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THE DETERMINATION OF TRACE CARBON IN METALS BY NONAQUEOUS TITRATION

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BY NONAQUEOUS TITRATION

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November 30, 1964

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BY NONAQUEOUS TITRATION

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Livermore, California

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ABSTRACT

This report describes a nonaqueous titrimetric procedure for determining the carbon dioxide evolved from metal samples which have been combusted in oxygen in an induction furnace. The carbon dioxide is titrated continuously using sodium hydroxide in pyridine as a titrant, acetone as the solvent, and thymol blue as the indicator. An independent standardization procedure is described and results are given showing the sensitivity, precision, and accuracy of the determination.

The determination of carbon in a wide variety of metals and alloys at the submilligram level is becoming a frequent task for the analyst servicing metallurgical samples. The analysis is usually accomplished in two steps; the combustion step in which the sample is burned, and the measurement step in which the resulting carbon dioxide is determined.

Some of the many different approaches to this problem have been summarized by Blom and Edelhausen(1) and by Dezirat(3). Walker and Kuo(8) have briefly reviewed some gas chromatographic procedures for the determination of carbon dioxide and described a procedure for carbon in ferrous

materials using this technique. Green, Still, and Chirnside(5) have reviewed the combustion step over a wide range of metals and presented information on methods of heating and the use of fluxes.

One of the more popular methods for trace carbon consists of measuring the change in conductivity of a barium hydroxide solution as the carbon dioxide is absorbed. Still, Dauncey, and Chirnside(7) have described the use of a conductometric procedure. Recently, Bruins(2) has discussed some of the disadvantages of using internal electrodes for measuring the conductivity of barium hydroxide solutions and described a series of vessels with external electrodes.

Very little use has been made of nonaqueous titrimetric procedures for the determination of carbon dioxide. Patchornik and Shalitin(6) have described a titration of carbon dioxide in benzylamine and applied it to biological samples. Grant, Hunter, and Massie(4) used dimethyl formamide as a solvent and used a titrimetric procedure for carbon in limestone, dolomite, organic compounds, and a high-carbon steel.

Blom and Edelhausen(1) have shown that the continuous titration of carbon dioxide in acetone with a methyl alcohol-pyridine solution of sodium methoxide using thymol blue indicator is a sensitive and accurate procedure for the determination of carbon dioxide in flowing systems. They used it for determining carbon in organic compounds. White(9) showed that the end-point drift in this system was due to the presence of water and excess methanol in the solvents and successfully applied the titration to microgram quantities of carbon derived from organic compounds and carbonates.

These titrimetric procedures require a relatively low flow rate of oxygen (30-60 ml/min), better suited to the determination of carbon in non-refractory, easily combusted materials. Preliminary experiments confirmed

the work of White. (9), and it was felt that if this procedure could be applied to the determination of carbon dioxide using higher oxygen flow rates and induction-furnace combustion techniques, a simple and accurate method for determining trace carbon in a wide variety of materials would result.

EXPERIMENTAL

Apparatus. Figure 1 is a schematic of the system with a second absorption cell shown connected in series with the first. Most connections on the incoming oxygen side of the small copper oxide furnace were constructed of 1/8-inch stainless-steel tubing which was silver-soldered to copper, and copper-glass housekeeper seals with glass spherical joints. The spherical joints were sealed with Apiezon W black hard wax. The oxygen pressure was controlled with a low-pressure pancake-type regulator after the usual oxygen pressure regulator. The oxygen of 99.5% purity was led by means of a coil of 1/8-inch stainless-steel tubing to a quartz tube 1-1/4 X 24 inch filled with wire-form copper oxide and heated to 800 to 900° C with a resistance furnace which was effective over 12 inches of the quartz tube. The oxygen plus any carbon dioxide impurity was then run through a Pyrex tube 1 X 18 inches filled with ascarite and anhydrone and from there entered the quartz combustion tube in a Leco induction furnace equipped with a variac control. The coils of stainless-steel tubing imparted a good deal of flexibility to an otherwise rigid system. A piece of flexible tubing connected the outlet of the induction furnace to a dust trap consisting of a small flask filled with glass wool, MnO₂ trap for absorbing oxides of sulfur and nitrogen, and finally a smaller copper oxide furnace heated to 800 to 900° C. The oxygen then went through a one-way check valve and was connected to the absorption cell by a short length of tygon tubing and plastic quick-connectors which were convenient for adding a cell or repositioning two cells.

Figure 2 is a sketch of the titration cell showing the buret attachment. It is a gas washing bottle of about 250 ml capacity (available from Houston Glass Fabricating Company, Houston, Texas). A small hole is blown in the shoulder or side of the bottle and a short length of glass tubing attached and fitted with a rubber syringe cap. A 19-gauge 4-inch stainless-steel hypodermic needle is used as a buret tip. It fits into a 5- or 10-ml microburet with detachable tip available from the Kimble Glass Company. An ascarite-filled drying tube can be placed on the funnel of the buret with a rubber stopper. Teflon sleeves are used to seal the standard tapered 29/42 caps to the tops of the cells.

Two of these cells may be connected in series for checking the completeness of carbon dioxide absorption, or they may be easily rearranged so that one may be used to generate a standard amount of carbon dioxide for titration in the second. Leco No. 528-35 crucibles for heavy duty use and Leco No. 528-42 porous covers were used throughout this investigation.

Reagents and Solutions. White (9) has shown that for a sharp end point free of excessive drift, the solvents should be dry and the titrant should not contain too much methanol. Satisfactory results were obtained using A. C. S. reagent-grade acetone and methanol without further drying. A. C. S. reagent-grade pyridine was distilled just before preparing solutions of sodium hydroxide.

0.2 M Sodium Hydroxide in Methanol. Quickly weigh approximately 800 mg of NaOH pellets and dissolve in 100 ml of methanol.

0.02 M Sodium Hydroxide. Take 10 ml of the 0.2 M stock solution and dilute to 100 ml with pyridine.

0.005 M Sodium Hydroxide. Take 2.5 ml of the 0.2 M stock solution and add about 90 ml of pyridine. If turbidity appears, add methyl alcohol

drop-wise with mixing until the solution clears; then complete the dilution with pyridine to 100 ml.

Sodium Bicarbonate Standard. 0.525 g of A. C. S. reagent grade NaHCO_3 per liter of water. (75.0 $\mu\text{g C/ml}$)

Indicator Solution. 0.1% solution of thymol blue in methanol.

Iron. Electrolytic iron ignited in moist hydrogen, available from the G. Frederick Smith Chemical Company (contains about 8 ppm C).

Tin. Leco No. 501-76 granulated tin (contains about 2 to 4 ppm C).

Copper Rings. Leco No. 550-184 (contains about 10 ppm C).

MnO_2 . Leco No. 501-60. Especially prepared for use as an absorbent. Reagent-grade MnO_2 is not effective. See for example Reference 10.

Procedure. Standardization of Sodium Hydroxide Solution. The titration cells are arranged so that CO_2 is generated and flushed out of cell number 1 into cell number 2. Put 30 ml of 10% H_2SO_4 into cell number 1 and attach the outlet of this cell to cell number 2 through a small (10 X 1.5 cm) drying tube containing silica gel. Add 150 ml of dry acetone and 30 drops of thymol blue indicator to cell number 2. Connect the purified oxygen from the induction furnace to the inlet of cell number 1. Adjust the oxygen flow rate to about 1 liter per minute and pretitrate with the appropriate NaOH solution to the final blue color of the indicator. The blue color of the indicator will gradually drift back to the yellow at a rate which must be predetermined and corrected for. This amounts to about 0.006 to 0.008 ml of 0.02 M NaOH per minute or 0.024 to 0.030 ml of 0.005 M NaOH per minute. After the system has been flushed out with oxygen as indicated by stable drift rates, an appropriate concentration of standard NaHCO_3 is allowed to enter cell number 1 from a buret. The CO_2 is titrated continuously as it is swept into cell number 2 by the oxygen without allowing the entire solution to turn

yellow at any one time. The cell is flushed out for 8 minutes and then the drift is checked for 5 minutes. The time required for the titration is recorded and the drift-rate correction is made.

Blanking. For the most precise results, the crucibles were individually prefired by the following procedure: A copper ring was placed in the bottom of the crucible. Two grams of iron and 2 grams of tin were added in alternating 1-gram layers. A porous cover was placed on the crucible and the variac control set at 70%. The crucible was placed in the furnace, the oxygen flow set at 1 liter per minute, and the furnace turned on. When the plate current meter indicated 400 milliamps, the variac control was slowly lowered over 5 minutes until the crucible gave only a faint red glow. The furnace was then turned off and the crucible allowed to cool in the closed furnace for 10 minutes. Residual carbon after a mock loading was not detectable.

Samples. The prefired crucible is removed from the induction furnace for ease of sample loading. It is placed on a clean porcelain plate and the sample (with extra flux, if necessary) added. The crucible is covered and returned to the furnace and the furnace is purged for 5 minutes with oxygen (1 liter/min). The titration cell is prepared as in the standardization step and then the furnace is turned on and the variac turned up until the sample "fires." The variac is adjusted so that the plate current is held at around 350 milliamperes. The CO_2 from the sample is continuously titrated as in the standardization step. The sample is burned for 10 minutes and then a drift is determined for 5 minutes. The drift-rate correction is made from the recorded titration time as before.

DISCUSSION AND RESULTS

Among the variables related to the use of the nonaqueous titrimetric procedure, the most important is the gradual drift of the end point. Our values are somewhat higher than those reported by White(9). However, the endpoints are sharp to 0.01 to 0.02 ml of 0.005 M reagent and the drift varies only slightly from run to run. The usual variation in drift is from 0.002 to 0.004 ml/min, which for a 10-minute run using 0.005 M titrant would amount to a difference of only 1 to 2 micrograms of carbon at most. The absolute rates are around 0.028 ml/min for the 0.005 M titrant and 0.010 ml/min for the 0.02 M titrant. Of course, accurate results require the determination of the drift after each run. Five minutes is sufficient for this determination. Typical drifts are included in some of the tables.

The values found for the rate of the drift of the end point vary somewhat depending on the experimental conditions. For instance, Table I, which gives results for the standardization of sodium-hydroxide solution, shows that the drift gradually increases as each run is made, but drops back again when the drying tube is replaced with a fresh one. Using a larger drying tube causes a higher rate of increase of the drift. Different desiccants had little effect. Using a small drying tube and changing frequently gave the lowest and most reproducible values.

The drift rate also depends, to some extent, on the amount of CO_2 that has been absorbed by the acetone. The acetone is usually replaced after three or four carbon determinations. A marked increase in the end-point drift rate resulted if the MnO_2 trap for oxides of sulfur and nitrogen became exhausted. A very large increase occurred if traces of acetone came in contact with the MnO_2 . This trap was replaced about once a week.

The lowest rate of the end-point drift was found for the oxygen stream going through the cold furnace and then entering the titration cell. A value of 0.016 to 0.020 ml/min (0.005 M) increased to about 0.028 ml/min (0.005 M) when a burned-out crucible was placed in the furnace and reignited. Evidently, some carbon is formed in the immediate combustion area of the furnace, possibly from the silicone rubber seal or the tube leading from the furnace. Again, the variation in drift from run to run was quite low as indicated in Table II.

The efficiency of absorption of the carbon dioxide in the titration cell can be indicated by connecting a second cell in series with the first as shown in Figure 1. Both cells are pretitrated to the end-point color and a slight excess of titrant added to the second cell. A standard carbon sample is burned in the furnace and the CO_2 titrated in the usual manner.

In this configuration the frit of the second cell over-pressurizes the first cell and this results in an excessive amount of acetone diffusing up the buret tip. The back-pressure also makes the buret drain slowly and hence it is difficult to continuously titrate the CO_2 as it is swept into the cell. Even under these conditions two samples containing 150 and 90 micrograms of carbon, respectively, and burned under oxygen flowing at 1.2 liters/minute showed only 3 micrograms of carbon appearing in the second cell. As mentioned previously, the color of the indicator should not be allowed to change to yellow during the titration, although some yellow color is sometimes observed as the titrant and CO_2 are mixed in the acetone.

Crucibles which have been prefired in the induction furnace will refire even though no additional flux or conducting sample has been added. Once the flux in the crucible has reached the molten state, even for the second firing, it will remain in this state for over an hour if the power is regulated

to keep the plate current to around 300 to 400 milliamps. If the copper ring was not present in the original flux mixture, a second addition of about 1 gram of iron is necessary to refire the crucible. If nonconducting samples are added to the prefired crucible, it is sometimes necessary to use extra iron and tin to refire the crucible.

Slow cooling of the crucible after the prefiring is necessary because, otherwise, the crucible may fail during the subsequent combustion step.

Table III indicates that the titrant is relatively stable. However, as the volume of titrant in a flask decreases the change in titer with time becomes pronounced unless precautions are taken to prevent CO_2 from coming in contact with the titrant. Also, in the 0.005 M solutions, a precipitate begins to form after a few days which tends to interfere with proper drainage of the buret. For these reasons it was found convenient to make a fresh dilution from the 0.2 M stock solution each day and restandardize each day.

N. B. S. standard sample 166B has been run using the NaHCO_3 standardization procedure and crucibles which have been prefired in the induction furnace. Table II gives the results on this sample for several runs of different sample sizes. The carbon contents of GFS iron and Leco tin and copper were also determined by this method.

The general procedure works well for other samples and has been used for determining trace carbon in such metals as uranium, beryllium, and boron, as well as various alloys and ceramics. Sometimes extra "flux" or "accelerator" must be added to a prefired crucible in order to obtain proper burning characteristics and insure complete combustion. In this case the blank on the added material must be determined.

A sample requires 35 minutes for completion using the single prefired crucible technique; that is about 15 minutes for the firing and slow cooling

and another 5 minutes for purging the system after sample loading. Ten minutes are taken to insure complete combustion and another 5 minutes for drift-rate check.

To reduce the time per sample in routine determinations, an average drift rate can be used which need be checked only once or twice a day.

The sensitivity of the determination using the dilute titrant is about $\pm 1 \mu\text{g}$ of carbon. The accuracy is the same. However, Table II suggests a possible negative bias in the results for the N. B. S. carbon standard at the higher carbon levels amounting to 2 or 3 micrograms.

The 0.02 M titrant is used when total carbon was expected to exceed $200 \mu\text{g}$. It is comparable to the more dilute titrant and no unusual problems were encountered in its use. The sensitivity was about $\pm 4 \mu\text{g}$ of carbon.

Although it is possible that the drift rates reported here could be lowered by some minor modifications of the furnace and by careful drying of the reagents, it is doubtful if much would be gained in accuracy and precision. The drifts are already reasonably stable for any series of runs.

Conclusion. The high oxygen flow rate, continuous visual observation of the CO_2 as it is titrated and the simplicity and sensitivity of the detection system affords a procedure well suited for trace carbon determinations in diverse materials and for investigational procedures for determining the proper conditions for the induction furnace technique.

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Table I. Standardization of 0.005 M Sodium Hydroxide in Pyridine
(NaHCO_3 Solution equivalent to $75.0 \mu\text{g C/ml}$)

$\mu\text{g Carbon}^a$ taken	Ml NaOH	Titer as $\mu\text{g C/ml}$	Drift, ml/min
84.8	1.68	50.4	0.024
148.5	2.97	50.0	0.026
79.5	1.57	50.6	0.028
152.3	3.00	50.7	^b 0.024
228.0	4.43	51.5	0.028
79.5	1.60	49.7	^b 0.022
153.8	2.99	51.4	0.030
213.8	4.30	49.7	0.032
220.5	4.37	50.5	0.028

^aThe order in which they were run. Mean = $50.5 \mu\text{g C/ml}$

^bDrying tube changed. Relative Standard Deviation = $\pm 1.3\%$

Table II. Determination of Carbon in N. B. S. Standard Sample 166B
Low-Carbon Stainless Steel 0.019₁ % C

$\mu\text{g C}^{\text{a}}$ taken	$\mu\text{g C}^{\text{b}}$ found	ppm C	drift, ml/min
19.7	21.5	208	0.022
19.1	19.4	194	0.020
19.2	18.9	189	0.024
38.5	38.3	190	0.026
38.5	38.3	190	0.026
38.0	38.9	195	0.022
76.2	75.2	188	0.024
76.6	75.2	187	0.028
77.0	77.3	192	0.020
116.6	115.4	189	0.026
115.6	112.8	186	0.028
115.2	111.8	185	0.026

^aSample weights ranged from 100 through 600 mg.

^b0.005 M titrant used.

Table III. Stability of Titrant

0.005 M titrant		0.2 M stock solution diluted to 0.005 M each day ^a	
1st day	51.1 $\mu\text{g C/ml}$	1st day	53.3 $\mu\text{g C/ml}$
2nd day	50.7 $\mu\text{g C/ml}$	3rd day	52.1 $\mu\text{g C/ml}$
5th day	48.8 $\mu\text{g C/ml}$	18th day	54.4 $\mu\text{g C/ml}$

^aResults reflect a volumetric error of about $\pm 5\%$ in making each dilution.

Figure 1. Schematic of apparatus. 1. Oxygen cylinder, 2. Pressure regulators, 3. 1/8-inch SS tubing, 4. Large furnace over quartz tube containing CuO, 5. Pyrex tube containing ascarite and anhydride, 6. Quartz combustion tube and induction furnace, 7. Spring-loaded handle, 8. Dust trap, 9. Trap containing MnO₂, 10. Small furnace over quartz tube containing CuO, 11. One-way check valve, 12. Absorption cells in series, 13. Burets, 14. Flowmeter, SL - Swagelok, HS - Housekeeper seals.

Figure 2. Sketch of titration cell.

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