

DETERMINATION OF CARBON ON NON-CONDUCTING CATALYSTS BY INDUCTION HEATING-CONDUCTOMETRIC METHOD

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Many catalysts used in petroleum processing are sensitive to small amounts of contaminants. One such material is carbon. To some types of synthetic catalysts, small amounts of carbon affect activity and/or selectivity appreciably; thus a rapid analytical procedure is needed to predict process controls. The search for a rapid procedure for determining total carbon on synthetic catalyst resulted in the development of a method which involves combustion followed by conductometric determination of the carbon dioxide formed.

Carbon on catalyst is generally determined by burning it in a resistance furnace and measuring the CO_2 evolved by gravimetric or volumetric methods. These methods proved inadequate because carbon trapped in catalyst pores could not be burned without first grinding the sample. This was time-consuming and, in addition, grinding did not necessarily release all of the carbon.

High frequency induction heating has also been used to burn carbon and it offered the advantage of higher temperatures whereby the sample is melted and entrapped carbon is exposed to oxygen. PEPKOWITZ¹ employed it in conjunction with a freeze-out technique for isolation of carbon dioxide, HOLLER *et al.*², absorbed the CO_2 in Ascarite, and SIMONS *et al.*³, developed a high frequency combustion-volumetric method. All of these procedures were applied to metals and were not applicable directly to non- or low-conducting materials. In addition, the techniques used to measure the carbon dioxide involved were either time-consuming, too sensitive to operator error for control work, or not applicable in the range below 0.1% carbon.

This paper describes a rapid and reasonably precise method for determining total carbon in non-conducting catalysts or other solids. The carbon dioxide evolved from the high frequency furnace is absorbed in dilute barium hydroxide. The change in conductivity of this solution is directly proportional to the amount of carbon dioxide absorbed.

Apparatus

A simple schematic diagram of the apparatus is shown in Fig. 1 and a photograph is shown in Fig. 2. (1) High frequency induction furnace, equipped with "Vycor" glass combustion tube. A Lindberg Model LI-501F was used for this work. Other suitable makes and models are available. (2) Conductometric carbon determinator, Leco Model 515, was employed for the finishing step.

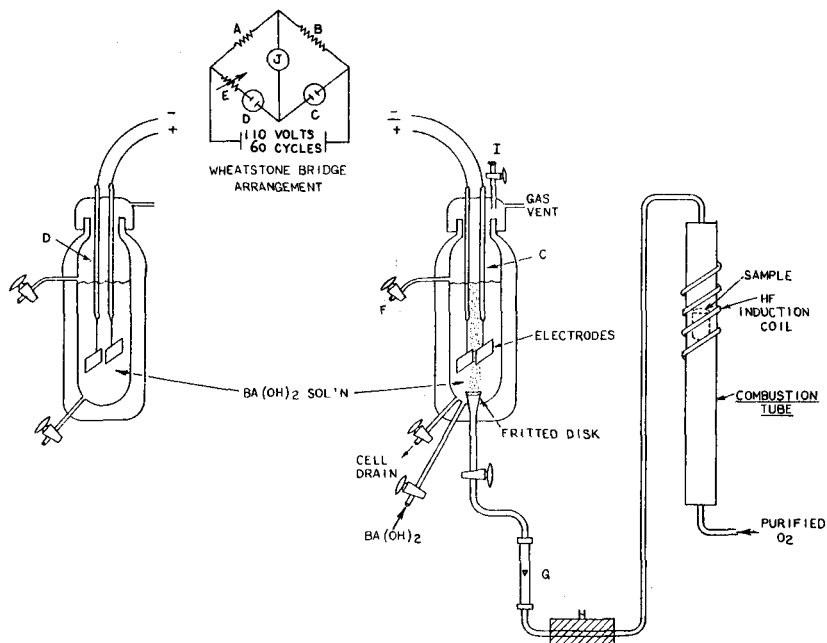


Fig. 1. Schematic diagram of apparatus. (A) fixed resistor; (B) fixed resistor; (C) measuring cell; (D) reference cell; (E) variable resistor; (F) cell leveling outlet; (G) rotameter; (H) sulfur scrubber; (I) wash solution inlet; (J) cathode ray tube.

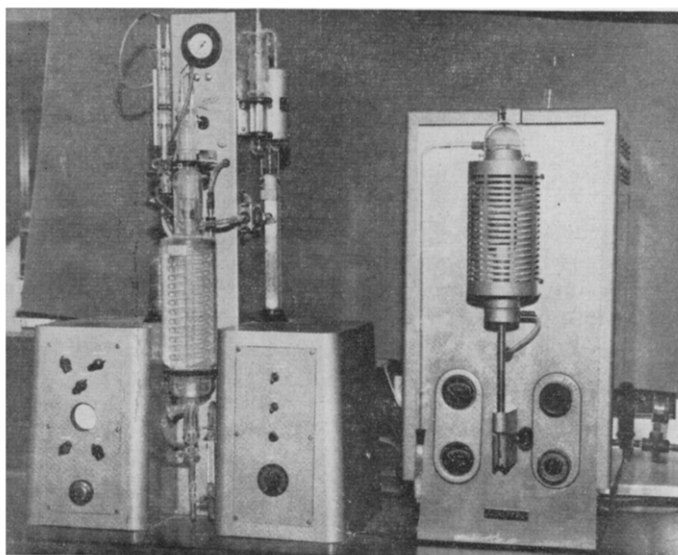


Fig. 2. Conductometric carbon determinator and high frequency furnace.

Reagents

Oxygen, prepurified grade, fed from a gas cylinder equipped with a reduction valve. It is further purified by passing it over an oxidation catalyst and then through Ascarite and a drying agent to remove carbon dioxide and water. Manganese dioxide, granular, non-carbon dioxide absorbing, Leco 501C. Iron chip accelerator, Leco 160 and tin, 20 mesh, carbon free, Leco 155. Barium hydroxide solution: Bubble carbon dioxide-free air through 16 l of distilled water for 1 h. Dissolve 15 g of $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ (reagent grade) in 500 ml of CO_2 -free water. Filter into the CO_2 -free 16 l of water previously prepared. Dissolve 2 g of Knox gelatin in 500 ml of warm CO_2 -free water. Add 5 ml of 2-ethylhexanol. Add this to large volume and bring up to 18 l with CO_2 -free water. Stopper bottle, shake contents thoroughly, then allow solution to stand for one week before using. NBS Standard No. 57 (Silicon), used for preparing calibration curve.

RECOMMENDED PROCEDURE

Calibration

Assemble apparatus according to manufacturer's instructions and as shown in Fig. 2. Turn on power and constant temperature bath switches on carbon determinator. Carefully place electrodes in cells C and D. Fill both cells with barium hydroxide solution to leveling outlet H. Adjust flow of oxygen to 250–300 ml/min and purge system while weighing sample.

To a dry carbon-free ceramic crucible add one scoop ($1/4''$ diameter by $1/4''$ deep) of iron and one scoop of tin. Weigh crucible, then add enough standard sample to give about 0.2 mg carbon. Reweigh to obtain exact sample weight. Add an additional scoop of iron and one of tin on top of the sample. Position crucible in "Vycor" glass combustion tube.

With oxygen flowing through the system, zero the decade reading on the Carbon Determinator and adjust lines on scope to coincide. Ignite sample for 5 min, then turn off furnace but continue flushing tube with oxygen. As oxygen flushes the combustion products from the furnace tube and into the scrubbing solution, the lines on the scope separate. Keep the lines together by increasing the decade (Ohms) reading. When all of the carbon dioxide has been absorbed in the barium hydroxide solution (total time is 10–15 min), the lines will no longer separate. Record this decade reading. Drain and rinse measuring cell with dilute HCl followed by water. Refill cell with barium hydroxide solution. Solution in the reference cell is changed whenever a new batch of barium hydroxide is put in use.

Burn increasing amounts of standard containing up to 0.6 mg carbon such as to permit construction of a calibration curve, decade reading *vs.* mg carbon.

Unknown samples

Unknown samples are analyzed in the same manner as described above. It has been found that 0.2-g samples are satisfactory. If samples much larger are taken, incomplete combustion is obtained. The final decade reading of the unknown is compared to the calibration curve in order to determine milligrams carbon burned.

A blank must be determined on the iron and tin and subtracted from values of the unknowns.

EXPERIMENTAL RESULTS

The precision of the method was established by repetitive analyses of plant samples. The standard deviation was found to be $\pm 0.007\%$ at the 0.07% carbon level. Ac-

curacy was demonstrated by the determination of NBS standard samples. These data are presented in Table I.

TABLE I
ACCURACY OF METHOD

Sample	No. of determinations	Carbon, wt. %	
		Certified value	Found
NBS-101C	5	0.072	0.065
NBS-57	10	0.087	0.081

It should be noted that the application of this method did not require better precision than shown, thus ultimate precision was not sought and may be better than indicated.

DISCUSSION

The measuring system of the conductometric apparatus is essentially a Wheatstone bridge, as shown in Fig. 1. Resistances A and B are fixed while E is variable, having a range of 0–100 Ohms. C and D are the glass cells containing barium hydroxide solutions, D being the reference cell and C is the measuring cell. J is an amplified cathode ray tube which indicates the state of balance of the bridge.

In operation, the bridge is balanced $A/B = D/C$. When the sample is burned, the carbon dioxide produced is introduced into cell C. This decreases the conductivity of the barium hydroxide solution due to formation of barium carbonate. The bridge is again balanced using the variable resistance E so that $A/B = D + E/C$, E then being directly proportional to the amount of carbon present.

The calibration curve should be checked daily. Investigation has shown that calibration does not shift during a given day but only when the instrument is shut down and restarted. Repeated efforts to establish a stable calibration curve failed. However, part of the shift in calibration was found to result from handling the measuring electrodes which were removed between analyses in order to rinse the measuring cell. The shift was lessened appreciably by adding glass tube I, whereby the HCl and water could be placed into the measuring cell without moving the electrodes.

Lines on the cathode ray tube should be parallel. Some difficulty with keeping them parallel was encountered and was traced to small variations in resistors. This difficulty was easily eliminated by connecting ten-turn helipot across each electrode and adjusting their resistances until the lines were parallel.

Success of this procedure depends, of course, upon complete oxidation of carbon to carbon dioxide. This is determined largely by temperature and the availability of oxygen at time of ignition. The excess supply of oxygen is easily maintained by increasing the input as the sample burns. Also, oxidizing agents may be used if needed.

Temperature presents a problem when low-conducting samples are to be analyzed. A conducting material must be added in proper amounts to insure an adequate temperature for oxidizing the sample. Electrolytic iron⁴ is suitable for this purpose. Tin is usually added to lower the melting point of iron. Various amounts of each were employed in burning synthetic catalysts and the amounts stated in the procedure were found to be optimum.

ACKNOWLEDGEMENTS

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SUMMARY

A method is described for the determination of carbon in non-conducting synthetic catalysts. Carbon is oxidized in a high frequency induction furnace and the evolved carbon dioxide is absorbed in a solution of barium hydroxide. The change in conductivity of this solution is directly proportional to the carbon burned. The method is rapid and reasonably precise at the 0.05% carbon level.

RÉSUMÉ

Une méthode est décrite pour le dosage rapide du carbone dans des catalyseurs. On procède par combustion dans un four à induction, à haute fréquence. L'anhydride carbonique obtenu est absorbé dans une solution d'hydroxyde de baryum. La variation de conductibilité de cette solution est proportionnelle à la quantité de carbone brûlée. La méthode est rapide et d'une précision satisfaisante au niveau de 0.05% de carbone.

ZUSAMMENFASSUNG

Beschreibung einer Schnell-methode zur Bestimmung des Kohlenstoffs in Katalysatoren durch Verbrennung in einem Hochfrequenz-Induktionsofen. Das gebildete Kohlendioxyd wird in Barytlauge absorbiert und die Änderung der Leitfähigkeit gemessen; diese ist dem Kohlenstoffgehalt direkt proportional. Die Exaktheit der Methode ist bei 0.05% Kohlenstoffgehalt zufriedenstellend.

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THE THERMAL PROPERTIES OF SOME AMINE TETRAPHENYLBORON SALTS 8-QUINOLINOL AND ITS DERIVATIVES

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In dilute acid solutions, many aliphatic and aromatic amines form insoluble salts with the tetraphenylboron ion, $[B(C_6H_5)_4]^-$, having the composition, $AmH^+[B(C_6H_5)_4]^-$ where AmH^+ is the amine onium ion. These salts have been useful for the qualitative and quantitative estimation of the amines¹⁻⁶. However, CRANE³ discovered that 8-quinolinol (oxine) forms a salt with the tetraphenylboron ion (TPB) which had the composition, 2 oxine: 1 TPB. On the basis of ionic charge considerations, the composition should be similar to that found for other amine salts, namely, 1 oxine: 1 TPB.

WENDLANDT⁷ has previously studied the thermal stability of the oxine-TPB salt

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