time is required to dissolve and allow the sample to attain the temperature of the thermostat. This is in contrast to the Wijs method which requires approximatley 60 minutes from receipt of sample to the time to obtain a result which can be used in quality control.

The amount of the sample taken for determining the iodine value by the proposed method depends upon the sensitivity of the system used and of the height of pulse expected. Generally it is found that a heat pulse of 200-250 mm allows measurement to better than 1%. Using the recorder sensitivity of 100 mV and the bridge sensitivity of 5.0 (arbitrary units) for assaying the iodine value of oils and fats which have iodine value up to 270, reasonable heat pulses can be obtained by the use from 0.05-0.10 grams of sample. It is possible to alter the sensitivity of the potentiometric recorder in steps (1, 2, 5, 10, 20, 50, 100, 200, 500 mV and 1 V) and this facility allows the system to be used for a wide range of materials, with good reproducibility and acceptable precision and accuracy.

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Zusammenfassung — Zur Ermittlung der Jodzahl von einigen im Handel befindlichen Speiseölen wurde ein einfaches, schnelles und genaues Enthalpimetrieverfahren mit Direkteinspritzung (DIE) entwickelt. Mittels Einspritzung einer Jodmonochloridlösung in die Probenlösung wird wegen der Halogenadditionsreaktion an den Doppelbindungen der ungesättigten Fettsäureester ein signifikanter Wärmeimpuls erzeugt. Die Methode wird anhand tatsächlicher Proben und Standardproben (Ölsäure, Linolsäure, Linolensäure) kalibriert, deren Jodzahl in Standardverfahren bestimmt wurde. Nach einmaliger Kalibration kann das Verfahren auch von angelerntem Personal routinemäßig durchgeführt werden. Das Verfahren besitzt eine ausreichende Empfindlichkeit und liefert Ergebnisse, die genauso akzeptabel sind, wie die in Standardverfahren erhaltenen Ergebnisse. Die Hauptvorteile dieser Methode bestehen in Zeit- und Kosteneinsparung bei der Analyse sowie in der Möglichkeit, das enthalpimetrische Verfahren automatisieren zu können.