Summary

The Toepler pump has been so modified that, with the aid of a common water pump, it will operate continuously and automatically, return the exhaust mercury to the reservoir, permit the collection of the exhaust gas, and guard against its contamination. The modified pump is no more difficult to construct than the simple Toepler pump. It will operate over long periods of time without attention.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, NATIONAL LAMP WORKS OF THE GENERAL ELECTRIC COMPANY]

THE VOLUMETRIC DETERMINATION OF SMALL QUANTITIES OF CARBON IN TUNGSTEN BY COMBUSTION

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The description of the volumetric method for the determination of carbon in tungsten by combustion, presented in this paper, is applicable to samples in which the total carbon is quite small (less than 0.2 mg.). The modifications in apparatus and technique have been developed for the analysis of carbon in tungsten filaments of incandescent lamps. A sensitive method is necessary, not only because the amount of carbon in the filaments is small (less than 0.05%) but because the weight of sample is frequently limited to a few milligrams of filaments or occasionally to the weight of a single filament.

Cain,[1] Brady,[2] Truog[3] and Hibbard[4] describe methods for the determination of carbon or carbon dioxide which depend upon the absorption of carbon dioxide in barium hydroxide solution and the titration of the excess of alkali with hydrochloric acid using phenolphthalein as indicator. These authors show that this adaptation of the titrimetric method using 0.1 to 0.5 *N* barium hydroxide is reliable for the larger amounts of carbon occurring in common steels and carbonate samples. No application of the method to small amounts of carbon is mentioned.

The present method of analysis depends upon the combustion of tungsten in oxygen, passage of the products of combustion into a special absorption apparatus containing hot 0.01 *N* barium hydroxide solution and titration of the cold, filtered solution with 0.01 *N* hydrochloric acid using thymolphthalein as indicator. Oxygen is purified by ignition over platinized porcelain and washing in concd. potassium hydroxide solution. A mercury seal and flexible plunger make possible the use of a closed system so

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[1] Cain, *J. Ind. Eng. Chem.*, **6**, 465 (1914).

[2] Brady, *ibid.*, **6**, 843 (1914).

[3] Truog, *ibid.*, **7**, 1045 (1915).

[4] Hibbard, *ibid.*, **11**, 941 (1919).

that carbon dioxide may be swept out and a satisfactory blank obtained before moving the sample into the combustion zone of the furnace. A special absorption apparatus provides for the complete absorption of carbon dioxide, the precipitation and filtration of barium carbonate in the hot solution, and finally a method of titrating the excess of barium hydroxide without transferring to a second vessel.

Apparatus

The dimensions of all apparatus may be had by referring to the length of Furnace B (Fig. 1) and the height of the water heater I (Fig. 2) both of which are 30 cm. Since all of the glass apparatus was made in the laboratory it seemed desirable to use Pyrex exclusively because of its greater strength and durability.

Combustion Train.—A detailed sketch of the combustion apparatus is shown in Fig. 1.

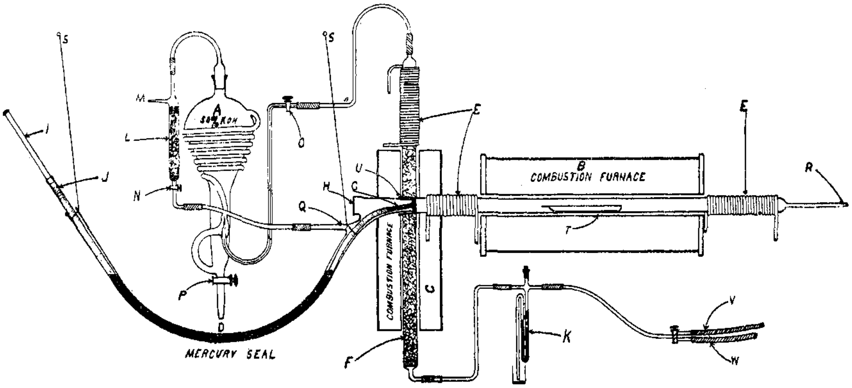

Fig. 1.

Air or oxygen is admitted at V or W as desired by operating the 3-way stopcock. Near the stopcock is a mercury trap K, which protects the apparatus from high pressures and also serves as a manometer. The combustion furnace C is constructed to give a temperature of 500° to 600°. It is supplied with a 2cm. silica tube F, filled with 10- to 20-mesh platinized, unglazed porcelain, and drawn down at the ends as shown in the sketch.

The rate of gas flow from Furnace C to Absorption Tower A is controlled by Stopcock O. Absorption Tower A consists of a 400cc. flask to which is attached 1.5 meters of spiral coil (5 mm. inside diameter) and an injector device so that the incoming gas passes out through a 1.5-mm. nozzle, causing an upward flow of gas and potassium hydroxide solution through the coil, and discharges in the top of the tower. The tower is drained by turning Stopcock P and is filled by removing the hollow, ground-glass stopper at the top, the stopper serving as an outlet for the washed gas. The purified gas from A passes into tube L which is packed with fine glass wool to insure removal of spray. M, a small jet (0.25 mm. in diameter), is kept permanently open to stabilize the flow of gas. Stopcock N regulates the flow of gas into the combustion furnace B. From L the combustion line enters the furnace B through the arm Q. Observations in the furnace are made through the sealed Pyrex glass window H. The furnace B is opened by swinging back D, a one-piece combination of mercury seal and furnace stopper, the latter making a ground-glass connection with the silica tube at U. The connection was prepared by flaring the silica tube, and shaping and grinding the Pyrex stopper to fit. Points S are supports from which D is swung. The Nichrome plunger G is made from heavy ribbon and attached to a 5mm. brass spring J. The glass rod I fits snugly into J and forms a convenient handle. By properly manipulating Handle I which operates plunger G the combustion boat can be pushed into the hot zone of the furnace. The combustion tube of B is a transparent silica tube (14 mm. in inside diameter) drawn down at one end and sealed with small tubing as shown at R. The exposed ends of the silica tubes, subjected to considerable heat, are cooled by water flowing through 5mm. copper coils E wound from annealed tubing. The boat T is a standard alundum combustion boat 13 mm. × 10 cm. Furnace C with the aid of a rheostat operates between 700° and 1000°.

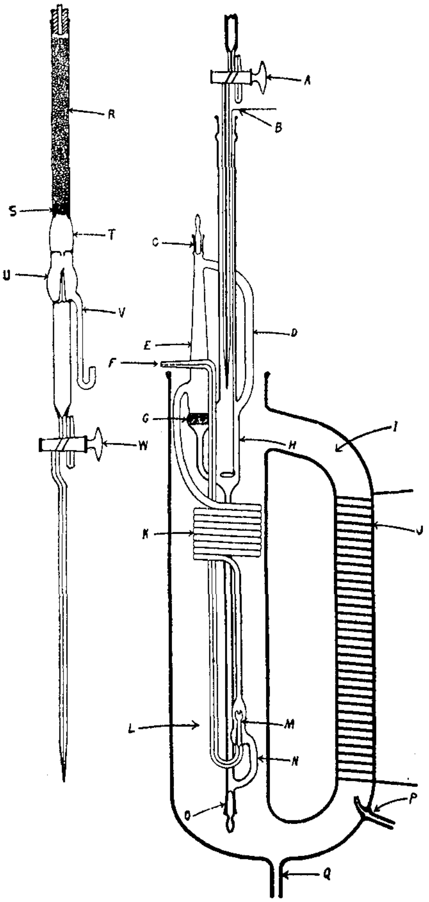

Fig. 2.

Absorption Apparatus and Pipet.—The carbon dioxide absorption apparatus, with buret and water heater in position, is shown in Fig. 2, at the right.

At the left is shown an automatic filling pipet with carbon dioxide trap. The combustion gases from Furnace B pass out R (Fig. 1) into the absorption apparatus at F (Fig. 2) down through a capillary tube and out the two 0.2mm. jets at M. During the mixing of the barium hydroxide solution and the gases, barium carbonate is precipitated and carried around the spiral coil K to Chamber E, where it is filtered upon a layer of fine glass wool, well cut up, evenly distributed and held in place by two perforated platinum disks. The filtered solution drains into H and down the vertical column, through N and again repeats the cycle. The inside diameter of the coil tubing from a point just above M to Chamber E is 2.9 mm. The gas delivered at E freed from carbon dioxide, passes out at the top of the chamber, through D, into the top of Chamber H and finally leaves the apparatus through the mouth near the handle of the stirrer B. The approximate gas flow through the apparatus at a mercury manometer pressure of 3 to 5 cm. is 75 cc. per minute. A continuous flow of gas escaping at B through the long, narrow neck of the absorption apparatus effectively prevents contamination by carbon dioxide from the air. Access to the apparatus for cleaning is provided by two ground-glass stoppers C and D and the mouth near B. Stirring of the solution in H during titration is accomplished with the platinum wire B, the stirrer having a gold-soldered, platinum disk small enough to pass through the mouth at B. The lower portion of the automatic filling buret A with 3-way stopcock is shown in position for titration. It is equipped with a carbon dioxide trap and is quite similar to the barium hydroxide pipet. Since 1 cc. of the buret scale is equivalent to 10 cm. of length, accurate readings can be made to ±0.01 cc. The total capacity of the buret is 5 cc.

The water heater I consists of a large tube 5 cm. in diameter, 30 cm. high, with a side arm 2 cm. in diameter. The side arm is wound with 40 turns of crimped Nichrome ribbon J (the resistance of which is 2.0 ohms per foot). This form of heating element used with a rheostat upon a 110-volt circuit gives ample heat control. Circulation of the water in the heater is promoted by bubbling air through P. The water in the heater is drained at Q, to which is attached a rubber hose with pinch clamp.

At the left of Fig. 2, a 4cc. automatic filling pipet suitable for handling barium hydroxide solution is shown. Tube R is filled with 20-mesh soda lime and supported by glass wool S. T is an air chamber to prevent liquid reaching the soda lime. The overflow of the pipet runs into U and passes out through the trap V; W is a 3-way capillary stopcock suitable for filling and emptying the pipet.

Standard Solutions and Indicator

Barium hydroxide and hydrochloric acid standard solutions are made to contain equal amounts of ethyl alcohol and barium chloride so that they will not change concentration in the solution being titrated. The alcohol, by lowering the surface tension of the aqueous solution, promotes smooth operations of the absorption apparatus. The presence of an excess of barium chloride decreases the solubility of barium carbonate. The prepared solutions are stored in bottles equipped with gravity siphons and soda lime traps.

0.01 *N* Barium Hydroxide.—A solution of barium hydroxide is prepared by diluting 0.02 *N* barium hydroxide with carbon dioxide-free water and neutral ethyl alcohol, and adding barium chloride so that the final solution after boiling and settling to clearness will have a normality between 0.010 and 0.011 and will contain 15% of alcohol and 1% of barium chloride.

0.01 *N* Hydrochloric Acid.—This solution is prepared by diluting 0.1 *N* hydrochloric acid with water and alcohol, so that after adding barium chloride it will have a normality of exactly 0.0105 and will contain 15% of alcohol and 1% of barium chloride. Carbon dioxide-free air saturated with the vapor of the same solution is bubbled through the solution for 24 hours. The solution is checked against pure sodium carbonate.

Thymolphthalein.—One-fourth g. of the dry indicator is dissolved in 100 cc. of neutral ethyl alcohol. One drop from the tip of a fine-tipped dropper is used. Thymolphthalein indicator is preferred to phenolphthalein because the end-point is sharper and because there is less risk of losing carbon dioxide near the end of the titration.

Method of Analyses

During the course of an analysis scrupulous care must be exercised to exclude carbon from every possible source. Freshly ignited alundum combustion boats which have been tested in blank determinations are used. All interior parts of the combustion line including the spring and plunger must be clean. Only a minimum exposure to the dust of the atmosphere is permitted. Blank and sample determinations are made under uniform conditions.

Preparatory to analysis, the combustion boat T (Fig. 1) is set into a larger alundum boat and the sample weighed into it. After removing the furnace stopper D, the boat with sample is grasped with crucible tongs and placed in the cold zone of the furnace and the stopper replaced.

With Outlet R (Fig. 1) connected to Inlet F (Fig. 2), the rate of gas flow through the absorption apparatus is adjusted so that uniform bubbling with the formation of alternate layers of gas and liquid results at M, forcing a continuous flow of liquid and gas through the coil K. After the apparatus is cleaned with hot 1:4 hydrochloric acid and washed free from acid, 6 cc. of water and 1 drop of thymolphthalein indicator are added and followed by 0.01 *N* barium hydroxide until the solution is permanently blue. Ten minutes after the sample has been placed in the cold zone of the furnace, the solution is treated with 0.01 *N* hydrochloric acid until 1 drop produces a colorless solution when observed in average north sky light against a flat, white background. After the apparatus has been drained by removing the stopper at O, 4 cc. of 0.01 *N* barium hydroxide solution is admitted at B from the delivery pipet (Fig. 2). This volume of liquid should be ample to operate the absorption apparatus. The water heater is placed in position and filled with hot water (68° to 70°). With the rate of gas flow properly adjusted and the temperature maintained at 65° by means of Nichrome heater J, the operation is continued for 13 minutes. The hot water is withdrawn through Q and replaced with water at 20°. When the apparatus is cooled, the heater is removed, indicator added, and the solution titrated with 0.01 *N* hydrochloric acid. The acid is added slowly, and the solution agitated thoroughly with Stirrer B, so that sufficient time is allowed for fresh alkali to circulate. At no time except near the end-point should the solution in H be colorless. This titration is designated as a blank determination. Blanks should check within ± 0.02 cc. of an established average before a sample analysis is made.

When a satisfactory blank is obtained and the titrated solution withdrawn, 4 cc. of 0.01 *N* barium hydroxide solution is added. With the water heater in position and filled, the sample is pushed into the hot combustion zone of the furnace, and the plunger quickly withdrawn to avoid heating the spring and plunger. The procedure from this point is identical with that in the blank determination. When the tungsten is in the form of fine wire or powder, the combustion is started with air and after two minutes switched to O by turning the 3-way stopcock at V and W. After titration of the sample the combustion boat T is removed in the customary manner with a heavy Nichrome wire bent at the end in the shape of a hook.

Analysis of Standard Sample

The volumetric method of analysis has been tested in a series of analyses of a standard sample of prepared tungsten powder. For this purpose a sample is prepared by mixing one part of tungsten powder, known to contain 0.50% of carbon, with nine parts of carbon-free tungsten, and passing twice through a 150-mesh sieve. An average of three analyses by a standard gravimetric combustion method, using large samples, gave 0.052% of carbon. The results of a series of analyses of this standard by the volumetric method are given in Table I.

TABLE I

DETERMINATION OF CARBON IN TUNGSTEN POWDER. STANDARD SAMPLE CONTAINING 0.052% OF CARBON

	Sample	Cc. of 0.011 N HCl			Mg. of carbon			% of carbon	
Detn.	G.	Blank	Samp.	Diff.	Present	Found	Error	Found	Error
1	0.0158	4.34	4.23	0.11	0.0082	0.0073	−0.0009	0.046	−0.006
2	.0230	4.33	4.14	.19	.0120	.0125	+ .0005	.054	+ .002
3	.0310	4.33	4.10	.23	.0161	.0152	− .0009	.049	− .003
4	.0380	4.34	4.03	.31	.0198	.0205	+ .0007	.053	+ .001
5	.0480	4.35	3.94	.41	.0250	.0271	+ .0021	.055	+ .003
6	.0580	4.34	3.85	.49	.0302	.0323	+ .0021	.055	+ .003
7	.0670	4.35	3.83	.52	.0348	.0343	− .0005	.051	− .001
8	.0770	4.34	3.71	.63	.0400	.0416	+ .0016	.054	+ .002
9	.0960	4.33	3.56	.77	.0500	.0508	+ .0008	.053	+ .001
10	.1150	4.33	3.40	.93	.0598	.0614	+ .0016	.053	+ .001
11	.1350	4.33	3.27	1.06	.0702	.0700	− .0002	.052	0
12	.1540	4.33	3.05	1.28	.0801	.0845	+ .0044	.055	+ .003
13	.1730	4.34	2.97	1.37	.0900	.0905	+ .0005	.052	0
14	.1920	4.34	2.95	1.39	.0998	.0918	− .0088	.048	− .004
15	.2880	4.34	2.25	2.09	.1500	.1380	− .0120	.048	− .004
16	.3840	4.34	1.70	2.64	.2000	.1742	− .0258	.045	− .007

1 cc. of 0.011 N HCl = 0.066 mg. of carbon. Blank HCl titr. = 4.2 cc. of $Ba(OH)_2$ soln.

A study of the analyses in this table indicates that 0.09 mg. of carbon is the maximum quantity that can be completely absorbed as carbon dioxide in this method of analysis. The first thirteen determinations show no significant variations and the errors in mg. of carbon found, with the exception of Determination 12, are not greater than the allowable errors of the volumetric apparatus. The remaining three determinations show an increasing loss of carbon dioxide, indicating that the maximum capacity of the apparatus for complete absorption has been reached.

Remarks

In an attempt to obtain uniform blank titrations it was noticed that the temperature and time of contact of the aqueous barium hydroxide solution with the glass influenced the titration. Above 95°, dissolved alkalies increased the acid titration 0.4 to 0.5 cc. during the usual interval of analysis. The corrosion decreased with temperature until at 70° no effect could be observed. The danger of corrosion was further diminished by mixing the alkali solution with ethyl alcohol. The presence of 15% of alcohol in the acid and alkali solutions, by lowering the surface tension of the solutions, eliminated most of the "grease trouble" incident to the use of lubricated stopcocks on a sensitive buret or pipet. A temperature of 65° was selected as being suitable to insure minimum corrosion of the glass and yet sufficient to permit complete carbon dioxide absorption and coagulation of the barium carbonate precipitate.

Acknowledgment

The writer wishes to thank Mr. J. G. Wild, Manager of the Chemical Laboratory, for suggestions and assistance in the development of this method.

Summary

Modifications in the volumetric method for the determination of carbon in tungsten by combustion are presented.

An absorption apparatus is described whereby carbon dioxide is precipitated and filtered as barium carbonate in the hot solution and the filtered solution titrated without transferring to a second vessel.

The addition of 15% of ethyl alcohol and 1% of barium chloride to the standard 0.01 N solutions of barium hydroxide and hydrochloric acid is recommended.

The use of a mercury seal and flexible plunger, providing for a closed combustion train during analysis, is shown.

A series of analyses of a standard sample of tungsten powder containing 0.052% of carbon shows that, in samples varying in weight from 0.016 g. to 0.288 g., the maximum error in the percentage of carbon found is 0.006 and the average error is 0.0026.

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