A sample of Merck's urea gave 20.28 per cent carbon against a calculated 19.99 per cent, while sucrose gave 41.98 per cent against a calculated 42.08 per cent. It is probable, as has already been noted by Salter,[1] that any oxides of nitrogen which may be formed are reduced in the zinc tube and hence are not a source of error in the determination.

SUMMARY

A simple, inexpensive apparatus is here reported for the determination of carbon in soils and similar substances by the wet combustion method, using chromic and sulfuric acids. The total time for the determination is about 25 min. Data have been presented showing that the method as outlined is subject to errors of small magnitude.

DIVISION OF SOIL CHEMISTRY AND BACTERIOLOGY
AGRICULTURAL EXPERIMENT STATION
BERKELEY, CALIFORNIA

EFFECT OF EXPOSURE ON RAW LINSEED OIL

By E. J. SHEPPARD

Received October 28, 1918

The most important property of linseed oil is that, when spread in thin layers and exposed to air, it absorbs oxygen and undergoes little-known changes in composition, yielding an elastic solid skin. This phenomenon is termed "drying" and on it depends the extensive industrial use of linseed oil in the manufacture of paint, varnish, linoleum, etc.

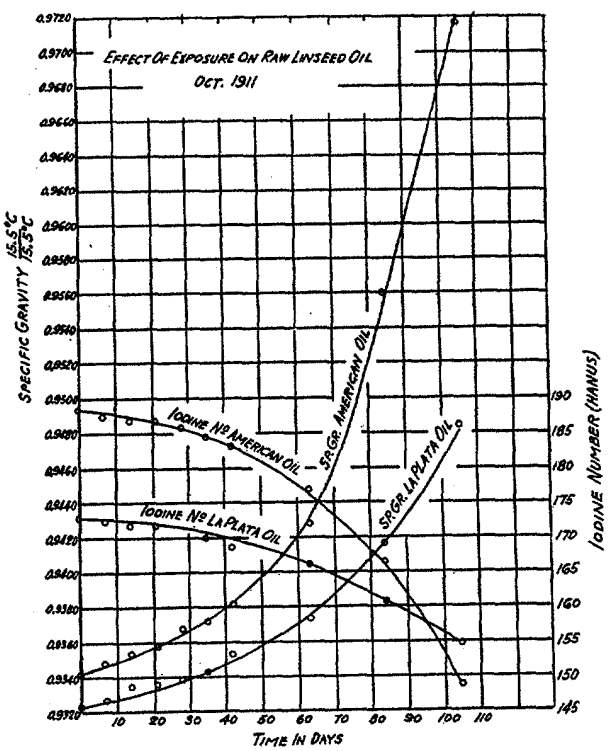

FIG. 1

The changes which take place in linseed oil when exposed to air have been studied by a number of investigators. Ballantyne[1] allowed linseed oil to stand in an uncorked bottle exposed to light. The oil was shaken daily and at intervals analyzed. Ballantyne found that under these conditions the iodine number decreased, while the specific gravity and acid number increased without a change in volume.

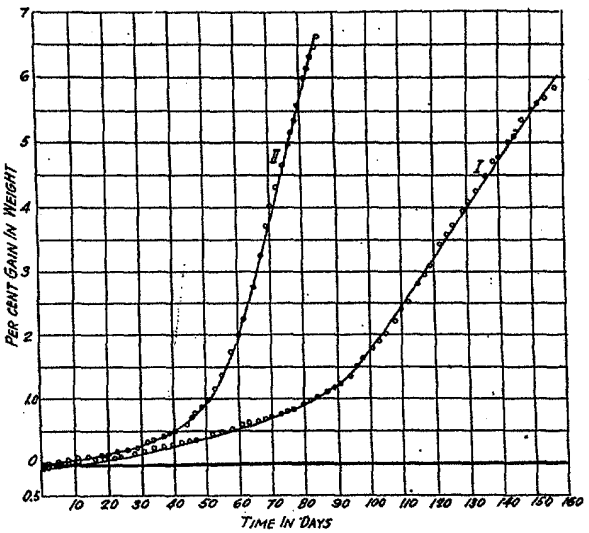

FIG. 2—EFFECT OF EXPOSURE ON RAW LINSEED OIL.
I = 0.95 Sq. Cm. Surface per Gram Oil
II = 2.00 Sq. Cm. Surface per Gram Oil

Sherman and Falk[2] studied the same question similarly and found a lower iodine number and higher specific gravity and a small increase in acidity. These authors found a 3.43 per cent increase in specific gravity calculated on the original weight, while elementary analysis showed that the oil had taken up 3.16 per cent oxygen. They concluded that the greater increase in specific gravity was probably due to a slight contraction in volume.

Sabin[3] exposed raw linseed oil in thin films for 8 mo. and found a specific gravity of 1.098 and a gain in weight of not more than 2 per cent. Assuming a specific gravity of 0.932 for the original oil, Friend[4] calculated a contraction in volume of 13.4 per cent for Sabin's film.

Thompson[5] exposed two varieties of raw linseed oil in thin films for 212 days and found

	Sp. Gr.	Gain in Wt. Per cent	Decrease in Vol. Per cent
North American Oil....	1.16	8.25	13.0
South American Oil.....	1.15	7.70	12.4

Friend[6] oxidized raw Calcutta oil by passing air through the oil and by spreading in thin films on glass. He found that as the oil gained in weight the density increased, while the volume increased to a maximum and then slowly decreased.

Except for the determinations of Sabin, of Thompson, and of Friend, there are no data known to the writer

[1] THIS JOURNAL, 8 (1916), 637.

[1] *J. Soc. Chem. Ind.*, 10 (1891), 29.
[2] *J. Am. Chem. Soc.*, 25 (1903), 711; 27 (1905), 605.
[3] THIS JOURNAL, 3 (1911), 84.
[4] *J. Chem. Soc.*, 111 (1917), 162.
[5] *Trans. Am. Inst. of Chem. Eng.*, 8 (1915), 251.
[6] *Loc. cit.*

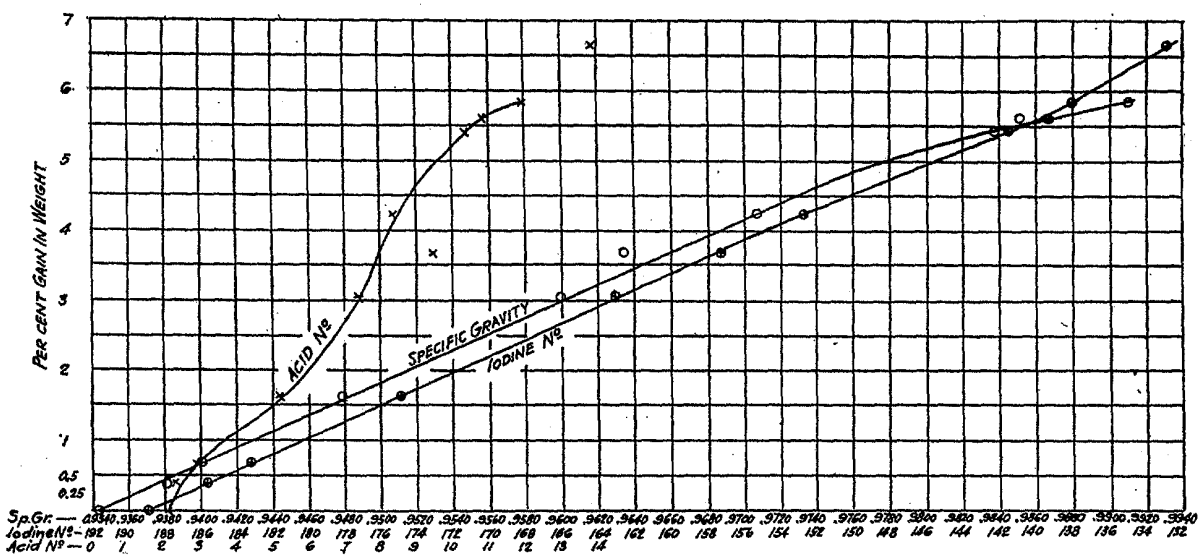

FIG. 3—CHANGES IN CONSTANTS WITH GAIN IN WEIGHT OF RAW LINSEED OIL

showing the variation of the constants with gain in weight of raw linseed oil on exposure to atmospheric oxidation. In 1911 the writer exposed two samples of raw linseed oil in shallow glass dishes of approximately 12.5 cm. diameter in a dust-proof glass top cabinet which permitted circulation of air. In order to prevent the formation of a skin, the oils were thoroughly stirred at least twice a day. At intervals the oil in each dish was thoroughly mixed and the specific gravity and iodine number determined, with the results as shown in Table I and Fig. 1.

TABLE I—EFFECT OF EXPOSURE ON RAW LINSEED OIL

	North American		La Plata	
Age Days	Sp. Gr. 15.5° C./15.5° C.	Iodine No. (Hanus)	Sp. Gr. 15.5° C./15.5° C.	Iodine No. (Hanus)
0	0.9342	188.4	0.9323	173.0
7	0.9348	187.3	0.9327	172.4
14	0.9355	186.8	0.9335	171.9
21	0.9357	186.8	0.9336	171.8
28	0.9368	185.6	0.9338	171.5
35	0.9372	184.6	0.9343	170.0
42	0.9382	183.2	0.9353	168.6
63	0.9428	177.0	0.9374	166.4
84	0.9561	166.4	0.9417	160.6
105	0.9717	149.0	0.9485	154.9

By withdrawing portions of the oils for determination of the constants, the volumes of the oils were gradually reduced, thus increasing the oil surface per gram of oil; or, in other words, decreasing the thickness of the oil layer. Now, since it is well known that, other things being equal, thin layers dry more rapidly than thick layers, these experiments suggested two questions: First, given layers of different thicknesses, are the changes in the constants the same for the same change in weight? Second, what is the quantitative effect of thickness of layer upon the rate of change in the constants?

In order to determine the variation of the constants for determined gains in weight, some pure, raw North American linseed oil was exposed in 10 shallow round glass dishes, eight of 9.2 cm. diameter and two of 9.7 cm. diameter, and the dishes kept in a glass top cabinet protected from dust but permitting circulation of air. About 70 g. of oil, accurately weighed, were placed in the eight smaller dishes, and about 36.9 g. in the two larger dishes. Each dish held throughout the test a glass stirring rod. Twice daily each sample was thoroughly stirred and at intervals the gain in weight noted. At longer intervals, the samples, one by one, were removed from the cabinet and certain constants determined. The length of exposure was limited by the formation of a skin, which would destroy the homogeneous character of the sample.

TABLE II—PER CENT GAIN IN WEIGHT OF RAW LINSEED OIL

Age Days	0.95 Sq. Cm. Oil Surface Per Gram Oil	2.0 Sq. Cm. Oil Surface Per Gram Oil	Age Days	0.95 Sq. Cm. Oil Surface Per Gram Oil	2.0 Sq. Cm. Oil Surface Per Gram Oil
1	—0.05	—0.04	71	....	4.14
2	—0.05	—0.015	72	....	4.30
3	—0.035	....	73	0.75	....
5	—0.025	+0.01	74	....	4.65
7	+0.01	....	75	0.80	4.78
8	....	0.05	76	....	4.96
9	0.03	....	77	0.88	5.14
11	0.04	0.065	78	....	5.33
12	0.04	....	79	....	5.58
14	....	0.10	80	0.92	....
16	0.06	....	81	....	5.99
18	....	0.115	82	0.96	6.14
19	0.07	....	83	....	6.31
20	....	0.135	84	1.01	6.46
22	0.08	....	85	....	6.63
23	....	0.18	87	1.11	....
24	0.11	....	89	1.18	....
26	....	0.20	91	1.23	....
28	0.15	....	94	1.36	....
29	....	0.24	96	1.50	....
31	0.19	0.32	98	1.64	....
34	0.23	0.36	101	1.79	....
37	0.25	0.42	103	1.91	....
39	....	0.47	105	2.01	....
40	0.28	....	108	2.21	....
41	....	0.50	110	2.42	....
43	0.33	....	112	2.57	....
44	....	0.61	115	2.80	....
45	0.34	....	117	2.95	....
46	....	0.70	119	3.09	....
47	0.35	0.77	122	3.41	....
49	0.39	0.86	124	3.58	....
51	....	0.99	126	3.72	....
52	0.45	....	129	3.93	....
53	....	1.16	131	4.08	....
55	0.48	1.37	133	4.23	....
58	0.525	1.74	136	4.49	....
60	....	2.00	138	4.69	....
61	0.60	....	140	4.76	....
62	....	2.25	143	5.00	....
63	0.625	....	145	5.09	....
65	....	2.76	147	5.33	....
66	0.655	....	150	5.49	....
67	....	3.25	152	5.60	....
68	0.69	....	154	5.68	....
69	....	3.71	157	5.84	....
70	0.71	4.02			

Table II and Fig. 2 give the time-gain in weight results. It is worthy of note that all samples showed a loss in weight during the first few days, although a well-settled oil was used. The longer the exposure the paler the oils became; Samples 6, 7 and 8, however, show practically no difference. The amount of oil placed in the large dishes made a layer about one-half as thick as the oil placed in the small dishes. In Fig. 2 the effect of thickness is clearly brought out showing that the thin layer gained in weight about twice as rapidly as the thick layer.

Without regard to the thickness of the layers, the evolution of pungent volatile products became distinctly noticeable when the oils had gained about one per cent in weight.

In Table III are assembled the analytical results shown in Fig. 3. Samples 7 and 8 skinned very slightly when 152 days old; this skin was stirred up with the oil and Sample 7 removed, while Sample 8 was continued 5 days longer, when it skinned again. It is remarkable to note, however, that Sample 10 did not skin, although it had gained about 1 per cent more in weight. There is a change in the specific gravity curve at the point of skinning of Samples 7 and 8 but no noticeable effect is produced in the iodine number curve. The acid numbers are rather irregular. Calculations of the per cent change in volume have been made but yield results not so decisive as those reported by Friend.

TABLE III—DATA SHOWING THE EFFECT OF EXPOSURE ON RAW LINSEED OIL

Sample No.	Age Days	Gain in Weight Per cent	Sp. Gr. 15.5° C. 15.5° C.	Iodine No. (Hanus)	Acid No.	Change in Volume Per cent	Relative Viscosity	Oil Surface per Gram Oil
Raw	0	....	0.9345	188.7	2.2	....	1.00	0.95
1	49	0.38	0.9383	185.2	2.4	—0.02	1.15	0.95
2	70	0.69	0.9403	183.0	3.0	+0.07	1.25	0.95
3	98	1.63	0.9481	174.6	5.3	+0.17	2.00	0.95
4	119	3.05	0.9602	162.8	7.5	+0.29	4.30	0.95
5	135	4.22	0.9710	152.4	8.5	+0.30	7.35	0.95
6	148	5.41	0.9840	141.2	10.5	+0.10	....	0.95
7	152	5.60	0.9854	139.2	11.0	+0.14	....	0.95
8	157	5.84	0.9913	137.7	12.1	—0.22	....	....
9	69	3.67	0.9638	157.0	9.6	+0.52	6.00	2.0
10	85	6.63	....	132.6	14.0	....	....	2.0

It was found that 1 g. of each of the oils would easily and completely dissolve in 100 cc. of benzene. The figures in column "Relative Viscosity" are rough approximations only and were obtained by measuring the time required for 10 cc. of the oil to flow from a pipette, taking the time of efflux of the raw oil as 1.00.

It will be observed in Fig. 3 that the iodine numbers of the oils in thin layers fall exactly on the curve of the oils in thick layers; while the specific gravity of Sample 9 is not far from the specific gravity curve of the thick layers.

SUMMARY

The effect of exposure on certain constants of raw linseed oil has been determined over a limited range of gain in weight. The thickness of the exposed layer of oil appears to affect only the rate of change in the constants. For any gain in weight over the range covered by these experiments, the changes occurring in the constants appear to be independent of the rate of gain in weight.

NATIONAL LEAD COMPANY
ST. LOUIS, MISSOURI

CARBON TETRACHLORIDE, CHLOROFORM AND CARBON HEXACHLORIDE FROM NATURAL GAS[1]

By G. W. JONES AND V. C. ALLISON

Received December 21, 1918

As a result of the war, the Government desired the maximum amount of carbon tetrachloride and chloroform to carry on the gas program. A great many of the gases used in modern warfare are derived from these sources. In view of the above fact, and also because after the war a great amount of chlorine, which is now being used for war purposes, will be turned back toward peaceful enterprises, the Bureau of Mines has undertaken an investigation on the production of useful products by the chlorination of natural gas and thus utilize part of this excess chlorine. The gas from many fields of natural gas in the United States which yield a pure methane gas, free from the higher saturated hydrocarbons, ethane, propane, etc., is especially desirable for making chlorinated products. The natural gas from several of these fields, notably those in Texas and Louisiana, in locations too far removed from industrial centers and large cities to warrant the expense of piping, could be successfully made into chlorinated products.

In this report only a preliminary survey of work done on a small scale is given and more elaborate results of the investigation will be published as the work develops.

A large amount of experimental work has been done along these lines during the last 25 years but so far nothing of practical value, that the authors are aware of, has been accomplished.[2] The general tendency has been to use a large excess of either chlorine or natural gas to prevent explosion. If a large excess of either gas is used the products desired are hard to separate from the excess of inert gas, since the deposition of the chloroform and carbon tetrachloride depends upon the partial pressure of these products in the gaseous state at the given temperature at which they are separated and the reaction cannot be controlled to produce the products desired. That the chlorination may work successfully there is required a catalyzer which will cause the reaction to proceed smoothly without explosions or deposition of carbon, and which will accomplish the substitution of the chlorine in the methane and ethane molecule according to the reaction $CH_4+4Cl_2=CCl_4+4HCl$ instead of the production of carbon and hydrochloric acid in accordance with the reaction $CH_4+2Cl_2=C+4HCl$. A great many catalyzers will cause chlorine and methane to react, when the temperature is high enough. In fact, no catalyzer is needed at all, but the reaction takes place violently and, being exothermic in character, explosively, and gives very little, if any, products other than carbon and hydrochloric acid. It is desirable to make the chlorination complete at one operation, hence if the desired product is carbon tetrachloride, four volumes of chlorine are caused to react with one volume of methane (natural gas), or in other words, the gases are caused to react in the ratios necessary to

[1] Published by permission of the Director of the Bureau of Mines.

[2] Phillips, Baskerville, and others.