THE PHOSPHOMOLYBDIC ACID TEST AS APPLIED TO LARD ANALYSIS.

By George F. Tennille.

Received November 5, 1894.

THE phosphomolybdic acid test has been of late so strongly recommended for use in the detection of cottonseed-oil in lard that it seemed to the writer that the record of the results of a rather thorough trial of this reagent would be of interest to chemists.

The test was originally proposed by P. Welmans in the *Pharm. Zeit.*, *1891*, **36**, 798. One gram of the oil or fat was dissolved in five cc. of chloroform, two cc. of phosphomolybdic acid solution were added, and the mixture shaken. On standing, the liquid separated into two layers, the lower of which was colorless and the upper of which had become green, if any vegetable oil were present. The addition of an alkali changed the green to a blue color. Lard, tallow, goose fat, and butter fat were said not to show any green coloration, and the only animal oil which gave the test was cod-liver oil.

It was supposed that at last the reagent had been discovered which would serve to detect any addition of cottonseed or other vegetable oils to lard, no such one test having previously been satisfactory. Very shortly this reaction was recommended for such a use by a number of chemists. Among others, Engler and Rupp, Wimmer, Mansfeld, and Goske approved of its efficacy. H. Schweitzer and E. Lungwitz (*J. Soc. Chem. Ind.*, *June*, *1894*, 614) state that they have found the reagent of great use.

Wallenstein, the first to criticise the test, (*J. Soc. Chem. Ind.*, *1893*, 55) states that tallow gives a green colóration when tested with the phosphomolybdic solution. To satisfy myself in regard to this point raised by Wallenstein I have tested a large number of samples of tallow, and other qualities of beef fat—such as might be used in adulterating lard or in the manufacture of compound lard—and have in no case obtained a green color.

J. Lewkowitsch (*J. Soc. Chem. Ind.*, *June*, *1894*, 617) has made an extended series of experiments with different fats and

oils in regard to the colors given with phosphomolybdic acid. He writes in part as follows: "Of all the samples only lard had remained colorless and there seemed to be ground for the opinion that cottonseed-oil or any other seed-oil employed for adulteration might easily be detected by phosphomolybdic acid. I prepared, therefore, a number of mixtures of pure, freshly rendered lard, yielding no coloration with Welman's test and of cottonseed-oil giving a distinct blue reaction." In testing these mixtures, he found that up to those containing thirty-five per cent. of cottonseed-oil the color of the upper layer was yellow, and at thirty-five per cent., on making this test alkaline, he only obtained a faint blue coloration. He continues: "This table clearly demonstrates the necessity of using Welman's test with great caution. In practical analysis an adulteration of ten per cent. cottonseed-oil would escape detection if freshly rendered lard had been used. Indeed, pure lard mixed with fifteen per cent. cottonseed-oil gave reactions just like sample number sixty-three in the preceding table." (Sample number sixty-three was a lard slightly rancid, six years old and gave a test remaining yellow when acid, and only faintly blue when alkaline.) "Welman's reaction can therefore be admitted only 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 given sample has to be carried out and may serve as a useful corroboration of results obtained by other methods."

Of course it is understood that the original color of the phosphomolybdic acid solution is a decided yellow. The green color produced by a certain sample is not of as deep a shade as the corresponding blue color when the acid has been neutralized by ammonia. Hence a light green tinge, which would be difficult to observe on account of the initial yellow color of the reagent, would be most readily seen when changed to a blue by the alkali.

Of all the samples of cottonseed-oil, which I have tested, each one gave a green color, though I find that the color varies much in depth with different oils. It seems to be a general rule that the more refined the oil the less heavy the coloration. Thus a crude oil will color intensely green, a yellow oil perhaps less so,

and a white oil still less. The age of the oil and the method of refining also in a great measure modify the color. In his tests on percentages, J. Lewkowitsch states that he used in making the mixtures a cottonseed-oil which gave a distinct blue reaction. The oil probably did not, therefore, show a deep green coloration and the test on the oil had to be made alkaline to produce a color which was decided. He must have used, I should judge, either an unusual oil or a weak solution of the reagent. For such oils as would commonly be employed for adulterations or compounding I think that ten to fifteen per cent. in a mixture would show a decided green coloration.

Samelson (*Ztschr. anal. Chem.*, *1894*, 189) comes to the conclusion that the phosphomolybdic acid test is of no value and that the iodine-absorption figure is the only reliable test for the detection of cottonseed-oil in lard. He states that six samples of American lard are undoubtedly impure because they have Hübl figures of from 64.7 to 67.2, which are higher than any figures hitherto recorded by scientific investigators for pure hog fat. On this assumption hangs the result of his investigation of Welman's test.

I have often tested lards of undoubted purity for their iodine-absorption figures and obtained results as high as from 62.7 to 66.4. On the other hand, as will be seen later, the Hübl figures for pure lard can run as low as 47.7. It must be remembered that lards are sold in large amounts in the American market which do not represent the whole fat of the hog, but simply a portion. It is a well-known fact that fats from different parts of the hog vary greatly in their iodine figures, hence, lards made from different portions of the fat would also vary. Wiley (U. S. Dept. Ag. Bul., 13, Lard and Lard Adulterations, 1889), states in order to show the great difference in the absorption power for iodine of the different fats of the hog, as follows, "For instance, a sample of intestine lard absorbed 57.34 per cent. of iodine; the leaf lard from the same animal absorbed 52.53 per cent.; the foot lard 77.28 per cent.; the head lard 85.03 per cent. In the prime steam lards mentioned the percentage of iodine absorbed was from 60.34 to 66.47 per cent., and the mean 62.86 per cent." The iodine test alone would certainly not be of much service for

the detection of vegetable oils in lard, when the iodine figure of the lard itself may vary as I have found, from 44.70 to 66.40. As may be calculated, thirty per cent. or more of cottonseed-oil could be added to a lard with an iodine figure of 44.7 without the iodine figure of the mixture reaching beyond the figures of pure lard. Hence it will be seen, I think, that the condemnation of a lard as adulterated with cottonseed-oil on the ground of a high iodine figure would be hasty and might easily be erroneous.

In the literature, then, of this test up to the present time, the preponderance of the writing is in its favor, and only two legitimate limitations are placed upon its accuracy, one, that tallow might give the same results as cottonseed-oil, and the other, that a certain comparatively small percentage of cottonseed-oil might escape detection. At first blush, one would think, therefore, that the test would be of value in preliminary examinations of samples suspected of sophistication; namely, that a negative test would show the lard contained not more than ten per cent. of cottonseed-oil, and, as the addition of less than ten per cent. would hardly pay the renderer, was, therefore, probably free from vegetable oils, and that a positive test would almost conclusively point to the presence of a vegetable adulterant.

After the careful examination of a great number of lards I have come to the conclusion that a positive test does not prove the presence of such an adulteration.

In my investigation the test has been carried out as follows:

About one gram of the melted fat is placed in a test-tube and dissolved in five cc. of pure chloroform, two cc. of a ten per cent. solution of phosphomolybdic acid are then added and the test-tube vigorously shaken. After standing, and the mixture having separated into two layers, the color of the upper liquid is observed by comparison with a test run in exactly the same manner on a sample of pure laboratory rendered lard. I do not consider a test as decisive unless a very apparent green tinge appears, relying more upon the green coloration than upon the slight blue shades produced after making doubtful greenish-colored tests alkaline with ammonia.

The lards upon which most of my tests were made were of

those grades known in New York City as No. 1 lard, Prime City lard, and Prime Western lard. A brief account of the manner in which these lards are rendered and their difference in fat composition may be of help to the better understanding of their often dissimilar chemical properties. These three grades of lard make up the bulk of the lard sold to the refiners in the vicinity of New York City.

No. 1 lard generally sells at a trifle lower figure than Prime City lard, say as a limit, half a cent per pound, though often it commands the same price. It is a harder fat than City or Western and is all steam-rendered. In color it often has a distinct green tinge and will generally carry a higher steam flavor. It is rendered by the slaughterers and is made up of gut fat with once in a while a little trimmings. No leaf lard is in it as the leaf is sold with the carcass to the butchers. After slaughtering, the fat is stripped from the still warm intestines and carefully washed and goes together with a certain proportion of trimmings to the rendering kettle, where it is subjected to steam under pressure. When the process is complete the water, etc., is drained off and the lard placed in tierces for sale. This lard is made in and about New York City, the hogs being brought from the West and slaughtered here.

Prime City lard is made by the butchers and may be either rendered in open kettles with free fire or steam-rendered in the same manner as No. 1 lard. This lard sells as a usual thing one-half cent per pound below Prime Western lard. The kettle-rendered is darker in color than the steam lard and has a characteristic taste and smell.

City lard is made of the trimmings, head fat, foot fat, backbone fat (perhaps some back fat), and any leaf which can not be sold over the counter, which fats accumulate in large amounts in the butcher shops. There is seldom any leaf lard in it as the leaf can be sold more profitably at retail for domestic rendering. The lard is usually a trifle softer than Western lard and not as good in color or flavor though better in these respects often than the No. 1 lard.

Prime Western lard is steam-rendered, of good color, high steam flavor, and a harder fat than City, but less so than No. 1.

It is rendered by the large slaughtering houses of the West in immense quantities and consists of gut fat and sometimes a little trimming.

Head fat often goes into this lard and the leaf at times may be a constituent. But only when the leaf can not be sold in the form of "neutral" lard for butterine does leaf lard find itself in the Western lard. Some back-bone fat at times may be present. The lard is shipped to the East in tierces and tank cars.

The first sample of No. 1 lard tested gave a decided green color. After further analysis the absence of any vegetable adulteration was pretty conclusively proven, and thinking that this might be a sporadic case only, samples of this grade of lard were obtained from all the firms who were rendering it in the vicinity of New York. On testing, each sample gave an undoubted green coloration, some, however, being more decided than others. After further examination of the lards it was decided that they

	Hübl figure.	Titre °C.	Rise of temperature with sulphuric acid, °C.	Bechi's silver nitrate test.	Milliau's silver nitrate test.	Wellman's phosphomolybdic acid test.	Microscope.	Free fatty acid. Per cent.	Specific gravity, 98° C. 15° C.
1.	54.5	41.4	30.5°	Negative.	Slight discoloration.	Decided green. Blue if alkaline.	Lard only.	...	.....
2.	55.6	41.4	31.8°	"	"	" "	"	...	.....
3.	58.6	40.2	34.8°	"	"	" "	"	...	.....
4.	53.7	41.4	30.0°	"	"	" "	"	0.73	0.8595
5.	55.4	41.4	31.5°	slight discoloration.	"	" "	"	...	.....
6.	56.1	41.4	31.7°	negative.	"	" "	"	...	.....
7.	47.7	42.4	25.5°	slight discoloration.	"	" "	"	...	.....
8.	51.7	41.8	31.5°	negative.	"	" "	slight indication of beef.	...	.....
9.	52.0	41.9	29.5°	slight discoloration.	"	" "	" "	...	.....
10.	48.9	...	...	.....	.....	" "	.....	...	.....

were pure hog fat. To corroborate the results a sample of the stock from which the lard is rendered was procured and after cleansing, was rendered in the laboratory. The resulting lard gave a decided green coloration with phosphomolybdic acid. The tests made upon nine samples of No. 1 lard and one sample of lard rendered in the laboratory from No. 1 lard stock may be seen in the table. Lards 1 to 9, inclusive, are those obtained

from the renderers. Lard 10 is that rendered in the laboratory.

The iodine-absorption figure was obtained in the usual manner, great care being taken in the manipulation, duplicates being run, blanks carried through with each test, and the flasks in which the determinations were made being furnished with ground-glass stoppers and gutters to hold a solution of potassium iodide seal, to prevent as far as possible any loss of iodine in vapor.

The "titre" is the crystallization temperature of the separated, washed, dried, and filtered fatty acids. The highest point which the mercury reaches, after the rise of temperature due to the liberation of the latent heat has begun, is the temperature recorded.

The rise of temperature with sulphuric acid is of no absolute value as each chemist has his own method of manipulation. The results of the test are simply given for comparison with each other in connection with the corresponding Hübl and "Titre" figures.

The Bechi test was carried out upon the glycerides using an alcoholic solution of silver nitrate. The words "slight discoloration" do not indicate the presence of cottonseed-oil which, in appreciable amounts, produces heavy blackening and often a silver mirror.

The Milliau modification of the Bechi silver nitrate test was carried out upon the fatty acids and the discoloration produced in each case was of a very slight character.

Welman's phosphomolybdic acid test on each sample showed a decided green color and on saturation of the mixture with ammonia the test turned a decided blue. By the words "decided green," in the table is meant, not a greenish yellow tinge, but a green color that was unmistakable to the eye. On the other hand, the tests were not of that deep emerald shade, such as a large percentage of cottonseed-oil would exhibit.

The microscopical examination was carried out upon crystals formed from saturated solutions of the fats in ether and showed in but one case any suspicion of the presence of beef fat, and here, sample 8, the result was doubtful.

The free fatty acid percentage was obtained in the usual way by titration and the use of phenolphthalein as indicator. The result was calculated to oleic acid.

The specific gravity was taken with a Westphal balance, the fat at a temperature of 98° C. being compared with an equal volume of water at 15° C. No correction was made for the expansion of the glass of the bob.

These lards were all hard fats with generally a high steam flavor, but with an inferior color.

It will be seen that there is quite a variation in the Hübl figures of the lards in the table; *viz.*, from 47.7 to 58.6. This is explained on glancing through the next column, when one notices that the titre decreases with approximately the same regularity with which the Hübl increases. The titre is a good guide to the hardness of the fat, that is, to the proportion of liquid to solid glycerides. As the amount of oleic glyceride increases in proportion to the amounts of stearic and palmitic glycerides, the fat becomes softer, the titre test is lower, and consequently, owing to the greater preponderance of unsaturated glyceride, the iodine-absorption figure becomes higher. The lards then owe their difference in Hübl figures to the difference in their fat composition. In the different rendering establishments, the proportion of fats used from different parts of the hog evidently varied. I consider that all the samples consisted of pure hog fat without any cottonseed or other vegetable adulteration. What constituent of this class of lards it is that has the reducing action upon the phosphomolybdic acid, I do not pretend to say. Whether it is a normal product of that portion of the fat of the hog, or simply an impurity introduced or not eliminated in the rendering process, or a peculiarity imparted to the fat at certain seasons of the year, or due to feeding, I am undecided.

Nearly all of the many samples of City lard, both steam and kettle-rendered, tested gave a negative result. In one or two cases, slight green tinges were observed. Of the fifty-seven undoubtedly pure samples tested, each representing on an average 100 tierces of lard, fifty gave no green color and seven gave a slight green tinge.

Western steam lard often gives a slight green test. Of the twenty-nine undoubtedly pure samples tested, each representing on an average 100 tierces, nineteen gave no green and ten a

slight green color. The tests were not as decided as those on the No. 1 lard but still distinctly visible. These results are probably due to the presence of the large percentage of No. 1 lard which the Western lard contains.

I might say further that lard rendered from the leaf alone, which does not, as far as I know, find its way to the lard market in this country, does not give a green color with the reagent. This fact may have been the cause of the many favorable endorsements which appeared after the first publication of the reaction. In order for the chemist to make a fair trial of the reagent, what, apparently, would appear fairer than to obtain a leaf and render it in the laboratory and make tests upon this lard?

In conclusion, I would say, that for the detection of less than ten to fifteen per cent. of cottonseed-oil the test is unreliable, as, in such an instance, no reaction may be produced. When a slight green is the result of a test, the presence of cottonseed-oil is not proven. When a heavy green color, deep emerald in shade, is obtained, the addition of a vegetable oil in considerable amounts is fairly certain. But it is easy to detect such large additions by other methods, and 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 cottonseed or other vegetable oils in lards.

LABORATORY OF THE CENTRAL LARD COMPANY,
October 29, 1894.

SOME NEW SOLVENTS FOR PERCHROMIC ACID.[1]

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Received November 8, 1894.

ON the addition of hydrogen peroxide to an aqueous solution of potassium dichromate acidified with sulphuric acid, a blue color is produced, which is supposed to be caused by the formation of perchromic acid. Ether dissolves the blue substance, forming an intensely colored, deep blue solution. On standing, the perchromic acid in this solution decomposes with the formation of chromic acid or salts of chromium.

Recently, Griggi (*J. Chem. Soc.*, **64**, 2,223) has stated that

[1] Read before the New York Section, December 8, 1893.