relatively small differences, samples of margarin from various sources, show much larger differences.

3. The viscosimetric determination can yield as good service in distinguishing butter-fat from margarin as any other physical method. The amount of margarin added to butter may also be approximately determined.

4. On account of its easy manipulation, its inexpensiveness, and the small amount of fat necessary, the "Fluidometer" is capable of yielding excellent results, not alone in the hands of experienced chemists, but likewise in those of government inspectors, etc.

THE EXAMINATION OF LARD FOR IMPURITIES.

By David Wesson.

Received June 22, 1895.

IN examining a sample of any material for impurities the analyst must first familiarize himself with the pure substance before he can detect wherein the sample under examination differs. If a definite compound is being dealt with, the problem is an easy one, but if we have an organic substance, which from the very nature of its origin is subject to many variations, the analyst is confronted with a problem of no small magnitude, and this is very true in regard to the accurate analysis of commercial lard, which is the fat rendered from various parts of the freshly slaughtered swine. Hogs being omniverous animals, it is reasonable to suppose that the fat will vary in accordance with the feed. It is a well-known fact that the lard from hogs which have been allowed to run in the woods and fatten on nuts of various sorts, preserves in a marked degree certain properties of the nut oils, and is much softer, containing more oil than that made from corn-fed hogs. That animals under proper conditions absorb food directly and deposit the same more or less unaltered in their tissues, seems to have been proven by experiments made some years ago at the Munich Physiological Institute.

That the fat varies greatly in different parts of the same animal has been demonstrated by various observers[1] as well as the writer.

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[1] Wiley: Bulletin 13. Part IV. U. S. Dept. of Agr.; R. T. Thomson and H. Ballantyne; *J. Soc. Chem. Ind.* 9. 589. (590).

E. Spaeth[1] gives table of analytical data showing variations between back, kidney, and intestinal fat, taken from eight different hogs, of different ages. His results show considerable difference between the different animals.

The modes of rendering make considerable differences in the character of the fat. The comparatively low temperature used in kettle-rendering produces a fat of quite different analytical nature from that produced by treatment under high steam pressure in a closed rendering tank (*autoclave*). As most American lard is prepared by this latter method, this fact must be well borne in mind in interpreting analytical results.

Time is an important factor in determining the condition of a lard. A lard several months old will give analytical data which if compared with those of a fresh sample, would indicate adulteration.

The lard analyst who knows nothing of the history of a sample, and without such experience as will enable him to judge by the senses what sort of lard he is dealing with, is extremely liable to misinterpret analytical results and fall into grievous errors.

The methods used for the detection of cottonseed-oil in lard depend upon specific color reaction with different reagents, different physical properties of the fats, and the differences between the fluid portion ("olein") of the lard and that of the cotton oil.

Considering these tests in their order, we will first consider the reaction with silver nitrate, commonly known as the "*Bechi Test*.

Cottonseed-oil when treated with an alcoholic solution of silver nitrate reduces the salt with formation of a brick-red or deep green color and deposition of metallic silver, while pure lard under like conditions should give little or no coloration and no metallic silver. The test has been applied in various ways by different chemists, but the writer has obtained the most satisfactory results by operating according to direction laid down by Dr. C. B. Dudley, in the Penn. R. R. specification for lard oil about six years ago. The solution used is made up with two grams silver nitrate, 200 cc. alcohol, and forty cc. ether. After expo-

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[1] *Ztschr. Angew. Chem. 1893*, 133-136; also abstract in *Journal of the Society of Chemical Industry*, **12**, 608.

sure to sunlight, till reaction ceases, the solution is decanted or filtered into a dark bottle.

In testing, ten grams of melted lard and five cc. of the solution are well stirred together on the water-bath at 100° C. for fifteen minutes, at the end of which time most of the alcohol will have passed off. With pure lard there should be no coloration, while in the presence of cottonseed-oil the depth of color varies according to the amount and character of the oil, and a metallic mirror is deposited on the surface of the liquid fat.

Applying the test, in the manner described, to samples of steam lard known to be pure, and representing many thousand tierces, the writer found that more or less coloration of a purple tint was the rule rather than the exception. Believing that this apparent reduction was due to organic matter of a reducing nature held in the lard as a result of the process of rendering, the experiment was tried of washing the lard with a two per cent. solution of nitric acid. For this purpose about fifty grams of melted lard in a flask are shaken up with twenty-five cc. of the diluted acid, and after allowing to settle on the water- or steam-bath, the acid water is removed and the lard washed once with fifty cc. of hot distilled water. After settling till clear, ten cc. of the lard are pipetted off and the test made as described. In nineteen cases out of twenty, pure steam lard after this treatment will give no reduction whatever or suspicion of reduction, the fat remaining colorless at the end of fifteen minutes, whereas the reducing matter of cotton oil being unaffected by this treatment would give an unmasked reaction with the silver nitrate. While in the majority of cases the above treatment is all that is necessary to remove accidental reducing matters, we occasionally meet lards which have been treated at very high temperature and for a long time, which show as a result a slightly higher than normal per cent of free acid (normal is four-tenths to one per cent) and contain decomposition products of the animal fiber which have a very strong reducing action on our silver solution. Such samples must be first washed with diluted caustic soda solution and distilled water, and afterward with the nitric acid. before any definite conclusion can be drawn from the results of applying the silver nitrate test.

The condemnation of a sample of lard which gives a coloration with silver nitrate, without first purifying the fat as indicated, would be as absurd as it would be unjust, yet many good analysts have been known to do this very thing.

Dr. Ernest Millau applies the silver nitrate to the freshly separated fatty acids, but insists most forcibly on a preliminary preparation of the fat for analysis by a purification somewhat similar to the one outlined above. (See pamphlet[1] published by Ministero de L'Agriculture.)

Exception is taken to the silver nitrate test by various writers because of the misleading reaction obtained with lard improperly prepared for analysis. and also because cotton oil can be refined with oxidizing agents and the use of very high temperatures in such a measure as to destroy the specific reducing agent. Also very old oil will sometimes refuse to give any reduction. If such an oil were mixed with lard. it goes without saying that no reduction would not necessarily indicate pure lard, but the writer can say, as a result of several years' experience, that he has never run across any sample of oil failing to give the reaction which would be suitable to use in the preparation of an edible fat. If a lard containing cotton oil should become so old that the oil should lose its reducing power. the lard would be fit only for the soap-kettle.

The preponderance of evidence seems to be in favor of the silver nitrate test as being the best single test which has yet been brought forward for the detection of cotton oil in lard. When properly applied it is the most reliable for detecting small quantities.

The phosphomolybdic acid test. otherwise known as the Welmans test, first described in the *Pharm. Zeit.*, *1891*, **36**, 798, has been highly recommended by several writers, of late, as of value for the detection of vegetable oils in lard. Among them may be mentioned Rupp, Wimmer, Mansfield, and Goske. while H. Schweitzer and E. Lungwitz[2] state that they have found the test one of great value.

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[1] Analyse Chemique des Matieres Grosses Agricoles. pas Ernest Millau, Directeur de Laboratoire d'Essais Technique de Marseilles.

[2] *J. Soc. Chem. Ind.*, 614. *June 1894*.

J. Lewkowitsch[1] says as the results of a series of careful experiments: "Welman's reaction can therefore be admitted as a preliminary test, the indications of which may, in some cases, give valuable hints as to the direction in which the examination of a sample has to be carried out and may serve as a useful corroboration of results obtained by other methods."

Samelson[2] concludes that the test is of no value and that the iodine figure is the only reliable test for the detection of cottonseed oil in lard. He bases the assumption on the fact that he found six samples of American lard with iodine numbers of 64.7 to 67.2, which were higher than any he had ever found recorded, whence he concluded that cotton oil must be present though not shown by the test.

George F. Tennille[3] publishes a very exhaustive paper on this test, and concludes that "the phosphomolybdic test may be considered to be of slight analytical value, and certainly does not fill that long-felt want of a simple test which will reliably indicate small percentages of cotton seed or other vegetable oils in lards." The writer has tried the test and arrived at the same conclusions.

Sulphuric Acid Test.—The color produced by the action of sulphuric acid on cottonseed-oil in a mixture with lard is often a good qualitative indication, but it so frequently happens that pure lards prepared under certain conditions will give similar coloration, that results must be taken with extreme caution, and in many cases had better not be taken at all.

Dr. J. Lewkowitsch[4] concludes: "The sulphuric acid color test may therefore only be used for purposes of preliminary information, and even then its indications should be interpreted with the greatest caution."

PHYSICAL TESTS.

Specific Gravity.—Lard freshly rendered in the writer's laboratory showed at $\frac{99^\circ}{15^\circ}$ C. a specific gravity of 0.8600 to 0.8610, while old samples of known purity have been observed running as high as 0.8620, while we have on record one specimen which

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[1] *J. Soc. Chem. Ind.*, 617. *June 1894.*

[2] *Ztschr. anal. Chem.*, 189. *1894.*

[3] This Journal, 17, 33.

[4] Contributions to the Analysis of Fats. IV, Color Reaction, *J. Soc. Chem. Ind.*, 617. *June, 1894.*

ran as high as 0.8640, and gave no indication of cotton oil by other tests. The lard was nearly a year old and had been stored in tierces. Cottonseed-oil shows under like conditions 0.8683. With fresh lard as a standard we would have a difference between lard and cotton oil of 0.0083. The lard cited would therefore show $\frac{0.0040}{0.0083}$ or forty-eight per cent. of cotton oil, which shows the test to give preposterous results when working on old lards. It is of use in obtaining the proportionate components of a mixture when the specific gravities of the identical fats used in preparing the mixture are known.

Refraction Index.—As this depends to a great extent on the relative amounts of olein and stearin and palmitin present, it is quite evident that two samples of lard containing these ingredients in different proportions would show different indices. Wiley has published a large number of refraction indices in Part IV, Bulletin 13, Dept. of Agriculture, 1889, Lard and its adulterations. In table 18, he gives the results of analysis of six samples of Prime Steam lard drawn by C. H. Mixer, the official inspector of the board of trade in Chicago, and accompanied by his affidavit. The lards were of unquestioned purity yet their indices varied from 1.4911 to 1.4675. which shows that the refraction index is little better than specific gravity as a test *per se.*

Melting-point.—Any one who has experimented much with the melting-points of lard and lard compounds will, it is believed, readily agree that no suitable method has yet been proposed which will give analytical indications of any value except in cases of large admixtures of beef fat. This determination depends so largely on the manner of cooling the fat and the time elapsing after the cooling that it is of no value whatever as an indication of small adulteration.

Crystallizing-point of the Neutral Fat.—The observation of the manner of crystallizing on cooling of the melted fat gives valuable indication regarding the presence of beef fat.

H. Schweitzer and E. Lungwitz,[1] give their mode of procedure and results obtained with it. They rely on the test to a

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[1] Commercial Analysis of Lard, *J. Soc. Chem. Ind.*, June. *1894*. 614. and July. *1894.* 709.

considerable extent for the detection of beef fat. Amthor and Zink[1] use this method among others.

The writer has derived very useful indications respecting the proportion of beef fat present in a mixture, by working in a somewhat different manner. As a rule pure lards chill below 30° before showing turbidity, while if beef fat is present crystallization begins at higher temperatures according to the amount present. A lard containing ten per cent. of beef stearin will cloud at a higher temperature than pure lard stearin.

Microscopical examination of the fat crystals deposited from ether is of value for the identification of beef fat when present in large enough amount. When only small amounts of oleostearine are present the test is not as conclusive as the cooling test, unless recrystallization is resorted to.

Crystallization-point of the Fatty Acids.— This method, first proposed by Dalican, has for a long time been considered a valuable criterion and is a very useful factor in passing upon the purity of a lard.

The crystallization-point depends upon the relative amounts of solid and fluid acids present, being higher of course in proportion to the increase in the former, but unfortunately the thermometer readings are not in exact ratio to the amounts added.

As the relative amounts of the fluid and solid acids vary in different parts of the same animal it is quite evident that pure lards will show quite different points of crystallization, according to the portion of the animal from which they have been prepared, and also according to the individual, as shown by the results on lards rendered in the U. S. Agricultural Laboratory in Washington and in the writer's laboratory in Chicago some years since.

Part of hog.	According to Wiley.	Wesson.
Head	36.6	35.4
Intestine	42.7	41.2
Leaf	41.3	41.5
Back and sides	...	39.7
Belly	...	39.7
Foot[2]	32.1	...

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[1] *Ztschr. Anal. Chem.*, *1892*, 584 to 537.

[2] This sample was prepared by a packer but well authenticated.

The crystallization-point of Prime Steam lard or the lard of commerce, varies from 35.5 to 38. The majority of receipts during the past year have shown an average to 36.5, which would indicate that more of the softer parts of the hog are now used than formerly, when the average was one degree higher.

Lard oil has a crystallization-point of 31°–32°, while well pressed lard stearin should show not less than 43.5°.

Considering the wide range in crystallization-point of pure lard, we can only regard the test as a corroborative one, and useful in connection with others in passing upon the purity of a lard, but of little value in proving presence of small amounts of either cotton oil or beef fat.

IODINE ABSORPTION.

As the amount of iodine absorbed by a fat depends upon the chemical nature and quantity of the fluid acids present it is evident that in the case of lards it is impossible to draw sharp conclusions, for the softer the lard the more iodine absorbed and conversely. If a standard for purity of lard should be established saying that the correct absorption should be a certain figure, there would be little trouble for the adulterator to make a mixture of cotton oil and beef fat which would fully meet the requirements, and thus make the iodine number prove nothing so far as purity of a lard is concerned. An example or two will make this apparent.

	Iodine number.		
Cotton oil	108	10 parts.	10.80
Oleostearin	21	10 "	2.10
Steam lard	64.5	80 "	51.80
Mixture has iodine number			64.50

and contains twenty per cent. of adulteration. The number 64.5 is very near the average for Prime Steam lard and well within limits. Another case would be that of a mixture of intestinal lard testing 52 and cottonseed-oil testing 108, which would contain twenty-five per cent. of the latter and still test 65, while with twenty per cent. cotton-oil the sample would have an absorption of but 63.

In our first example the Dalican temperature of crystallization would be raised a little above normal by the oleostearin, while in the second instance it would be about normal for pure lard. By normal we mean the temperature of crystallization corresponding to the amount of fluid acid indicated by the iodine number.

Besides the variations caused by the fat being taken from different parts of the hog, we have the difference in individual animals, caused by difference in feed. For instance, Wiley.[1] found on testing the lard rendered in his laboratory from different parts of the same animal, figures which differ considerably from the writer's, as shown in the following table:

	Wiley		Wesson.	
Portions of animal.	Iodine No.	Point of crystallization.	Iodine No.	Point of crystallization.
Head	85.03	36.6	60.35	35.4
Intestine	57.34	42.7	52.14	41.2
Leaf	62.55	41.3	56.88	41.5
Back and sides	. . .	...	57.41	39.7
Belly	....	...	58.82	37.7

The results would seem to indicate that one of these hogs judged by the others must have been sadly adulterated. In the writer's opinion, the animal operated on by Wiley, which was purchased in Washington, was very likely one which had gathered a portion of its adipose in the woods of Virginia and adulterated its fat with the oils from beechnuts and acorns. while the writer's hog was a plain, every day Western corn-fed specimen, such as generally comes to the Chicago packers.

The crystallization-points would certainly indicate that considerable differences in the character of the oleins must be the cause of the great differences in the iodine numbers.

To observe the effects of age on samples, those of the writer cited above were tested again after three months standing in the laboratory at from 20° to 30° C., with the following results:

Head	63.64
Intestine	58.05
Leaf	61.02
Back and sides	60.50
Belly	63.95

Comparing these figures with those obtained on the fresh samples, which, if considered a standard of purity, would lead us to the conclusion that time had been adding some cotton oil. In

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[1] Lard and Adulteration Bulletin 13. Pt. IV. U. S. Dept. of Agriculture.

the case of the leaf lard the quantity would appear to be eight per cent.

That age acts in a similar manner on steam rendered lard we can see no reason to doubt.

As a rule the iodine numbers of steam lards run considerably higher than most of the published results on lards.

The iodine numbers of prime steam lard range as follows :

Sample.	Crystallization-point.	Iodine number.	Remarks.
5662	39.30	61.95	Wiley : Lard and Adulterations: samples drawn and sworn to by C. H. Mixer. the official inspector at Chicago.
5663	38.05	63.82	
5664	....	60.34	
5665	....	65.12	
5666	39.10	60.85	

Sample.	Crystallization-point.	Iodine number.	Remarks.
1	36.3	67.22	Lard from 400 tierces and different packers. Age of samples. six to twelve months. All samples prime merchantable lard. and unquestionably pure. Tests made in our laboratory.
2	36.0	65.25	
3	36.3	69.06	
4	36.5	69.26	
5	35.6	67.30	
6	37.0	65.31	
7	37.3	64.31	
8	35.0	68.48	

L. E. Spaeth[1] gives results on fats from different parts of eight different hogs and draws the conclusion that a lard must not be considered adulterated merely because its iodine number surpasses sixty. Spaeth's results are :

	Iodine number of fat from		
Age of hog.	Back.	Kidney.	Intestines.
Two years	63.25	61.15	62.90
Six to eight months	62.95	49.35	57.25
Ten months	55.50	55.88	50.60
Six months	60.10	55.80	52.30
Five to six months	57.08	50.20	51.75
Six to seven months	63.61	52.35	49.85
Ten months	60.95	46.60	47.60
Six to seven months	61.20	51.50	52.85
Mean	60.58	52.60	53.10

The above results are especially instructive as showing the great difference which exists between different animals as well as different parts of the same animal.

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[1] *Ztschr. Angew. Chem. 1893*, 133-136.

As commercial lard is nowadays made largely from heads, back, and side fat, it is easy to account for the high iodine absorption of prime steam lards.

IODINE NUMBER OF THE FLUID ACIDS.

As the fluid acids are the portion of the fat which absorb the iodine, and as the amount of fluid acids present in the fat determine its absorption, which also varies with the nature of the fluid acids present, it follows that the truly scientific method of analyzing a lard is to first determine the percentage of fluid acids present, and then from the iodine number of the fluid acids calculate the proportion of lard and cotton oil present.

This system of analysis was first published by Muter.[1] His process consists in precipitating the lead salts from a neutral solution, extracting the oleate with ether, decomposing the lead soap in the solution with dilute acid, determining the amount of oleic acid present by titrating a measured portion with standard alkali, and then determining the iodine number, using half a gram of the fluid acids under standard conditions. The process though tedious, gives very satisfactory results. Messrs. Muter and DeKoningh published some of the results of the process in the *Analyst*, *Feb. 1890*. They obtain for the fluid acids of tallow, 90; for lard, 93–94; while for cotton oil, 135.

N. J. Lane[2] reviews Dr. Muter's method, and describes an improvement which gives the results in much shorter time. His results, which were obtained in our laboratory, were as follows:

	Fluid Acids. Per cent.	Iodine number of same.	Hübl number of fat.	Saponification equivalent.	Crystallization-point of fatty acids.
Cottonseed stearin ·······	68.05	141.09	99.3	288.21	36.6
Summer yellow cotton oil	75.16	141.96	108.36	397.51	32.4
Winter yellow cotton oil··	77.64	143.49	110.96	296.27	30.4
Cotton oil, Columbia, S. C.	76.73	141.97	108.95	284.75	33.8
Cotton oil, New Orleans··	76.67	140.59	109.23	288.94	33.4
Steam lard, ave'ge sample	64.15	99.48	64.96	287.85	37.4
Corn oil (maize oil)······	83.97	144.40	121.7	·····	····
Arachide oil··············	79.84	114.00	93.55	·····	····

In studying the above table it will be noted in the case of cot-

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[1] *Analyst 1889.*

[2] This JOURNAL. 15, 110.

ton oil, that whatever variation there may be in the other constants, the iodine number of the fluid acids shows comparatively little variation.

The sample of steam lard mentioned was a composite sample of a number of lots of known purity, representing the article as made at that time.

Wallenstein and Finck[1] work with a modification of the Muter method, which guards more fully against oxidation of the fluid acids by contact with air.

They say: "In deciding qualitatively as to the purity of a fat it may be assumed that below the limit of ninety-six (iodine number of fluid acids) there is no admixture of vegetable oil (except it be cocoanut oil, which is however revealed by the saponification number of the sample). *Between ninety-six and 105 much depends on the origin of the fat.* For instance, Central European lards show ninety-three to ninety-six, while American lards vary between 103 and 106, and additional confirmation by Welman's or Bechi's test will be required to form a decisive opinion."

Results obtained are as follows:

	Iodine number of fluid fatty acids.	Iodine number of Glycerides.
Berlin ox tallow	92.2	38.3
Australian tallow	92.4	45.2
Hungarian mutton tallow	92.7	38.6
American western steam lard	104.5	65.4
Berlin hogs' lard	96.6	52.7
Hungarian hogs' fat	96.2	60.4
Viennese hogs' fat	95.2	60.9
Roumanian hogs' fat	96.0	59.5
White American cottonseed-oil	147.5	108.0
Yellow American cottonseed-oil	147.3	107.8
Yellow Egyptian cottonseed-oil	148.2	108.0
White English cottonseed-oil	146.8	106.5
White German cottonseed-oil	147.1	107.1
Yellow Peruvian cottonseed-oil	147.8	106.8
Maize oil	140.7	122.0
Arachis oil	128.5	98.5

The above results agree fairly well with Lane's, and are another contribution to the variation of hog fats. The authors attribute the high iodine absorption of the American lard to the

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[1] *Chem. Ztg.* 12, 1189-1191; also *J. Soc. Chem. Ind.* Jan. 31, *1895*, 78.

difference in feeding methods pursued in America and Europe. They are no doubt right, though the mode of rendering also differs.

At the present time the writer is aware of no method of analysis approaching the modified method of Muter for accuracy, and invariably applies it in doubtful cases.

G. Halphen[1] gives results of a method of separating the fluid and solid fatty acids based on difference in solubility of zinc salts in carbon bisulphide. Their results show that very imperfect separations are obtained and the process has little practical utility. The writer tried the same method in 1888, using gasoline, and obtained better but not satisfactory results.

In conclusion, I would say that working with the best analytical methods at our command, unless the origin of samples is known, the analyst is frequently at a loss to interpret results, in much the same manner as in passing upon a potable water of unknown history, and often when we see the self-confident manner in which small percentages of cotton oil are announced on very questionable data, we feel like exclaiming with the poet,

> "Fools rush in where angels fear to tread."

March 12, 1895.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 7.]

THE ACTION OF HALOID ACIDS IN GAS FORM UPON THE SALTS OF ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

BY EDGAR F. SMITH AND FRED. L. MEYER.

Received May 3, 1895.

AFTER observing the conduct of salts of the acids of elements of Group V toward hydrochloric acid gas, it was but natural that we should, with some interest, note the results arising when the other haloid acids, in gas form, were substituted for hydrogen chloride. It was useless to predict what might occur, and. therefore, the slight variations from preconceived notions were in no wise surprising. Taking up the study of the haloid acids and the various salts in the order of increasing molecular magnitude, we began with

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[1] *J. de Pharm. et Chim.*. 30, 241-247. *1894.*