A COMPARISON BETWEEN THE BROMINE AND IODINE ABSORPTION FIGURES OF VARIOUS OILS.

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An examination of the existing tables for the bromine and iodine figures for the various oils discloses so many inconsistencies and obvious inaccuracies that the need for a revision of these tables is apparent. Such a revision is offered as the result of the present investigation. The work has been very carefully carried out in accordance with the methods described below, and the figures given are the results of so many repetitions that there is comparatively little opportunity for error.

In regard to the comparative accuracy of the two figures, the bromine absorption figure presents some decided advantages. Errors in the determination of this are largely due to faulty manipulation, while the iodine absorption is affected by many outside circumstances, such as change in temperature, during the much longer time required for the operation. Furthermore, in the case of bromine, loss from substitution can be readily determined by the use of potassium iodate, while, in the case of iodine, this test is of comparatively little value. On the other hand, substitution is much more likely to occur in the case of bromine, which offsets, to a great degree, the objections to the use of iodine named above.

The details of the methods employed in the present investigation are as follows:

1. Iodine Absorption Figure.—A solution of mercury bichloride and one of iodine were made up according to the original method of Baron Hübl, that is, with at least one molecule of $HgCl_2$ to every 2 atoms of iodine. A solution of 0.10 normal sodium hyposulphite was then prepared and standardized by means of potassium bichromate. Equal parts of the first two solutions were mixed together and allowed to stand for twelve hours in the dark before use. Thin Erlenmeyer flasks, having ground-glass stoppers with gutter between flask and stopper, were used for this operation. A weighed portion of the oil was dissolved in 10 cc. chloroform, 25 cc. of the previously prepared mixed Hübl solution added, the flask sealed by filling the gutter with a solution of potassium iodide, and the whole set away in the dark for twenty-four hours. A blank was run in connection with each determination. A solution of potassium iodide was then added in sufficient quantity to prevent precipitation, and the contents of the two flasks titrated with the sodium hyposulphite solution. The flasks should be frequently shaken during the titration, in order that the layer of chloroform may be gradually deprived of color, and a sharp end reaction may be had. When the operation was nearly completed, a few drops of starch solution were added in order to obtain a sharper change in color. The starch solution should be added as late as possible in order to prevent carbonization.

2. *Bromine Absorption Figure.*—The determination of this figure was carried out almost exactly as proposed by Dr. McIlhiney[1] except that the wait before titration was increased to from twenty to thirty minutes. The end reaction is less sharp by this process than in the Hübl determination on account of a yellowish tinge in the liquid which masks, to some extent, the disappearance of the starch blue. It is to be noted also that, bromine being more unstable in character than iodine, decomposition of the addition-product more readily takes place and, therefore, a return of the blue color is more likely to follow decolorization. On this account the determination of the substitution-figure should be hastened as much as possible.

A table showing the results obtained with fifteen different oils, by the methods described above, follows. In this table the oils are given in the order of increasing divergence between the bromine and iodine figures. The oils examined are divided into five classes according to the characteristics which they present. The first class, comprising eight oils, shows so close an agreement between their bromine and iodine figures that it evidently makes but little difference in which way their addition-factor is determined. In fact, reasoning from analogy, we may assume that this is true of all vegetable oils of simple constitution, together with whale and lard oils.

Sperm oil, being a wax, is placed in a class by itself and, as might perhaps be expected, gives somewhat erratic figures.

The class comprising rape and castor oils presents marked char-

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acteristics. In the former oil, substitution seems to take place to a greater extent with iodine than with bromine; this is probably due to the greater length of time necessary to carry out the Hübl process. Traces of sulphur in rape oil, acquired during the process of manufacture, may also exert some influence upon the action of iodine on this oil. In the case of castor oil, the dihydroxy group may set up an oxidation which would account for the difference observed between the two values.

The complex structure of the three fish oils following, probably causes some absorption of bromine which is not direct substitution, but which accounts for the greater bromine figure observed.

		Iodine.	Iodine calculated from bromine.	Difference of averages.	Difference of nearest figures.
I.	Olive oil	79.70–80.40	80.31	0.26	0.09
	Cottonseed oil	97.50	97.41–97	0.295	0.09
	Poppyseed oil	127.98–128.55	128.37	0.055	0.28
	Linseed oil	155.12-155.52	154.80	0.52	0.32
	Sw't almond oil	90.53–89.64	90.20–89.64	1.08	0.33
	Peanut oil	100.71–100.76	101.26	0.523	0.50
	Whale oil	128.00	127.45–127.38	0.585	0.50
	Lard oil	76.99–77.36	76.03–75.88	1.22	0.96
II.	Sperm oil	79.95–79.76	82.39–82.08	2.422	2.13
III.	Rape oil	103.69–103.37	99.03–98.56	4.60	4.17
	Castor oil	86.32–87.15	78.74–78.71	8.01	7.58
IV.	Seal oil	93.31–93.99	103.09–103.74	9.765	9.10
	Cod-liver oil	122.09–122.79	132.86–132.18	10.08	9.39
	Menhaden oil	176.5–175.65	186.94–186.86	10.825	10.36
V.	Resin oil	59.67–58.95	10.60–10.26	48.845	48.35

Examination of numerous samples of many different oils would probably disclose some regularity of action, and might lead to the formulation of some rules and tests for the detection of oils, either in combination or separately, from the relation between their bromine and iodine figures. For example, the presence of menhaden oil in linseed oil could be easily detected in this manner.

The following table gives the substitution figures of all those oils tabulated above which show themselves at all capable of forming substitution products. It will be noticed that only six out of the fifteen oils figure in this table.

	Total bromine.	Addition figure.	Substitution figure
Cod-liver oil........	85.16-84.67	84.52-84.09	0.63-0.58
Average........	84.91	84.305	0.605
Menhaden oil.......	120.10-120.30	118.88-118.93	1.22-1.27
Average........	120.15	118.905	1.245
Sweet almond oil....	59.54-59.15	57.38-57.02	2.16-2.13
Average........	59.345	57.20	2.145
Sperm oil	54.61-54.56	52.41-52.21	2.20-2.34
Average........	54.585	52.31	2.27
Castor oil	52.62-52.80	50.09-50.07	2.53-2.73
Average..... ..	52.71	50.08	2.63
Resin oil...........	108.67-109.23	6.74-6.47	101.93-102.76
Average........	108.90	6.605	102.345

As will be seen upon examination, the foregoing table gives results differing widely from those of other experimenters. In cases where the substitution is small this is probably due, in part at least, to experimental error, as great care is necessary in the conduct of the operation. Errors are titrated for, along with substitution, and the result obtained is compounded of these two items. In connection with this investigation, the recent article of Marshall[1] on the "Iodine Value of Oils" should also be noted.

Attention should also be called to the fact that several of the oils examined above were somewhat rancid and it is probably due to this fact that sweet almond oil shows substitution.

THE USE OF METALLIC SODIUM IN BLOWPIPE ANALYSIS.

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THE use of sodium carbonate to assist the action of the reducing flame has long been customary in blowpipe analysis, and is adopted by all text-books on the subject. The reducing action is partly due to the formation of sodium cyanide but more largely to the formation of gaseous sodium and carbon monoxide. At best its action is slow and nothing more severely tests the skill of the beginner than the attempt to obtain a button of metallic tin from cassiterite, or the sulphur reaction from gypsum. In general it is much more difficult to reduce an oxide or sulphide before the blowpipe, than it is to cause the opposite reaction to take place by means of the oxidizing flame.

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[1] *J. Soc. Chem. Ind.*, (1900), p. 213.