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SODIUM MASS TRANSFER: XIII THE DETERMINATION OF TOTAL CARBON IN SODIUM

By

W.W. SABOL
D. DUTINA
D.E. REY
J.L. SIMPSON

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GENERAL ELECTRIC

ATOMIC POWER EQUIPMENT DEPARTMENT
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THE DETERMINATION OF TOTAL
CARBON IN SODIUM

W. W. Sabol
D. Dutina
D. E. Rey
J. L. Simpson

Approved: *R. W. Lockhart*

R. W. Lockhart, Project Engineer
Sodium Mass Transfer Program

D. H. Ahmann

D. H. Ahmann, Manager
Chemistry and Chemical Engineering

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SODIUM MASS TRANSFER: XIII
THE DETERMINATION OF
TOTAL CARBON IN SODIUM

ABSTRACT

A modification of the classical Pepkowitz-Porter method for determining the carbon content in sodium has been made. In the new approach, carbon-containing gases released during dissolution of the sodium (gases that were discarded in the original work) are collected and are added to the CO_2 found by the customary wet oxidation. Improvements in preparing the Van Slyke oxidant have reduced the blank by a factor of 2.5. The sensitivity is 10 ± 5 ppm C with sample sizes ranging from 1.5 to 8.0 grams. All manipulations are performed in a closed system which eliminates the need for sweep or carrier gases and reduces the possibility of introducing contamination. Gas chromatography is used to determine the quantity of carbon evolved as CO_2 or other gaseous forms during the analysis. Results of analyses of samples removed from sodium mass transfer loops are presented.

The technique established for collecting and identifying the components of the gas mixture released during the main steps in the procedure has provided evidence for the presence of more than one type of carbon (i. e. , elemental) in the sodium.

INTRODUCTION

It has been recognized for some time that carburization of stainless steels and decarburization of ferritic steels occurs in systems that are in contact with high-temperature flowing sodium.⁽¹⁾ Mass transport of metals also occurs in these systems and results in the formation of corrosion deposits. The quantity of material moved is dependent upon parameters such as (1) the temperature, (2) the oxygen content of the circulating sodium, (3) the material, (4) the rate of sodium flow, (5) location in the system, and (6) configuration of flow passage. The effects of these parameters on the corrosion processes occurring on combinations of three types of structural materials are being studied with six dynamic test loops of identical configuration.⁽²⁾

In support of these studies, it was necessary to monitor the total carbon in the sodium during the course of a loop run. The development program undertaken to provide an analytical method for this purpose is described herein.

Classically, the determination of carbon is performed after quantitative oxidation of the element to carbon dioxide. Stoffer and Phillips⁽³⁾ applied this principle to the analysis of sodium-potassium alloy, using gaseous oxygen as the oxidant. This approach was modified by Mungall, and co-workers⁽⁴⁾ and applied to the analysis of sodium metal. In their modification, the absorption of CO_2 by the Na_2O produced is prevented. Kallman⁽⁵⁾ described a similar combustion technique, but chose a lower temperature to ensure the absorption of all the CO_2 by the Na_2O

produced. The carbon dioxide which is released by dissolving the Na_2CO_3 and Na_2O matrix in an acid system, is collected and measured. Pepkowitz and Porter⁽⁶⁾ used wet combustion. After the sodium sample is dissolved in water, the resultant caustic solution is acidified with sulfuric acid, and then evaporated to a slurry of sodium sulfate. The carbon in this residue is oxidized with Van Slyke reagent,⁽⁷⁾ a mixture of sulfuric, phosphoric, and chromic acids.

Aside from the oxidation techniques, analytical methods also differ in ways of measuring the CO_2 evolved. In many of the earlier procedures, manometry, conductimetry, and titrimetry are used and it is assumed the gas being measured is CO_2 . These methods are being replaced by the specific, and generally more sensitive techniques of gas chromatography⁽⁴⁾ and mass spectrometry,⁽⁸⁾ which identify as well as measure the quantity of gases found.

Before choosing the most suitable method for total carbon, current theories regarding the carbon species responsible for transport in sodium were examined. Just which form of carbon takes part in these reactions is not known, although there are strong proponents for the belief that carbon and oxygen, paired in some fashion, are responsible for the movement of carbon. Lyushenko and Nevzorov,⁽⁹⁾ for example, propose that transport occurs by carbon monoxide. The possibility that carbonates and carbonyls are present in sodium,^(10, 11) and are playing an active part in the process, cannot be ignored. Oxygen-free species, such as elemental carbon and heavy metal carbides, must be considered.

As a result of the uncertainty about the variety of forms of carbon that may exist under loop conditions, the primary requisite for an analytical method is that all the carbon, regardless of its form, be measured. Secondly, it was desirable that the method provide, if possible, information about the nature of the species of carbon present. Finally, the sensitivity of the method must be such as to permit accurate measurement at the expected concentration levels. Because appropriate solubility data for carbon in sodium was lacking at the specified test operating conditions (see Gratton⁽¹²⁾ for example) it was only possible to make the rough estimate that a sensitivity of 10 ppm would meet the data requirements.

Generally, the choice of an adequate method for measuring the gas evolved is not difficult; often it is made on the basis of the equipment already on hand or within the experience of the analyst. The choice of the oxidation method to provide a measure of total carbon as well as information on the source of the specific carbon species involved, however, is not made so easily. It was decided that the wet combustion method used by Pepkowitz, after certain modifications, would best meet the requirements.

In the present version, the gases liberated during the dissolution of the sample, as well as those released upon acidification and evaporation of the dissolver solution, are collected and measured. This is a departure from the method as originally developed, wherein these gases were discarded. In the remainder of the method, oxidation by means of Van Slyke solution, as described by Pepkowitz is used.

To perform these operations initially, a flowing system utilizing purified helium as a carrier gas was used. ⁽¹³⁾ However, for the present analytical scheme, a closed system, without a sweep or carrier gas, was designed to accommodate all the main steps in the method, i. e., dissolution, neutralization, evaporation, and wet oxidation. In this way, contamination from air or loss of carbon containing gases by entrainment in the carrier gas stream was avoided, as was the need for equipment to ensure the purity of such a gas. Heated copper oxide was used to convert hydrogen released during dissolution into water. Thus, the need for large expansion volumes in the system was eliminated. Coincidentally, some of the carbon-containing gases (CO) evolved were oxidized to CO₂ by passing them through this heated, dry oxidant. The gases from the dissolution and acidification steps were examined together, but separately from the gases evolved during the wet oxidation. The total carbon, then, was calculated as the sum of the amounts of carbon found in each of these two steps.

Gas chromatography was substituted for the simple manometric measurement to identify, as well as measure, the quantity of gases liberated in the determination. If carbon were present as carbides, as carbonyls or as carbonates it would be released in the gaseous state in the milder steps of the sample treatment and before wet oxidation. Specifically, CO could indicate the presence of carbonyls; hydrocarbon gases could indicate the presence of carbides; and CO₂ could indicate the presence of carbonates. The potential ability to differentiate between the various carbon-containing species is an advantage over the high-temperature, dry combustion methods which use gaseous oxygen. While such methods may be adequate for determining total carbon content, they cannot readily give much information about specific carbon species.

The sensitivity of the Pepkowitz method was marginal for the requirements of the program. This was due primarily to a high reagent blank coupled with a restriction on the size of the sample that could be handled. It was also due to the use of a fairly crude, by today's standards, manometric measurement.

The Pepkowitz-Porter method had a blank of 30 ppm. They required 5 ml of the Van Slyke reagent which contained 6 µg of C per ml to react with a 1 gram sample. This is clearly unsatisfactory where analysis at the 10 ppm level is required. An improved Van Slyke reagent was prepared which contained 2.5 times less carbon (2.3 µg per ml) than the solution used by Pepkowitz. This was accomplished by substitution of concentrated acid for fuming sulfuric and by heating at 140°C for 6 hours. The mixture is allowed to cool to room temperature under vacuum. The detailed procedure for the preparation of this reagent appears in the Appendix. In addition an apparatus capable of handling a 5 gram sample was designed and assembled. Ten milliliters of the reagent are required in the modified procedure and thus it can be calculated that the blank has been reduced to 5 ppm when a five gram sodium sample is used. This is satisfactory on the basis of the usual rule that an acceptable sensitivity is that equal to twice the blank value. Although gas chromatography was primarily introduced to enable identification of the gases released in the determination, it has the added advantage of providing a means for the quantitative measurement of these gases at

concentrations of 1 ppm or less. A Perkin-Elmer model 154L Vapor Fractometer was satisfactory for these measurements after it was modified. A second detector was added to the circuit to correct errors in results due to flow interruption which were caused by the valving arrangement associated with the use of a single detector. These changes are discussed in the Appendix and illustrated in Figures A-2 and A-3.

The major emphasis in this report will be placed on describing the method for determining the total carbon content in sodium. Some typical results obtained on sodium samples removed from dynamic loops will be presented. Also, some observations on the nature of the gases evolved during the determination will be included.

ANALYTICAL METHOD

The steps in the analytical method are summarized briefly in this section. The step-by-step procedure on sampling, analyzing, and calculating appears in Appendix A. The apparatus is shown in Figure 1.

Sampling Techniques

Sodium is removed from the loops by evacuated, long-stemmed, Pyrex glass bulbs of approximately 40 gram capacity.⁽¹³⁾ The bulbs are cut open in a glove box containing a controlled atmosphere of argon. Small pieces of sodium (1/4 inch diameter) are removed from each bulb and several pieces are combined to provide several 2.0-to-3.0 gm samples. These pieces are weighed and then placed in individual reaction flasks. The flasks are sealed, by closing the cocks on the connecting funnel and flask, transferred from the glove box, and attached to the analytical apparatus:

Analytical Procedure

1. Releasing, Trapping, and Measuring Carbon Attacked by Water and Acid

After evacuating the closed system to 1 torr, the sample is dissolved with 0.1 N H_2SO_4 . The hydrogen released is oxidized to water by copper oxide at 360°C, and is collected on magnesium perchlorate (Anhydron). The basic solution is acidified with an excess of concentrated sulfuric acid (determined from the amount of sodium sampled) and the resulting sulfate slurry is then boiled to decompose carbonates, releasing carbon dioxide. The gases evolved during this treatment are contained in the closed system and are transferred by a Toepler pump into a copper U-trap containing silica gel cooled with liquid nitrogen. The trap is removed from the system and the contained gases are separated and measured by gas chromatography. Molecular sieve and silica gel columns controlled to 75°C are used, with He as the carrier gas. The carbon content calculated from the gases determined at this point is identified as "water-acid" carbon.

FIGURE 1 APPARATUS FOR THE DETERMINATION OF CARBON IN SODIUM

2. Releasing, Trapping, and Measuring Carbon Attacked by Van Slyke Reagent

The remaining sulfate slurry is wet-oxidized with Van Slyke reagent. The gases released within the closed system are again collected in the U-trap and measured by gas chromatography as described previously. The carbon in these gases is identified as "Van Slyke" carbon.

Calculations

The volume of each carbon-containing gas is converted to micrograms of carbon by application of the perfect Gas Law. This quantity is corrected for the blank (where necessary), related to the amount of sodium analyzed, and reported as parts per million of total carbon.

DISCUSSION OF RESULTS

1. Blanks

Although there is a small blank associated with the analytical system, the main contribution to the blank can be attributed to the Van Slyke reagent. The carbon content of a typical batch of reagent is reported in Table I. The average carbon content of the blank, 23 ± 3 micrograms per 10 ml is a decided improvement over the 60 ± 12 micrograms attained by Pepkowitz for an equivalent amount of reagent. Batches of the reagent have been used over a period of two months with no change in carbon content.

TABLE I
DETERMINATION OF THE VAN SLYKE REAGENT BLANK

<u>Run</u>	<u>Volume of Reagent (ml)</u>	<u>Carbon Found (μg)</u>	<u>Carbon Concentration (μg/10 ml)*</u>
1	10	20	20
2	20	54	27
3	30	57	19
4	10	24	24
5	20	44	21
6	10	25	25
7	20	54	27

Average Value 23μ g
Standard Deviation, $1\sigma \pm 3 \mu$ g

*Volume used in analysis.

Blanks due to the system have been determined to be 0.5 ppm or less. Because this amount is negligible compared to the reagent blank, no attempt has been made to identify the source or eliminate it.

2. Recovery of Added Gases

The ability to transfer, collect, and measure those gases (CO_2 , CO , and CH_4) normally observed in the analysis was tested by injecting known amounts of these gases into the apparatus with a calibrated gas syringe through a rubber septum attached at the top of the addition funnel. Four hundred cubic centimeters of hydrogen were also introduced to simulate the conditions existent during the time the sample is being dissolved in water. The gases were then manipulated in the system and measured in a manner analogous to that used in the actual analysis. The results are summarized in Table II. The quantitative recovery of the added gases attests to the validity of this part of the procedure.

TABLE II
RECOVERY OF ADDED GASES WITH 400 ml OF H_2 PRESENT

<u>Gas</u>	<u>μl Introduced</u>	<u>μl Recovered</u>	<u>% Recovery</u>
CO_2	440	435	98.9
	240	238	99.2
	140	139	99.3
CH_4	440	437	99.3
	240	233	97.1
	140	133	95.0
CO^*	440	448	101.8
	240	238	99.2
	140	142	104.4

Average = 99.0%

Standard Deviation, 1σ , = $\pm 2.1\%$

*CO was oxidized by CuO and measured as CO_2 .

2. Recovery of Added Carbon

The ability to recover carbon added as sodium carbonate was a test of the accuracy of those steps in the procedure which led to the calculation of "water-acid" carbon. Aliquots of a solution containing a known concentration of this salt were introduced into the reaction vessel and the analysis was carried out in the described manner. The results presented in Table III show an average recovery of $105.9 \pm 11.2\%$ for 4 runs in which the carbon content ranged from 24 to 250 micrograms.

TABLE III
RECOVERY OF CARBON ADDED AS Na₂CO₃

<u>Carbon Added (μg)</u>	<u>Carbon Recovered (μg)</u>	<u>Recovery, %</u>
24	29	120.0
48	51	106.0
96	90	93.8
240	246	102.5

Mean Recovery 105.9%

Standard Deviation, $1\sigma \pm 11.3\%$

Although the efficacy of Van Slyke solution in oxidizing carbon was demonstrated by Pepkowitz, ⁽⁶⁾ some of the work was repeated with the improved solution. The work also served to test the equipment and manipulations used in this part of the procedure. Tables IV and V give the recovery data obtained for carbon introduced as sucrose and as graphite yarn. These results show that the effectiveness of the reagent has not changed. They also show that the transfer and trapping techniques are quantitative.

TABLE IV
RECOVERY OF CARBON ADDED AS SUCROSE

<u>Carbon Added (μg)</u>	<u>Carbon Recovered (μg)</u>	<u>Recovery, %</u>
162	137	84.6
162	167	103.1
162	138	85.2
162	143	88.3
324	326	100.6
324	323	99.7
758	766	101.1

Mean Recovery 94.7%

Standard Deviation, $1\sigma \pm 8.2\%$

TABLE V
RECOVERY OF CARBON ADDED AS GRAPHITE YARN

<u>Carbon Added (μg)</u>	<u>Carbon Recovered (μg)</u>	<u>Recovery, %</u>
305	317	104.0
115	106	92.0
126	123	98.0
281	303	107.0

Mean Recovery 100.0%

Standard Deviation, $1\sigma \pm 6.6\%$

4. Precision of the Analysis

In the absence of a standard sample of carbon in sodium, the precision of the method was determined by analyzing some actual program test loop sodium. Three sodium-filled bulbs were each analyzed in triplicate. The sodium analyzed varied in weight from about 1.5 to more than 8.0 grams. The data in Table VI show that a standard deviation for the determination of ± 5 ppm is attainable.

TABLE VI
PRECISION OF THE ANALYSIS

<u>Bulb</u>	<u>Sample Weight, (g)</u>	<u>Carbon Concentration, (ppm)</u>
4-2-7	1.52	34.2
	2.99	25.4
	5.75	20.2
		29.9 ± 7.0
*54	2.52	77.4
	4.63	69.3
	6.05	69.9
		72.2 ± 4.5
4-4-3	3.30	21.2
	5.71	16.6
	8.30	15.5
		17.7 ± 3.0
Average Standard Deviation 1σ		± 4.7 ppm

*Barrel No. 2 of reactor grade sodium.

The agreement among the total carbon results obtained for a given bulb regardless of the sample size, Table VI, gives further confidence in the over-all method. These results indicate too, that samples as large as 8.0 grams can be analyzed by the procedure.

Further evidence of the good precision attainable may be found by examination of the total carbon results listed in Table VII, where the results of duplicate analyses on 6 additional bulbs of test loop sodium are presented. In this case, each sample of the pair taken from a bulb was analyzed by a different operator.

5. Observations Concerning Gaseous Carbon Compounds Released During Analysis

In the preliminary stages in the development of the method, a flowing argon⁽¹³⁾ system was used to carry the gases. Particular attention was paid to the examination of the gases evolved during sample dissolution and of those gases released during neutralization and acidification. In these early experiments, methane, ethane, and carbon monoxide were identified after the dissolution, and carbon dioxide and traces of methane were observed during the acidification. These observations encouraged the effort to employ a wet determination.

TABLE VII
COMPLETE ANALYSIS OF TYPICAL SAMPLES
OF SODIUM FROM MASS TRANSFER TEST LOOPS

ALL RESULTS IN ppm CARBON

Sample	Sample Weight (g)	Operator	Water-Acid Carbon Measured From			Van Slyke Carbon	Total Carbon
			CH ₄	CO	CO ₂		
1-6-4	2.80	A	ND*	0.3	21	51.8	73.1
	2.15	B	ND	ND	21	51.8	71.0
2-5-14	2.22	A	T **	0.2	12.0	39.4	51.6
	2.70	B	T	0.7	11.3	33.6	45.6
3-10-4	3.60	A	ND	T	8.0	19.0	27.0
	3.11	B	T	0.2	9.0	17.4	26.6
4-8-4	2.19	A	T	ND	13	22.0	35.0
	4.05	B	T	ND	5.5	39.2	45.0
5-6-8	3.06	A	ND	0.1	4.9	49.6	54.6
	4.12	B	ND	0.2	5.1	48.0	53.3
6-6-5	2.41	A	ND	0.4	10.0	23.0	33.1
	2.59	B	ND	0.3	10.0	21.0	31.0

*ND = Not Detected

** T = Trace < 0.1 ppm

The total carbon analyses of several typical loop samples are shown in Table VII, confirming the early observations that CO , CH_4 , and CO_2 are present in the gases released during the water-acid treatment. Roughly 20 to 25% of the total carbon in a typical loop sample is in a form that can be released in a gaseous form by this relatively mild treatment. However, the absolute distribution among these three gases, as shown in Table V, is misleading. It should be remembered that in the present procedure, all the gases evolved from both dissolution and acidification steps are passed over hot copper oxide. Consequently, it is possible that much of the CO_2 measured comes from the oxidation of gases such as carbon monoxide and hydrocarbons rather than being entirely caused by the decomposition of carbon forms such as carbonates that might also be present in the original sample. It should be remembered too, that in the present apparatus, no attempt is made to separate those gases released during dissolution from those evolved during acidification. Because of these limitations on the observations, no unambiguous conclusion concerning the nature of carbon species in sodium can be made to date. What is important, however, is that the presence of the various gases does give strong evidence for the existence of more than one form of carbon in the sodium.

Current work is directed toward an improved separation and identification of these gases. Thus far, success has been attained in revising the procedure and separating the carbon related to the dissolving step from that related to the acidification step. However, oxidation of the gases over copper oxide has yet to be eliminated. Changes in the apparatus to eliminate this treatment and to introduce more efficient cold traps to separate the gases from bulk quantities of H_2 appear warranted. Early results show that at least one third of the total gases evolved arise during the dissolution step and that both methane and carbon dioxide are present. The latter gases, of course, represents oxidation of some more reduced form of carbon.

CONCLUSIONS

1. The Pepkowitz-Porter wet oxidation method for the determination of small amounts of elemental carbon in sodium has been modified to permit the determination of total carbon in a sodium sample.
2. Carbon can be measured at concentration levels of 10 ppm or greater with a precision of ± 5 ppm.
3. Identification and measurement by gas chromatography of gases evolved during sample dissolution and acidification has provided evidence that some readily decomposed species of carbon are present in the Sodium Mass Transfer sodium samples.
4. More work is needed to relate the off gases observed to carbon species in sodium that has been exposed to steel above 1050°F .

APPENDIX A

I. SAMPLING TECHNIQUESA. Sampling of the Sodium From the Program Test Loops

The equipment and techniques used to take sodium from the project test loops has been described in detail. ⁽¹³⁾ Sodium is received for analysis in a 4-inch-long, 1-1/8-inch diameter Pyrex bulb which holds about 40 grams. A tube, 24 inches long, 1/4 inch in diameter, and sealed with de Khotinsky cement, extends from the bulb. Before the bulb is placed in the dry box, all but 2 inches of the tube is cut off and discarded.

B. Sampling of the Sodium-Filled Bulbs

The sodium-filled bulbs are opened and sampled in a glove box which contains a purified argon atmosphere. The box is designed so that it can be alternately evacuated and purged with argon. Special butyl gloves which minimize the diffusion of gases and moisture into the box are used. The argon is purified by passage through Ascarite and Anhydrone traps before entering the box. The purity of the argon is checked periodically by gas chromatographic analysis.

The bulbs are loaded into the vestibule of the box while the box itself is under 1 psig argon. The vestibule is then evacuated to 0.1 torr and refilled with purified argon. Next, the bulb is transferred into the box through the connecting port. Then, both the box and the vestibule are evacuated to 0.1 torr and the box is refilled with argon to 1 psig. Argon is then allowed to purge through the box and out into the atmosphere for 15 minutes before samples are removed from the bulbs. The purge is continued until these samples are taken, loaded into the reaction flasks, and the flasks sealed with a connecting funnel. The sampling operation consists of cutting the glass bulb, separating the sections of sodium with a spatula, and removing 2 to 3 grams of sodium in 1/4-inch-diameter pieces from the separated sections. The sample, comprised of these pieces, is weighed to the nearest milligram and loaded into the reaction vessel. The connecting funnel is then attached to this vessel and the stopcocks on the flask and funnel are closed.

The vestibule is filled with freshly purified argon and the reaction vessel is transferred into it. The box is re-pressurized to 1 psig. The vestibule is opened to the atmosphere, the reaction vessel removed, and transferred to the analytical system.

II. DETAILED ANALYTICAL PROCEDUREA. Apparatus (Figure A-1)

- A. Closed end Hg manometer.
- B. Vacuum stopcock.
- C. Three-way vacuum stopcock.

FIGURE A-1 SCHEMATIC DETAILED DRAWING OF APPARATUS

- D. Addition funnel.
- E. Teflon stopcock.
- F. Reaction flask.
- G. Teflon stopcock.
- H. CuO furnace tube. (The CuO is purified by heating for 24 hours at 400°C under a vacuum of 1.0 torr.)
- I. Tube furnace.
- J. Anhydrous tube.
- K. Three-way stopcock with offset bore.
- L. Toepler pump.
- M. Four-way "Circle Seal" valve of stainless steel.
- N. Gas collection trap, 1/4-inch copper tubing, packed at bottom, of loop with 1/2-inch 30 to 60 mesh silica gel.
- O. Vacuum stopcock.
- P. Cold trap.

Components made of Pyrex are interconnected by O-ring joints and screw clamps. The O-rings are made of Teflon-coated "Viton." The flask and CuO furnace tube are designed so that the joints are sufficiently removed from any hot zones. In some sections the connections are made with short lengths of heavy-walled Tygon tubing to reduce the probability of breakage during manipulations of the apparatus.

B. Releasing, Trapping, and Measuring Carbon Attacked by Water and Acid

Reagents

0.1 N H_2SO_4 - Use doubly distilled water, boiled to remove CO_2 . Add the H_2SO_4 while the water is hot. Cool and store in a tightly-capped reagent bottle.

Concentrated H_2SO_4 - Heat to vigorous fuming. Cool and store in a Pyrex reagent bottle.

Procedure

1. Connect the reaction flask and the addition funnel to the analytical system with O-rings and screw clamps.
2. Evacuate the system to less than 1.0 torr up to the stopcock on the side arm of the reaction flask.

3. Open the stopcock on the side arm of the reaction flask and evacuate the entire system to less than 1.0 torr.
4. Isolate the vacuum pump and leak-test the system. The system is considered to be sufficiently tight if there is no change in the level of Hg on the manometer after a period of 10 minutes.
5. Pipet 5 ml of 0.1 N H_2SO_4 into the additional funnel for each 3.0 grams of sample.
6. Turn the stopcock on the Toepler pump so that the pump is in line with the reaction flask. Place a cold water bath around the flask.
7. Add a sufficient amount of the 0.1 N H_2SO_4 dropwise to the sodium sample to dissolve the metal. (Do not drain the funnel.)
8. Use the Toepler pump to pass the gases evolved through the CuO furnace. Continue the pumping until all the visible moisture formed is absorbed on the Anhydron.
9. Close the stopcock on the side arm of the reaction flask. Pipet 4.5 ml of concentrated H_2SO_4 into the addition funnel for each 3.0 grams of sample.
10. Add the concentrated H_2SO_4 to the caustic slurry in the reaction flask. Leave sufficient acid in the funnel to act as a seal against the atmosphere. Remove the water bath and heat the bottom of the flask at 80°C with a heating mantle for 15 minutes. Cool the upper portion of the dissolution flask with an air line to allow the water to condense and reflux.
11. Open the stopcock on the side of the dissolution flask to allow any visible water to trap on the Anhydron.
12. Reduce the temperature on the flask to 50°C. Place a Dewar flask containing liquid nitrogen around the gas collection trap.
13. Transfer the gases from the system into the trap with the Toepler pump. The Hg is lowered while in-line with the dissolution flask and raised while in-line with the trap. This is repeated seven times to ensure complete transfer of all gases.
14. Turn the four-way valve to isolate the gas collection trap. Remove the Dewar flask and the heating mantle. Turn the stopcock on the Toepler pump so that the pump is again in-line with the reaction flask.
15. Detach the gas collection trap from the system and attach it to the gas chromatograph.

16. Purge the bypass line on the chromatograph for 10 minutes while the trap warms to room temperature. Introduce the trapped gases into the chromatograph and analyze.

C. Releasing, Trapping and Measuring Carbon Attacked by Van Slyke Solution

Reagent

Van Slyke Solution - Combine 400 ml concentrated H_2SO_4 , 100 ml concentrated H_3PO_4 , and 15 grams CrO_3 . Heat the mixture at 140°C for 6 hours. Cool under vacuum, then store in Pyrex reagent bottle.

Procedure

1. Reattach the gas collection trap to the system, evacuate it, and then isolate the vacuum pump.
2. Place 10.0 ml of the Van Slyke solution in the addition funnel, then add the reagent to the dissolution flask. Leave a few drops in the funnel to act as a seal against the atmosphere.
3. Place a heating mantle under the dissolution flask and heat the solution at 180°C for 1 hour.
4. Collect the evolved gases in the trap as described in Step 13. Remove the trap and analyze the gases in the manner previously described, Part B, Steps 14-16.

D. Blanks

The blank value used for the calculations is the average carbon content obtained from repeated analyses of each Van Slyke reagent prepared. The reagent is added to the evacuated reaction flask through the reagent funnel in the described manner. The remainder of the procedure is then followed to completion. An occasional run is made without sodium starting with distilled H_2O and sulfuric acid, but since it is found that the contributions from these reagents is not significant (1 or 2 μg) only the Van Slyke reagent is tested on a regular basis. A blank is run with every group of six analyses.

E. Gas Chromatography

The instrument used in this laboratory is a Perkin-Elmer Vapor Fractometer, Model 154 L. The operating parameters are:

1. Columns
 - 10-foot, 30 to 60 mesh silica gel.
 - 8-foot, 30 to 60 mesh molecular sieve 5A.
2. Carrier Gas
 - Reactor grade helium, initial pressure 9 psig, outlet flow 35 cc/min.

3. Temperature

70°C regulated to $\pm 0.1^\circ\text{C}$.

4. Detectors

Hot wire (tungsten filaments operated at 300 ma for silica gel effluents. Thermistor for molecular sieve effluents.

5. Introduction of Standard Gases

Six-way valve (Perkin-Elmer) with accurately calibrated loop.

6. Introduction of Unknown Gases

Double 4-way valve (Circle Seal) arrangement to allow purge of lead lines before sample entry.

7. Standards

Matheson, C. P. grade CO_2 , CO , CH_4 , C_2H_2 , H_2 .

The arrangement of the two columns, the direction of gas flow, and the bridge circuitry are shown in Figures A-2 and A-3. Both CH_4 and CO are detected with the thermistor detector as effluents off the molecular sieve column and the CO_2 and C_2H_2 are detected with the hot wire detector as effluents off the silica gel column. These compounds are identified by their retention times on the particular column. Each of these compounds appears as a peak area on the recorder.

F. Calculations

The quantity of a particular compound is determined by comparing its recorded peak area to the recorded area obtained from a known volume of the same pure compound. The volume of the unknown gas is calculated and corrected to carbon concentration in the original sodium sample by suitable application of the Gas Law and from the weight of the sodium sample. The calculations are as follows:

$$\mu\text{l gas from sample} = \mu\text{l standard gas} \times \frac{\text{peak area sample}}{\text{peak area standard}} \quad (1)$$

$$\mu\text{g C} = \mu\text{l gas from sample} \times 12.011 \text{ P}/760 \text{ RT} \quad (2)$$

where:

$$R = 0.08205 \text{ l-atm-deg}^{-1}\text{-mole}^{-1}$$

P = barometric pressure in millimeter

$$T = 273.15 + ^\circ\text{C}$$

FIGURE A-2 ARRANGEMENT OF COLUMNS AND DETECTORS

FIGURE A-3 DETECTOR CIRCUITS

Equation (2) can be simplified with negligible loss in accuracy. Since operating conditions at this laboratory are generally 21°C and 760 mm Hg, the substitutions of these values give:

$$\mu\text{g C} = \frac{\mu\text{l gas from sample}}{2} \quad (3)$$

Then:

$$\text{ppm C} = \frac{\mu\text{g C} - \text{blank}}{\text{g of sodium}} \quad (4)$$

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