

3. The effect of the addition of various amounts of potassium hydroxide to the alcoholic solution of fluorescein, due to the formation of the dipotassium salt of fluorescein, has been studied.

4. The absorption of fluorescein in strong aqueous potassium hydroxide undergoes a progressive change, indicating the occurrence of two processes: (1) the rupture of the pyrone ring and (2) the possible formation of a carbinol followed by some other disruptive process.

ITHACA, NEW YORK

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

## THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS<sup>1</sup>

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Many methods for the determination of oxygen in organic compounds have been described.<sup>4</sup> In all these methods it is necessary to perform a *separate* experiment for the determination of oxygen. In the new method proposed here we determine the amount of oxygen consumed *during* the combustion of an organic compound *gasometrically* and are thus able to analyze for Carbon, Hydrogen *and* Oxygen in *one* operation.

We used the modification of Wise's<sup>5</sup> semi-micro combustion method which has been developed and used in this laboratory by Dr. W. M. Lauer

### Apparatus and Procedure

The apparatus used is shown in Fig. 1. Oxygen was made from solid potassium permanganate and measured (N. T. P.) in a Ramsay buret. The combustion tube contained platinized asbestos only. The use of copper oxide was avoided at this time following a suggestion of Professor W. H. Hunter. It is possible that copper oxide wire reduced to copper during the combustion may not be reoxidized to the same extent as it had been originally. The sample was weighed on an ordinary analytical balance, as were the absorption tubes.

<sup>1</sup> This method was devised in examining the liquid product obtained in the course of the investigation on "the effect of electrical discharge on gaseous hydrocarbons," listed as research project No. 8 of American Petroleum Institute Research. Financial assistance for this work has been received from a research fund of the American Petroleum Institute, donated by the Universal Oil Products Co. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

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<sup>4</sup> Older work: "Analyse, etc., org. Verbind.," Hans Meyer, 3rd ed., Julius Springer, Berlin, 1916, p. 301; M. C. Boswell, *THIS JOURNAL*, **35**, 284 (1913); **36**, 127 (1914); R. Strebinger, *Z. anal. Chem.*, **58**, 97 (1919); H. Ter Meulen, *Rec. trav. chim.*, **41**, 509 (1922); **43**, 899 (1924); *Chem. Weekblad*, **23**, 348 (1926).

<sup>5</sup> Wise, *THIS JOURNAL*, **39**, 2055 (1917).

At the beginning of an analysis the apparatus was brought to atmospheric pressure by opening stopcock A. Sample and absorption tubes were, of course, in place. The mercury in vessel B was placed on the mark C and stopcock D was closed. Room temperature and barometer were noted. Oxygen sufficient for the combustion was transferred to the vessel B so that all of it would take part in the flow through the combustion tube. The circulation was started by causing the Sprengel pump to operate. By a previous calibration we had determined the proper rate of dropping the mercury so as to produce the usual flow of oxygen through the combustion tube. We allowed forty-five minutes for complete combustion and fifteen minutes for further sweeping.

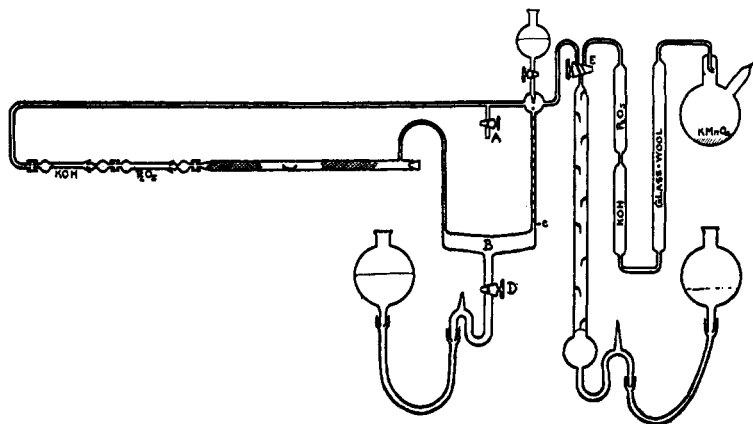


Fig. 1.

At the end of the experiment the apparatus was brought into its initial condition by removing the three pieces of triangular iron which comprised the furnace and all the hot asbestos shields and allowing room temperature to be attained. The remaining oxygen was now removed from vessel B, which was again filled with mercury to the mark C. Stopcock D was closed. The gas was thus transferred to the Ramsay buret, which was set to atmospheric pressure and stopcock E was closed. The oxygen remaining in the buret was measured and the absorption tubes were removed and weighed. An analysis can be carried out in two hours.

Blank experiments were run which showed some consumption of oxygen and gain of weight in the potassium hydroxide and pentoxide absorption tubes. However, oxygen thus treated and run through a second blank shows a negligible decrease in volume and the gains in the absorption tubes are also negligible. In further work we expect to pretreat the oxygen as it comes from the generator, thus avoiding the necessity of making blank experiments.

A very important feature of our apparatus is that the system is closed

and any gases due to cracking or incomplete combustion (such as methane and carbon monoxide) are carried back through the hot combustion tube several times in the period allowed for the combustion. Thus our method tends to insure complete combustion.

### Results

That the method yields good results can be seen from the data on benzoic acid<sup>6</sup> given in Table I. The calculation of the percentage of oxygen found by our method (Col. 5) is obvious and need not be given in detail.

TABLE I  
DATA ON BENZOIC ACID

Sample taken, mg.	H, %	C, %	Oxygen, %		Total	100 - Total
			By difference 100% - %H - %C	From O <sub>2</sub> consumption		
30.1	5.93	69.45	24.62	24.59	99.97	+0.03
34.5	5.51	67.92	26.57	26.04	99.49	+ .51
34.8	4.93	68.14	26.93	25.00	98.07	+1.93
33.65	5.12	69.30	25.58	26.45	100.87	-0.87
Average	5.37	68.70	25.93	25.53	99.60	+ .40
Calcd.	4.96	68.82	26.22	26.22	100.0	
	0.41	0.12	0.29	0.69	0.40	

That the method here proposed is of value was shown by combustions made on a volatile oil obtained from ethane under the influence of electrical discharge in an ozonizer.<sup>7</sup> Combustions were made of this oil by the ordinary semi-micro method which indicated that carbon and hydrogen together amount to only 87%. The individual experiments checked satisfactorily. Had the ordinary procedure of the organic chemist been adopted it would have been concluded that the oil contained 13% of oxygen. However, from its origin from ethane in a closed system this appeared improbable. By special experiments it was shown that it did not absorb oxygen rapidly. This perplexity led to the method of combustion described, by which it was immediately possible to show that the oil in question contained carbon and hydrogen only and no oxygen. In this case the failure of the ordinary method of combustion is evidently due to some form of incomplete combustion.

It is in cases like the one described above that the method will find its greatest use. One would naturally take the per cent. of oxygen as obtained by difference as the more accurate figure after having demonstrated by this method that oxygen actually is contained in a given compound.

<sup>6</sup> Bureau of Standards Sample.

<sup>7</sup> Paper (Preprint No. 6) presented by S. C. Lind and Geo. Glockler at the September 5, 1927, Meeting of the American Electrochemical Society held at Minneapolis, Minnesota.

We wish to thank Professor S. C. Lind for suggesting the method of attack and Professor W. H. Hunter for his interest in our work and helpful suggestions.

### Summary

A new method is proposed which permits the determination of oxygen during the combustion of organic compounds containing carbon, hydrogen and oxygen. The amount of oxygen consumed is measured volumetrically. The arrangement of the combustion train in a closed circulating system insures complete combustion.

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[CONTRIBUTION FROM THE BAKER CHEMICAL AND ROCKEFELLER PHYSICAL  
LABORATORIES OF CORNELL UNIVERSITY]

## THE ABSORPTION SPECTRA OF BENZENE AND TOLUENE IN ALCOHOLIC SOLUTION. THE SPECTROSCOPIC DETECTION OF BENZENE AS AN IMPURITY IN ORGANIC COMPOUNDS<sup>1</sup>

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Since Henri<sup>4</sup> succeeded in ordering the numerous lines in the absorption spectra of benzene vapor, in accordance with the modern view of band spectra, there has been a revival of interest in the absorption of the aromatic hydrocarbons. Henri and Walter<sup>5</sup> followed with a study of the vapor of toluene and Klingstedt<sup>6</sup> reported on its absorption spectrum in hexane solution. The latter was able to show that the relatively broad solution bands follow the same law that applies to the band heads in the vapor spectrum. Kronenberger and Pringsheim<sup>7</sup> have measured the absorption spectrum of solid benzene at  $-180^{\circ}$ . They found that the diffuse bands of liquid benzene break up into many narrow bands of about 1 Å. in width, of which they record 62. These vary considerably in intensity, the most prominent being associated with the strong bands

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<sup>4</sup> Henri, *J. phys. radium*, **3**, 181 (1922). For a fairly complete bibliography of the early work on the absorption spectra of benzene and toluene, see "Report of the British Association for the Advancement of Science," 1916, p. 131.

<sup>5</sup> Henri and Walter, *Compt. rend.*, **176**, 746 (1923).

<sup>6</sup> Klingstedt, *ibid.*, **175**, 1065 (1922); *Acta Acad. Abo. Math. Phys.*, **3**, 1 (1924).

<sup>7</sup> Kronenberger and Pringsheim, *Z. Physik*, **40**, 75 (1926).