dehyde gave the same characteristic coloration in the same period of time. It is necessary for accurate work that equal amounts of the unknown and known solutions be taken, and that the amounts of the morphine solution used should be the same; also the evaporating dishes and the watch-glasses should be alike both in size and shape.

SUMMARY.

This method gives not only a simple means of detecting formaldehyde, but in the case of liquids allows of its estimation. It is applicable when the formaldehyde is present with a great variety of substances and can be adapted with almost equal facility to both liquid and solid products.

In conclusion I wish to thank Dr. L. W. Andrews for his kind suggestions.

WORCESTER POLYTECHNIC INSTITUTE,
February 16, 1905.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 105.]

THE INFLUENCE OF ATMOSPHERIC OXIDATION UPON THE ANALYTICAL CONSTANTS OF FATTY OILS.

(SECOND PAPER.)

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IT HAS been shown[1] that non-drying and semi-drying oils, on exposure to air, undergo changes similar to those which take place when the corresponding fatty acids are treated with potassium permanganate in alkaline solution, oleic acid being apparently converted into dioxystearic, and linoleic into sativic acid. The "oxidation," therefore, appears to result mainly in the addition of hydroxyl groups, two of these groups taking the place which, in the determination of the iodine number, would have been taken by two halogen atoms. If, as stated by Ballantyne,[2] atmospheric oxidation causes no change in the volume of the oil, the increase in specific gravity and the decrease in iodine absorbing power are to each other as the weight of the hydroxyl group is to that

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[1] This Journal, **25**, 711 (1903).

[2] *J. Soc. Chem. Ind.*, 10, 29 (1891).

of the iodine atom. Calculating both of these changes on the basis of the original weight of oil the relation would be:

Percentage increase in specific gravity : Decrease in iodine number : : OH : I or as 1 : 7.46.

This calculation was applied to "exposed" samples of olive, lard, cottonseed, maize and poppy-seed oils, and has been used successfully by students in identifying "unknown" oils, which had been so altered by exposure as to give iodine numbers considerably below the normal limits. Additional experiments have recently been made to determine whether the proportion applies with equal accuracy, when the oxidation is allowed to go farther. Determinations of acidity and of index of refraction have also been made in some cases.

The principal results are shown in the following table:

INFLUENCE OF EXPOSURE UPON SOME OF THE ANALYTICAL "CONSTANTS."

Description of oil.	Specific gravity $\frac{15.5^\circ}{15.5}$ (D)	Iodine number.	Free acid calculated as oleic. Per cent.	Index of refraction at 15.5° (N)	Specific refractive power $\left(\frac{N-1}{D}\right)$
Neatsfoot, fresh	0.9160	60.9	....	1.4685	0.5115
" after exposure	0.9285	51.2	10.67	1.4692	0.5053
Lard oil, I, fresh[1]	0.924	69.3	....	......	......
" after exposure	0.943	54.6	9.98	......	......
Lard oil, II, fresh	0.917	73.3	0.90	1.4697	0.5122
" after exposure	0.943	56.2	4.96	1.4724	0.5010
Sperm, fresh	0.886	78.5	....	......	......
" after exposure	0.926	48.9	5.85	1.4724	0.5102
Olive, fresh	0.9165	83.8	2.65	1.4712	0.5141
" after exposure	0.924	77.3	....	1.4722	0.5100
Almond, fresh	0.919	97.0	5.92	......	......
" after exposure	0.9355	83.9	7.84	......	......
Cottonseed, I, fresh	0.920	102.8	0.14	......	......
" after exposure	0.938	89.9	2.96	......	......
Cottonseed, II, fresh	0.923	105.2	....	1.4737	0.5132
" after exposure	0.939	90.2	....	1.4779	0.5090
Maize, I, fresh	0.924	117.2	....	......	......
" after exposure	0.939	105.7	....	......	......

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[1] This sample may have begun to change before the first examination, as the specific gravity is abnormally high.

Description of oil.	Specific gravity $\frac{15.5^\circ}{15.5}$ (D)	Iodine number.	Free acid calculated as oleic. Per cent.	Index of refraction at 15.5° (N)	Specific refractive power $\left(\frac{N-1}{D}\right)$
Maize, II, fresh[1]	0.9213	118.6	1.13	1.4764	0.5171
" after exposure	0.990	63.4	12.52	1.4779	0.4827
Linseed, I, fresh	0.934	177.1	1.26	1.4835	0.5177
" after 1st exposure	0.954	148.1	2.05	......	......
" " 2nd "	0.969	136.9	....	1.4886	0.5042
Linseed, II, fresh	0.934	180.2	1.33	......	......
" after 1st exposure	0.942	165.8	2.23	......	......
" " 2nd "	0.966	140.1	4.48	......	......
Linseed, III, fresh	0.934	184.8	....	......	......
" after exposure	0.951	160.0	....	......	......
Linseed, IV, fresh	0.9345	186.3	....	......	......
" after exposure	0.948	159.1	....	......	......

It will be seen that, in the case of every oil examined, the index of refraction had increased at the same time with the specific gravity, but not to the same extent, so that the specific refractive power calculated by Landolt's formula $\left(\frac{N-1}{D}\right)$ is in each case considerably diminished.[2]

In testing oils of unknown history, this fact will be found useful. An oil having low iodine number and specific refractive power, with high specific gravity, index of refraction and Maumené number may be considered as having undergone partial oxidation, as the result either of exposure or of "blowing."

When the iodine numbers of the oxidized ("exposed") oils are corrected on the basis of the change in specific gravity, according to the theory, as explained above, the results obtained are all within the normal variations of oils of the same species;[3] but

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[1] This was one of the samples used by Vulté and Gibson in their investigation of maize oil (this Journal, **22**, 453 (1900); **23**, 1 (1901). Professor Vulté having kindly furnished one of us a small portion of the sample at that time, it was kept in a partially filled bottle for five years. When examined at the end of this time the oil had become so viscous as to be barely fluid at 15.5° so that the specific gravity could not be determined with certainty to the third decimal place.

[2] Compare the results obtained in the examination of a rancid butter fat by Browne, whose paper (this Journal, 1899, **21**, 975-994) includes a review of the earlier work.

[3] The discussion in the text applies only to non-drying and semi-drying oils. The results of our experiments on partially oxidized linseed oils are included in the table for comparison and reference although they are not sufficiently uniform to suggest a factor for correcting the iodine numbers of such oils.

the agreement with the original iodine numbers is not always as close as the accuracy of the analytical methods would allow. Probably a simplified method of correction will be found fully as accurate and more convenient. The following is suggested:

To find the original iodine number of a semi-drying or non-drying oil, which has been altered by atmospheric oxidation, add 0.8 to the iodine number found on the altered sample for each increase of 0.001 in the specific gravity $\left(\text{taken at } \frac{15.5^\circ}{15.5^\circ}\right)$

The last column in the following table shows the results obtained by correcting according to this rule.

CORRECTION OF IODINE NUMBERS OF OXIDIZED OILS.

			Iodine number after exposure.		
No.	Description.	In fresh condition.	Without correction.	Corrected according to theory.	Corrected by simplified method.
1.	Neatsfoot oil	60.9	51.2	61.9	61.2
2.	Lard oil, I	69.3	54.6	71.0	69.8
3.	Lard oil, II	73.3	56.2	78.8	77.0
4.	Sperm oil	78.5	48.9	84.7	80.9
5.	Olive oil	83.8	77.3	83.8	83.3
6.	Almond oil	97.0	83.9	97.8	97.1
7.	Cottonseed oil, I	102.8	89.9	106.2	104.3
8.	Cottonseed oil, II,	105.2	90.2	104.7	103.0
9.	Maize oil, I,	117.2	105.7	119.4	117.7
10.	Maize oil, II	118.6	63.4	124.1	118.4
	Average	90.86	.....	93.24	91.27
	Average omitting (No. 3)	92.81	.....	94.84	92.86

It will be seen that the simple rule suggested above, gives results sufficiently accurate for all ordinary purposes, even when applied to oils which had lost from 15 to 45 per cent. of their original iodine absorbing power. It is applicable to sperm oil as well as to fatty oils.

When the original specific gravity is not known, the calculation must be based on the average specific gravity for the species of oil under examination. Any error involved in this assumption will be too small to affect seriously the interpretation of the results.

QUANTITATIVE LABORATORY,
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