[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

A RAPID METHOD OF DETERMINING CARBON IN ORGANIC COMPOUNDS

BY H. D. WILDE, JR., AND H. L. LOCHTE

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A series of hydrazine derivatives obtained in recent investigations in the Texas Laboratory gave low results for carbon and hydrogen because, in spite of the greatest precautions in making the ordinary copper-oxide or lead-chromate combustion analysis, the compounds could not be burned completely. The nitrogen obtained in the Dumas determination was usually mixed with an inflammable gas, the nature of which has not yet been determined. In the case of a beautifully crystallizing and easily purified oxidation product of acetone-α-phenyl-semicarbazone, $C_6H_5N(CONH_2)$-$N{=}C(CH_3)_2$, obtained by Goodwin and Bailey,[1] the ordinary combustion method failed completely whereas in the calorimetric bomb this substance burned readily as did all difficultly-burned hydrazo, azo and hydrazone compounds analyzed.

No method has heretofore been perfected for determining carbon by burning the substance in oxygen under pressure in a calorimetric bomb and absorbing the resulting carbon dioxide in standard alkali *within* the bomb. Quantitative estimation of carbon has been proposed repeatedly,[2] but the products formed during the combustion have invariably been absorbed outside the bomb, except in the case of von John[3] who analyzed steel samples by burning them in oxygen in an Erlenmeyer flask and absorbing the carbon dioxide within the flask. It is true that Eiloart,[4] in 1888, suggested the desirability of determining carbon and hydrogen by absorbing the products of combustion within the bomb, but made no practical application of the idea.

In the method developed by us the compound is burned in a calorimetric bomb with oxygen under pressure, the carbon dioxide absorbed by shaking with 0.5 N barium hydroxide contained in the bomb and the carbonate formed determined by titration with 0.5 N hydrochloric acid. The amount of acid required between the phenolphthalein and the methyl orange end-points is equivalent to the carbon dioxide formed. The carbon dioxide in the air may be neglected, provided the work is carried out rapidly in a well ventilated laboratory.

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[1] In unpublished work.

[2] Berthelot, *Compt. rend.*, **114**, 317 (1892); **129**, 1002 (1899). Hempel, *Ber.*, **30**, 202 (1897). Kroker, *Ber.*, **30**, 606 (1897). Langbein, *Z. angew. Chem.*, **1900**, 1229. Fries, THIS JOURNAL, **31**, 272 (1909). Zuntz and Frentzel, *Ber.*, **30**, 380 (1897). Higgins and Johnson, THIS JOURNAL, **32**, 547 (1910).

[3] Von John, *Chem.-Ztg.*, **37**, 426 (1913).

[4] Eiloart, *Chem. News*, **58**, 284 (1888).

By this method substances containing no halogen may be analyzed at the rate of one determination every 20 to 30 minutes with an accuracy equal to that obtained in the Liebig method of combustion analysis. In the case of substances containing halogen, oxyhalogen compounds are formed which interfere with the method as outlined. By reducing any such oxyhalogen compounds and determining the carbonate present according to the technique described below, the process becomes applicable to halogen compounds.

Experimental Work

In the experimental work the Parr illium bomb with its smooth unlined construction was found to be particularly well suited for the type of work involved, but other forms of bombs could undoubtedly be employed. Inasmuch as the solution used is alkaline, a plain steel bomb should prove satisfactory in case only carbon is to be determined. Such a bomb should be much cheaper than the rather expensive ones employed in calorimetric work.

The substance to be analyzed is prepared and burned according to the methods in use in calorimetry, but the sample used should weigh only from 80 to 200 mg. The heavy iron wire furnished with the Parr peroxide calorimeter gives more reliable ignition than the finer wire often used.

Analysis of Solids.—Solids should be compressed into pellet form before weighing. In case the sample by itself does not burn completely, it should be placed in an ordinary gelatin capsule that has been previously weighed. These capsules are very uniform in their carbon content and therefore the proper correction is easily determined by running a series of blanks on each box. The supply of capsules should be kept in a desiccator, since Roth[5] found that they are hygroscopic.

We find that ignition is certain when the gelatin container is used if the wire is threaded through needle holes in the sides of the capsule. In case no igniter is employed, the pellet is placed in the cup provided with the bomb and the ignition wire adjusted so as to press against the sample sufficiently to maintain contact during the jars incident to closing and charging the bomb.

A definite volume of 0.5 *N* barium hydroxide solution, at least 10% greater than that required to neutralize all acids formed, is next placed in the bottom part of the bomb.[6] Ordinary Linde process oxygen at a pressure of 25 atmospheres was employed in all the experimental work.

After ignition of the sample in the usual manner, the bomb is placed

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[5] Roth and Wallasch, *Ann.*, **407**, 140 (1915).

[6] Due to the slight solubility of $Ba(OH)_2$ in cold water, a more dilute solution must be employed during cold weather. In case no check on the amount of other acids formed is desired, a saturated solution may be employed in the bomb and a 0.2 *N* solution used in back titration.

in a mechanical shaker and agitated vigorously for about ten minutes. It is then removed from the shaker and allowed to stand for a few minutes before admitting an additional 5 atmospheres of oxygen. The pressure may then be released slowly without danger of losing more than traces of carbonate during the process of relieving the pressure.

The reaction mixture is rapidly washed into a beaker, phenolphthalein added and the mixture vigorously stirred while 0.5 *N* hydrochloric acid is admitted until the pink color is just discharged. The barium carbonate will not be affected appreciably before this point is reached, if the acid is added slowly during effective stirring. Methyl orange and about 20 g. of C. P. sodium chloride are next added and the titration with acid is continued until about 5 cc. has been added beyond the methyl orange end-point. The excess of acid is determined by back titration with standard barium hydroxide solution.

The exact color of the methyl orange end-point is best found by means of preliminary analyses of benzoic acid. The color so obtained is preserved by means of methyl orange in a sodium acetate-acetic acid buffer solution made up to match the color obtained in the trial runs. The acid used between the phenolphthalein and the methyl orange end-points is equivalent to the amount of barium carbonate formed. Lindner's[7] method of determining carbonate is slightly more accurate, but requires much more time than our simple scheme.

Analysis of Liquids.—In the case of liquids that do not react with or dissolve gelatin, capsules are the most convenient containers so far tried in this work. Only the half of the capsule having the smaller diameter is used, the cap serving only as a holder during filling and handling. Two such inner parts are weighed. Into one the liquid is introduced by means of a small pipet and the other, perforated with two needle holes near the rim, serves as a stopper. Although the two parts have the same diameter, they are elastic enough to permit the use of one as a stopper for the other. The capsules and contents are then weighed, the fuse wire is led through the holes in the stopper, and fixed in such a position that the capsule is suspended in an upright position. In filling and in the subsequent handling of the container, care must be taken to keep the liquid from touching the joint between the two parts of the capsule, as experience seems to show that there is almost invariably a slight loss if the liquid wets the joint. In all but the very volatile liquids a tiny needle hole should be pierced in the bottom of the stopper just before closing the bomb. The hole prevents the collapse of the container at the moment when oxygen pressure is applied. In the cases of the few liquids that destroy the capsule in the short time interval involved, one of the regular methods of burning such liquids in calorimetric work must be resorted to.

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[7] Lindner, *Ber.*, **55**, 2025 (1922).

The subsequent steps in the analysis of liquids are identical with those described for solids. Naturally, the carbon dioxide formed in the combustion of the gelatin capsule must be subtracted from the total amount found.

Analysis of Halogen Compounds.—The simple method outlined above has been found to be applicable to a large number of compounds containing carbon, hydrogen, oxygen, nitrogen and sulfur, or any of the usual combinations of these, but when a carbon determination is attempted on an organic halogen compound the value of the carbon found is always too high while the calculated amount of halogen is too low. This appears to be due to the formation of small amounts of oxyhalogen compounds which interfere with the titration for carbonate. The following modification of our method has been found to be satisfactory for a number of compounds containing chlorine. It has not been tried on bromine or iodine compounds although there is no reason why satisfactory results should not be obtained on such substances by the same method.

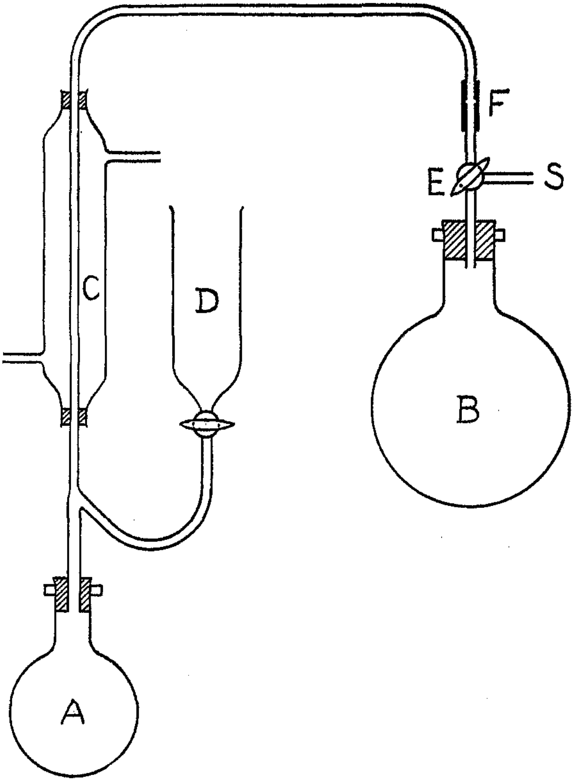

Fig. 1.—Apparatus for analysis of halogen compounds.

The sample is prepared, weighed and burned according to the method described above. Instead of directly titrating the contents of the bomb, they are washed into a 250cc. flask in which 3 to 4 drops of hydrazine hydrate and about 10 mg. of aluminum foil have been placed. This evolution flask is then connected to a condenser as shown at A, Fig. 1.

Fifty cc. of the standard barium hydroxide solution is placed in the 500cc. flask B which is connected as shown and then evacuated through S by means of a water-jet pump and the stopcock E turned to connect the two flasks and disconnect the pump. An excess of 1:3 hydrochloric acid is then added to the flask A by means of the dropping funnel D. The liquid in the flask A is slowly heated to the boiling point and boiled for about five minutes. All of the carbon dioxide is thus liberated without completely relieving the vacuum in the system. Finally the flask A is just filled with distilled water through the dropping funnel D and the carbon dioxide in the condenser and tubing rinsed into the flask B by letting air enter through the funnel D until the system is at atmospheric pressure. The stopcock E is turned to close the flask and disconnected from the condenser and pump. The carbon dioxide in the flask B is completely absorbed by shaking the latter for five to ten minutes. The barium carbonate formed is then determined in the usual manner.

The titration should show that less than 0.3 to 0.4 cc. of 0.5 N acid was carried over during the distillation. A complete carbon determination can readily be completed in an hour by this method with an accuracy equal to that of the simple method used for halogen-free compounds.

Results

The following compounds were purified until one of their physical constants agreed with that given in the literature and were then analyzed by our method: benzene; benzoic acid; urea; dibenzoyl-hydrazine; 1,2-dibenzoyl-1-phenyl-2-*iso*propyl-hydrazine, $C_6H_5N(COC_6H_5)(C_6H_5CO)NC(CH_3)_2$; *m*-nitrobenzoic acid; furfuralazine; nitrobenzene; sulfanilic acid(*p*); phenyl mustard oil; carbon disulfide; saccharin; aniline hydrochloride; *sym*-di-*iso*propyl-hydrazine hydrochloride; and benzyl chloride. In addition to these, since this work was completed, a large number of analyses have been run on coal, fuel oil and various compounds encountered in work in this Laboratory. The results in all cases tried were satisfactory and the method is now in use not only for accurate carbon determinations,

TABLE I

ANALYTICAL RESULTS

Compound	Sample G.	Capsule G.	Vol. of 0.5 N HCl consumed Cc.	Wt. C found G.	Wt. C in capsule G.	Wt. C in sample G.	% C Found	% C Calcd.
Phenyl mustard oil	0.0959	0.0763	30.40	0.09120	0.03148	0.05972	62.27	62.15
	.1389	.0640	37.48	.11244	.02641	.08603	61.93	
	.0892	.0694	27.96	.08388	.02864	.05524	61.93	
	.0919	.0805	29.88	.08964	.03322	.05642	61.39	
	.0912	.0670	28.09	.08427	.02765	.05662	62.08	
*Sym*di-*iso*propyl-hydrazine hydrochloride	.1562	....	24.63	.07389	.....	.....	47.30	47.21
	.0886	....	13.88	.04164	....	....	47.00	
	.1603	....	25.46	.07638	....	....	47.65	
	.1001	...	15.75	.04725	....	....	47.20	

but also for rapidly establishing the probable structure of substances obtained in research work.

The results which are tabulated in Table I were obtained in *consecutive* runs on two typical compounds and give an idea of the accuracy and reliability of the method in the hands of an average advanced student.

The volume of hydrochloric acid consumed is determined by calculating the volume of acid neutralized between the phenolphthalein end-point and that of methyl orange.

In the case of compounds containing sulfur, this element may be estimated gravimetrically in the titrated solution from the carbon determination, thus combining the analysis of these two elements. The estimation of sulfur by calculation from the data obtained in the carbon determination is possible, but is not very accurate, as the amount of nitric acid obtained varies somewhat.

Contrary to our expectations, the nitrogen in organic compounds is usually burned to free nitrogen, thus yielding only a small fraction of the nitric acid expected. Even in the case of such compounds as nitrobenzene the amount of nitric acid produced is less than 10% of that calculated, so that we have here instances in which nitrogen is reduced during combustion in compressed oxygen. Mr. G. B. Boone, to whom credit is due for a number of analyses made in this work, is continuing the study of this behavior of nitrogen compounds.

Numerous refinements such as the use of more dilute acid, use of a larger sample, different method of determining the carbonate formed, and a correction for the carbon dioxide in the air suggest themselves, but as such refinements call for a greater consumption of time and for more complex manipulation and calculations, such modifications were not considered in this work of which the sole object has been the development of a method of analysis as simple and rapid as is consistent with the degree of accuracy required in regular research work as well as control work.

In conclusion we wish to point out the fact that this method could easily be modified to make it applicable to micro-analysis. The construction of a bomb of one-tenth the capacity of the ordinary bomb should present no difficulties and all other steps in the determination are now part of micro-technique. Gelatin capsules of such size as to weigh only a few milligrams are not being manufactured, as far as we know, but could no doubt be produced easily if there were a demand for them.

Summary

1. A rapid method of analyzing organic compounds for carbon has been developed. The compound is burned in the presence of compressed oxygen and of standard barium hydroxide in the calorimetric bomb. The carbon dioxide formed in the combustion is absorbed by shaking the bomb and its contents.

2. The carbonate formed is determined, in the case of compounds not containing halogen, by titration with standard hydrochloric acid using phenolphthalein and methyl orange as indicators.
3. The amount of sulfur in a sulfur compound may be determined gravimetrically on the titrated solution used in the carbon analysis.
4. In the case of halogen compounds, any oxyhalogen compounds formed are destroyed by some reducing agent such as hydrazine hydrate, the solution is then acidified and boiled, and the carbon dioxide thus liberated is reabsorbed by barium hydroxide and titrated in the usual manner.
5. Nitrogen from nitrogen compounds does not interfere with the carbon determination and seems to escape almost entirely as free nitrogen.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

THE OCCURRENCE OF FREE PENTOSES IN PLANTS. THE EFFECT OF EXTRACTION OF THE SUGARS WITH AMMONIACAL ALCOHOL

BY DUANE T. ENGLIS AND CEDRIC HALE

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Introduction

In 1914 Davis and Sawyer[1] offered the first evidence for the occurrence of pentoses in the free state. Further evidence by Spoehr[2] confirmed such occurrence. Still, Davis and Sawyer based their conclusions on the fact that a non-fermentable reducing sugar residue was obtained from a plant extract after fermentation with yeast and also on the fact that by running the Krober-Tollens determination of pentoses by distillation with hydrochloric acid, a greater precipitate was obtained with phloroglucinol than could be accounted for as due to hexoses. They also showed that the furfural-like compounds produced from sugars other than pentoses are of very little significance in the majority of cases.

However, for the purpose of neutralizing any organic acids that were present, these investigators added to the alcoholic extract of the sugars ammonium hydroxide (d., 0.88) in a proportion of 1% by volume. This treatment would tend to throw some doubt as to the conclusiveness of their evidence. Perhaps enough isomerization of fructose to glutose or some other sugar, non-fermentable by yeast, could have taken place to give a residue after fermentation which would reduce Fehling's solution. Furthermore, it is possible that some intramolecular change or some degradation of the hexose sugars could have given rise to a product which

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[1] Davis and Sawyer, *J. Agr. Sci.*, **6**, 406 (1914).

[2] Spoehr, *Carnegie Inst. Pub.*, **1919**, 287.