NASA TECHNICAL MEMORANDUM

NASA TM-75259

# DETERMINATION OF CARBON BY THE OXIDATION-REDUCTION REACTION WITH CHROMIUM

L. Mashkovich and A. F. Kuteynikov



Translation of "Opredeleniye ugleroda po okislitel'no-vosstanovitel'noy reaktsii s khromon", In: Sovremennyye metody khimicheskogo i spektral'nogo analiza materialov, (Modern Methods of Chemical and Spectral Analysis of Materials) 1967, pp. 217-220


NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

MARCH 1978

STANDARD TITLE PAGE

| 1. Report No. | 2. Government Accession No. | 3. Recipient's Catalog No. |
|---|---|---|
| NASA TM-75259 | | |

4. Title and Subtitle

DETERMINATION OF CARBON BY THE OXIDATION REDUCTION REACTION WITH CHROMIUM

5. Report Date: March 1978

6. Performing Organization Code

7. Author(s)

L. Mashkovich and A. F. Kuteynikov

8. Performing Organization Report No.

10. Work Unit No.

9. Performing Organization Name and Address

Leo Kanner Associates, Redwood City, California 94063

11. Contract or Grant No.: NASw-2790

13. Type of Report and Period Covered: Translation

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration, Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Opredeleniye ugleroda po okislitel'no-vosstanovitel'noy reaktsii s khromom", In: Sovremennyye metody khimicheskogo i spektral'nogo analiza materialov, (Modern Methods of Chemical and Spectral Analysis of Materials) 1967, pp. 217-220

16. Abstract

Free carbon was determined in silicon and boron carbides in ash, oxides, and other materials by oxidation to carbon dioxide with a mixture of $K_2Cr_2O_7 + H_2SO_4$. The determination was made from the amount of Cr(VI) consumed, by adding excess Mohr's salt and titrating with a standard solution of $KMnO_4$. The amount of Cr(VI) self-reduced was determined in a blank test. Optimum oxidation conditions were achieved when the volumes of 5% $K_2Cr_2O_7$ and $H_2SO_4$ were equal. The mixture was boiled for 1-2 hours using a reflex condenser. The volume should not be reduced, in order to avoid an increase in the sulfuric acid concentration. The relative error was 4-7% for 0.005-0.04 g C and $\leq$ 3.5% for 0.1 g C.

| 17. Key Words (Selected by Author(s)) | 18. Distribution Statement |
|---|---|
| | Unclassified-Unlimited |

| 19. Security Classif. (of this report) | 20. Security Classif. (of this page) | 21. No. of Pages | 22. Price |
|---|---|---|---|
| Unclassified | Unclassified | | |

# DETERMINATION OF CARBON BY THE OXIDATION-REDUCTION REACTION WITH CHROMIUM

L. Mashkovich and A. F. Kutejnikov

A method is developed for determining carbon according to the reaction with a mixture of potassium bichromate and sulfuric acid, by means of the determination of reduced chromium. The method is used for determining carbon in materials containing boron carbide, silicon carbide, and fluoroplastic.

/217*

In order to determine free carbon in materials containing chemically stable carbides, methods are used which are based on the capability of free carbon to be oxidized to a dioxide by various oxidants and mixtures of them [1].

Corleis developed the principle of the method of damp oxidation of carbon and used it to determine combined carbon. The procedure is based on the dissolving of cast irons, steels, iron, and ferroalloys in a mixture of $H_2SO_4 + CuSO_4 + H_2CrO_4$ with the absorption of $CO_2$ by soda lime [2]. The mechanism of the reaction is expressed [2, 3] by the equation $3C + 2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3CO_2 + 8H_2O$.

Carbon black, coal, coke, and graphite behave differently toward oxidants, with graphite being the most stable.

We tested the oxidizing capacity of a number of mixtures with respect to different types of graphite and to the compounds which are contained in the materials being studied. It was established that the chromium mixture $H_2SO_4 + K_2Cr_2O_7$

*Numbers in the margin indicate pagination in the foreign text.

is the most suitable. It oxidizes carbon completely and does not affect silicon carbide, boron carbide, fluoroplastic, ash, oxides, and silicon. The chromium mixture was used earlier [4, 5] for oxidizing free carbon in $B_4C$, with absorption of carbon dioxide by asbestos or barite.

We propose a method for determining carbon, based on the determination of the chromium consumed in oxidation.

The method was tested on spectrally pure graphite, using a mixture with various chromium and sulfuric acid contents for oxidation. An increase in acidity accelerates the process of oxidation of the carbon (Fig. 1), but at the same time /219
assists self-reduction of the chromium (Fig. 2). This phenomenon was observed in a blank test, i.e. through heating of the mixture without carbon. Self-reduction of chromium disturbs the stoichiometric character of the reaction and causes errors in the determination of carbon by chromium.

Comparison of the obtained results made it possible to establish the optimal composition of the mixture and the oxidation conditions under which the oxidation-reduction reaction between carbon and chromium occurs stoichiometrically. This mixture should consist of a 5% solution of potassium bichromate and concentrated sulfuric acid in a 1:1 ratio. An increase in the chromium concentration, with heating and subsequent cooling, leads to the precipitation of $K_2Cr_2O_7$ crystals. It is necessary to conduct the heating without reducing the volume, so as not to increase the sulfuric acid concentration.

The given mixture oxidizes 1 g of graphite in 2-2.5 hours. In this case, the amount of self-reduced chromium is $\sim$0.3%. Taking this amount into account according to a blank test, one may preclude error or reduce it to a minimum.

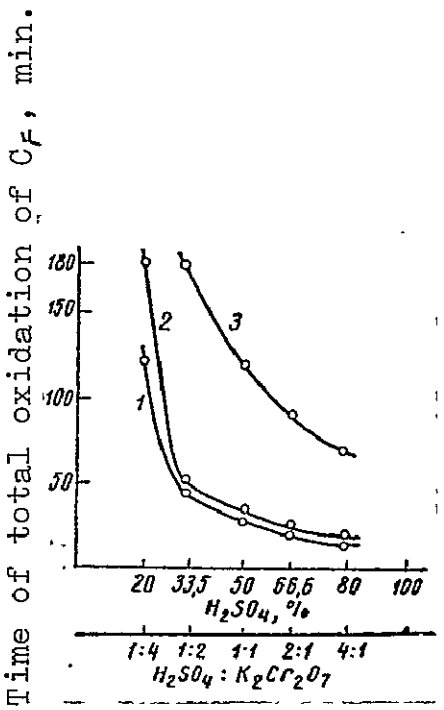


Fig. 1. Dependence of the rate of oxidation of free carbon on the sulfuric acid concentration in the chromium mixture:
1—0.01 g $C_F$, 2—0.05 g $C_F$, 3—1.00 g $C_F$

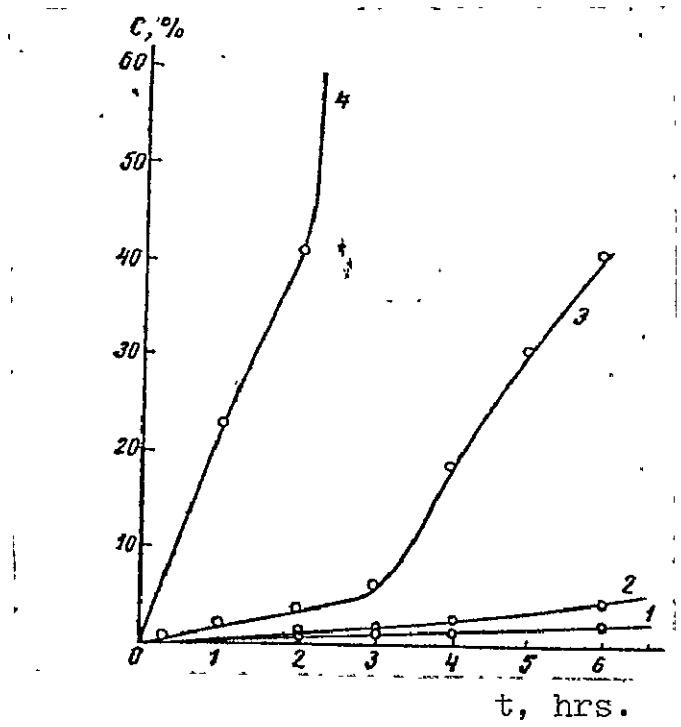


Fig. 2. Effect of boiling time and composition of chromium mixture on the reduction of chromium in the blank test. Curves 1-4 correspond to the ratio of $H_2SO_4$ (1.84): 10% $K_2Cr_2O_7$ = 1:4; 1:2; 1:1; 2:1.

Given in Table 1 are the results of determining spectrally pure carbon using chromium. The relative error of determination was 4-7% for 0.005-0.04 g C and $\leqslant 3.5\%$ for 0.1 g C. The time of a single determination was 20-30 minutes. This method makes

TABLE 1

RESULTS OF THE DETERMINATION OF CARBON ACCORDING TO THE OXIDATION REACTION WITH CHROMIUM (n=10)

| a Количество графита, мг | b Расход Cr (VI), мг | | e Найдено С мг | f Ошибка % (отн.) |
|---|---|---|---|---|
| | c рассчитано по реакции | d найдено | | |
| 5,0 | 28,9 | 30,5 | 5,3 | 5,6 |
| 10,0 | 57,8 | 58,7 | 10,2 | 2,0 |
| 20,0 | 115,7 | 118,1 | 20,4 | 2,0 |
| 40,0 | 231,1 | 231,6 | 40,1 | 0,25 |
| 60,0 | 346,7 | 344,3 | 60,0 | 0 |
| 80,0 | 462,2 | 449,7 | 77,8 | 2,75 |
| 100,0 | 577,8 | 579,0 | 100,2 | 0,20 |

Key: a. Amount of graphite, mg
b. Consumption of Cr(VI), mg
c. Calculated according to the reaction
d. Found
e. C found, mg
f. Error, % (relative)

it possible to determine from several to dozens of per cents of carbon, and may be recommended for the analysis of materials containing oxides, ash, silicon, fluoroplastic, boron carbide, and silicon carbide.

A 0.1-2 g sample of the material, finely divided to -150 +200 mesh, was processed by boiling with a 5% solution of potassium bichromate, accurately measured with a buret, and with the same amount of concentrated sulfuric acid. The processing was conducted in a conical flask of 200-300 ml volume with a ground reflux condenser for 1-2 hours. A blank test was performed at the same time. After dissolving, the /220

contents of the flask, with the precipitate, were transferred to a 250 ml volumetric flask.

If necessary, the precipitate was filtered through a glass filter and weighed.

A 0.05 n. solution of Mohr's salt, the excess of which was back-titrated with 0.05 n. potassium permanganate, was added from a buret to the aliquot portion (25/250 for the sample and 5/250 for the blank test) [6]. The carbon content was calculated according to the formula

$$X = \frac{A \cdot 100}{5{,}78a}\ \%,$$

where $a$ is the sample in g; 5.78 is the amount of Cr(VI) going into the oxidation of 1 g of carbon; A is the amount of Cr(VI) going to the oxidation of $C_{св}$ in the sample; $A = B_1 - B$ ($B_1$ and B are the amounts of Cr(VI) taken for oxidation and remaining after oxidation of carbon).

The developed method was tested on artificial mixtures and production samples. The most reliable results were obtained with a content of > 1% C in the sample. The results are given in Table 2.

TABLE 2

RESULTS OF DETERMINING FREE CARBON BY DIFFERENT METHODS

| a Исследуемый материал | b Содержание $C_{св}$, % | c Найдено $C_{св}$, % | | |
|---|---|---|---|---|
| | | d предлагаемым способом | e методом выжигания | f газообъемным методом [6] |
| g | | | | |
| h Карбид бора . . . . . | ⩽18 | 10,60 | — | 10,07 |
| Графит + SiC: | | | | |
| № 1 . . . . . | — | 1,34 | 1,20 | 1,27 |
| № 2 . . . . . | — | 61,47 | 61,10 | — |
| № 3 . . . . . | — | 61,08 | 60,50 | — |
| № 4 . . . . . | — | 67,02 | 67,7 | — |
| № 5 . . . . . | — | 81,44 | 82,1 | — |
| 0,1 г SiC+0,1 г C . . . . . | 50 | 50,10 | 50,0 | — |
| 0,18 г SiC+0,02 г C . . . . | 10 | 10,13 | 9,85 | 9,96 |
| B—Si—C . . . . . | — | 63,75 | 44,82 | 62,62 |
| | | 63,38 | | 65,81 |
| i Фторопласт . . . . . | 0 | 0 | — | — |
| j Фторопласт + графит: | | | | |
| 0,9 г + 0,1 г C . . . . . | 10 | 9,86 | — | — |
| 0,92 г + 0,08 г C . . . . . | 8 | 7,94 | — | — |
| № 1 . . . . . | 50 | 50,30 | — | — |
| № 2 . . . . . | 50 | 52,10 | — | — |
| № 3 . . . . . | 65 | 66,80 | — | — |

Key: a. Material being studied
b. $C_f$ content, %
c. $C_f$ found, %
d. By the proposed method
e. By the roasting method
f. By the gas volume method [6]
g. Boron carbide
h. Graphite + SiC
i. Fluoroplastic
j. Fluoroplastic + graphite

REFERENCES


1. Analiz tugoplavkikh soedinenii [Analysis of High-Melting-Point Compounds], Metallurgizdat (1962).

2. Corleis, E., Stahl und Eisen, 14, 1894, 589.

3. Lendel', G., et al., Analiz chernykh metallov [Analysis of Ferrous Metals], Goskhimizdat, 182 (1934).

4. Meerson, G.A., Samsonov, G.V., Zavodskaya laboratoriya XVI/12 (1950).

5. Kitakhara, Asakhara, Atodi, RZhKhim, No. 78324 (1959).

6. Dymov, A.M., Tekhnicheskii analiz rud i metallov [Technical Analysis of Ores and Metals], Metallurgizdat, 194 (1949).