5-1943

Gas - Volumetric Semimicrodetermination of Carbon: A Wet Method for Aliphatic and Cyclic Compounds

Roger P. Staiger

Gas - Volumetric Semimicrodetermination of Carbon

Roger P. Staiger
Department Honors
Ursinus College
May 1943

This thesis submitted in partial fulfilment of Department Honors.

Group Adviser-

Roger P. Staiger

Russell D. Sturgis.

Gas - Volumetric Semimicrodetermination of Carbon

A wet method for aliphatic and cylic compounds.
Taken, with modifications, after a paper by
E. Berl and W. Koerber
Published in Industrial and Engineering Chemistry
May 1943

Roger P. Staiger
Honors Paper for Chemistry

Introduction

The purpose of this paper is to do further research into a quick and easy gas-volumetric semimicrodetermination of carbon. The general theory was taken from a paper of the same name by E. Berl and W. Koerber. A number of difficulties arose in the course of the work necessitating numerous elaborations and changes.

Within the time limited for the submission of this paper definite conclusions have been reached, but there is still room for great improvement in technique and expansion in the field of the material analysed.

The past few years have brought forth much literature on the topic of semimicrodeterminations, especially in the field of organic chemistry. It seems fitting that in times when everything is accelerated that work on easier and quicker means of analysis in a less expensive manner should be adopted.

The following work will try to explain the technique and apparatus of this method, and to show the accuracy which can be obtained.

Explanation of the Method

The apparatus is especially adapted for determining the carbon content of organic compounds containing carbon, hydrogen, and oxygen; for example, carbohydrates, aromatic and aliphatic acids, organic salts, and neutral substances. Coal and inorganic substances containing mixed carbon, such as asbestos paper, are also applicable; carbonate salts, which easily give up carbon dioxide are easily determined.

By oxidizing the weighed sample in the oxidizing flask with strong chromic and sulphuric acid, all of the carbon present is converted to carbon dioxide. This is driven into a gas buret with hot concentrated sodium sulphate. Hot sodium sulphate is used for its low absorption tendencies toward CO_2. The water level in the gas buret is regulated to keep it at atmospheric pressure by the leveling flask, and a reading on the buret is taken.

At this time a fifty per cent solution of potassium hydroxide is introduced which absorbs the carbon dioxide present and raises the water level; again the leveling flask adjusts the gas to atmospheric pressure. The change in volume is equal to the amount of CO_2 absorbed and the percentage of carbon can be calculated directly.

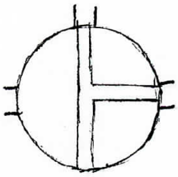
Apparatus

Many additions and corrections have been made to the material outlined by Berl and Koerber, due to the different style gas buret used.

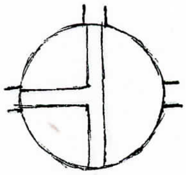
An explanation is more easily understood when referred to Figure 1, diagram of apparatus:

1. Filter flask-connected to water vacuum pump as a safety flask.
2. Manometer-to read vacuum in apparatus.
3. Wide mouth wash bottle-safety flask to prevent liquid from entering manometer.
4. Jacket-water cooler for buret.
5. Gas buret.
6. Thermometer in water jacket.
7. Funnel-for concentrated KOH-attached to buret.
8. Oxidizing flask-for oxidation of organic material.
9. Funnel-attached to oxidizing flask to contain oxidizing acids.
10. NaOH wash bottle-removes CO_2 from air entering buret.
11. Leveling flask-to adjust water levels to maintain atmospheric pressure.
12. Bunsen burner-to heat oxidizing flask.

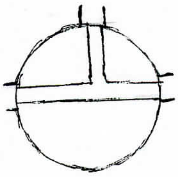
Stopcock D is a three way stopcock which can be adjusted to allow any two or all three passages to be connected.



1.



2.



3.

The oxidizing flask is not a standard piece of apparatus and was constructed by a glassblower. The actual dimensions are illustrated in Figure 11

Solutions

1. Concentrated sodium hydroxide solution for NaOH wash bottle to free air from CO_2.
2. 100% viscous phosphoric acid for stopcocks.
3. Concentrated chromic acid solution.
4. Concentrated sulphuric acid solution.
5. Saturated sodium chloride solution acidified with hydrochloric acid and colored with methyl orange.
6. Concentrated hot sodium sulphate solution.
7. 50% potassium hydroxide solution.
8. Concentrated sodium chloride solution.

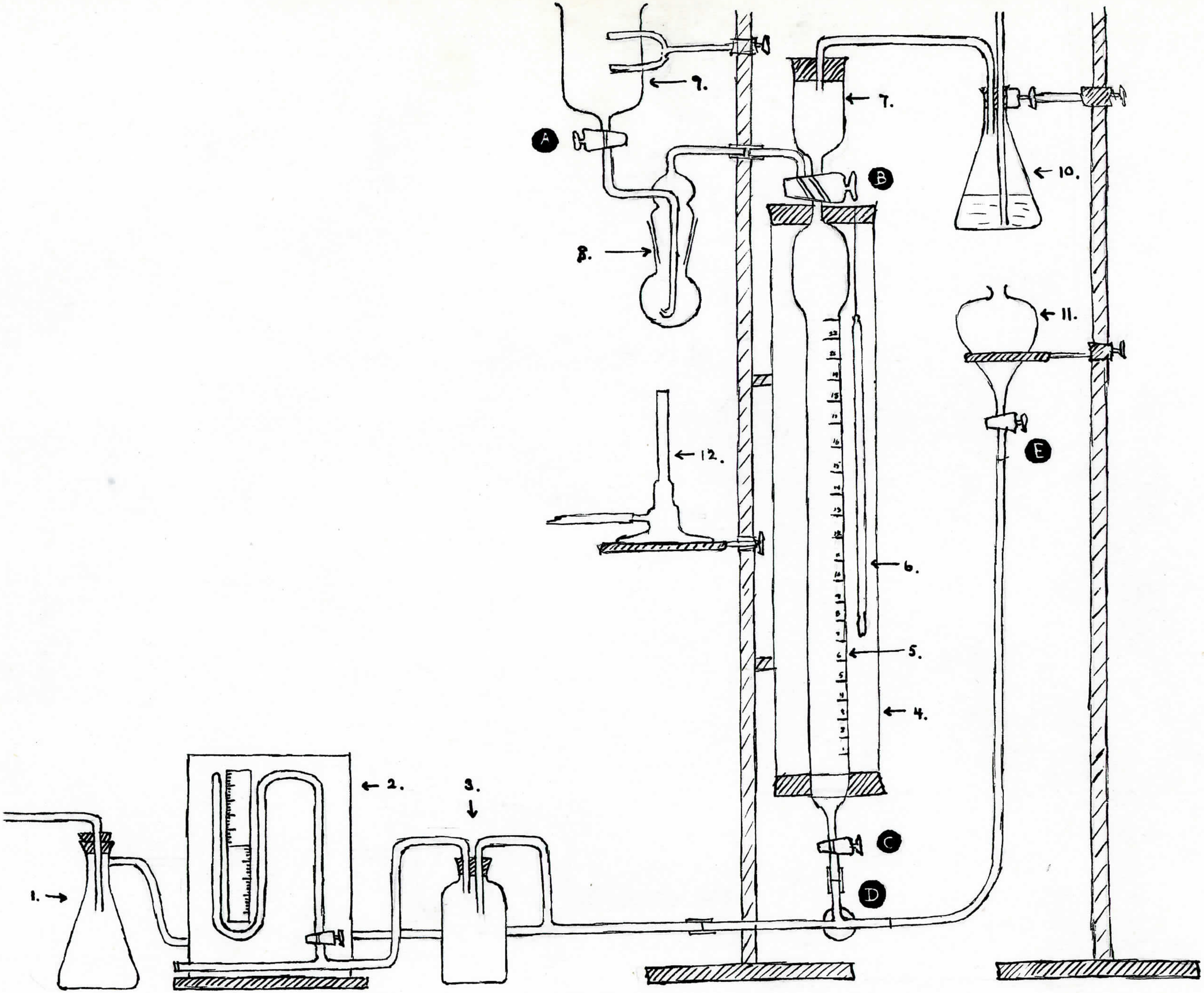


Figure1. Diagram of Apparatus

Figure1. Diagram of Apparatus

Difficulties Arising in Establishing a Technique

In the original paper the oxidizing solution was specified as concentrated chromic acid followed by concentrated phosphoric acid. This mixture was to be heated to boiling in the vacuum for five to eight minutes. It was found that either the oxidation wasn't conplete or that decomposition occurred liberating other gases which created an over pressure--this varied with both the time of heating and the intensity of heating. Therefore the stronger oxidizing agents were resorted to.

In thecase of sodium carbonate, the reaction with hydrochloric acid gave a low reading. This could be due to two the greater absorption tendencies for carbon dioxide in the hydrochloric acid solution then in the chromic acid, sulfuric acid solution.

The style of gas buret used was not calibrated to the top. Therefore some means for getting the reading portion of the gas absorption within the calibrated range had to be considered . The first method was to draw off the liquid from the absorbed gas to the first reading of the unabsorbed gas, and measure this volume. This method proved to be too inaccurate. It was then that the method of allowing 50cc of CO_2 free airfill the uncalibrated portion was devised. In this way greater accuracy was obtained.

In the original paper it was advised to place a small pellet of CO_2 free sodium hydroxide in the flask with the sample to be oxidized. Much better results were obtained when this was omitted.

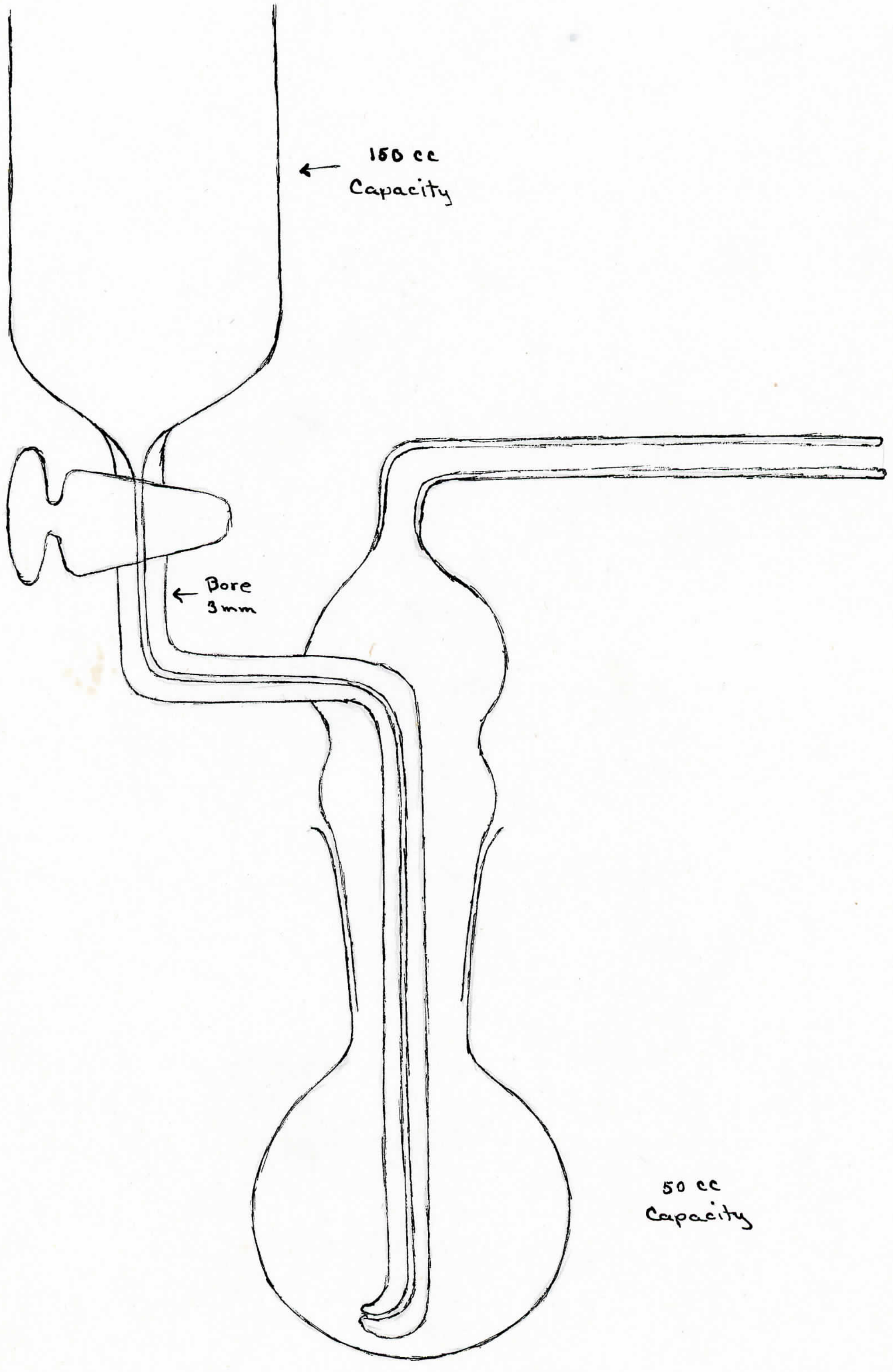


Figure 2. Oxidizing Flask (Actual Size)

Method of Procedure

The weight of the sample should be calculated to allow approximately 45cc of CO_2 to be produced. This depends upon the carbon content of the material being analysed. The sample with one drop of mercury is placed in the oxidizing flask and put in position. Stopcock A and the standard taper joint on the oxidizing flask are lubricated with vixcous 100% phosphoric acid. Any stopcock grease might be oxidized and give a faulty determination.

Stopcock A is closed. Stopcock B is open between the oxidizing flask and the buret, C is open and D is open between water vacuum pump and buret. The apparatus is then evacuated. After reaching good vacuum stopcocks B and C are closed and D is open between leveling flask and buret. Stopcocks C and E are then opened and saturated salt solution is allowed to fill buret. Stopcock B is then opened between NaOH wash flask and buret, and just 50cc of CO_2 free air is allowed to pass into the buret to fill upper bulb. B and C are then closed and D is opened between water vacuum pump and buret C is reopened to allow 45cc of liquid to be drawn from the buret and create a partial vacuum. It is then closed.

Five milliliters of concentrated chromic acid solution are poured into the funnel at A. Carefully opening A, practically all the liquid is introduced into the flask, but no air should be allowed to enter. Five milliliters of concentrated sulphuric acid are poured into the funnel and introduced into the flask, again no air should enter the evacuated apparatus.

As soon as the reaction starts, stopcock B is opened between the oxidizing flask and the buret. The flask should be heated gently so its contents just boil slightly for a period of one half minute and the contents shaken thoroughly. After a period of five minutes the reaction can be considered complete. Care must be taken that no air is allowed to enter the apparatus.

At this time stopcock D is opened between the leveling flask and the buret and stopcock C is opened slightly to see if an over pressure has been produce. If the water level falls it is best to discard the determination and use a smaller sample

After the sample has been oxidized B is closed and concentrated hot sodium sulphate solution is added to funnel A. A is opened, and the flask is filled with this solution. No air should enter through A. When no further sodium sulphate solution enters the flask, B is opened. The sodium sulphate solution fills the capillary between the combustion flask and the buret and reaches the lower part of the bore of stop cock B, B is closed. A period of about five minutes is required for the warm gas in the buret to reach the temperature of the water in the jacket. A thermometer in the jacket determines the temperature of the water and the gas in the buret.

Then C is opened and saturated acidified colored sodium chloride solution is introduced until the levels in the buret and in the leveling flask are the same. The volume of the gas, carbon dioxide plus foreign gas, mostly air, in the buret is now read. A slight vacuum is created in the buret by lowering the leveling flask, closing C, introducing 60% potassium hydroxide solution through the funnel above B. B is closed and the solution is allowed to rise until an equilibrium is reached. After the carbon dioxide absorption is finished, some concentrated sodium chloride solution is added through funnel above B. Then the volume of non-absorbed gas is read with the help of the leveling flask.

The entire apparatus can be washed out by applying a vacuum and draining water from the funnels above A and B through the apparatus into the vacuum pump safety flask.

Treatment of Results

Calculating the percentage of carbon by the slide rule:

$$\%C = \frac{Wt\ Carbon}{Wt\ Sample} = \frac{Wt\ CO_2 \times .273}{Wt\ Sample}$$

$$= \frac{44 \times Moles \times .273}{Wt\ Sample}$$

$$= \frac{44 \times V_2 \times .273}{22,400 \times Wt\ Sample}$$

$$= \frac{44 \times V_1 \times .273 \times P_1 \times .273^\circ}{22,400 \times 760 \times T_1 \times Wt\ Sample}$$

$$\%C = \frac{V_1 \times P_1 \times 19.25}{T_1 \times Wt\ Sample}$$

$$\frac{V_1\ P_1}{T_1} = \frac{V_2\ P_2}{T_2} \qquad V_2 = \frac{V_1\ P_1\ .273^\circ}{T_1\ 760}$$

Calculating the percentage of carbon by logarithms

% Carbon determination form

Wt of substance		log	
cc of CO_2 measured		log	
temperature		log	
pressure		log	

log of cc		760 log of P'	2.88081
log of P		log of T	
273° log of T	2.43616		2.
	1.		

Subract #2 from #1		log of V'	

log of V'		log of 22,400	4.35625
log of 44.01	1.64355	log of total gms	
log of $\frac{C}{CO_2}$ factor	9.43599		4.
	3.		

Subtract #4 from #3		log of %C	
		%C	X 100

Filter Paper- Phosphoric acid, NaOH, Chromic acid, Hg. Cat., theoretical 44.4%, calculated 40.8%.

Weight	47.2 mg.
Pressure	760.6
Volume	40.0
Temperature	297.0

Filter Paper- Sulfuric acid, Chromic acid, Hg. Cat., theoretical 44.4%, calculated 43.7%.

Weight	55.3mg.
Pressure	759.6
Volume	48.6
Temperature	297.0

Cinnamic Acid- Sulfuric acid, Chromic acid, Hg. Cat., theoretical 73%, calculated 67.5%.

Weight	31 mg
Pressure	764.8
Volume	42.2
Temperature	296.5

Cinnamic Acid- Sulfuric acid, Chromic acid, Hg. Cat., theoretical 73%, calculated 68.6%

Weight	729.6
Pressure	759.6
Volume	41.3
Temperature	297.0

Lactose- Sodium hydroxide, Phosporic acid, Chromic acid Hg. Cat.,
theoretical 40%, calculated 41.25%

Pressure	761.6
Weight	51.8
Volume	43.4
Temperature	298.0

Lactose-

Phosphoric acid, Sodium hydroxide, Chromic acid, Hg. Cat.,
theoretical 40%, calculated 41.47%

Weight	50.0
Volume	41.9
Temperature	296.0
Pressure	76o.6

Lactose-

Sulfuric acid, Chromic acid, Hg. Cat.,
theoretical 40%, calculated 40.2%.

Weight	54.0
Temperature	298.5
Volume	44.6
Pressure	753.2

Resorcinol-

Sulfuric acid, Chromic acid, Sodium hydroxide, Hg. Cat.,
theoretical 65.3%, calculated 61.5%

Weight	30.0
Temperature	299.5
Volume	38.1
Pressure	753.2

Resorcinol-

Sulfuric acid, Chromic acid, Hg. Cat., Sodium hydroxide,
theoretical 65.3, calculated 63.7%.

Pressure	759.6
Weight	30.6
Volume	39.5
Temperature	296.0

Resorcinol-

Sulfuric acid, Chromic acid, Hg. Cat.,
theoretical 65.3%, calculated 65.1%.

Pressure	765.4
Weight	30.7
Volume	40.1
Temperature	296.0

Sodium Benzoate- Sulfuric acid, Chromic acid, Hg. Cat.,
theoretical 58.3%, calculated 52.1%.

Weight	42.0
Pressure	764.0
Volume	44.3
Temperature	297.0

Sodium Benzoate- Sulfuric acid, Sodium hydroxide, Chromic acid, Hg. Cat.,
theoretical 58.3%, calculated 55.6%.

Weight	29.6
Pressure	764.0
Volume	33.4
Temperature	298.0

Sodium Benzoate- Sulfuric acid, Chromic acid, Hg. Cat.,
theoretical 58.3%, calculated 58.6%.

Pressure	765.4
Weight	41.2
Volume	48.6
Temperature	297.0

Sodium Carbonate- No oxidizing reagent, No catalyst
theoretical 11.3%, calculated 10.7.

Pressure	764.4
Temperature	297.5
Volume	43.4
Weight	201.8

Sodium Carbonate- Sulfuric acid, Chromic acid, Hg. Cat.,
theoretical 11.3%, calculated 11.3%

Pressure	764.4
Temperature	297.0
Volume	44.5
Weight	201.0

Asbestos-

Sulfuric acid, Chromic acid, Hg. Cat.
first sample-3PM
calculated 6.68%

Weight	312 mg
Volume	42.2
Temperature	297.0
Pressure	761.0

Asbestos-

Sulfuric acid, Chromic acid, Hg. Cat.
second sample-3PM calculated 6.36%

Weight	315 mg
Volume	41.0
Temperature	297.0
Pressure	756.2

Asbestos-

Sulfuric acid, Chromic acid, Hg. Cat.,
third sample-3PM
calculated 6.16%

Weight	314.0
Volume	39.2
Temperature	297.0
Pressure	757.4

Asbestos-

Sulfuric acid, Chromic acid, Hg. Cat.,
first sample No. 10 JM
calculated 2.6%

Weight	510.5
Volume	26.4
Temperature	297.0
Pressure	757.4

Asbestos-

Sulfuric acid, Chromic acid, Hg. Cat.,
second sample No. 10 JM
calculated 2.63 %

Weight	514.0
Volume	27.6
Temperature	298.0
Pressure	757.9

Asbestos-

Sulfuric acid, Chromic acid, Hg. Cat.,
third sample No. 10 JM
calculated 2.63%

Weight	509.5
Volume	27.3
Temperature	298.0
Pressure	757.9

Asbestos-

Sulfuric acid, Chromic acid, Hg. Cat.,
first sample 12 NOon
calculated 1.12 %

Pressure	752.0
Temperature	294.0
Volume	16.6
Weight	722,5

Substance	Oxidizing Agent	Weight mg.	CO_2 ml.	T	P mm. Hg	Carbon	
						found	cal.
Filter Paper $C_6H_{10}O_5$	P. C. NaOH	47.2	40.0	297	760.6	40.8	44.4
	S. C	55.3	48.6	297	797.0	43.7	44.4
Cinnamic Acid $C_6H_5CHCHCOOH$	S. C. NaOH	31.0	42.2	296.5	764.8	67.5	73.0
	S. C. NaOH	29.6	41.3	297	759.6	68.6	73.0
Lactose $C_{12}H_{22}O_{11}H_2O$	P. C. NaOH	51.8	43.4	298	761.6	41.25	40.0
	P. C. NaOH	50.0	41.9	296	760.6	41.47	40.0
	S. C.	54.0	44.6	298.5	753.2	40.2	40.0
Resorcinol $C_6H_4(OH)_2$	S. C. NaOH	30.0	38.1	299.5	753.2	61.5	65.3
	S. C. NaOH	30.6	38.5	296.0	759.6	63.7	65.3
	S. C.	30.7	40.1	296.0	765.00	65.1	65.3
Sodium Benzoate C_6H_5COONa	S. C. NaOH	42.0	44.3	297.0	764.0	52.1	58.3
	S. C. NaOH	39.6	33.4	298.0	764.0	55.6	58.3
	S. C.	41.2	48.6	297.0	765.4	58.6	58.3
Sodium Carbonate Na_2CO_3	HCL-no oxid. agent no cat.	201.8	43.4	297.5	764.4	10.7	11.3
	S. C. Hg. cat.	201.0	44.5	297.0	764.4	11.3	11.3