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

A NEW MICRO METHOD FOR DETERMINING CARBON IN ORGANIC COMPOUNDS

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A recent article[1] describes a rapid and accurate method of determining carbon by combustion of the sample in a calorimetric bomb, absorption within the bomb of the carbon dioxide and subsequent determination of the amount of carbonate formed. It was pointed out that the method could probably be applied to micro determination of carbon. Experiments show that the method, modified as indicated below, may be employed to advantage in micro analysis. The results are as accurate as those reported for other micro methods, while the procedure is simpler and more rapid.

Apparatus

Preliminary experiments with a steel bomb gave satisfactory results but showed that the unprotected metal corrodes too rapidly to permit its use under conditions obtaining in micro analysis. The chemistry mechanician, Mr. W. L. Benson, then constructed a Monel-metal bomb that has proved satisfactory except in the case of halogen compounds. Some of the acid-resisting alloys may be found to give good results even in the case of chlorine compounds. If these fail, enameling or some special treatment such as that described very recently for such cases by Roth[2] should produce a bomb that would resist the action of the corrosive gases resulting when compounds containing more than small amounts of halogen have to be analyzed by this method. In case such compounds are not involved the Monel metal does not corrode appreciably and gives satisfactory results.

The structural features of the bomb are, in general, similar to those of the Parr oxygen bomb. To prevent too rapid cooling of the cup the heavy ring of the cup holder is omitted and the light platinum-foil cup is supported by clamping in the slotted end of the heavy wire serving as cup holder and terminal for the ignition wire. The dimensions of the bomb are decreased to 180 by 30 mm. so that a 200 by 30 mm. Pyrex test-tube, cut to the proper length, readily slides into the bomb as a temporary lining. The use of this tube as titration vessel obviates all rinsing but prevents vigorous shaking and exposes the metal of the bomb to any corrosive gases formed.

Instead of a shaking apparatus an adjustable rotating machine is used and set at such an angle that about 75% of the inside surface of the test-tube is exposed to the absorbing liquid while the bomb is rotated at the

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[1] Wilde and Lochte, THIS JOURNAL, **47**, 440 (1925).

[2] Roth, Ginsberg and Lasse, *Z. Elektrochem.*, **30**, 417 (1924).

rate of about 100 revolutions per minute. With saturated barium hydroxide as absorbing medium no carbon dioxide could be detected after the bomb had been rotated for 30 minutes.

Solutions

In case carbon is the only element to be determined, the most convenient absorbing medium is a saturated solution of barium hydroxide. Ten cc. of this solution is placed in the Pyrex tube by means of a buret sealed to a 3-way stopcock in such a manner that it may be connected either to the supply bottle or to the delivery tube. Naturally, all barium hydroxide solutions are protected, wherever possible, from contact with the carbon dioxide of the air.

The excess of base in the test-tube is neutralized by means of approximately 0.5 *N* hydrochloric acid. This solution is employed in preference to the more dilute standard acid used subsequently to avoid the less sharp end-points that would be obtained with the large volume of solution that would result.

A carefully standardized solution of 0.2 *N* hydrochloric acid is used for the carbonate titration. It may be measured from a carefully calibrated 10cc. buret, but a more rapid and accurate plan uses a special buret made by sealing a piece of capillary tubing to each end of the bulb of a 5cc. pipet. This is then sealed, at its lower end, to the stopcock of the supply line and to a buret stopcock rather than sealed to a 3-way buret stopcock which is little more rapid and much more liable to error in manipulation. This buret is then carefully calibrated by weighing the water (not mercury) delivered between marks on the capillary tubing, allowing only as much time for drainage as is to be used in measuring out the acid during titrations. In this way the standard acid is added in multiples of about 5 cc., with the volume used definitely known to 0.01 cc.

The 0.1 *N* barium hydroxide solution used in back titration to determine the excess of acid added is measured by means of a protected 10cc. buret reading directly to 0.05 cc. This permits estimating accurately to about 0.01 cc. The buret tip should be drawn out to a fine point to decrease the drop size. In case the Lindner scheme is employed a micro buret reading directly to 0.01 cc. may profitably be used since the end-point could be determined to less than 0.01 cc.

Procedure

Analysis of Solids.—In the case of solids containing no chlorine, the material is compressed into pellets weighing 10 to 30 mg. These are weighed on a micro or an assay balance, the pellet is placed in the cup and the usual ignition wire adjusted. Ten cc. of saturated barium hydroxide[3]

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[3] In case the laboratory temperature does not drop below 15° a standard 0.4 *N* solution may be used in place of the saturated one.

solution is added to the tube in the bomb. Further steps in ignition are identical with those used in the macro method. The bomb is rotated for 30 minutes before it is opened and the carbonate formed determined. The excess of base is neutralized carefully since losses will occur here unless the acid is added carefully during thorough stirring. Just before the phenolphthalein end-point is reached the tube is transferred to the buret of 0.2 *N* hydrochloric acid and the titration continued to the exact end-point; 2 to 7 cc. more than enough 0.2 *N* hydrochloric acid to react with all carbonate present is then added, using methyl orange to indicate the approximate end-point. The exact volume of 0.2 *N* hydrochloric acid so added must, of course, be known. After all specks of carbonate have disappeared, the excess of acid used is determined by back titration with 0.1 *N* barium hydroxide solution to the methyl orange end-point. It is advisable in all cases, and necessary when samples contain less than 5 mg. of carbon, to obtain the exact end-point with methyl orange by matching a standard color such as that of methyl orange in a sodium acetate-acetic acid buffer solution, or, more conveniently, that of a mixture of ferric chloride and cobalt nitrate recommended by Kolthoff.[4] The procedure of Lindner,[5] using only phenolphthalein as indicator, requires boiling under a reflux air condenser for 30 minutes and hence prolongs the procedure by that amount, but the end-point in removing the excess of hydrochloric acid is very sharp and permits readings to less than 0.01 cc. of 0.1 *N* solution. This procedure is recommended for samples containing less than 5 mg. of carbon unless the operator has high ability to distinguish shades of orange. The Lindner procedure was employed in the last two analyses reported in Table I. Unless the laboratory is especially well ventilated a correction for carbon dioxide in the air must be made, but this correction is practically constant from day to day (0.05 ± 0.01 cc. in all but the analyses on urea; negligible in the case of the series on urea).

Analysis of Liquids.—In the case of liquids the sample is most conveniently weighed from a small bulb with fine capillary tip or from a Sprengel type of pycnometer of about 1 cc. capacity. In either case the second weighing may be made while the bomb is in the rotating machine. In the case of low-boiling compounds losses occur even if the sample is ignited immediately after being placed in the cup. These difficulties are discussed by Roth and Wallach[6] and by Richards and Barry[7] and remedies are suggested. Some of these schemes could doubtless be employed, but they appear to be too intricate and time-consuming to be used in routine micro analysis. If tiny celluloid capsules were available, they would offer

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[4] Kolthoff, "Der Gebrauch von Farbenindikatoren," Julius Springer, Berlin, 1921, p. 84.

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

[6] Roth and Wallach, *Ann.*, **407**, 134 (1914).

[7] Richards and Barry, THIS JOURNAL, **37**, 1009 (1915).

the simplest solution to this problem. In the case of liquids boiling above about 100° a weighed pellet of ignitor such as benzoic acid is placed in the platinum foil cup and a tiny drop of the liquid placed on the pellet and ignited as soon thereafter as possible. Further steps in the procedure are identical with those for solids.

Effect of Other Elements.—Nitrogen, oxygen and sulfur do not interfere with the use of the micro method. No compounds containing phosphorus have been analyzed. If phosphorus does interfere, the use of the halogen modification recommended in the previous article would doubtless yield correct results. In the case of aniline hydrochloride the steel bomb gave fair results when the halogen modification was employed in micro analysis, but the metal corroded rapidly. In the case of the Monel-metal bomb the mixture of gases formed also produce considerable corrosion accompanied, for some reason, by low results for carbon so that the Monel-metal bomb, as constructed, cannot be employed for the analysis of chlorine compounds.

TABLE I

ANALYTICAL RESULTS

	Weight in milligrams of					Carbon, %	
Material analyzed	Sample	Ignitor	C in ignitor	Total C	C in sample	Found	Calcd.
Benzoic acid	14.04	.....	...	9.666	9.666	68.85	68.83
	13.98	.....	...	9.597	9.597	68.65	
	16.02	.....	...	11.010	11.010	68.73	
	7.18	.....	...	4.959	4.959	69.20	
White cotton	18.23	.....	...	7.842	7.842	43.02	
Thread pellet	18.80	.....	...	8.098	8.098	43.07	
Phenyl mustard oil	10.70	18.45[a]	7.943	14.623	6.680	62.43	62.22
	8.96	9.62[b]	4.252	9.825	5.573	62.20	
	14.36	8.92[b]	3.943	12.895	8.952	62.34	
Urea pellet	28.623	4.970[c]	4.274	9.966	5.692	19.88	20.00
Crystals	8.700	8.200[c]	7.052	8.774	1.722	19.79	
Crystals	16.93	3.55[c]	3.053	6.442	3.389	20.02	

[a] Pellet of white thread.

[b] Gelatin capsule.

[c] "Nujol," 86.00% of carbon.

The complete determination, including weighing and titrating, requires 50 to 60 minutes. In case a series of analyses is to be made the time required is considerably less since weighing and titration may occupy the analyst while the bomb is in the rotating machine. Aside from the technique of handling and weighing micro samples, the operations are as simple as those of the macro method.

Summary

1. By using a modification of the bomb method of analysis described by Wilde and Lochte, the carbon content of samples weighing 10 to 30 mg. may be determined accurately and rapidly.

2. Nitrogen and sulfur do not interfere with the use of the method, but the bomb described is corroded when chlorine compounds are burned.

3. No practical method of using this method in analyzing micro samples of liquids boiling below 100° has been developed.

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[CONTRIBUTION FROM THE EXPLOSIVES CHEMICAL LABORATORY, EXPLOSIVES SECTION, PITTSBURGH EXPERIMENT STATION, UNITED STATES BUREAU OF MINES]

THE PROPERTIES OF GLYCOL DIACETATE[1]

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Until recently the prohibitive cost of glycol diacetate, $CH_3.COO.CH_2.$-$CH_2.OOC.CH_3$, prevented its use as a solvent; but now it is prepared on a large scale with a high degree of purity and is finding extensive application in the arts. Having a high boiling point, high solvent power, low vapor pressure and being non-inflammable, it was thought possible that this compound might be of use in the purification and crystallization of explosives. With this in view, a study of its physical properties was made in the Explosives Chemical Laboratory of the Pittsburgh Experiment Station of the Bureau of Mines, at the suggestion of and on material procured by Dr. Charles E. Munroe of the National Research Council.

Properties

Pure glycol diacetate is a colorless, neutral, mobile liquid possessing a slight, characteristic, though unobjectionable, odor. It may be prepared (1) from ethylene dibromide or diiodide and silver acetate,[4] (2) from ethylene dibromide and anhydrous potassium acetate[5] at 150° to 200°, or (3) by boiling a mixture of 74 g. of ethylene dibromide, 80 g. of sodium acetate, and 200 g. of glacial acetic acid for 35 hours.[6] It is now prepared on a large scale from derivatives of the chlorination of natural gas.[7]

A quantity of commercial glycol diacetate[8] of high purity, boiling at 188° to 189.6° (739.2 mm.), was purified in the following way. The water that may have been present was removed by treatment with calcium chloride. The clear filtrate was kept from contact with moist air and fractionally distilled at about 125° and 85 mm. The middle (and largest) of three

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

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[3] Assistant Explosives Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[4] Wurtz, *Ann. chim. phys.*, [3] **55**, 433 (1859).

[5] Demole, *Ann.*, **177**, 49 (1875).

[6] Seelig, Ger. pat. 41,507 (1887).

[7] Meyer, Ger. pat. 332,677 (1921). Rodebush, U. S. pat. 1,430,324 (1922).

[8] Supplied by courtesy of the Carbide and Carbon Chemicals Corp.