

linkage, as in cellobiose. The molecules are arranged parallel to the fiber length; lateral spacings between chains are relatively great. In agreement with Wooster's<sup>32</sup> and Bragg's<sup>33</sup> generalizations, the highest refractive index is found for vibrations lengthwise of the chain structure. Greatest deformability, and the consequent maximum photochemical degradation, should take place crosswise of the chains, since their length and parallelism would prevent lengthwise deformation.

It is generally accepted that photochemical degradation of cellulose fibers results in shortened chain length with an increase in reducing and acidic properties due to the breaking of oxygen linkages, and a consequent increase in copper number. Comparisons of chain length by viscosity, etc., were not feasible on the small samples irradiated, but the chemical changes observed correspond to those to be expected from the above process, if the light energy by virtue of its transverse vibrations breaks some of the oxygen links in the cellulose chain.

The present work illustrates qualitatively the generalization that the properties of crystalline

(32) Wooster, *Z. Krist.*, **80**, 495 (1931); "Crystal Physics," Cambridge Univ. Press, Cambridge, 1938, pp. 175-187.

(33) Bragg, "The Crystalline State," Vol. 1, G. Bell and Sons, London, 1933, p. 186; "Atomic Structure of Minerals," Cornell Univ. Press, Ithaca, 1937, p. 120.

matter differ with direction, a factor that should never be ignored in dealing with ordered structures. With the recent development of methods for producing oriented aggregates of other long chain compounds such as oils, the study of the anisotropic photochemical properties of their molecules becomes possible.

**Acknowledgment.**—This work was carried out under a Fellowship supported by the Procter and Gamble Company. The authors are also indebted to E. B. Ashcraft for valuable advice.

### Summary

Using a silica "pile of plates" polarizer, to give polarized ultraviolet light, parallel ramie fibers were irradiated, in a cell containing metallic sodium, to eliminate air or moisture that might cause secondary non-directional reactions. With light vibrating crosswise of the fibers, degradation was greater than with vibrations lengthwise, by about 25%, as measured by copper number determined on 10-mg. samples. From analogy with simpler compounds, it is concluded that photochemical degradation of cellulose chains is greatest if they are oriented so that the light energy vibrates in the direction in which they are most deformable.

ITHACA, N. Y.

RECEIVED SEPTEMBER 2, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

## A Simple Wet Combustion Method for the Determination of Carbon, Oxygen Equivalence and Empirical Formula by Iodic Acid Oxidation\*

BY BERT E. CHRISTENSEN AND J. FRED FACER

More work pertaining to organic combustions has been described in the literature than perhaps any other single analytical procedure. The fact that so much attention has been devoted to this determination testifies to its importance. The problem of determining carbon and hydrogen has been approached in several ways.<sup>1-6</sup> In spite of all these developments there is still need for simpler techniques, less expensive equipment and

(\* Published with the approval of the Monographs Publication Committee, Oregon State College, Research paper No. 24, School of Science, Department of Chemistry.

(1) Glocker and Roberts, *THIS JOURNAL*, **50**, 828 (1928).

(2) W. R. Kirner, *Ind. Eng. Chem., Anal. Ed.*, **6**, 358 (1934).

(3) H. Lieb and H. G. Krainick, *Mikrochemie*, **9**, 367 (1931).

(4) J. Lindner, *Ber.*, **59**, 2561, 2806 (1926).

(5) M. Nicloux and A. Boivin, *Compt. rend.*, **184**, 890 (1927).

(6) E. Sucharda and B. Bobranski, *Z. anal. Chem.*, **77**, 462 (1929).

methods by which the occasional determination can be made with some degree of ease.

A study of the means by which the above problem may be answered leads to one possibility, the wet combustion process. This would entail the measurement of "oxygen consumed" as an alternative for the determination of moisture. Dichromate and iodate have been cited as excellent reagents for this purpose. Of these iodate is outstanding<sup>7</sup> since little, if any, decomposition (unless carried out above 200°) or carbon monoxide formation accompanies its reduction.

A survey of the literature reveals that Strebinger<sup>8</sup>

(7) Christensen, Williams and King, *THIS JOURNAL*, **59**, 293 (1937).

(8) Strebinger, *Z. anal. Chem.*, **58**, 97 (1919).

was among the first to use iodate in this connection. He determined the oxygen requirement of an organic compound and from this and the known carbon and hydrogen content he calculated the percentage of oxygen in the compound. Later Stanek and Nemes<sup>9</sup> used this same reagent to determine not only the "oxygen consumed," but in addition the carbon dioxide evolved. The hydrogen content was calculated from the "oxygen consumed" plus other values by means of rather complicated equations.

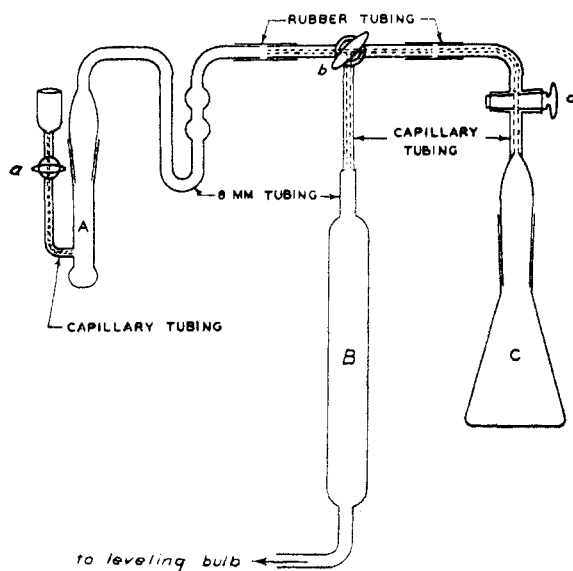


Fig. 1.

Williams<sup>10</sup> also has pointed out the importance of being able to determine the amount of oxygen required for complete combustion of organic material. He has developed this idea and in his paper on "Oxidation Equivalent Analysis"<sup>11</sup> describes a simple method for the determination of molecular structure based only on "oxygen consumed" and molecular weight data. The success of this method, however, hinges upon a fairly accurate means of obtaining the molecular or equivalent weight of the compound in question.

It was the opinion of the authors that the ideas presented by Williams could be much further utilized as a tool for the determination of molecular structure. Such an objective would only require the development of a simple procedure for the determination of carbon dioxide evolved from the reaction mixture. Due to the nature of the

evolved gases ( $\text{CO}_2$ ,  $\text{I}_2$ ,  $\text{Cl}_2$ ) it is apparent that a gravimetric method, such as described by Stanek and Nemes<sup>9</sup> for the determination of carbon dioxide, would not be as desirable as a volumetric procedure. For this reason a modified Pettenkofer method<sup>12</sup> using a volumetric principle was devised.

**Apparatus.**—This apparatus is illustrated diagrammatically in Fig. 1. The reaction vessel A (total volume 20 ml.) was constructed from no. 15 standard taper joint and a capillary stopcock. The gas reservoir B consisted of a three-way stopcock, a 100 ml. buret and a leveling bulb. Mercury was used as the confining fluid. The reaction flask for the analysis of carbon dioxide was designed from a 250-ml. Erlenmeyer flask, a no. 20 standard taper joint and capillary stopcock.

**Procedure.**—The conditions for iodate oxidation are described adequately in the literature.<sup>9,11</sup> The analysis as modified for measurement of carbon dioxide is very simple.

The reaction vessel is charged with 10–20 mg. of organic material<sup>13</sup> and sufficient potassium iodate to constitute approximately 100% excess<sup>14</sup> and the system flushed with carbon dioxide free air.

Closing capillary stopcock a, the three-way stopcock b is then opened so as to permit the flow of emitted gases into the gas reservoir which is maintained at a slight vacuum by means of the leveling bulb.

The carbon dioxide flask is then charged with 10 ml. of approximately 0.25 *N* barium hydroxide, partially evacuated, and then connected to the other arm of the three-way stopcock.

Three ml. of pure concentrated sulfuric acid (carbon free) are now introduced into the reaction vessel by means of the stopcock a. The charge is now ready for combustion.

By means of a phosphoric acid bath<sup>15</sup> the temperature of the reaction chamber is kept at approximately  $190 \pm 5^\circ$  for twenty to forty minutes. The gases which are generated during this time pass through the U-tube containing approximately 1 ml. of concentrated potassium iodide solution, to the gas holder B. By operating stopcocks b and c the carbon dioxide is readily transferred to the reaction flask C.

At the end of the heating operation stopcock a is opened and 5 ml. of 50% sulfuric acid (to decrease the free air space) is introduced. The gas which has accumulated in gas reservoir B is then transferred to reaction flask C.

An Ascarite tower is now connected to the apparatus

(12) Lunge and Ambler, "Technical Gas Analysis," Gurney and Jackson, London, 1934, p. 221.

(13) Samples such as hydroquinone which are rapidly oxidized in the cold by iodic acid can be treated successfully by first wetting the sample with a drop or two of 50% sulfuric acid before introducing the concentrated acid. The presence of a platinum boat in the reaction mixture should be avoided since it apparently catalyzes the decomposition of iodate.

(14) One milli-equivalent of oxygen will completely oxidize 2 mg. of paraffin, 7.5 mg. of glucose, or 4 mg. of benzoic acid. From the nature of an unknown compound one can approximate in most cases the iodate requirement with sufficient accuracy as to make a preliminary oxidation unnecessary.

(15) Christensen and King, *Ind. Eng. Chem., Anal. Ed.*, **9**, 194 (1936).

(9) Stanek and Nemes, *Z. Anal. Chem.*, **98**, 244 (1933).

(10) R. J. Williams, *This Journal*, **59**, 288 (1937).

(11) Williams, Rohrmann and Christensen, *ibid.*, **59**, 291 (1937).

through stopcock a, and sufficient air (carbon dioxide free) is flushed through the system to sweep all the carbon dioxide into the evacuated flask C, bringing it to atmospheric pressure.

**Determination of Carbon Dioxide.**<sup>16</sup>—The flask C is now removed and allowed to stand for twenty minutes. Ten ml. of water and 5 ml. of acetone (to improve end-point) are then added and the excess barium hydroxide is neutralized to the thymol blue end-point. In order to give as sharp a change as possible 0.8 *N* hydrochloric acid is added at the rate of approximately one-half drop per second. When within about 0.3 to 0.4 ml. of neutrality, 0.05 *N* acid is used to establish the end-point. In case of oxidation of an unknown compound the 0.8 *N* hydrochloric acid required can be approximated sufficiently for this purpose so as not to introduce any complications.

To prevent the diffusion of air into the flask during titration, a rubber sheet (such as is used for dental dam) was fitted loosely over the mouth of the flask. The tip of the buret was inserted through a small hole in the rubber. This arrangement kept out the air without complicating the procedure whatsoever.

Having neutralized the excess barium hydroxide, the solution containing the barium carbonate precipitate is then made slightly acid to methyl red with a known amount of 0.05 *N* hydrochloric acid. In order to ensure removal of the last traces of carbon dioxide, the solution is boiled for five minutes. The amount of standard acid required to neutralize the barium carbonate can now be determined accurately by back titration with 0.05 *N* sodium hydroxide to the methyl red end-point. From these data the amount of carbon dioxide evolved can be computed.

Preliminary experiments using either carbon dioxide evolved from sodium carbonate or direct titration of solutions of sodium carbonate consistently gave high values for recovered carbon dioxide. This constant deviation was found to depend on quantity of precipitate and was thought to be due primarily to the apparent adsorption of barium hydroxide by the barium carbonate. In order to avoid using a blank, the hydrochloric acid was standardized with the carbon dioxide (evolved from either sodium carbonate or from the combustion of succinic acid) by means of the above procedure.

**Determination of Oxygen Consumed.**—The reaction vessel A is removed and the mixture transferred to a 1-liter Erlenmeyer flask, then diluted to approximately 100 ml. and steamed until disappearance of the iodine color. Sufficient sodium carbonate to neutralize about all but 1 ml. of the concentrated sulfuric acid is now added. Two grams of potassium iodide are introduced and the solution is then titrated with 0.1 *N* sodium thiosulfate. This measures the excess iodate.

The amount of iodate used was found to be consistently greater than the theoretical due to traces of organic matter in the sulfuric acid and to thermal decomposition. This necessitated the use of a blank which amounted to 0.90 mg.

(16) This procedure was later modified as follows: 10 ml. of standard barium hydroxide was measured by automatic pipet and introduced into vessel C. The amount of carbon dioxide absorbed was determined by titrating the excess barium hydroxide with 0.05 *N* hydrochloric acid to thymol blue end-point. The same precautions such as use of rubber sheet, acetone, etc., were taken here as in the case of the titration of barium carbonate.

## Discussion and Results

The results of a number of typical runs are tabulated in Table I.

**Calculation of Hydrogen.**—Having determined both the percentage of carbon and the oxygen requirement of the compound, the percentage of hydrogen can be calculated readily from the equations of Strebinger

$$\% \text{H} = \frac{(\% \text{O}_R + 100 - 11/3\% \text{C})}{8.93}$$

where  $\text{O}_R$  is the oxygen requirement in grams per hundred grams of sample. With compounds containing other elements in addition to carbon, hydrogen and oxygen, these calculations can be applied to the residue after correcting for such elements.

**Determination of the Empirical Formula.**—From the above data it is possible to make some very interesting calculations. By way of illustration one may take a specific case in which the following designations can be used

$\text{C}_x\text{H}_y\text{O}_z$  = formula of unknown

$M$  = molecular weight

$N$  = number of atoms of oxygen required to oxidize one molecule of compound

$E$  = grams oxidized by 1 gram atom of oxygen

then

$$M = \frac{12x}{\% \text{C}}$$

$$M = NE$$

$$NE = \frac{12x}{\% \text{C}}$$

$$\frac{N}{x} = \frac{12}{\% \text{CE}} = R$$

$$N = Rx$$

Since  $N$  and  $x$  are integers, there must be one integer which multiplied by  $R$  will give the other integer. The possible integers (which fit this equation) can be ascertained rapidly with a slide rule.

Suppose that from the analysis of an unknown compound (benzoic acid) one obtains the following data:  $E = 8.12$  (8.14 calcd.),  $\% \text{C} = 69.3$  (68.8 calcd.). Calculating the value of  $R$  we obtain 2.13. This would give  $x$  and  $N$  the possible integral values listed below.

$x$	$N$	$M^{17}$
7	14.92	122
8	15.05	138
15	32.00	260

Which value of  $x$ ,  $N$  and  $M$  is the correct one can be established readily by means of the Diofantine equations derived by Milne<sup>10</sup> in which

$$(a) \quad y = (6N - M + 22x)/2$$

$$(b) \quad z = (M - 6N + 2y)/22$$

$$(c) \quad x = (M - 2N - 18z)/8$$

(17)  $M$  is always an even integer except in the case of odd molecules.

TABLE I

Mg sample	Taken	Mg. KIO <sub>3</sub> Used	Corr.	Ml. HCl used (Neutralize BaCO <sub>3</sub> )	Milli-eq. CO <sub>2</sub> found	Carbon, % Found	Calcd.	Hydrogen, % Found	Calcd.	Found	<sup>E</sup> Calcd.
Succinic acid											
16.34	255.3	83.4	82.5	22.12	1.107	40.66	40.68	5.16	5.12	16.96	16.88
16.38	251.5	83.7	82.8	22.21	1.111	40.71		5.12		16.93	
18.44	253.2	94.8	93.9	25.02	1.250	40.67		5.18		16.81	
15.15	256.7	78.0	77.1	20.68	1.033	40.91		5.08		16.82	
Hydroquinone											
14.19	254.3	144.3	143.4	30.91	1.545	65.34	65.44	5.55	5.49	8.47	8.48
11.76	252.7	119.5	118.6	25.69	1.283	65.46		5.49		8.49	
15.60	251.4	158.6	157.7	34.00	1.699	65.33		5.55		8.47	
Benzoic acid											
10.04	258.7	107.0	106.1	23.13	1.156	68.84	68.84	4.88	4.95	8.13	8.14
12.94	252.0	137.2	136.3	29.78	1.488	69.05		5.08		8.10	
12.05	251.1	128.3	127.4	27.68	1.383	69.02		4.97		8.10	
Cinnamic acid											
10.12	256.1	117.4	116.5	24.55	1.227	72.73	72.96	5.44	5.44	7.44	7.41
15.07	251.6	175.1	174.2	36.70	1.833	72.96		5.43		7.41	
10.38	254.8	120.2	119.3	25.22	1.261	72.88		5.48		7.42	
Vanillin											
16.47	252.3	158.7	157.8	34.70	1.735	63.22	63.15	5.35	5.30	8.93	8.95
12.13	250.5	116.4	115.5	25.55	1.277	63.18		5.23		8.99	
Sucrose											
15.69	252.6	96.1	95.2	21.94	1.097	41.94	42.10	6.67	6.48	14.11	14.25
13.09	257.9	79.3	78.4	18.36	0.9181	42.08		6.43		14.29	
12.24	253.4	74.5	73.6	17.22	0.8613	42.22		6.46		14.25	
Acetylsalicylic acid											
9.94	249.8	85.8	84.9	19.90	0.9952	60.07	60.00	4.43	4.47	10.02	10.00
15.17	253.7	131.5	130.6	30.45	1.522	60.21		4.58		9.94	
14.15	250.4	122.8	121.9	28.52	1.425	60.44		4.48		9.94	
Phenyl salicylate											
10.41	250.8	117.0	116.1	25.28	1.263	72.82	72.89	4.66	4.71	7.68	7.66
12.82	251.4	144.7	143.8	31.21	1.560	73.08		4.71		7.63	
12.37	248.7	139.4	138.5	30.00	1.500	72.94		4.72		7.65	
13.69	249.8	155.0	154.1	33.34	1.667	73.04		4.80		7.60	

$x$ ,  $y$ ,  $z$ ,  $N$  and  $M$  are integral values. Below are listed the values of  $y$  and  $z$  derived from equations (a), (b), and (c).

Value of $x$	Corresponding value of $z$	Corresponding value of $y$
7	2	6
8	2.22	4
15	4.23	10

It is evident that the formula can be none other than  $C_7H_6O_2$ .

In certain cases where molecular weight is large or where considerable error is made in the determination of either  $E$  or percentage carbon, several *possible* solutions may be obtained. Even under these rather adverse conditions it is still possible to determine the correct formula. In such cases differences in chemical behavior, the determination of molecular or equivalent weights

are a direct aid in determining the correct solution.

With the percentage carbon and "oxygen consumed" data it is also possible to ascertain the nature of the errors made during a determination (such as incorrect weights, wet or partially dehydrated samples, incomplete combustion) merely from the nature of carbon to oxygen ratios which are obtained.

**Other Applications.**—On many occasions it is only necessary to determine the percentage carbon to serve as a check on the purity of a preparation. For such purposes this method is especially adaptable, particularly on the micro scale. Furthermore, certain compounds which are not completely oxidized at 200° can be treated successfully at a higher temperature. In such cases

oxygen equivalent data may be obtained by the dichromate method.

**Limitations.**—The one limitation to this method is the use of iodic acid as an oxidizing agent. Not all compounds are completely oxidized by this reagent at 200°. The literature, however, reveals that a great many compounds can be oxidized successfully by iodic acid under conditions here specified.

In the case of compounds with high molecular weights, the determination of the molecular formula has the same limitations in accuracy as do the traditional combustion methods.

The question of compounds containing nitrogen, sulfur and halogens has not yet been investigated in this Laboratory. However, both Strebinger, and Stanek and Nemes have oxidized successfully a number of such compounds with iodic acid. It is the opinion of the authors that the presence of nitrogen, halogen, or sulfur in an organic compound which can be completely oxi-

dized should offer no complications to the method here described.

When one considers (1) the simple apparatus, (2) adaptability of the procedure to intermittent operation, (3) the amount of information derived from a single analysis, and (4) rapidity of analysis (less than two hours), it is evident that this method offers at least a partial solution to an important organic technique.

### Summary

A simple apparatus for the determination of oxygen equivalence and percentage carbon by means of iodic acid oxidation has been described.

A modification of the Pettenkofer method for the determination of carbon dioxide has been devised.

Equations have been derived by means of which the empirical formula of an organic compound can be established readily from the data supplied by the above method.

CORVALLIS, OREGON

RECEIVED MAY 10, 1939

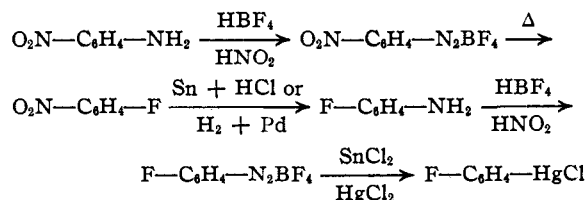
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SCHOOL OF PHARMACY, UNIVERSITY OF MARYLAND]

## Fluorinated Aromatic Mercurials

BY MELVIN F. W. DUNKER AND EDGAR B. STARKEY

The preparation and properties of some fluorinated aromatic mercurials are described. These compounds have been tested for antiseptic activity and the results are reported in detail elsewhere.<sup>1</sup>

The direct mercuriation of fluorobenzene by refluxing in glacial acetic acid with mercuric acetate yielded about 10% of *o*-fluorophenylmercuric chloride. The mercuriation of *p*-fluorophenol with mercuric acetate in water at room temperature yielded a monomercurial assumed to have the mercury ortho to the hydroxyl since *p*-chlorophenol is reported to mercurate in that position.<sup>2</sup> The fluorophenylmercuric chlorides were prepared as shown by the equations below



While the replacement of the diazonium group with mercury does not always give yields which are entirely satisfactory, yet the compounds so prepared are generally obtained more pure, or in a form more easily purified, than when other methods are employed. This has been noted before.<sup>3</sup>

### Experimental

**Fluoronitrobenzenes.**—The diazotization of *p*-nitroaniline as previously described<sup>4</sup> yielded the theoretical quantity of *p*-nitrobenzenediazonium fluoborate (ortho, 92%; meta, 92%). The decomposition of the diazonium fluoborate was carried out as described by Schiemann,<sup>5</sup> the same sand being used for repeated decompositions of the same diazonium compound. The decomposition of 1 mole of *p*-nitrobenzenediazonium fluoborate in 20-g. portions gave 82 g. of *p*-nitrofluorobenzene or 58% of the theoretical (ortho, 13%; meta, 43%).

**Fluoroanilines.**—The reduction of 100 g. (0.7 mole) of *p*-nitrofluorobenzene with tin and hydrochloric acid yielded 58 g. (75%) of *p*-fluoroaniline (ortho, 70%; meta, 89%).

(3) Nesmejanow, *et al.*, *Ber.*, **62**, 1010 (1929); *ibid.*, **67**, 130 (1934).

(4) Dunker, Starkey and Jenkins, *THIS JOURNAL*, **58**, 2308 (1936).

(5) Schiemann and Pillarsky, *Ber.*, **62**, 3035 (1929).

(1) Accepted for publication in the *Journal of Bacteriology*.

(2) German Patent 234,851.