Modified Thiocyanogen Reagent and Method

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Historical

REFERENCE to thiocyanogen, $(SCN)_2$, *per se*, first appears in the literature in 1829 when Liebig (22) attempted to prepare the "free radical" by passing a stream of chlorine over silver and lead thiocyanates. Failing in this effort, he tried bubbling chlorine through a hot concentrated solution of potassium thiocyanate and obtained a yellow precipitate which closely approximated the composition of $(SCN)_2$. In announcing his discovery, Liebig mentioned his surprise at the inert nature and nonvolatility of his product which was contrary to all expectations. Linnemann (23), in 1861, obtained silver iodide and a readily volatile red-brown liquid by allowing silver thiocyanate to react with an ethereal solution of iodine. Because of the extreme instability of the liquid product Linnemann did not pursue his researches further and therefore never knew that he had actually been the first to prepare free thiocyanogen.

Schneider (32), in 1866, allowed sulfur chloride in carbon disulfide solution to react with silver cyanide with the expectation of obtaining thiocyanogen as one of the products. Instead he obtained some "white crystals with a penetrating odor invoking tears." These crystals, though possessing the theoretical composition $(CN)_2S_2$, were shown under the microscope to be a heterogeneous mixture and later were recognized to consist of $(CN)_2S$ and $(CN)_2S_3$. Other investigators made equally futile attempts to obtain this elusive substance, and in 1901 Goldberg (11) concluded that since no one had as yet isolated free thiocyanogen, such radicals could not be obtained in the free state from their compounds and they must of necessity exist in solution in the ionic state.

In the course of an investigation of the complex, gold thiocyanogen, Bjerrum and Kirschner (4) determined the standard potential of thiocyanogen/thiocyanogen-ion and found it to be 0.796 volts. This E.M.F. value places free thiocyanogen between bromine (1.09 volts) and iodine (0.54 volts) if it is classified in the halogen series, and it follows therefore that bromine would displace thiocyanogen from a solution of its salt while thiocyanogen would likewise replace iodine. Bjerrum and Kirschner (4) found that the instability of free thiocyanogen in an aqueous solution soon vitiated its capacity for displacing iodine. They refrained from undertaking the logical investigations into the behavior of $(SCN)_2$ in non-aqueous solutions when they became cognizant of the fact that a contemporary had previously isolated thiocyanogen in the free state.

In 1919 Söderbäck (33) published his classic researches on thiocyanogen in which he described the preparation of the elusive $(SCN)_2$. The product was obtained by reacting iodine with an ethereal suspension of silver thiocyanate. In the course of this work Söderbäck investigated many different solvents and also all of the available metallic thiocyanates as possible reagents for preparing $(SCN)_2$. He replaced iodine by bromine which he found more satisfactory because the reaction went to completion with the latter reagent. Upon the publication of Söderbäck's work interest in thiocyanogen was reawakened and in 1921 cryoscopic measurements were made by Lecher and Goebel (21), who showed that, in a bromoform solution of less than 0.5 normal concentration, the thiocyanogen molecule existed in the associated biradical form, $(SCN)_2$.

Soon afterwards (1923) Kaufmann (15) conceived the notable idea that thiocyanogen, dissolved in a suitable solvent, would attach itself to double bonds in unsaturated hydrocarbons in the same manner as bromine or iodine. It was but one step further to substitute unsaturated fatty acids for the hydrocarbons and to the discovery (16) that the reagent would react quantitatively if only one double bond was present in the unsaturated aliphatic acid and that, if expressed in terms of iodine absorbed, the thiocyanogen value would equal the iodine value. He found in the case of linoleic acid that only one of its two double bonds reacted with thiocyanogen and in the case of linolenic acid that only two of its three double bonds reacted with thiocyanogen.

Having definitely established these facts Kaufmann (17) devised a series of stoichiometric equations for use in calculating the composition of glyceride mixtures, using the iodine and thiocyanogen values for this purpose. No absorption of thiocyanogen occurs in the case of triply bonded compounds such as stearolic and behenolic acids. Because of the specificity of the addition of thiocyanogen its use as a reagent for the determination of the composition of mixtures of fatty acids and glycerides and for establishing the constitution of long chain polyethenoid fatty acids (34) has achieved considerable importance in fat and oil chemistry.

The first published report of any practical application of the thiocyanogen method in this country was made by Barbour (3) in 1930, who definitely established the superiority of this method over the lengthy and cumbersome Twitchell lead salt procedure then employed in determining the composition of fats and oils and as a means of controlling the hydrogenation of unsaturated glycerides.

Actually, Martin and Stillman (24) were the first to standardize the method to a point where it assumed importance and recognition as a valuable aid to chemists engaged in the field of fats and oils, and the present American Oil Chemists' Society (2) thiocyanogen method is essentially as described by them.

As the method became more generally used, various investigators (13, 14, 30, 35) reported notable variations in their results when calculated by means of Kaufmann's original equations. These discrepancies arose from the fact that when two double bonds are present in an aliphatic chain as in linoleic acid, slightly more than one of them is saturated with thiocyanogen. If, on the other hand, there are three

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double bonds present in the molecule as in linolenic acid, addition of thiocyanogen corresponds to slightly less than two of them. The discrepancies have been overcome by the application of a set of empirical constants (27) in place of the stoichiometric equations originally proposed by Kaufmann.

Introduction

IN THE course of work involving the determination of the thiocyanogen value of several hundred samples of fats and other lipids the present authors experienced considerable difficulty in obtaining consistent and reproducible results. In an effort to ascertain the cause of the poor reproducibility of thiocyanogen values practically every variable inherent in the different methods now in use for the determination of this characteristic of fats and oils was investigated. These investigations included the preparation of the reagent, factors affecting its stability, and the apparatus used in carrying out the determination. As a result of this work it has been possible to eliminate certain difficulties and to improve the accuracy and precision of the thiocyanogen method, and to broaden its applicability.

The principal difficulties encountered arose from (a) the incomplete solubility of certain fats and fatty products in the reagent, (b) the tendency for resin-like products to form during the reaction with consequent occlusion of iodine, (c) poor stability of the reagent on storage, especially when reducing substances were present in any of the original components of the mixture, (d) insufficient potassium iodide in the reaction mixture, (e) the presence of unsuspected traces of moisture, and (f) the source and method of preparation of the original lead thiocyanate.[2]

Each of these factors was investigated, and modifications and improvements were made in the thiocyanogen method to obviate or minimize specific difficulties. In general, this was accomplished by careful preparation of the thiocyanogen reagent and incorporation of carbon tetrachloride as one of its components; increasing the quantity of potassium iodide to at least twice the theoretical weight per aliquot of reagent; improvement in the method of preparing the original lead thiocyanate; and proper drying and handling of all reagents and glassware used in the determination. The nature of the difficulties encountered by the authors in applying the thiocyanogen method and the steps taken to overcome them are set forth herein in some detail because similar difficulties have confronted many others who have had experience with this method and because of the economic implications involved in its application to industrial fats and fat products.

Application of the official A.O.C.S. method (2) to the determination of thiocyanogen values of a large number of samples led to the observation that reagent blanks frequently did not check. Most of the fats and oils under examination did not dissolve completely in the reagent, and some hardened fats were found to be almost completely insoluble. Where attempts were made to dissolve the hydrogenated fats in carbon tetrachloride prior to addition of the reagent, other difficulties were encountered, primarily as a result of the decreased normality of the reagent which introduced errors in applying the accepted equations for calculating the composition of the sample. The reagent, itself, was extremely unstable and often was subject to unpredictable changes in a very short period of time. It was subsequently found that these changes in the reagent were attributable to the presence of reducing substances or to traces of moisture in one or more of the original components of the solution mixture and to the fact that the reagent had to be stored above the freezing point of acetic acid. In contrast to this behavior it was observed that when 25% of the required volume of acetic acid normally used in preparing the thiocyanogen reagent was replaced by an equivalent volume of carbon tetrachloride, the stability of the reagent was increased by virtue of the fact that it could be stored at the conveniently low temperature of 5°C., and at the same time complete solubility was imparted to a wide variety of samples.

These observations indicated the need for a stable, all-purpose thiocyanogen reagent and method which would be capable of being applied with equal reliability to glycerides, fatty acids, and hydrogenated fats and which would yield accurate values throughout the entire range of anticipated thiocyanogen values. Such a reagent should be applicable without changing its normality at the beginning of the reaction through addition of another solvent to dissolve the sample. A constant ratio of thiocyanogen to sample can be maintained in each case, and at the same time the original sample and all end reaction products remain soluble.

The idea of replacing part of the glacial acetic acid with carbon tetrachloride in the thiocyanogen reagent is not a new one. As a matter of fact, it was first used by Kaufmann (19). According to a more recent publication (20) by this same author, 30% by volume is a suitable quantity of carbon tetrachloride to use. The A.O.A.C. (1) recommends that 20% of the total volume of the reagent be replaced by carbon tetrachloride while Matthews, Brode and Brown (25) found that as little as 10% was suitable to their needs. The present A.O.C.S. method (2) excludes carbon tetrachloride entirely in either the reagent or as a solvent for the sample. Application of this reagent has repeatedly led to the formation of a very undesirable resinous-like product which results from the introduction of water into the reaction mixture following the addition of powdered potassium iodide. This behavior is particularly likely to occur when the reagent is applied to glycerides. As far as can be ascertained, the resinous product appears to occlude a small though definite quantity of the free iodine which is subsequently released on the addition of potassium iodide and water, consequently requiring vigorous and prolonged shaking to remove it completely from the product during titration. In the case of fatty acid mixtures having low thiocyanogen values large weights of the sample are used, and the addition of water precipitates a thick layer of the acids which floats on the surface of the aqueous layer and thus further complicates the titration.

Two schools of thought apparently exist with regard to the addition of potassium iodide. Kaufmann (18) recommends the use of a 10% aqueous solution of potassium iodide which is also specified in the present A.O.A.C. (1) method. Matthews, Brode and Brown (25), however, used 3.5 ml. of 50% aque-

[2] The methods of preparation and purity of lead thiocyanate is the subject of a separate communication.

ous potassium iodide. The use of potassium iodide in the dry powdered form was first employed by Martin and Stillman (24) and appears to have definite advantages but when used in quantities of one gram per 25 ml. aliquot of reagent it produces erratic results. When, however, the weight of potassium iodide is increased to twice, or slightly more than twice the theoretical weight necessary to react with 25 ml. of 0.2 N reagent, the discrepancies disappear. The necessity for the use of the larger quantity of potassium iodide is clearly demonstrated by the apparent normalities obtained on a thiocyanogen solution using both 1.0 gram and 1.8 gram (calculated 1.66 g./25 ml. 0.2 N reagent) quantities of finely powdered, dry potassium iodide. The weights of potassium iodide and corresponding apparent normalities are shown in Table 1.

TABLE 1.

Effect of Various Weights of Finely Ground, Dry Potassium Iodide on the Apparent Normality of 25 ml. Aliquots of a Thiocyanogen Solution.

No.	Wt. of KI used	Type of shaking	$Na_2S_2O_3$ used	Average normality
	g.		*ml.*	
1	1	Vigorous	50.03	0.1998
2	1	Vigorous	50.00	
3	1	Gentle	49.75	0.1989
4	1	Gentle	49.80	
5	1.8	Vigorous	50.70	0.2027
6	1.8	Vigorous	50.80	
7	1.8	Gentle	50.71	0.2026
8	1.8	Gentle	50.73	
9	1.8[1]	Vigorous	50.40	0.2017
10	1.8[1]	Vigorous	50.60	

[1] Coarsely ground.

Purification of Components of Thiocyanogen Reagent

THE preparation of a stable and reliable thiocyanogen reagent rests almost entirely on the rigorousness with which the individual components have been purified.

Purification of acetic acid and acetic anhydride. Reducing substances must be removed from the acetic acid by oxidation with 2% by weight of chromic oxide, refluxing for two hours and then distilling (28). Care must be exercised to prevent any trace of the chromic oxide being carried over in the distillation process. Generally, the first fractions should be discarded and the purity of the middle cut ascertained by subjecting it to the A.C.S. permanganate test for reducing substances in acetic acid (8). In applying the test, the required quantity of N/10 permanganate solution should be added to the test sample and a similar volume of distilled water as a control. After two hours the test sample should show no more than a perceptible decrease in color compared to the control. If an empyreuma-free acetic acid can be purchased, the purification process can be reduced to the removal of moisture which is accomplished by refluxing the pure acetic acid for four hours with 5% by volume of acetic anhydride.

The acetic anhydride itself must also be free of reducing substances otherwise little or no purification is accomplished. It, too, must be subjected to the same test for reducing substances as is used on the acetic acid. This may be accomplished by converting a sample of the anhydride to the acid by heating with a small amount of distilled water before applying the permanganate test.

An efficient fractionating column is required to produce pure cuts of acetic anhydride. One type which has been found satisfactory and which is now generally available in most laboratories is the Widmer column.

Purification of carbon tetrachloride. Purification of the carbon tetrachloride is accomplished by shaking it in a separatory funnel with successive portions of concentrated sulfuric acid (50 ml. conc. H_2SO_4 to 1 l. of CCl_4) until no further color develops in the acid layer on standing for two hours. The two layers are separated and the portion of the acid remaining in the carbon tetrachloride is washed out with distilled water. The last traces of sulfuric acid are neutralized by washing with two consecutive 50 ml. portions of 50% potassium hydroxide solution.

Partial drying may be accomplished by allowing the carbon tetrachloride to remain over night in large Erlenmeyer flasks in contact with a layer of potassium hydroxide pellets after which it is decanted, filtered, and distilled. The distillate in this state may be used for the determination of iodine values, but it must be further dried for use in thiocyanogen determinations. More complete drying may be achieved by permitting the carbon tetrachloride to stand over a charge of phosphorus pentoxide (50 gms. P_2O_5 to 1 l. of CCl_4) for several hours during which it is shaken occasionally. It is then filtered into a previously dried flask which is attached to a completely moisture-free distillation unit protected from outside moisture by a calcium chloride drying tube. The carbon tetrachloride is finally distilled from a second charge of phosphorus pentoxide (10 gms. P_2O_5 to 1 l. of CCl_4) as recommended by Kaufmann (19).

Preparation of potassium iodide. The potassium iodide should be ground to pass a 60-mesh sieve. This may be done conveniently in a ball mill using approximately one-half pound of potassium iodide per pint-size jar containing 24 three-quarter-inch diameter porcelain balls. The grinding should be continued for 48 hours. On removal from the jars the potassium iodide should be dried in a vacuum oven at 60° C. for two hours. The fine powder has a tendency to cohere in lumps during drying, and these should be broken up by crushing with a mortar and pestle prior to sifting through a 60-mesh stainless steel wire sieve.

Preparation and Use of Thiocyanogen Reagent

THE individual steps followed in the preparation of the thiocyanogen reagent are not materially different from those described by Kaufmann (17) and elaborated upon and standardized by Martin and Stillman (24).

All of the glassware used in the preparation of the reagent is dried in an oven for two hours at 110° C. and stoppered until cooled sufficiently for use.

Into a dried two-liter bottle are placed 50 gms. of lead thiocyanate, freed of moisture by allowing it to stand over phosphorus pentoxide for eight days in a vacuum desiccator. Five hundred milliliters of pure, dry acetic acid are poured into the bottle containing the lead thiocyanate. Into a 500-ml. bottle is poured 25% of the total volume of acetic acid along with an equal volume of carbon tetrachloride, previously purified and dried as described above. To this same bottle is added from a 10-ml. micro-burette 5.15 ml. of pure bromine. The large bottle containing the lead thiocyanate is securely fastened in a mechanical shaker,

and the bromine mixture from the smaller bottle is added in approximately 10 ml. volumes followed by shaking after each addition until all the color due to bromine has disappeared. After the first few 10-ml. portions have reacted, the bromine solution can be added in increasingly large volumes until all of the mixture has been poured into the larger bottle. It is well to shake the reaction mixture an extra five minutes after all traces of bromine have disappeared.

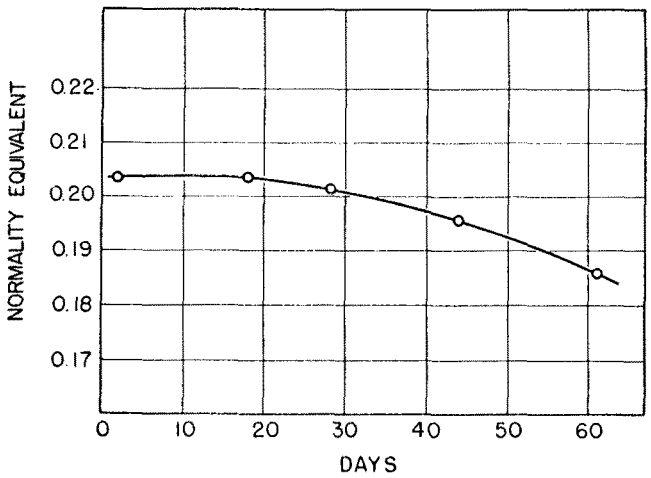

Fig. 1. *Rate of deterioration at 5°C. of approx. 0.2 N $(SCN)_2$ reagent containing 25% by volume of carbon tetrachloride.*

The precipitated lead bromide is then allowed to settle and the liquid decanted and filtered with the application of suction into one of the vacuum flasks, using the Büchner funnel fitted with two layers of filter paper. The filtering process is repeated using the second vacuum flask but the same funnel and filter paper. The reagent, which at this stage is a clear, pale straw-colored liquid, is transferred to the third bottle with the aid of the powder funnel. The bottle is protected from atmospheric moisture by covering the top with parafilm and from sunlight and glare by encasing it in a paper sack. It is now ready for storing at a temperature of 5° C. It must be remembered that during the entire preparation procedure the reagent must be protected from direct sunlight and strong glare and be exposed only to diffused light.

Prior to its use for determining thiocyanogen values the cold reagent is allowed to come to room temperature after which 20-ml. aliquots are pipetted into 125-ml. glass-stoppered Erlenmeyer flasks containing the previously weighed portions of sample in micro beakers. The sample weight to be used is calculated so that it will react with only one-third of the reagent present leaving a 200% excess. The reaction period which has been used in this laboratory is the recommended 24 hours for a 0.2 N reagent, the reaction mixtures being maintained in the dark at 19° C. The normality of the reagent has generally varied within the limits of 0.196 N to 0.206 N. At least three blanks are run with each short series of determinations, but the number of blanks is increased as the series lengthens.

At the expiration of the reaction period, twice the theoretical quantity of finely powdered potassium iodide is added to each flask and the flask swirled two minutes if it contains a sample, or three minutes if it is a blank. Twenty milliliters of distilled water is then added and the mixture is gently swirled until all solid potassium iodide is dissolved. The reaction mixture is now ready for titration with 0.1 N sodium thiosulfate solution using a starch indicator.

The stability of the thiocyanogen reagent prepared in the above-described manner is shown graphically in Figure 1 in which the ordinates represent the change in normality and the abscissae the storage period in days. The solution was maintained in the dark at a temperature of 5° C. during the entire storage period but was periodically brought to room temperature during occasions when it was in use for determining thiocyanogen values.

Weight of sample. In order to obviate making calculations for each sample requiring analysis a table of sample weights corresponding to every fifth increment in thiocyanogen value was prepared. These sample weights are calculated to produce an approximate excess of 200% when used with 20 ml. of 0.2 N thiocyanogen reagent prepared as previously described. The sample weight corresponding to each thiocyanogen value between 15 and 169 is given in Table 2.

TABLE 2.

Calculated Sample Weights Equivalent to Approximately 200 Per Cent Excess of 0.2 N Thiocyanogen Reagent When Using 20 ml. of Reagent per Sample.

T. C. Value	Sample Wt.	T. C. Value	Sample Wt.
	grams		*grams*
15	1.130	95	0.1782
20	0.8465	100	0.1693
25	0.6772	105	0.1612
30	0.5643	110	0.1539
35	0.4837	115	0.1472
40	0.4233	120	0.1411
45	0.3762	125	0.1354
50	0.3386	130	0.1302
55	0.3080	135	0.1254
60	0.2821	140	0.1209
65	0.2604	145	0.1167
70	0.2418	150	0.1128
75	0.2257	155	0.1092
80	0.2116	160	0.1060
85	0.2000	165	0.1026
90	0.1881	169	0.1000

Reproducibility of results. The variation which may be expected in duplicate determination is indicated in the data of Table 3 which represents two series of determinations made on different days. The samples comprise various fatty acid fractions obtained in the course of a solvent fractionation experiment. Predetermined iodine values were the only basis available for predicting the probable thiocyanogen value. Samples 63 to 91, covering a range of values from 72 to 87, indicate an average reproducibility of ± 0.13 unit; samples 93 to 123 covering a range of values from 28 to 65, indicate an average reproducibility of ± 0.07 unit.

During one three-month period more than 250 samples of fats and fatty products were analyzed, using 11 different preparations of the thiocyanogen reagent and a total of 41 reagent blanks. As indicated in Table 4 the average deviation of these blanks was ± 0.02 ml. Redetermination of some of these same samples three weeks to six months apart, using different preparations of the reagent, gave a maximum deviation 0.4 units.

Application of the Thiocyanogen Method

THE thiocyanogen reagent and method described above has been in constant use in this laboratory for more than a year. During this period it was applied to the analyses of more than 700 samples having a range of thiocyanogen values from 14 to

TABLE 3.

Reproducibility of Duplicate Thiocyanogen Determinations of Two Series of Mixed Fatty Acids.

Sample No.	Thiocyanogen value	Difference	Excess of reagent %
Thiocyanogen value range, 72 to 87			
63	81.99 81.74	0.25	181 186
65	86.38 86.60	0.22	186 183
67	83.22 83.07	0.15	182 182
69	77.95 78.01	0.06	184 188
71	72.46 72.34	0.12	185 189
73	78.88 78.70	0.18	191 189
75	83.22 82.96	0.26	183 187
77	77.86 77.91	0.05	193 191
79	85.84 85.69	0.15	178 181
81	86.72 86.55	0.17	182 184
83	72.92 72.84	0.08	192 196
85	78.71 78.16	0.65[1]	200 189
89	78.77 78.80	0.03	191 207
87	84.01 83.99	0.02	185 187
91	83.90 83.78	0.12	178 188
Thiocyanogen value range, 28 to 65			
93	34.71 34.58	0.13	179 179
95	46.22 46.17	0.05	181 188
97	38.12 38.20	0.08	185 183
99	35.93 36.08	0.15	187 187
101	35.26 35.33	0.07	188 193
103	42.33 42.21	0.12	188 192
105	36.89 36.81	0.08	189 190
107	33.00 33.02	0.02	183 183
109	37.96 38.00	0.04	180 195
111	27.95 27.98	0.03	192 185
113	34.01 34.05	0.04	200 200
115	39.40 39.56	0.16	201 198
117	42.19 42.28	0.09	151 188
119	36.83 36.95	0.12	209 206
121	27.55 27.60	0.05	183 191
123	65.19 65.18	0.01	182 182

[1] Excluded from average.

167. These samples included purified unsaturated fatty acids, mixed fatty acids from various oils, natural fats and oils, hydrogenated fats, and other products.

TABLE 4.

Average Deviation Observed in the Titer of 41 Reagent Blanks.

Date	Number of blanks	High	Low	Average	Average deviation
		ml.	*ml.*	*ml.*	*ml.*
7/13/44	5	40.96	40.90	40.92	±0.02
7/14/44	5	40.10	40.05	40.08	±0.01
7/14/44	5	39.50	39.40	39.45	±0.04
7/17/44	5	39.34	39.30	39.32	±0.02
7/25/44	3	38.90	38.89	38.89	0.00
8/ 9/44	3	39.94	39.90	39.92	±0.02
8/17/44	3	40.22	40.20	40.21	±0.01
9/27/44	3	39.92	39.88	39.90	±0.02
9/27/44	2	39.80	39.80	39.80	0.00
10/21/44	4	40.00	39.95	39.98	±0.03
10/21/44	3	40.08	39.94	40.03	±0.06

Purified unsaturated acids. The pure acids were separated and purified according to generally accepted methods observing certain precautions pertinent to the acid being prepared. Pure oleic acid was isolated from olive oil and purified in the form of the methyl ester by the method of Wheeler and Riemenschneider (35). The final ester fraction was further recrystallized from 10 volumes of acetone at —37° C., and the oleic acid obtained by saponification was distilled at 0.1 mm. pressure.

The tetrabromides of linoleic acid were prepared from the fatty acids of corn oil according to the procedure of McCutcheon (26). The tetrabromides were further purified by recrystallizing once from ethyl ether and twice from Skellysolve L, using Skellysolve F to wash the filter cake. Decolorizing carbon (Darco) was used during the first crystallization from Skellysolve L to aid in the purification. The white crystalline tetrabromostearic acid (M.p. 115.5-115.8° C., total immersion thermometer) was debrominated in peroxide-free ethyl ether to yield pure linoleic acid by the method described by Frankel and Brown (10). The debromination and all further treatment of the free acid was carried out in an atmosphere of oxygen-free nitrogen. The acid itself was finally fractionated in a molecular pot-still at 1×10^{-4} to 4×10^{-5} mm. pressure. The fraction, on which the following analyses are reported, distilled at a temperature of 113° C.

The hexabromides of linolenic acid were prepared from linseed oil according to the method of Rollett (31). Decolorization with activated carbon (Darco) and five recrystallizations from toluene produced a white crystalline hexabromostearic acid (M.p. 185.5-186.0° C., total immersion thermometer). The acid sample and thermometer were placed in an oil bath preheated to 170° C. Thereafter, the temperature was increased at the rate of 1-2° per minute until the melting point was reached. Debromination of the hexabromostearic acid was carried out according to the method of Frankel and Brown (10), using peroxide-free ether in an atmosphere of carbon dioxide. Following the removal of the solvent, the acid was fractionated in a molecular pot-still at 1×10^{-5} mm. pressure. The fraction representing the pure acid distilled at 115.5°-116.0° C. In the case of both linoleic and linolenic acids the fractions used were

immediately weighed into micro beakers which were transferred to 125 ml. ground-glass stoppered Erlenmeyer flasks. The reagent was pipetted into the flasks at once, thus precluding all possibility of oxidation. This same precaution was observed in all the analyses.

The method of G. W. Ellis (9) was employed in the preparation of elaidic acid from oleic acid.

The iodine and thiocyanogen values were determined on each of the above-described acids and on methyl oleate with the results shown in Table 5. Peroxide values determined for linoleic and linolenic acids were 2.66 and 4.0 milliequiv. per kg. respectively.

TABLE 5.

Thiocyanogen values of the unsaturated acids and ester.

Product	Iodine value		Thiocyanogen value	
	Found [1]	Theory [2]	Found	From literature
				Average values
Elaidic acid	89.5	89.9	89.7	89.3 (13, 14, 27)
Oleic acid	89.6	89.9	89.6	89.3 (13, 14, 27)
Linoleic acid	180.2	181.0	97.0	96.7 } (13, 14, 27, 29)
Linolenic acid	272.1	273.5	167.1	167.1 }
Methyl oleate	84.8	85.6	85.0	85.3 (27, 29)

[1] Iodine values were determined with 150% excess of 0.2 N Wijs reagent and a reaction period of one hour.
[2] Calculated with latest official International Atomic Weights (1941).

Further evidence of the purity of the above acids was obtained by measurement of their ultraviolet absorption spectra in the regions of absorption of diene, triene, and tetraene conjugation. These data and the percentage of conjugation calculated therefrom are presented in Table 6. The complete spectral absorption curves from 225 mμ to 325 mμ at 2 mμ intervals are shown in Figure 2. The almost complete absence of maxima in the regions of absorption of diene, triene, and tetraene conjugation indicates that negligible amounts of conjugated isomers are present in these acids.

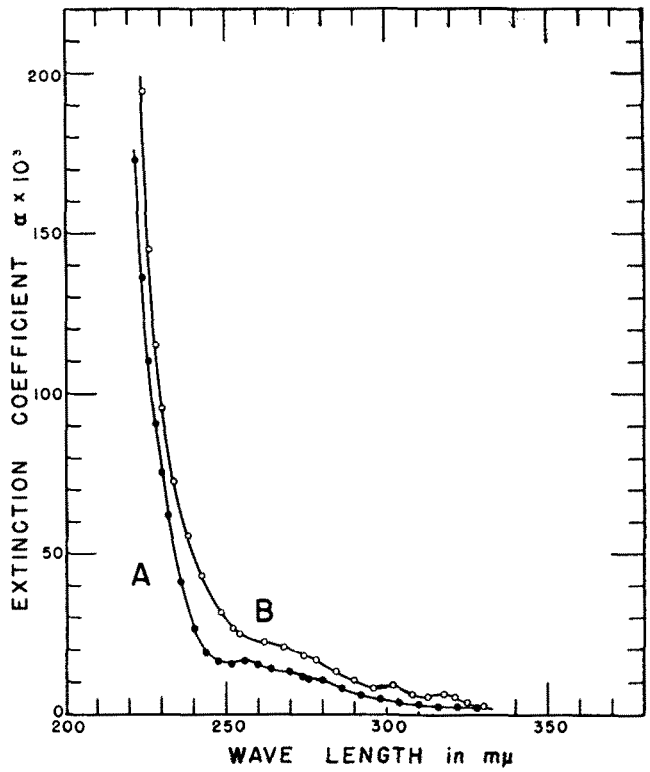

FIG. 2. Extinction curves for (A) linoleic acid and (B) linolenic acid in cyclohexane.

TABLE 6.

Spectrophotometric Analyses of Linoleic and Linolenic Acids.

Extinction coefficients			Type of conjugation	Percentage of conjugation	
Wave length [1]	Linoleic	Linolenic		In linoleic acid	In linolenic acid
mμ					
232	0.0618	0.083	Diene[2]	0.0248	0.047
262	0.0149	0.022	Triene[2]	0.0001	0.000
270	0.0133	0.020	Tetraene[2]	0.0019	0.0047
274	0.0115	0.018			
280	0.0102	0.016	Diene[3]	0.0051	0.068
308	0.0033	0.0065	Triene[3]	0.0007	0.011
310	0.0031	0.0058	Tetraene[3]	0.0012	0.0029
316	0.0026	0.0061			
320	0.0025	0.0059			
322	0.0024	0.0049			

[1] The extinction coefficient equals $a = \frac{\log \frac{I_o}{I}}{c\,l}$ where $\log \frac{I_o}{I}$ is the optical density, c is the concentration in grams per liter, and l is the length of the absorption cell in centimeters.
[2] Calculated according to Brice (5, 6).
[3] Calculated according to Brode (7).

All absorption spectra data were obtained from measurements made with a Beckmann quartz spectrophotometer. Solutions of the acids were obtained by weighing the samples directly into volumetric flasks and diluting to volume with cyclohexane purified according to the method described by Graff, O'Connor, and Skau (12).

Fats and miscellaneous fat products. The utility of the above-described thiocyanogen method is attested by the fact that it has been applied without modification to a heterogeneous class of fat products. These products together with the corresponding range of thiocyanogen values are shown in Table 7.

TABLE 7.

Fats and Fat Products With Range of Thiocyanogen Values Determined With Modified Thiocyanogen Reagent and Method.

Range of thiocyanogen values			
15 to 89	23 to 90	52 to 72	14 to 80
Glycerides	Mixed fatty acids	Hydrogenated oils	Esters of fatty acids
Rice bran oil	Cottonseed oil, hydr.	Peanut oil	Babassu
Pecan oil	Cottonseed oil, unhydr.	Cottonseed oil	Methyl oleate
Babassu oil	Gutcha nut oil	Shortenings	Methyl linoleate
Peanut oil	Coyol nut oil		
Cottonseed oil	Human fat		
Soybean oil	Coyol (crude pulp)		
Corn oil	Peanut oil		
Coyol nut oil			
Human fat			
Gutcha nut oil			
Distilled glycerides[1]			

[1] Glyceride fractions obtained by molecular distillation of a variety of oils.

All of the products listed in Table 7 were soluble in the reagent and no additional solvent was required to effect complete solution, consequently the reagent/sample ratio remained constant and the A.O.C.S. (27) equations for calculating their compositions were, therefore, applicable.

With carbon tetrachloride in the reagent the formation of the objectionable resinous-like product was entirely eliminated and both the original and end-reaction products remained soluble throughout the titration. Since this is consistently the case regardless of the type of sample analyzed, no occlusion of free iodine occurs. In addition, large-size samples of fats having low thiocyanogen values remain in solution. Under these conditions all of the titrations can be performed with ease and rapidity; the endpoint is

definitely clearcut and good checks are obtained in replicated determinations of a given sample.

Summary

A general reagent applicable to a wide range of thiocyanogen values and capable of reacting with practically all types of fats and oils has been described.

The principal features of the method include rigorous purification of all reagents; replacement of 25% of the volume of glacial acetic acid normally used in preparing the thiocyanogen reagent with an equal volume of carbon tetrachloride; use of finely powdered, dry potassium iodide; increase in the amount of potassium iodide added prior to titration from 1.0 gram to twice the equivalent weight calculated for the volume of standard reagent used; and complete exclusion of water from all reagents and glassware.

The value of the modified reagent is attested by data indicating its improved stability, accuracy when applied to pure unsaturated fatty acids, and its general applicability to a wide variety of fats and fat products.

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Soybean Oil

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SOYBEAN OIL is "coming of age" in the United States. Figure No. 1 shows the relative United States production of the six most important vegtable oils, and Table No. 1 (appended) shows also the annual disappearance of these six oils.

An examination of these data shows that the United States consumed annually over 100,000,000 lbs. soybean oil for five consecutive years during World War I (1916 to 1920, inclusive), reaching a high of 335,000,000 lbs. in 1918. All of this oil was imported, and much of it was of relatively poor quality with the result that United States usage dropped markedly after 1920.

It was not until 1922 that *domestic* soybean oil was produced in marketable quantities. The growth of production was slow at first and then progressed at a more rapid pace, as shown by the solid curve in Figure No. 1, until in 1944 it well exceeded the billion-pound mark and equalled the production of cottonseed oil for the first time.

How much of this record current high domestic production is a result of World War II, brought about because of curtailment of importation of vegetable oils from the Pacific islands regions? How much of this current high production and usage is likely to remain in post-war times? Perhaps an examination of the usage of soybean oil in the past decade will help in part to answer these questions.

Usage of Soybean Oil

The tabulation in Table No. 2 shows the main usage of soybean oil and the relative growth in terms of usage in the various products.

The tabulation shows also the marked increase in usage of soybean oil in recent years for edible purposes, namely, in shortenings, margarine, and salad oils and the relative slower increased usage of soybean oil for "drying oil" purposes.

For example, in 1943 the usage of soybean oil in edible products was 891,000,000 lbs., or about 90% of the total. This was due in part to the allocation of oils in 1943, but even in 1940 and 1936 the respective percentage usage of soybean oil in edible products was 86% and 87%. The main usage of soybean oil in the United States in the past 10 years has been in edible products.

Usage of Soybean Oil and Competing Oils in Products

Table No. 2 lists the various products in which soybean oil has been used and shows the annual amounts thus consumed. The relative importance of