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DETERMINATION OF THE IODINE VALUE OF OILS AND FATS

Results of a Collaborative Study

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Determination of the iodine value of oils and fats: results of a collaborative study

Abstract - This report outlines the study protocols and compares the results obtained for the iodine values of a wide range of fats and oils when using the published standardised method (which specifies the use of carbon tetrachloride) with the results obtained when using a mixture of cyclohexane and glacial acetic acid. The values reported for the iodine values indicate that the latter solvent system can be recommended for use in place of carbon tetrachloride in the determination of iodine value without loss of precision.

INTRODUCTION

As a consequence of the recognition of the potential carcinogenic risk when using carbon tetrachloride for analytical purposes, the Commission decided to carry out an investigation into whether this solvent could be satisfactorily replaced by a non-toxic reagent when determining iodine values by the published standard method which specifies the use of carbon tetrachloride.

Before organising a comprehensive interlaboratory study it was considered advisable to conduct a preliminary investigation involving three laboratories experienced in the determination of iodine values. For this investigation, samples of crude fish oil, tung oil, tallow and sunflower seed oil were provided. Each sample was required to be analysed in duplicate, with each solvent, and when determining the iodine value of the tallow the effect of adding tetrachloroethane immediately before the titration of excess iodine was to be checked. The volume of Wijs' solution and solvent to be used were 25 ml and 15 ml as specified, respectively, in the present IUPAC and ISO standardised methods. [Note:† The AOCS method prescribes a reaction solvent volume of 20 ml.]

The results of this preliminary investigation are given in Table 1. It will be seen that the agreement between the overall mean values obtained for the determined iodine values by both solvents was generally satisfactory. The difference in the results obtained for duplicate analyses (not shown in the table) by each laboratory appeared to indicate that the precision of the method was unaffected by the choice of solvent. It was not established that the use of tetrachloroethane, when determining the iodine value of the tallow, made a significant improvement to the performance characteristics of the method and this aspect was not studied further. On the basis of these preliminary results it was decided to proceed with a comprehensive collaborative study.

1st COLLABORATIVE STUDY AND RESULTS

For the 1st study (1989), which was undertaken in co-operation with members of ISO/TC 34/SC 11, eleven fats and oils were selected to represent the wide range of lipid materials for which the determination of iodine value is of commercial importance viz.: 7 vegetable oils (olive oil, refined palm kernel oil, crude and refined palm oil, tung oil, sunflower seed oil, hydrogenated soya bean oil), 3 animal fats (crude and hydrogenated fish oil, tallow) and a used frying oil. Each of the 11 materials were provided as blind duplicates (i.e. a total of 22 samples) and participants were required, for each sample provided, to determine the iodine value once only using carbon tetrachloride, and once only using a 1:1 mixture of cyclohexane and glacial acetic acid. The procedure to be followed was based on the IUPAC method 2.205 (ISO 3961) and participants were requested to confirm, or otherwise, that the Wijs' reagent (see *Appendix* to this report) did not contain carbon tetrachloride.

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The results of a statistical evaluation of the iodine values obtained in the 1st collaborative study (in which 11 laboratories from 9 countries participated) are summarised in Table 2. For reasons of space the raw data (i.e. individual results submitted by each laboratory - see Reference below) are not reproduced in this report, but a comparison (see Table 2) of the mean values and the values for r and R (repeatability and reproducibility limits, respectively) shows, except in the case of the hydrogenated oils, that the type of solvent used for the determination has little or no influence on the precision of the determination. Since the method is based on an empirical procedure the "true" iodine values are unknown, but it will be noted that for each material the iodine values reported by the participants for the iodine values can be considered to be in agreement and independent of the solvent system used. It will be seen, however, (from Table 2) that the precision experienced during the analysis of the hydrogenated oils was unsatisfactory.

TABLE 1. Results of the preliminary study

sample	Lab 1		Lab 2		Lab 3		mean value	
	CTC	CHX	CTC	CHX	CTC	CHX	CTC	CHX
solvent used*	CTC	CHX	CTC	CHX	CTC	CHX	CTC	CHX
fish oil, crude	110.4	109.4	106.2	103.4	110.0	103.7	108.9	105.5
tung oil	169.8	171.8	133.8	134.6	167.0	168.7	156.9	158.4
sunflower seed oil	134.5	135.0	131.1	131.6	133.6	131.3	133.1	132.6
tallow, without TCE	40.4	39.8	45.5	46.0	47.1	46.9	44.3	44.2
with TCE	54.6	47.4			49.0	47.9	51.8	47.7

*[CTC: carbon tetrachloride; CHX: cyclohexane + glacial acetic acid (1:1)]

Table 2. Statistical analysis of results obtained in the 1st collaborative study

sample	mean value		r		R		no. of accepted results
	CTC	CHX	CTC	CHX	CTC	CHX	
solvent used*	CTC	CHX	CTC	CHX	CTC	CHX	(CTC, CHX)
sunflower seed oil	133.6	132.9	3.0	3.6	7.2	4.8	(20,20)
palm oil, refined	53.1	53.0	0.65	0.82	1.43	1.90	(20,20)
fish oil, crude	109.1	108.5	1.67	1.40	4.35	2.80	(18,14)
tung oil	164.5	163.1	3.47	2.39	5.27	4.32	(14,12)
tallow (beef fat)	47.2	46.9	1.37	1.33	2.75	3.10	(20,20)
soyabean oil, hydrog.	63.3	65.3	1.86	13.8	17.2	14.9	(12,16)
palm oil, crude	52.5	52.6	1.29	2.15	2.19	2.89	(18,20)
frying oil, used	37.7	37.7	0.97	1.38	1.18	2.48	(14,14)
fish oil, hydrog.	63.3	68.6	3.61	1.69	17.2	11.0	(12,12)
palm kernel oil	18.2	18.3	0.17	0.14	0.51	0.64	(16,14)
olive oil	82.3	82.2	0.75	1.75	1.86	2.62	(14,10)

*[CTC: carbon tetrachloride; CHX: cyclohexane + glacial acetic acid (1:1)]

Scrutiny of the titre values reported in the case of the hydrogenated materials revealed that the amount of residual iodine (available for titration following the reaction with Wijs' solution) was much lower than the minimum level recommended in the text of the method. This had arisen as a result of incorrect test sample weights for the hydrogenated oils being advised by the study co-ordinator - the degree of hydrogenation of the materials provided for the study was much less than that assumed. It was therefore agreed that a further study should be carried out in order to ascertain the correct precision characteristics of the method when applied to the determination of the iodine value of hydrogenated materials.

2nd COLLABORATIVE STUDY AND RESULTS

For the 2nd study (1990), in which members of ISO/TC 34/SC 11 again participated, three materials were provided, viz: hydrogenated soya bean oils at two levels of hydrogenation, and a hydrogenated fish oil. The three materials were provided as blind-coded duplicates to give a total of six samples. Participants were requested to carry out one determination only of the iodine value on each sample using carbon tetrachloride, and one determination only using a mixture of cyclohexane and glacial acetic acid (1 + 1). Test sample weights of 0.13 g for the more lightly hydrogenated soya bean oil and 0.2 g for the other two oils were advised in accordance with the assumed iodine values of these materials. The procedure to be followed was that as adopted for the 1st collaborative study.

Table 3. Statistical analysis of results obtained in the 2nd collaborative study

Sample#	SB01	SB01	SBO2	SBO2
Solvent*	CTC	CHX	CTC	CHX
Number of laboratories	17	17	17	17
Number of results	34	34	34	34
Number of laboratories retained after elimination of outliers	16	17	17	17
Number of accepted results	32	34	34	34
Mean value	102.6	102.3	74.7	74.8
Repeatability limit (r)	1.4	2.2	1.7	1.5
Reproducibility limit (R)	4.8	5.1	3.7	2.1
Sample#	HFO		HFO	
Solvent*	CCT		CHX	
Number of laboratories	17		17	
Number of results	34		34	
Number of laboratories retained after elimination of outliers	16		17	
Number of accepted results	32		34	
Mean value	73.0		72.8	
Repeatability limit (r)	1.7		1.6	
Reproducibility limit (R)	2.5		2.3	

#SBO - hydrogenated soya bean oil; HFO - hydrogenated fish oil

*CTC - carbon tetrachloride; CHX - cyclohexane + glacial acetic acid (1:1);

Statistical analysis according to ISO 5725-1986.

Results for this 1990 study were submitted by 18 laboratories from 11 countries: China, Czechoslovakia, the Federal Republic of Germany (3), Finland (2), Hungary, Japan (2), Malaysia, Netherlands, New Zealand (2), South Africa, the United Kingdom (2), and the United States. Again, for reasons of space, the raw data is not reproduced in this report (*see Reference below*) but the calculated statistical parameters are collated in **Table 3**. Only two sets of results were identified as Cochran outliers; results from one laboratory were received too late for inclusion in the statistical analysis. It will be noted that the iodine values obtained when using either solvent are in good agreement and also that the *precision* of the determination is not affected when cyclohexane + glacial acetic acid is used in place of carbon tetrachloride. In view of the diminished carcinogenic risk when using cyclohexane the Commission agreed to recommend that the latter solvent (as a 1:1 blend with glacial acetic acid) should replace carbon tetrachloride in the method for the determination of iodine value.

The results of the study have been submitted to the ISO/TC 34 SC 11 Secretariat with a view to a similar recommendation being made for incorporation in a revision of the present text of the equivalent standardised method [ISO 3961-1989] published by the International Organization for Standardization.

REFERENCE

The raw data for the results obtained in all three studies have been reproduced in the Commission's Working Reports and Minutes for 1989/1990. Copies of the data are available on request from the Secretary of the Commission.

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APPENDIX

Preparation and composition of Wijs' reagent

Wijs' reagent is a solution of iodine monochloride in acetic acid and can be prepared from a mixture of iodine trichloride and iodine or, alternatively, from iodine monochloride and chlorine gas. Since the preparation of the reagent is time consuming most laboratories use commercially-produced Wijs' reagent. However, it has been found that there is a variation in the composition of the commercial Wijs' reagent currently available - in some case the solvent used is acetic acid alone (as required by the original Wijs' procedure and specified in the *AOCS* method) and in other cases the product sold as Wijs' reagent has been found to be a mixture of acetic acid and carbon tetrachloride (i.e the modified Wijs' reagent specified in the texts of the current *ISO* and *IUPAC* methods.) Following revision the texts of the latter methods will indicate that carbon tetrachloride-free Wijs' reagent is to be used for iodine value determinations.