equal to 2.53 specific gravity. The determinations made with doubtfully pure specimens vary from 2.4 to 2.58.

Sulphur.—Deville's results for monoclinic sulphur.

Thallium.—The chart indicates a somewhat higher gravity (11.98) than Crookes obtained from the metal in the form of wire (11.91).

Zirconium.—The atomic volume apparently should be a little greater than 21.2.

THE OIL OF CORN.[1]

BY C. G. HOPKINS.

Received September 22, 1898.

THE presence of oil in the corn kernel was discovered by Bizio[2] in 1823. A partial analysis by Hoppe-Seyler[3] gave the following as the percentage composition[4] of the oil:

Cholesterol	2.65
Protogon	3.95
Saponifiable fats, etc	93.40

The statement is made that the oil contains stearin, palmitin, and much olein, and the melting-point of the fatty acids is given as 51° to 54° F. (11° to 12° C.).

Some of the so-called physical and chemical "constants," which have been determined by several investigators are given below:

	Specific gravity of oil at 15° C.	Unsaponifiable substance. Per cent.	Iodine absorption. Per cent.
Spüller[5]	......	1.35	119.7
Smith[6]	0.9244	....	122.9
Hart[7]	0.9239	1.55	117.0
Rokitianski[8]	0.8360	....	75.8

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[1] From advance sheets of the author's thesis "The Chemistry of the Corn Kernel," for the degree of Doctor of Philosophy, Cornell University, 1898, which will be published as Bulletin No. 53 of the University of Illinois Agricultural Experiment Station.

[2] *J. Chem. u. Phys.*, *1823*, 37, 377.

[3] *Med. Chem. Untersuchungen*, 1, 162; *Bull. Soc. Chim.*, *1866*, [2], 6, 342; *Jsb. Fortschritte der Chem.*, *1866*, 698.

[4] I have not been able to see Hoppe-Seyler's original paper. Presumably the protogon is the substance now termed lecithin, and the methods employed in estimating it and cholesterol were similar to those which are discussed herein.

[5] Dingler's *poly. J.*, *1887*, 264, 626.

[6] *J. Soc. Chem. Ind.*, *1892*, 11, 504.

[7] *Ibid.*, 1894, 13, 257, from *Chem. Ztg.*, 17, 1522.

[8] Inaugural Dissertation, St. Petersburg, *1894*; *Pharm. Ztschr. Russland*, *1894*, 33, 712; *Chem. Centrbl.*, *1895*, [4], 7, 1, 22.

The oil used by Spüller was the ordinary ether extract. Rokitianski used a petroleum ether extract. Hart worked with a "dark brown" sample presumably found on the market. Smith's material was obtained on the market, but was of a "bright golden color" and was probably a fair sample of corn oil.

Spüller observed that the oil absorbed no oxygen from the air even after fourteen days' exposure. Smith states that the freezing-point of the oil is below —20°. Hart gives the melting-point of the fatty acids as 25°. Rokitianski reports further qualitative chemical work which showed the oil to contain oleic and linolic acids. It is evident from the specific gravity and the iodine absorption that the material with which he worked was not ordinary corn oil.

Wiley and Bigelow[1] have recently found the heat of combustion of oil of corn to be 9280 calories per gram.

EXPERIMENTAL.

In a preliminary study a small amount of oil was obtained by collecting the ether extract from a large number of proximate analyses of corn. In this, advantage was taken of the fact that the oil is moderately soluble in alcohol when hot and but slightly so at ordinary temperatures.[2]

The oil was transferred from the small flasks, used in its extraction, by means of hot alcohol to a single vessel. On cooling the oil precipitated and settled to the bottom, the alcohol being each time decanted from the collected oil, and used in transferring the next lot. Finally the alcohol was evaporated, and the oil dried to constant weight in a water oven. When freshly obtained from white dent corn the oil is nearly colorless, but on standing a pale yellow and finally a deep golden color develops, plainly indicating a gradual change in its condition, presumably due to absorption of oxygen. This was confirmed by determining the iodine absorption which was found to be 115.5 per cent.

A large quantity of corn oil, including samples from four different sources,[3] was then secured in order to make a more

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[1] This Journal, 20, 309.

[2] Smith has found the solubility of corn oil in alcohol by volume to be two per cent. at 16° and thirteen per cent. at 63°.

[3] Samples of corn oil were very kindly furnished me by President Wm. F. Piel, Jr., of The National Starch Manufacturing Company, New York City; by The Chas. Pope Glucose Company, Geneva, Ill.; by The Glucose Sugar Refining Company, Chicago; and by Messrs. Elbert and Gardner, New York City.

thorough investigation. The oil is obtained as a by-product in the manufacture of corn-starch and glucose-sugar, and all of the samples secured were of a pale straw color and evidently fresh and pure.

SPECIFIC GRAVITY.

Three of these samples of corn oil were sufficient in quantity to enable me to make determinations of their specific gravity by means of a delicate Westphal balance which by trial gave the specific gravity of pure water at 15° as 1.000°. The samples of oil gave the following results :

	I.	II.	III.
Specific gravity at 15°........	0.9245	0.9262	0.9258

MELTING-POINT.

Preliminary experiments confirmed the observation of Smith that the oil is still fluid at —20°, a temperature of —23° (obtained with snow and concentrated sulphuric acid) failing to solidify the oil. It was found, however, that the oil became hard and solid at about —36°.

The melting-point was determined by a modification of the method of the Association of Official Agricultural Chemists.[1]

In a tall beaker of about two and five-tenths liters' capacity was placed a small quantity of concentrated sulphuric acid (to absorb water vapor so that the apparatus would remain transparent at low temperatures). A second beaker of about two liters' capacity was placed in the first, being supported by the rim without touching the bottom. A one-liter beaker taller than the second was placed in the latter and filled with alcohol, the space between the two being filled with solid carbon dioxide. A glass tube thirty mm. in diameter and closed at the bottom was fitted into the inner beaker with a large cork, the tube being about one-third filled with a mixture of one volume of concentrated sulphuric acid and three volumes of absolute alcohol, and then nearly completely filled with absolute alcohol. The temperature of the alcohol in the beaker was kept uniform throughout by constant stirring with a wire which passed through the cork and terminated in a ring surrounding the glass tube. A heavy glass spoon and a glass spatula were placed in the alcohol.

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[1] U. S. Dept. of Agr., Div. of Chem., Bull. 46, 34.

When the temperature reached —50°, the spoon was removed and a drop of the oil at once let fall upon it. A thin, solid, white, opaque disk formed, and was quickly made to drop into the inner tube by using the glass spatula. The disk of solidified oil settled through the absolute alcohol to the denser liquid below and there remained in suspension.

The beaker which had contained carbon dioxide was replaced by another and the temperature allowed to slowly rise. An alcohol thermometer was used for reading the temperatures below the freezing-point of mercury. Above —38° a delicate mercury thermometer was employed.

As the temperature rose the disk remained unchanged until at —19° it began to lose its opacity. At —14° it had become perfectly transparent, but no change in shape could be detected below —7°. The disk was much contracted and thickened at —5° and became entirely symmetrical in form at —2.3°. A second determination gave practically the same results, the final reading being −2.4°. The change in temperature (when near the melting-point) required five to six minutes for one degree.

To determine the change in the consistency of the oil, a thin-wall tube of eight mm. diameter, closed at the bottom and containing one cm. of the oil, was placed in alcohol at —45°. After the oil had become solid a glass rod twenty cm. long and two mm. thick (the lower end being widened to five mm. diameter), was placed in the tube so that its weight was entirely supported by the solidified oil. At —13° the oil had become transparent but still supported the rod. At —10° the rod began to settle appreciably and at —9° it had passed through the centimeter of oil to the bottom, although a disk of oil suspended beside the tube in the same liquid had not changed appreciably in shape. The change of temperature from —10° to —9° required five minutes.

IODINE ABSORPTION.

The method of Hübl[1] was employed for this determination, except for certain details of the process.

Standard sodium thiosulphate solution was prepared by dissolving 47.2 grams of the crystallized salt ($Na_2S_2O_35H_2O$) in water and diluting to two liters. From theory one cc. of this

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[1] *J. Soc. Chem. Ind.*, *1884*, 3, 641.

solution should be equivalent to 12.06 milligrams of iodine if the salt were pure.[1] The solution was standardized with resublimed iodine with the following results :

Iodine taken	0.5160	0.5574 gram.
Thiosulphate solution required	42.9	46.4 cc.
Iodine equivalent to one cc	12.03	12.01 milligrams.

The average of these results, 12.02, was used in the following work :

The iodine solution, containing fifty grams iodine, and sixty grams mercuric chloride in two liters of alcohol, was standardized whenever used.

Little pipettes of about five-tenths cc. capacity were placed in five cc. vials nearly filled with the corn oil, the bulb of the pipette being immersed, and the whole weighed. The measure of oil was then transferred to a 500 cc. glass-stoppered bottle, the pipette returned to the vial, and the exact weight of oil taken determined by difference. The duplicate is taken immediately and necessitates only one more weighing. Ten cc. of chloroform and forty cc. of iodine solution were added to the oil. After two hours twenty-five cc. of ten per cent. potassium iodide solution and about 125 cc. of water were added and the excess of iodine determined by titrating with the sodium thiosulphate solution, starch indicator being added near the close of the reaction.

Duplicate determinations of four different samples of oil from as many different sources gave the following results :

	Oil taken. Gram.	Iodine absorbed. Gram.	Iodine absorbed. Per cent.
1	0.3473	0.4255	122.5
	0.3844	0.4729	123.0
2	0.4251	0.5179	121.8
	0.4714	0.5729	121.5
3	0.4281	0.5212	121.7
	0.4742	0.5772	121.7
4	0.4326	0.5324	123.1
	0.5168	0.6351	122.9

OXYGEN ABSORPTION.

In order to afford a large surface for the absorption of oxygen, the oil was placed in a large crystallizing dish of seventy-five

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[1] Sutton's Volumetric Analysis, *1890*, 115, states that standard sodium thiosulphate solution may be made by simply dissolving an exact weight of the crystallized salt, $Na_2S_2O_35H_2O$, in water and diluting to a definite volume.

mm. diameter. This was allowed to stand at the room temperature, the weight of the oil being determined from time to time as follows:

	Grams.
Weight of oil taken	2.1732
Weight after 1 day	2.1722
" " 7 days	2.1718
" " 11 days	2.1718
" " 12 "	2.1718

These results confirm those of Spüller, showing that the oil does not take up oxygen under these conditions.

The dish was then placed in a water-oven and the following data[1] obtained:

	Grams.
Weight after 1 hour	2.1726
" " 1 day	2.1996
" " 2 days	2.2488
" " 3 "	2.2590
" " 4 "	2.2588
" " 5 "	2.2558
" " 6 "	2.2513
" " 7 "	2.2448

The first action of air upon the hot oil is evidently the direct addition of oxygen; but after two or three days the oil began to turn noticeably darker in color and finally to lose weight, evidently due to a secondary reaction which effects some decomposition of the oil with formation of volatile products.

LECITHIN.[2]

A weighed quantity of oil was mixed with potassium nitrate and sodium carbonate in a platinum dish and ignited until the carbon was completely burned. The fused mass was dissolved in dilute hydrochloric acid, and the total phosphoric acid determined.[3] The amount of lecithin was calculated by multiplying the weight of magnesium pyrophosphate obtained by the factor

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[1] These results emphasize the importance of avoiding the presence of oxygen in drying corn or corn oil in analytical work.

[2] Lecithin is commonly regarded as a compound of the base, neurine, with distearylglycerophosphoric acid, although one or both of the stearic acid radicals may be replaced by radicals of palmitic or oleic acid, and the neurine (trimethylhydroxyethyl ammonium hydroxide) is sometimes replaced by another base; *e. g.*, betaine.

[3] Cf. Hoppe-Seyler, *Jsb. Fortschritte der Chem.*, *1866*, 744; Schulze and Frankfurt, *Landwirtschaftliche Versuchs-Stationen*, *1893*, **43**, 207.

7.25.[1] Duplicate determinations gave the following results:

	Grams.	Grams.
Oil taken	10.728	6.435
KNO_3 used[2]	10.0	35.0
$Mg_2P_2O_7$ obtained	0.0221	0.0132
Lecithin	0.1602	0.0957
	Per cent.	Per cent.
Lecithin in oil[3]	1.49	1.49

CHOLESTEROL.[4]

To determine cholesterol[5] about fifty grams of the oil were saponified on the water-bath with twenty grams of potassium hydroxide and 100 cc. of seventy per cent. alcohol. The soap was transferred to a large separatory funnel with 200 cc. of water and shaken first with 500 cc. of ether and then three times with 250 cc. of ether. The four portions of separated ether were combined, and the ether distilled, the residue being resaponified with two grams of potassium hydroxide and ten cc. of seventy per cent. alcohol. The solution was then transferred to a small separatory funnel with twenty cc. of water and shaken with 100 cc. of ether. After separating the aqueous layer the ether solution was washed four times with ten cc. of water, the ether solution being finally transferred to a weighed flask, the ether distilled and the weight of the dry residue (cholesterol) determined. Three determinations gave the following results:

	Grams.	Grams.	Grams.
Oil taken	50.16	53.50	54.24
Cholesterol obtained	0.7002	0.7114	0.7512
	Per cent.[6]	Per cent.	Per cent.
Cholesterol in oil	1.40	1.33	1.38

The cholesterol was recrystallized from absolute alcohol in characteristic glistening plates, melting at 137° to 137.5°. It also gave the characteristic color reactions[7] for cholesterol: (1)

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[1] 7.25 parts of lecithin ($C_{44}H_{90}O_9PN$) yield one part of magnesium pyrophosphate.

[2] The proportions of potassium nitrate used were purposely varied, but the results indicate that the smaller proportion was sufficient.

[3] By extracting corn with ether and alcohol, successively, Schulze and Frankfurt (reference above) have obtained amounts of phosphoric acid equivalent to 0.25 to 0.28 per cent. of lecithin in the corn.

[4] A monatomic alcohol, $C_{26}H_{43}OH$.

[5] Cf. Bömer, *Ztschr. für Untersuchung der Nahrungs- und Genussmittel*, 1898, 21, for recent work on the details of this method.

[6] Spüller had obtained 1.35 per cent. and Hart 1.55 per cent. of unsaponifiable matter.

[7] Watts' Dictionary, *1889*, **2**, 147.

when shaken with chloroform and sulphuric acid; (2) when evaporated to dryness with nitric acid; (3) when warmed with hydrochloric acid and ferric chloride.

TOTAL FATTY ACIDS.

After removing the cholesterol from about fifty grams of oil the remaining soap solution (about 500 cc.) was acidified with hydrochloric acid and shaken in a separatory funnel. An ethereal layer of about 150 cc. at once separated. After adding 100 cc. more ether and thoroughly shaking, the aqueous layer was drawn off, the ether solution of the fatty acids washed with several portions of water and then transferred to a weighed flask, the ether distilled off, a few cubic centimeters of absolute alcohol dissolved in the residue and evaporated to remove traces of water, and the weight of the total fatty acids determined:

	Grams.
Oil taken	50.160
Fatty acids obtained	46.935
	Per cent.
Fatty acids in oil	93.57

The fatty acids form a solid mass at 15°, but melt nearly completely at one or two degrees above, the last particles of solid disappearing at 23°. Prepared as described the fatty acids absorbed only 126.4 per cent. of iodine instead of 130.7 per cent. as calculated from the iodine absorption of the oil. This indicates that oxygen had been absorbed by the acids during the process of separation. It was found that oxygen is slowly absorbed by the fatty acids while standing in a desiccator at the ordinary temperature. At 100° the absorption is much more rapid although, as with the oil, secondary reactions soon begin at the higher temperature. The change in weight was found to be as follows:

Time. In days.	In desiccator. Grams.	In water-oven. Grams.
0	1.9685	2.2740
1	1.9692	2.3106
2	1.9717	2.3366
3	1.9777	2.3366
4	1.9847	2.3282
8	2.0231	...
12	2.0665	....
16	2.0911	....
22	2.1157	....
28	2.1293	....
34	2.1297	....

All action apparently ceased after about one month's time. A considerable portion of the fatty acids had separated in the solid form and of a pure white color, while the other portion remained a colorless, oily liquid.

It is of interest to note the apparent relation between the iodine absorption and the oxygen absorption by the fatty acids. As already shown the fatty acids as prepared absorbed 126.4 per cent. of iodine. If an equivalent amount of the bivalent oxygen may be absorbed instead of the univalent iodine then eight per cent. of oxygen should be taken up. The results show that 1.9685 grams of the fatty acids absorbed 0.1612 gram of oxygen, an amount equal to eight and two-tenths per cent.

Time would not permit the preparation of the fatty acids in a manner which would prevent the absorption of oxygen during the process, and then a repetition of the quantitative determination of the absorption. This is especially desirable in order to confirm the results as given above, and the writer expects to investigate this point more fully in the future.

VOLATILE ACIDS.

About five grams of oil were saponified in a 500 cc. flask with two grams of potassium hydroxide and forty cc. of eighty per cent. alcohol. After evaporating the last of the alcohol, 100 cc. of recently boiled water were added, the soap solution acidified with forty cc. of dilute sulphuric acid (1:10), a few pieces of freshly ignited pumice-stone added, the flask connected with a condenser by means of a safety bulb tube, and 110 cc. of distillate collected. After mixing, 100 cc. were passed through a dry filter and titrated with one-twenty-fifth normal barium hydroxide solution.

Four determinations gave the following results :

	Grams.	Grams.	Grams.	Grams.
Oil taken	4.506	5.894	5.671	5.718
	cc.	cc.	cc.	cc.
N/25 barium hydroxide required	1.3	1.5	1.4	1.3

As two blank determinations required one and three-tenths and one and five-tenths cc., respectively, of the barium hydroxide solution it is evident that the oil contains no volatile acids.[1]

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[1] Spüller gives Reichert's number for the volatile acids as 0.33; Smith states that the oil examined by him contained volatile acids equivalent to 0.56 per cent. of potassium hydroxide; and Morse (New Hampshire Experiment Station Bulletin, *1892*, 16, 19) gives volatile acids as three and two-tenths per cent. in a sample of corn oil which absorbed 112.8 per cent. of iodine.

SEPARATION AND DETERMINATION OF FATTY ACIDS.

It has been found especially by Hazura[1] and his associates that the oxidation of unsaturated fatty acids by alkaline potassium permanganate serves as a basis for the approximate separation of several fatty acids. Under proper conditions the oxidation is chiefly confined to the direct addition of the hydroxyl group (OH) wherever "free valences" exist. The following shows the relations among several acids in the series containing eighteen atoms of carbon in the molecule :[2]

Unsaturated acids. Saturated acids.
Stearic, $C_{18}H_{36}O_2$.
Oleic, $C_{18}H_{34}O_2$, oxidizes to..dihydroxy stearic, $C_{18}H_{34}(OH)_2O_2$.
Linolic, $C_{18}H_{32}O_2$,, oxidizes to tetrahydroxy stearic, $C_{18}H_{32}(OH)_4O_2$.
Linolenic, $C_{18}H_{30}O_2$, oxidizes to hexahydroxy stearic, $C_{18}H_{30}(OH)_6O_2$.

After removing the cholesterol from 53.5 grams of oil, the combined soap solution was heated till the dissolved ether was distilled, cooled, and diluted to two liters. Two liters of a one and five-tenths per cent. potassium permanganate solution were then gradually added with constant stirring. After ten minutes the precipitated manganese hydroxide was filtered off, and the clear filtrate acidified with hydrochloric acid. The precipitate thus formed was filtered off, washed, air-dried, and then extracted with ether. The residue insoluble in ether weighed, after drying, eighteen grams. It was extracted with boiling water until but two grams remained, which, when again extracted with ether, left a residue of six-tenths gram and soluble in boiling water.

The substance dissolved in hot water was practically completely precipitated as the solution cooled[3] and proved to be sativic acid (tetrahydroxystearic acid), as is indicated by the method of formation and by its solubility in hot water. The melting-point[4] of the dried substance was 157°–159°.

The quantitative synthesis of the potassium salt was effected by dissolving a weighed amount of the acid in warm alcohol and titrating with standard alcoholic potassium hydroxide solution :

[1] *Monatsh. Chem.*, *1886 to 1889*, 7 to 10.

[2] Cf. Hazura: *Ibid.*, *1887*, **8**, 269.

[3] 2000 cc. of the filtrate from the precipitated sativic acid required only five-tenths cc. of fifth-normal potassium hydroxide to show alkalinity with phenolphthalein.

[4] Bauer and Hazura, *Monatsh. Chem.*, *1886*, 7, 225, give 160° as the melting-point of several samples of sativic acid, prepared in a manner similar to the above.

Sativic acid taken.	Potassium hydroxide required.	Per cent. potassium in product.[1]	Per cent. potassium (theory).[2]
1.000	0.1604	10.08	10.14

The ether solutions obtained as described above were combined and the ether distilled. The residue was solid at the room temperature, melted gradually as the temperature rose from 40° to 60°, and was found to absorb 79.2 per cent. of iodine, thus showing very incomplete oxidation of the unsaturated acids.

A second lot of corn oil (54.24 grams) was oxidized by alkaline permanganate, the cholesterol and then the dissolved ether having been previously removed. The soap was diluted to two liters and cooled to 0° by ice kept in the solution. A solution of potassium permanganate containing eighty grams in two liters of water was slowly added with constant stirring. After thirty minutes precipitated matter was filtered off and washed ; the clear filtrate was acidified with 150 cc. of concentrated hydrochloric acid ; the precipitated acids were filtered off, dried, and extracted with ether. The residue insoluble in ether (17.7 grams, was dissolved in boiling ninety-five per cent. alcohol. On cooling, the sativic acid separated in the crystalline form, melting at 161°-163°.

By distilling the ether from the solution obtained as above described, a brown residue (nine and five-tenths grams) was obtained which melted at 55° to 60° and showed an iodine absorption of only nine and two-tenths per cent.

The aqueous acid solution from which the insoluble organic acids had been precipitated by hydrochloric acid was evaporated nearly to dryness, a black tarry mass gradually separating, showing that, although a small amount of unsaturated acids had been unacted upon, the oxidation had gone far beyond the simple addition of hydroxyl groups to the unsaturated compounds.

To further investigate the fatty acids, a method essentially that of Muter[3] was tried for their separation and determination. It is based upon the fact that the lead salts of the unsaturated acids, oleic, linolic, etc., are soluble in ether; while the lead salts of the saturated acids, stearic, palmitic, etc., are not.

[1] Calculated weight $= 1.000 + 0.1604 \frac{39.14 - 1.008}{56.148}$

[2] For $C_{18}H_{31}(OH)_4O_2K$.

[3] *Analyst*, 1877, **2**, 73.

About one and five-tenths grams of the oil were saponified with alcoholic potash and the soap dissolved in water, the unsaponifiable substance (cholesterol) being separated from the soap solution by shaking with ether. The solution was then neutralized with acetic acid, and the fatty acids precipitated with lead acetate, a slight excess being added. The lead salts were washed with water, and then transferred with fifty cc. of ether to a glass cylinder of about sixty cc. capacity, which was stoppered and then violently shaken for five to ten minutes. The small quantity of matter insoluble in ether was then allowed to settle. A stopper carrying two glass tubes similar to those used in the ordinary washing bottle was placed in the cylinder, the long tube reaching nearly to the undissolved sediment. By blowing in the short tube the clear solution is transferred almost completely without disturbing the sediment. The undissolved substance was then shaken with more ether, allowed to settle, and the ether transferred as before as completely as possible. This treatment was twice more repeated. The undissolved lead salt was then warmed with about twenty-five cc. of dilute hydrochloric acid, till the fatty acid separated; and, after cooling sufficiently, the whole was transferred to a 250 cc. graduated bulb tube, ether being used to complete the transfer. The portion of the tube below the bulb contained fifty cc. and was graduated to two-tenths cc. A small glass tube carrying a stopcock was sealed in just below the fifty cc. mark. The tube was filled to the 250 cc. mark (above the bulb) with ether, and thoroughly shaken. The aqueous layer, containing the excess of hydrochloric acid and the precipitated lead chloride was allowed to separate.

The volume of ether solution was observed, and 200 cc. of it were drawn off into a weighed flask, evaporated to dryness, and the weight of the residue determined.

Duplicate determinations gave the following:

	Grams.	Grams.
Oil taken	1.60	1.610
	cc.	cc.
Volume of ether solution	222.4	221.0
Ether solution taken	200.0	200.0
	Gram.	Gram.
Saturated acids obtained	0.0670	0.0648
	Per cent.	Per cent.
Saturated acid in oil	4.66	4.44

The residue of saturated acids formed a white solid mass. It was dissolved in hot alcohol and allowed to crystallize. The melting-point was 57°. The quantity of the saturated acids thus obtained was considered too small for further satisfactory examination (see foot-note below).

Before the lead salts of the saturated acids were completely washed by decantation[1] the clear ether solution of the lead salts of the unsaturated acids absorbed oxygen, and became cloudy, a white precipitate forming in considerable amount. Two samples of the atmosphere in the cylinders above the solutions were drawn off in gas burettes; and, after removing the ether vapor, the residual air was found to contain only 15.3 per cent. and 13.9 per cent., respectively, of oxygen instead of 20.8 per cent. as found in the air of the laboratory.

By subtracting the percentage (4.55) of saturated acids found in the oil from that of the total fatty acids (93.57) the amount of total unsaturated acids is found to be 89.02 per cent., consisting of oleic and linolic acids. (The melting-point of the sativic acid obtained and the composition of its potassium salt prove the absence of linusic acid in the products of oxidation, and, hence, of linolenic acid in the total fatty acids.)

From the iodine absorption, the amounts of oleic and linolic acids can be accurately determined. Thus:

Oleic acid, $C_{18}H_{34}O_2 + I_2 = C_{18}H_{34}I_2O_2$, diiodostearic acid.
Linolic acid, $C_{18}H_{32}O_2 + 2I_2 = C_{18}H_{32}I_4O_2$, tetraiodostearic acid.

As 89.02 grams of these unsaturated acids in the ratio in which they exist in corn oil absorb 122.3 grams of iodine the following equation can be stated, x being the number of grams of oleic acid:

$$x\frac{254}{282} + (89.02 - x)\frac{508}{280} = 122.3$$

The oleic acid is found to be 42.92 grams and the linolic acid 46.10 grams.

By subtracting from the amount of saturated acids the equiv-

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[1] At least two days' time is required for this process, and even this was found more satisfactory than filtration. I have no doubt that, if centrifugal force were substituted for gravity, the washing by decantation could be done much better and so quickly that the unsaturated acids could also be determined before the absorption of any appreciable amount of oxygen. Quantities of the separated materials sufficient for further examination could doubtless be obtained in a short time. No suitable centrifugal was at hand for this work.

alent of the stearic acid contained in the lecithin, and calculating to the respective glycerol esters the remaining saturated acids (as stearic acid), the oleic acid, and the linolic acid, the following summary is obtained as the composition of the oil of corn:

	Per cent.
Cholesterol	1.37
Lecithin	1.49
Stearin (?)	3.66
Olein	44.85
Linolin	48.19
Total	99.56

SOME ERRORS IN THE DETERMINATION OF NITROGEN.[1]

BY C. G. HOPKINS.

Received September 22, 1898.

THE determination of nitrogen was made by the ordinary Kjeldahl method. The metallic mercury used in the digestion was measured in a capillary tube, one end of which is doubly bent so as to form a loop, the short arm of which is turned back upon itself near the end while the long arm serves as a handle. The loop is made sufficiently narrow to pass into the mercury bottle, and of sufficient length to retain, when raised above the liquid, the exact quantity of mercury required for a single determination. By blowing in the longer arm the mercury is emptied into the digestion flask.

Heavy copper flasks were used in the distillation with much satisfaction, the sodium hydroxide solution (containing the necessary amount of potassium sulphide) being added in sufficient excess to "bump" before the contents may become dry, thus serving as a signal that the distillation has gone far enough.

Two common sources of error in the nitrogen determination were found and investigated. In titrating an acid solution in an open vessel with standard ammonia solution a very appreciable error is introduced by the volatility[2] of the ammonia, although the only possible loss is from the tip of the burette and from the falling drops.

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[1] From advance sheets of the author's thesis. "The Chemistry of the Corn Kernel," for the degree of Doctor of Philosophy, Cornell University, 1898, which will be published as Bulletin No. 53 of the University of Illinois Agricultural Experiment Station.

[2] Rempel has already shown that dilute ammonia solution drawn into beakers or evaporating dishes and then titrated suffers marked loss.—*Ztschr. angew. Chem.*, *1889*, 331.