Combustion studies of natural gas with special reference to the Bozeman supply
by Albert D Ford

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the Degree of Master of Science in Mechanical Engineering at Montana State College
Montana State University

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Bozeman, Montana
June, 1938

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ABSTRACT

This thesis discusses tests of combustion products from natural gas, burned in warm air furnaces and steam boiler furnaces.

Charts are included and explained which may be constructed and used to check the completeness of combustion of any gas from the Orsat analysis even though the analysis of the fuel gas is not known. These charts were checked by other methods which showed that when CO was indicated H_2 was found in the flue gas. Other combustibles were also found when an excess of O_2 was indicated by the Orsat analysis even though CO was not present.

INTRODUCTION

It has been known for several years that when natural gas, such as the Bozeman supply, is burned, the calculations of weights of materials leaving the furnace, based upon the Orsat analyses of the products of combustion do not agree with the calculated values of materials entering the furnace as closely as they do when other types of fuel, such as coal and oil, are burned. As long as the CO_2 content of the flue gas is below certain limits the agreement is fairly close but as the air supply is decreased toward the theoretical air requirements, a discrepancy is noted, and this discrepancy increases as the air supply is decreased.

The percentage of CO_2 which it is possible to obtain seems to vary considerably, due to difference in installations burning natural gas even from the same supply mains.

It has also long been known by chemists that intermediate products are formed which may be carried over with the products of complete combustion.

Professor W. A. Bone (4, 5) and his associates conducted many experiments on the combustion of hydrocarbons but they worked with the pure gases, mostly methane, but also hydrogen, the latter produced in the laboratory, by the electrolysis of water.

They found that even under carefully controlled conditions

the $CH_4 + CO_2$ did not always burn to $CO_2 + 2H_2O$ and if insufficient O_2 was present formaldehyde was formed to some extent. They found that the higher hydrocarbons formed other products by adding oxygen rather than by breaking up to form the simple products of CO_2 and H_2O.

This work of Professor Bone's suggested to the writer that these laboratory experiments might offer the explanation for the failure of Orsat measurements when used with natural gas combustion products; and also gave him a clue as to what products might be present in the flue gases not indicated by the Orsat analysis.

PURPOSE OF INVESTIGATION

The purpose of this investigation is to find out why the Orsat analysis does not balance out when natural gas is burned in domestic hot air furnaces or industrial steam boilers with very nearly the theoretical requirements of air.

More specifically stated, the purpose is to study the combustion of natural gas in commercial furnaces to determine why the weights of materials entering the furnace as calculated from a slow combustion analysis of the fuel gas, do not check with the weights of materials leaving the furnace as calculated from the Orsat analysis of the combustion gases.

The occasion for the study was the failure of purely mechanical measurements of fuel gas and air supply entering the furnace to check with the weights of chimney gases as made by a previous investigator. (6)

BASIC PREMISES

The first of the tests were conducted on domestic furnaces in actual use that could be equipped with the various measuring devices for measuring the air and gas intake and flue gas output. One small upright fire tube steam boiler located in the Montana State College Creamery was also used. In this case the conditions of combustion could be varied over a large range at will. On these, changes and alterations could be made to vary conditions.

The later work on steam boiler burners was done on installation under actual operating conditions as found in practice.

1. METHODS PREVIOUSLY USED:

a. The common method of testing the completeness of the combustion of any furnace is by means of Orsat analysis or Carbon Dioxide indicators and recorders of which there are several different types. These instruments show the amount or proportion of the carbon that has been burned either to carbon dioxide or carbon monoxide and the oxygen remaining, but give no indication directly of any hydrogen or other compounds that may be present. Much discussion has been carried on through the power plant magazines (7,8,9,10,11,12,13) as to the merits of these instruments. Many ingenious charts and formulas have been devised to calculate the losses and completeness of combustion from the instrument data. However, most of the writers have assumed that CO is the only combustible formed in the flue gas.

The Bureau of Agricultural Engineering, U. S. Department of Agriculture, in cooperation with the Bureau of Home Economics (33) have made a study of domestic oil burners. They have worked out methods of checking the completeness of combustion of oil burners by means of Ostwald Diagram (28) and Orsat analysis.

b. Methods have been devised, by means of Orsat analysis and exhaust gas analyzers, to analyze and detect combustibles in the exhaust gas from gasoline engines. (24) Much has been accomplished in obtaining better operation as well as saving in fuel. However, this problem is different from burning fuel in a furnace because the gasoline engine operates best with a slight excess of fuel while the furnace operates best under our present system of firing with a slight excess of air in the air fuel ratio.

c. The method of measuring the intake of air, the fuel gas, and the flue gas by means of orifice meters (1,2,6) has also been tried. This method gives some very interesting data which checks very closely with the Orsat as long as combustion is complete. However, when the intake air approaches the theoretical requirements the incoming and outgoing do not balance and there is no indication as to the cause of the discrepency.

2. OTHER METHODS ATTEMPTED

a. Because of the high humidity of the flue gas from the combustion of natural gas it was thought some tests of the dew point might be of interest. (See Appendix A)

b. Another method available for testing is to determine the unburned carbon and hydrogen by complete analysis.

This may be done by means of explosion or slow combustion pipettes.

The flue gas is sometimes tested for hydrogen and carbon monoxide by the copper oxide tube method. (21,22, 23) A platinized silica gel tube is also used in testing for free hydrogen in both flue gas and natural gas. (25)

Mr. F. G. Philo (29) of Southern California Edison Company mentions, but does not describe, an instrument that analyzes and burns a check sample automatically to record the combustibles in the flue gas from boiler furnaces using both oil and natural gas.

APPARATUS USED FOR TESTING

The apparatus used for testing consisted of the following:

1. Common Orsat
2. Differential micromanometer and calibrated orifices. (1, 2, 6, 17, 27, 32, 34)
3. Several types of dew point indicators.
4. Burrell Orsat (31) with slow combustion pipette and copper oxide tube. (18, 21, 22, 23)
5. Burrell Orsat with slow combustion pipette and platinized silica gel tube. (25, 26)

The Burrell Orsat with slow combustion pipette and copper oxide tube was somewhat similar to the equipment described in "Methods of the Chemist of the United States Steel Corporation for Sampling and Analysis of Gases". (31) Both mercury and acidulated water, saturated with the gas being analyzed, were tried as confining fluids. (26)

Item number five was of the same type except that it had been originally fitted with palladium tube which the author removed and replaced with a U-tube filled with platinized silica gel. (25,26) Considerable experimenting was done with different confining fluids both for flue gas and natural gas analysis to see which would give the best results with this experiment. Water with one-half cubic centimeter hydrochloric acid and two drops of methyl orange in each leveling bottle gave the best results when used by the procedure outlined on pages 18 and 19.

TYPES OF BURNERS TESTED

The domestic furnaces tested were of the warm-air type; one was equipped with Roberts conversion burner and the other with Killiams conversion burner; both set in furnaces originally designed to burn coal.

The steam boilers tested included three installations:

The Bozeman Canning Company plant consisted of three horizontal return tubular boilers, one of about 150 H. P. and two of about 125 H. P. These boilers were originally installed with underfeed stokers but later converted to gas burners by removing stokers and installing 4 N. G. E. burners of the natural draft inspirating type in the front wall of each furnace to replace fire doors and arches.

The Montana State College Creamery boiler installation consisted of a vertical fire tube boiler, equipped with a group of N. G. E. burners of the same type as the above but smaller size set vertically in the furnace. The faces of the burners were set at about the height of the original coal grate. Air was admitted to the original ash pit opening which was equipped with a damper so that intake could be varied at will but no adjustment could be made between primary air which entered through the burner with the gas and the secondary which entered through the openings between the burners.

The University of New Mexico installation consisted of two Babcock and Wilcox type H boilers of 320 H.P. each, equipped with three Babcock and Wilcox combination oil and gas burners per boiler and Bailey automatic control of gas supply, forced draft and induced draft from master pressure controller through Bailey ratio meters.

NATURAL GAS ANALYSIS

The slow combustion apparatus was supplied by the Chemical Engineering Department and a few analyses were by the author under Dr. Ward's supervision. Then the apparatus was moved to the calorimeter room in the Mechanical Engineering Laboratory where the work was continued at weekly intervals.

Analysis of the fuel gas could not be made that would check. Though the ratio of C to H was very close, the percentage of N_2 as calculated from the residue of burning the sample varied from 7 to 13.6%. So a study was made of the available works on natural gas combustion. (21, 22, 23) "Flame and Combustion in Gases", by Bone and Townsend (4) was the most extensive work found. They reported the finding of aldehydes in the condensate from the combustion of many hydrocarbons. These authors also disprove the preferential combustion theory of both carbon and hydrogen.

They also found that when CO was present after combustion, H_2 was also frequently present and in some cases even CH_4 was present. On this authority it was assumed that something of this kind was happening in the combustion pipette and in the commercial furnace.

Frequent explosions were experienced. All of the explosions occurred just as the last of the gas had passed into the combustion pipette or as the products of combustion were passing back to the measuring burette. Finally at Dr. Ward's suggestion

the current was turned off the ignition coil as soon as the gas had all been passed into the combustion pipette. Then the gas was nearly all passed back to measuring burette and the current turned on the ignition coil again and the mixture of gas and O_2 passed through again.

It was found that the mixture continued to contract each time it was passed over the hot ignition coil. The source of trouble was never found even though the apparatus was checked repeatedly for leaks.

Later, better results were obtained by mixing the sample of gas to be analyzed with an equal amount of nitrogen from which every trace of oxygen had been removed. The nitrogen, of course, was carefully measured just before mixing with the gas sample.

The best results were obtained by having the sample of gas and nitrogen, about ten c.c. of each, mixed and in the slow combustion pipette when the current was turned through the ignition coil. Then as soon as the coil was a clear red heat the oxygen was slowly added.

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2. The latter part of the research work on this project was done at the University of New Mexico and the analysis of natural gas there is not exactly the same but the behavior and the heating valve is very nearly the same as that supplied to the city of Bozeman, Montana.

METHOD OF PROCEDURE

The thesis by Gordon Conrad "A Method for Testing Gas Fired Furnaces" (6) was taken as a guide and starting point. The furnace and most of the equipment were the same as he used and the same readings were taken. In addition a dew point indicator was used to indicate the absolute humidity of the air going into the furnace and the flue gas leaving the furnace.

The first tests were run and the dew point taken by drawing a sample of flue gas from Orsat sampling tube by means of rubber tubing. Then it was found that condensate was forming in the rubber tubing and readings were of no value. The polished cylinder of the dew point indicator was installed directly in the flue pipe by suspending it in the pipe and installing a glass window in the flue pipe through which to make observations.

This did not work well because the high temperature of the flue gas and the moisture formed a deposit on the polished surface after a few minutes which could not be distinguished from the dew point cloud. Next the original dew point indicator, which had been made by blowing glass connections on a Keldahl flask, was installed to take the sample of flue gas directly from the flue. This did not work satisfactorily because the gas was not directed so that it impinged directly on the polished surface. The cloud of moisture then ran down the glass into the sampling tube to be picked up by the

entering gas to give a reading which was probably too high. The indicator was changed to use copper tubing for a sampling tube. The end was bent and flattened to direct a wide stream of flue gas onto the polished surface of the indicator.

This worked best of anything tried up to this time. It was easy to watch the cloud come and fade with a change in temperature of 1° F. or less but it is too fragile for rough use. The results of these tests are shown in Table 1.

These values checked closely with the calculated values till the excess air was reduced nearly to the calculated requirements, then the dew point lowered sometimes even before CO was indicated by the Orsat analysis. No readings of the lowered dew point are included because it always took so long to get the indicator adjusted to the lower temperature that other conditions would change. Several times one observer read the Orsat while another operated the dew point indicator but check readings could not be obtained of the lowered dew points.

Another dew point indicator was made on the suggestion of Don Asbury of Montana Power Company. This was on the same principle of one used at the gasoline plant at Cutbank, Montana. It consisted of a 3/8" copper curved tube 16" long, polished on the inside, fitted with a flashlight at one end and a window at the other. The copper tube through which a small part of the flue gas was drawn by an aspirator, was installed inside a

larger tube containing the cooling liquid. When the temperature of the tube walls was above the dew point the light was reflected at the opposite end. When the temperature of the tube walls was lowered to the dew point a cloud formed, and the light was no longer reflected out the window.

This did not work so well because it required a rise of from 3° to 5° to remove the cloud.

At this point it seemed that no more information could be obtained whether by the dew point indicator or by measuring the fuel gas and air entering or the flue gases leaving the furnace. So an attempt was made to obtain a sample of the flue gas, take it to the laboratory and test it by the copper oxide tube and slow combustion pipette for hydrogen and other combustibles. Consistent results could not be obtained by this method because it seemed the gas or gases formed were unstable or were absorbed by any moisture in the sample container. See page 32.

No further attempt was then made to analyze the combustibles in the flue gases for several months but several hundred Orsat analyses were made and tabulated on different types of steam boiler installations. Many of these were made on an installation at the University of New Mexico, equipped with Bailey Ratio Meter by which both gas flow and air flow could be noted at the time the sample was taken. Conditions of fire were also noted.

Then a Burrell type of Orsat equipped with slow combustion pipette was fitted with a tube filled with platinized silica gel. (25, 26) The apparatus was set up in the boiler room so that the flue gas sample could be drawn directly from the boiler flue into the Orsat burrette. The regular Orsat analysis was made and each reading rechecked to a constant volume.

The curve fig. 1 was constructed to show the theoretical values of CO_2 and O_2 for all values of CO_2 from zero to perfect combustion. This curve will be discussed more later. The results of Orsat analysis were checked against this graph and if the point fell below the line the residue of the flue gas remaining in the burette after the regular Orsat analysis was analyzed as follows:

The sample of flue gas was stored in the CO_2 pipette and the manifold filled with water from the burette leveling bottle. The beaker under the platanized silica gel U tube was filled with water and brought to boiling by means of the alcohol lamp and kept at that temperature through the remainder of the analysis. Then O_2 from a Linde oxygen drum was passed into the burette and allowed to bubble through the confining water in the leveling bottle to make sure the water was saturated. The stop cock to the U tube was opened and O_2 passed through that and bubbled through the combustion tube and pipette leveling bottle until that water was saturated. The O_2

was closed off at the drum. Water was leveled at the top of the combustion pipe with the U tube submerged in boiling water and the stop cock closed. Then the water in the burette was raised and leveled in the burette to retain about 10 c.c. of pure O_2, and the volume recorded.

The sample of gas was then brought back from the CO_2 pipette and the total volume again recorded and carefully checked. The stop cock to the U tube was then opened and by alternately raising and lowering the two leveling bottles the gas was passed back and forth through the U tube three times. The water in combustion pipette was again leveled and when it had reached a constant reading the results were recorded and the contraction calculated as due to $2H + O$ burning to H_2O.

The water level in slow combustion tube was then lowered allowing enough gas to pass through the stop cock to expose the platinum coil and the current turned through the coil to heat it to clear red. The gas was passed three times through the coil and the current turned off.

Water in combustion pipette was then leveled as before and the gas cooled, measured, and recorded. The regular Orsat analysis was then run on the gas sample again and the results recorded as unburned fuel in original sample.

With the Bailey Ratio Meter and the Bailey selector controls it was very easy to vary the gas air ratio to increase or decrease the excess air by any desired amount.

TABLE I

Orsat analyses from Roberts conversion burners in hot air furnace. See page 12. All percentages are by volume.

Date	Time	CO_2%	O_2%	CO%	Dew Point	Flue Gas Temp.
3-16 1935	7:30	7.4	7.4	.0	118°F	425°F
	7:50	7.8	6.4	.0	122	425
	8:10	9.8	3.0	.2	131	440
	8:30	10.2	1.7	.2	134	440
3-20 1935	7:30	6.8	8.8	0	117	480
	7:45	7.2	7.4	0	120-	468
	8:00	9.4	4.0	0	127	442
	8:10	9.2	4.6	0	127	445
	8:30	10.3	2.8	0	*	457

*Dew point too low to catch before other conditions had changed.

These data illustrate how the dew point increases with the CO_2 but it also shows how misleading the dew point reading might be if no information is also obtained on the amount of moisture taken in with the air. See Appendix A. These data plotted as crosses on chart of fig. 1.

TABLE II

Tests conducted at Montana State College Creamery.

N. G. E. burners in vertical tube boiler.

Date	Time	CO_2%	O_2%	CO%	H	C*	Dew Point	Flue Gas Temp.
8-12	9:55	10.0	1.2	0	0	0	128°F	710°F
	10:37	9.0	.4	.1	2.7	1.0	124	670
	4:00	8.0	.2	2.6	4.0	1.4	126	620
	4:25	7.8	.2	2.4	4.7	1.6	125	610

These data plotted as dots on chart of fig. 1.

All percentages are by volume.

TABLE III

Tests conducted at University of New Mexico

Date	Time	CO_2%	O_2%	CO%	Free H	Combine H	C*
12-27	8:00	10.2	1.6	.2	.2		
	9:10	9.2	1.8	0	0	3.6	2.4
	10:40	11.4	1.2	.4	.2	T	.2
	1:50	10.0	.6	0	.2	3.9	2.6

These data plotted as squares on chart of fig. 2.

These data illustrate how combustibles may be present in the flue gas and still not be indicated by common Orsat analysis. All percentages are by volume.

* See Page 42

TABLE IV

Orsat Analyses for Industrial Boilers Before Adjusting

(Bozeman Canning Company, 1935, See Page 12)

Time	Boiler Number	CO_2%	O_2%	CO%	Flue Gas Temp.
11:10	2	8.2	2.0	1.6	385°F
11:35	2	8.0	2.0	2.0	385
1:08	1	6.0	6.4	1.2	330
3:05	3	7.2	4.4	1.6	410

Plotted as squares on chart of fig. 1.

All percentages are by volume.

TABLE V

Orsat Analyses from Industrial Boilers of Table IV After Adjusting

Time	Boiler Number	CO_2%	O_2%	CO%
12:30	3	10.6	2.6	.0
12:52	1	10.6	1.9	.1
1:38	2	9.6	3.4	.0

Plotted as circles on chart of fig. 1.

These tables illustrate losses which may occur in steam boilers unless combustion is closely checked as explained on page 35.

All percentages are by volume.

TABLE VI

Orsat analysis, University Heating Plant--Babcock and Wilcox combination oil and gas burners under Babcock and Wilcox type H water tube boilers. This data is plotted as circles on fig. 2. All percentages are by volume.

Date	Time	CO_2%	O_2%	CO%	Gas Flow	Air Flow
1-31-38	5:15AM	10.2	3.0	0	18,500	19,000
	6:05AM	9.4	4.0	0	21,500	21,500
	7:05AM	9.3	3.9	0	17,000	17,500
	9:50AM	9.6	4.2	0	15,500	15,500
	4:30PM	8.0	6.0	0	12,000	12,000
2-4-38	5:15AM	8.8	5.0	0	14,500	14,500
	6:30AM	9.4	3.2	0	16,500	16,500
	11:45AM	9.0	5.6	0	8,500	8,500
3-5-38	5:30AM	9.2	3.9	0	15,000	15,000
	6:35AM	9.9	3.5	0	20,000	20,000
	7:30AM	10.5	2.4	0	13,700	13,500
	1:10PM	10.3	3.3	0	10,250	10,250
3-6-38	7:05AM	10.2	2.8	0	17,000	17,000
	7:45AM	9.6	4.0	0	17,500	17,500
3-7-38	5:40AM	10.1	2.8	0	18,000	18,000
	6:35AM	11.0	1.7	0	20,000	20,000
	7:25AM	10.6	2.0	0	18,500	18,500
	10:08AM	10.8	2.2	0	16,500	16,500

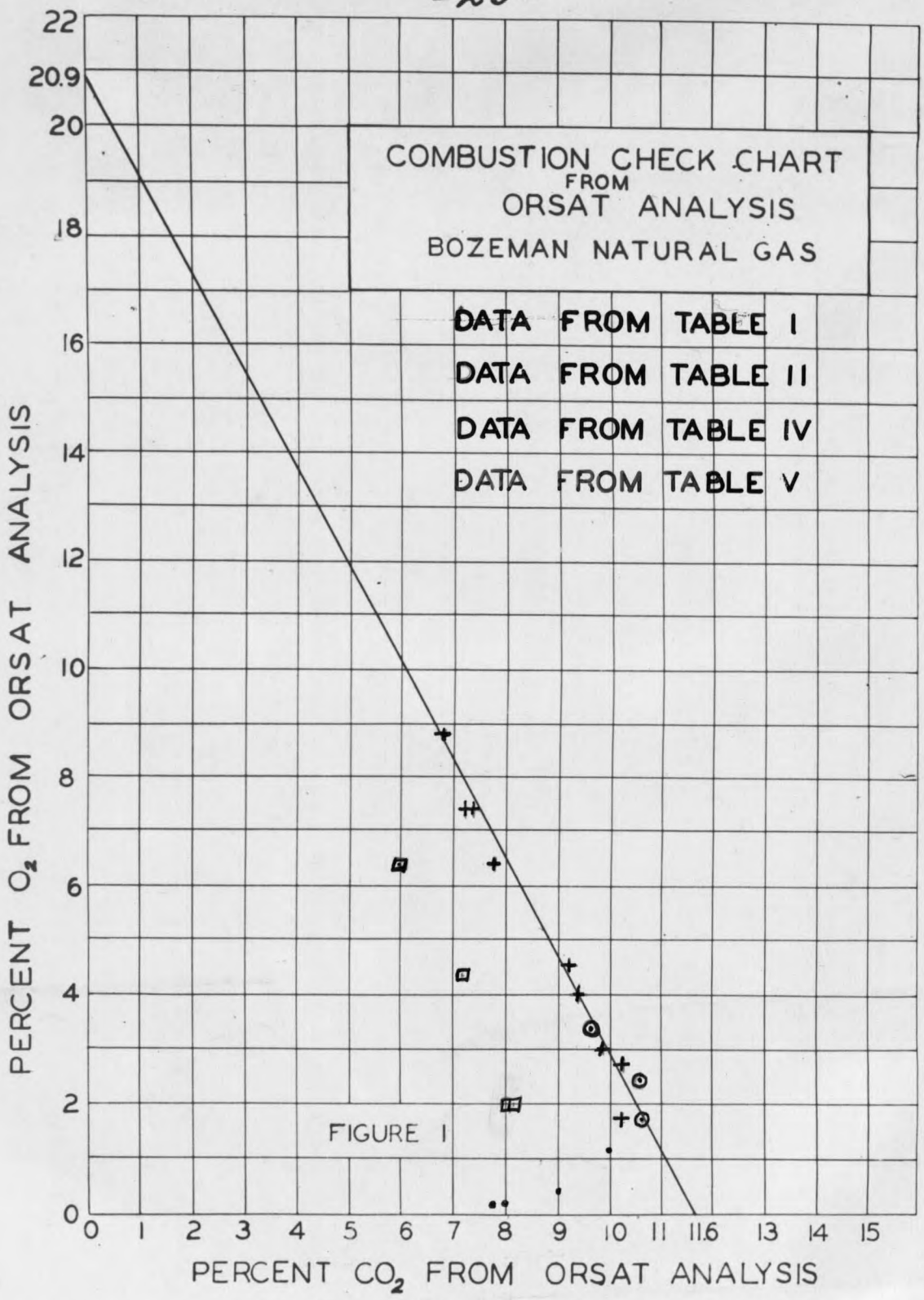
COMBUSTION CHECK CHART
FROM
ORSAT ANALYSIS
BOZEMAN NATURAL GAS
DATA FROM TABLE I
DATA FROM TABLE II
DATA FROM TABLE IV
DATA FROM TABLE V
PERCENT O_2 FROM ORSAT ANALYSIS
PERCENT CO_2 FROM ORSAT ANALYSIS
22
20.9
20
18
16
14
12
10
8
6
4
2
0
0 1 2 3 4 5 6 7 8 9 10 11 11.6 13 14 15

FIGURE 1

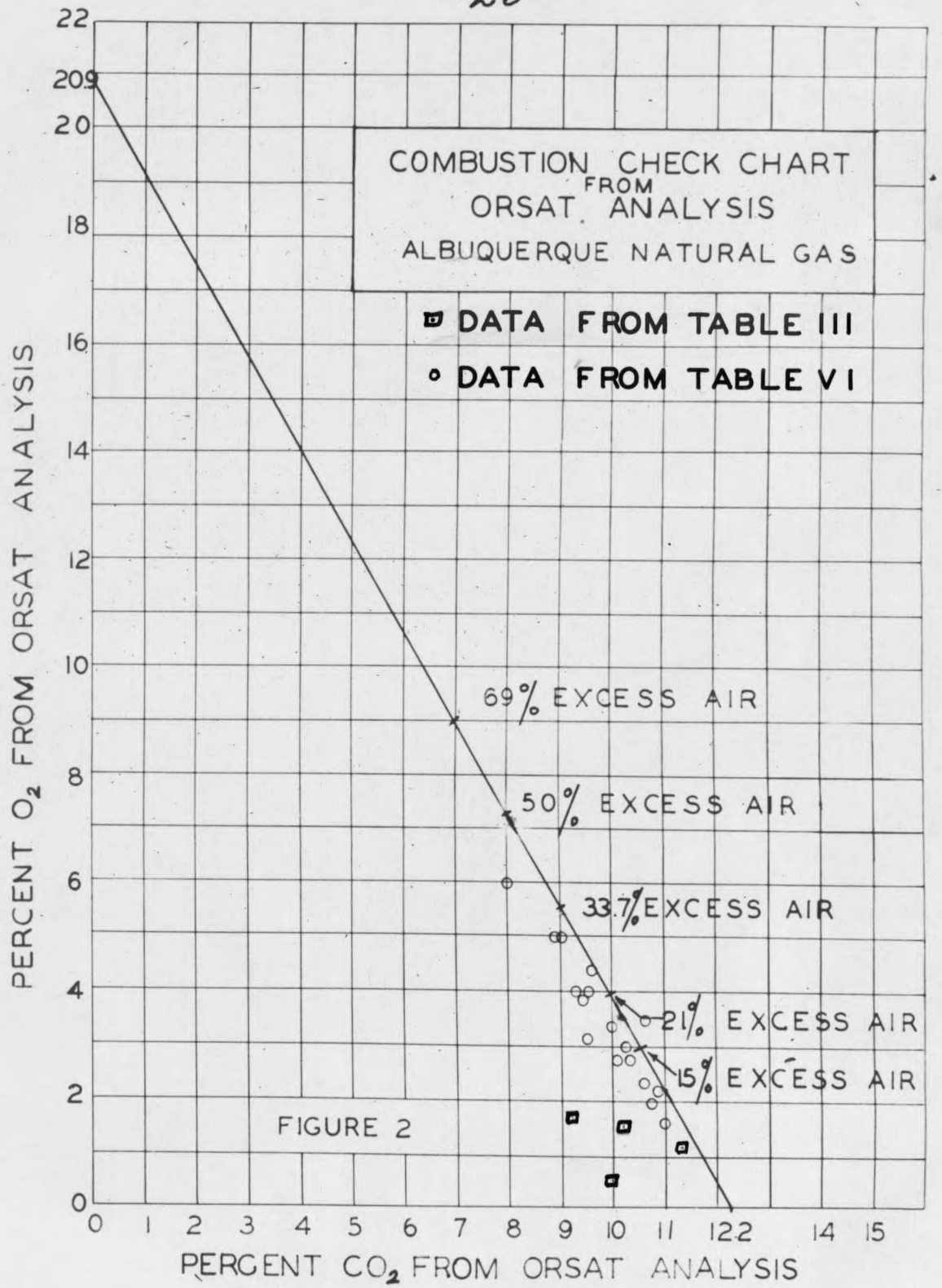
COMBUSTION CHECK CHART
FROM
ORSAT ANALYSIS
ALBUQUERQUE NATURAL GAS
DATA FROM TABLE III
DATA FROM TABLE VI
69% EXCESS AIR
50% EXCESS AIR
33.7% EXCESS AIR
21% EXCESS AIR
15% EXCESS AIR
PERCENT O2 FROM ORSAT ANALYSIS
PERCENT CO2 FROM ORSAT ANALYSIS
0 1 2 3 4 5 6 7 8 9 10 11 12.2 14 15
0 2 4 6 8 10 12 14 16 18 20 20.9 22

FIGURE 2

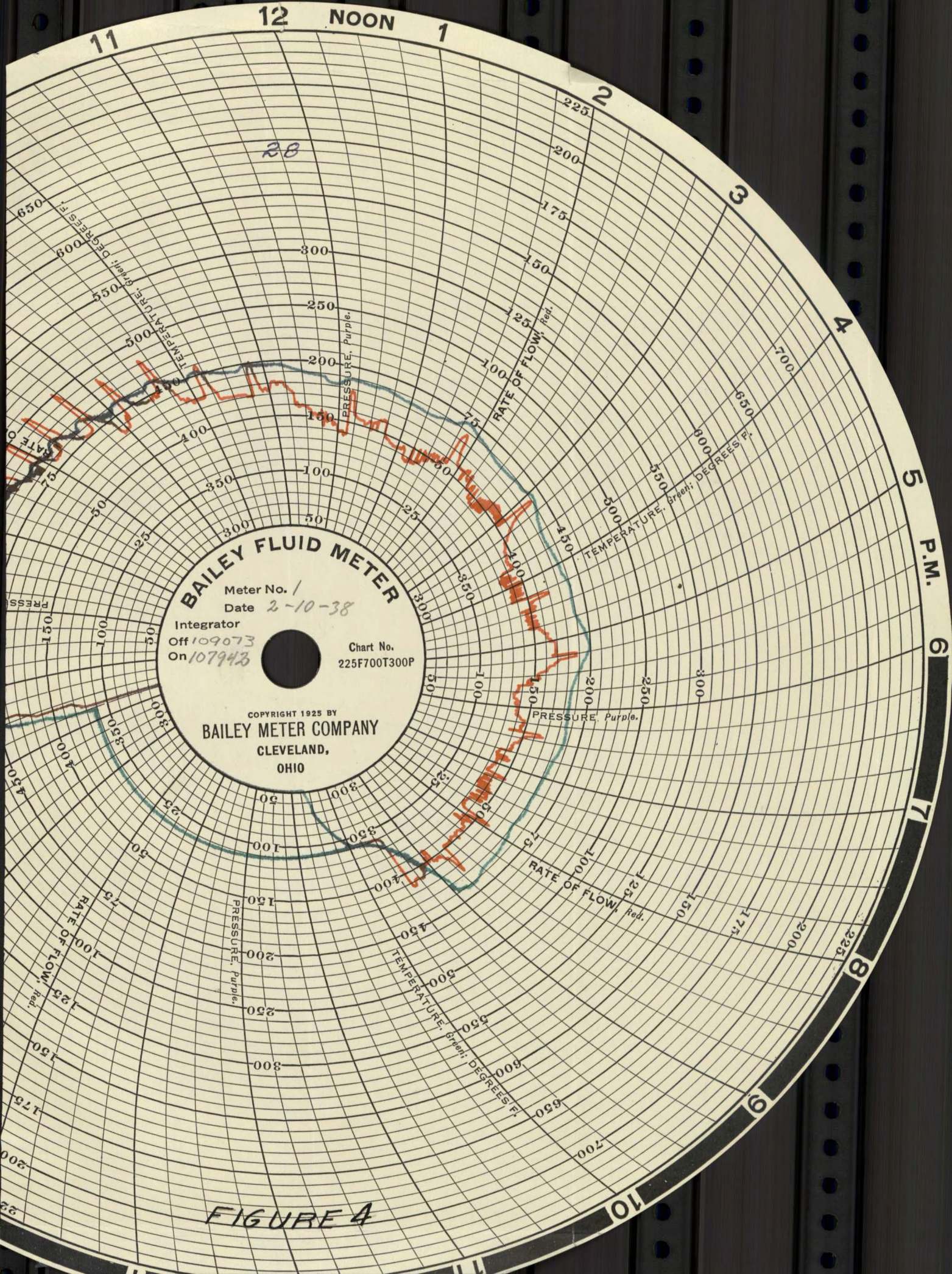
12 NOON
1
2
3
4
5 P.M.
6
7
8
9
10
11
28
BAILEY FLUID METER
Meter No. 1
Date 2-10-38
Integrator
Off 109073
On 107942
Chart No.
225F700T300P
COPYRIGHT 1925 BY
BAILEY METER COMPANY
CLEVELAND,
OHIO
PRESSURE, Purple.
RATE OF FLOW, Red.
TEMPERATURE, Green; DEGREES F.

FIGURE 4

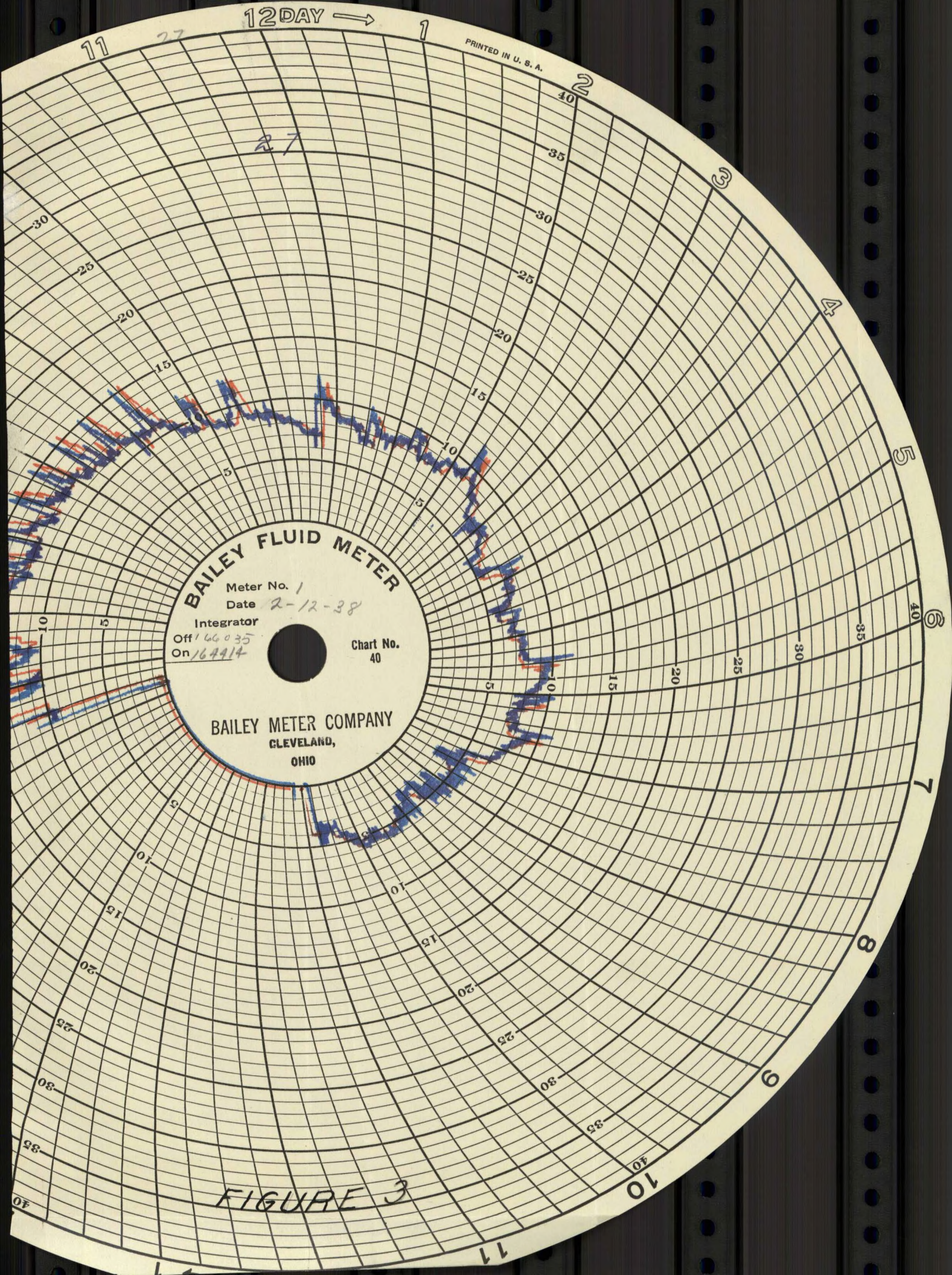
12 DAY
1
2
3
4
5
6
7
8
9
10
11
PRINTED IN U. S. A.
BAILEY FLUID METER
Meter No. 1
Date 2-12-38
Integrator
Off 166035
On 164914
Chart No. 40
BAILEY METER COMPANY
CLEVELAND,
OHIO

FIGURE 3

DISCUSSION OF RESULTS

Table 1 indicates the first results obtained with the dew point indicator. As the CO_2 increased the dew point increased accordingly and did not vary much from calculated dew point. In other words within this range the completeness of combustion might be indicated by the dew point as well as by the Orsat, but are misleading unless corrected for humidity of air.

This series of tests were run on the same furnace, measuring the air intake, and flue gas output by means of orifices in intake and stack with micromanometer so connected that the pressure differential across either orifice could be read within a few seconds of each other. And following the procedure outlined by Gordan Conrad (6) the results checked very closely to his data. As the CO_2 rose toward ideal conditions the quantity of flue gas always exceeded the intake (air plus gas) by a larger difference so the attempt to solve the problem from this angle was abandoned.

At this point in the investigation an attempt was made to plot the results of a large number of Orsat analyses to see what relation could be worked out.

The CO_2 readings were laid off as abscissa and the O_2 as ordinates and within the limits of common errors in reading, the upper curve was a straight line for most values up to 9.5% or 10% CO_2. And if this line was extended it cut the x

axis at theoretical CO_2 for perfect combustion with no excess of O_2.

This curve is very similar to the Ostwold diagram (28). However, quoting Mr. G. H. Senner (33): "The Ostwold diagram was originally devised on the assumption that the only product of incomplete combustion was CO and the various values of CO were represented by lines parallel to the line of complete combustion, and below it. If a given Orsat reading showed a percentage of CO_2 below the complete combustion line for a given O_2 reading, it was assumed that incomplete combustion existed and the distance below the complete combustion line represented the amount of CO present. When the products of combustion of the domestic oil burner were studied it was found, on the contrary, that no matter how imperfect the combustion, the point almost invariably fell on the complete combustion line, even when there was a deficiency of air for combustion." This was not the case when this diagram was used to check the Orsat analyses of the flue gas from natural gas burners.

The graph, figure 1, was drawn from an analysis of Bozeman natural gas but it was found if a large number of Orsat analyses were made of the flue gas and the values plotted, a line could be drawn from the point $CO_2 = 0$ as $O_2 = 20.9$ through the highest points and extended to intersect the CO_2 axis. Figure 2 was

was constructed in this way.

This graph was then used to check the Orsat analysis. If the analysis was carefully made any deviation from the straight line was immediately investigated. A point above the line usually indicated a leak in the Orsat but in one case points consistently above the line for several days indicated a change in the analysis of the natural gas furnished, probably by a change in the source of supply, but in that case it was evident a new line could be drawn through these points but the change lasted only a few days.

During the latter part of this work the graph was used as a guide almost entirely. If the Orsat analysis was carefully made and checked at each reading and the point did fall 1% to 2% away from the line, an analysis of the residue gas in the sample always showed combustibles either as H or some hydrocarbon compounds.

Table II shows some of the results of the test on the small vertical steam boiler at the Montana State College Creamery.

The dew point indicator here was arranged so that the sample taken for the Orsat analysis was drawn through the dew point indicator so there would be little chance for the two samples to differ.

In these results the dew point rose consistently as the

CO_2 increased as there was no indication of CO in the Orsat analysis but as shown in reading No. 10:37 when CO was found the dew point dropped indicating less H was being completely burned to water vapor.

Samples of flue gas were collected at the same time the Orsat samples were taken and if the Orsat indicated CO the other sample was taken to the laboratory and analysis made in the Burrell Orsat with slow combustion pipette and copper oxide tube. These analyses always showed some H present in the flue gas if CO had been found in Orsat analysis. As other combustibles were found they could not be positively identified because the ratio of C and H were seldom ever the same in any two samples.

This method of procedure was abandoned because it was impossible to get a gas sample container that was satisfactory. If a metal container was used the gas had to be displaced by water or other liquids and the solubility of these combustibles was so high that by the time the first analysis was run most of the combustible gas had dissolved and a check run always showed a much smaller percentage of combustible as well as CO_2.

Various types of rubber containers (balloons) were tried but most of the H escaped from these in a few hours and since it took about an hour to complete an analysis these were not a success.

Table VI shows a few of the hundreds of the Orsat analyses run at the University of New Mexico Heating Plant. The most of the results are self explanatory but "gas flow" and "air flow" might be confusing. Gas flow indicates the cubic feet of gas flowing through the burners per hour corrected to 12.6 pounds per square inch absolute pressure and at 60° F. The air flow indicates the number of cubic feet per hour of gas that would be used if a predetermined air to gas ratio was being maintained. This ratio was 15% excess air when operating with all three burners in operation. But when only one or two burners were in operation there was always some air leakage through the louvres and hence these conditions were not obtained.

The Bailey Ratio Meter measures the flow of gas delivered to the burners through the regular thin plate orifice and meter. The air flow is measured by the differential in the furnace draft across the boiler tube bank. The indicator is calibrated and adjusted so that the two pens, indicating air flow and gas will be together for a predetermined CO_2 and they will maintain this ratio very nearly as the load varies from maximum to minimum and visa versa. The chart reading gives the gas input directly but the chart reading must be multiplied by the air-gas ratio to give the cubic feet of air at any instant. This equipment works very well and maintains a nearly constant CO_2 for a steady load or a slowly changing load but for a rapidly

fluctuating load the automatic equipment does not always make both air and gas adjustments simultaneously as shown on the chart. The readings from 1-31-38, 6:05AM to 3-5-38, 5:30AM inclusive in table VI represent the operation of this equipment on rapidly changing load. The remainder of the table is typical of the readings for steady load operation. These points are plotted on figure 2. Hundreds of Orsat analyses were made at lower values of CO_2 which lie exactly on the line, but these were chosen to illustrate that as the theoretical air requirements are approached the points tend to fall below the line indicating that even with this equipment some combustibles escape unburned. Figure 3 is a chart from the Bailey Ratio Meter, the red curve indicates gas flow while the purple indicates air flow. Figure 4 is a chart from the Bailey Steam Flow Meter, the red line indicates steam flow and the green line indicates flue gas temperature.

RESULTS OBTAINED

Table IV is a typical example of the operating conditions often found in a natural gas fired boiler plant. These Orsat analyses were obtained from a plant where three coal fired horizontal return tubular boilers had been converted to gas firing by removing the stokers and installing four N. G. E. gas burners of the inspirating natural draft type to each boiler.

These readings were taken after the chart, figure 1 had been worked out for checking the combustion. Referring the first reading to the chart, 8.2% CO_2 would indicate 6.3% of O_2 should have been present. Instead only 2% was present and 1.6% CO. Even if all the CO was assumed to be CO_2 and 3.3% O_2 even then the Orsat analysis indicated something more must be present that could not be accounted for. At the time these analyses were made, the system had not been worked out of analyzing the flue gases with hydrogen tube and slow combustion pipette.

The condition was remedied by lowering the gas pressure on the burners from five to three pounds per square inch. Table V gives the Orsat analyses from the same three boilers after the gas pressure to the burners had been reduced. A check by the chart shows that combustion was still not perfect

but very much improved. This example is only one of several similar ones that were run.

Most of the homemade devices and ideas for checking the combustion in natural gas furnaces, such as checking the tubes for soot or the color of the flame were of little value. And the Orsat and CO_2 indicators and recorders were not infallable in the hands of inexperienced operators. The common mistake made by most steam boiler plant operators, when the boiler was operating near capacity and the steam demand was increased, was to increase the gas supply without regard to air. This might even work to decrease the output.

For example in table III, .2% H was indicated in the flue gas but since only about 8.0%by volume of intake was fuel gas, then nearly 30% of the H in fuel was wasted.

A complete analysis by slow combustion pipette or other means was the only way found to determine exactly the amount of combustibles in flue gas from natural gas combustion. This was a slow tedious job for a chemist or experienced engineer.

The method of plotting CO_2 against O_2 and checking all Orsat analyses by this graph gave a quick and easy method of determining the completeness of combustion.

Many attempts were made to find out exactly what chemical change took place when natural gas was burned with insufficient air in the furnace but the results were very contradictory.

No two samples could be obtained in which the ratio of C to H were exactly the same. However, it was found that whenever CO was indicated in the Orsat analysis, free H_2 was also detected if the sample was tested by either the copper oxide tube or the platinized silica gel method.

CONCLUSION

In conclusion it has been found that the Orsat analysis of flue gas from natural gas fired warm air furnaces and industrial steam boilers does not balance out as the air supply is reduced toward the theoretical requirements because:

1. Whenever CO was found in the flue gas, free H_2 was also present when tested by copper oxide tube, platinized silica gel tube or slow combustion pipette, but since it is not absorbed by any of the absorbent solutions it showed up as N_2 in the measurements.

2. Combustibles were found in some cases in the flue gas even when no CO was present and where an excess of O_2 was indicated by the Orsat analysis.

APPENDIX A

DEW POINT

The dew point obtained experimentally was compared with the calculated value but since both changed with every change of humidity in the intake the dew point indicator was of very little practical value.

To obtain the theoretical dew point of the flue gas the amount of water formed in 100 mols of flue gas was computed by the combustion chart (35) by which the ratio of the C in CO_2 plus CO must have the same ratio to the H_2 of the H_2O as the C to H_2 in the fuel if combustion is complete. The water entering in the air must be added and the sum divided into the volume of flue gas per 100 mols. This gives the volume of one pound of water vapor under operating conditions.

By comparing this volume with psychrometric tables the dew point may be obtained and compared very closely with the experimental results but since the humidity might change considerably during a test a table could not be worked out relating the dew point to CO_2. This is shown in table I for two different days.

The dew point does show, though, in the last reading that some radical change was taking place in the combustion and was the first indication obtained in this investigation that all of H_2 was not being burned to H_2O even though Orsat analysis did not show any CO present.

APPENDIX B

COMBUSTION CHECK CHART

The chart figure 1 was drawn by calculating the CO_2 contained in the flue gas when the Bozeman natural gas is burned completely to CO_2 and H_2O with no excess air. The analyses of gas were as follows: C--66.1±%; H_2--22.4±%; N_2--11.5±%. All percentages were by weight. Assuming 100 pounds of fuel were taken, this would contain 66.1 pounds or 5.51 mols of carbon, 22.5 pounds or 11.25 mols of H_2, and 11.4 pounds or .4 mols of N_2. If combustion were perfect there would have been 5.51 mols of CO_2, 11.25 mols of H_2O, and .4 mols of N_2 in flue gas from the fuel. This would have required 5.51 mols of O_2 for the CO_2 and 5.62 O_2 for H_2O or a total of 11.1 mols of O_2 which would include (11.1 x 79.1) ÷ 20.9 or 42.0 mols of N_2. The flue gas from 100 pounds of fuel gas would then contain 5.51 mols CO_2 plus 42.0 mols of N_2 from air and .4 mols from fuel or 47.9 of which 5.51 is approximately 11.6%.

Figure 2, as explained earlier in the text, was drawn by extending a straight line from 20.9 on the O_2 axis. This point for Albuquerque natural gas proved to be 12.2% CO_2 when there was no O_2. Then if it was considered that 100 mols of air were taken to start with and 20.9 mols of this were O_2 and 79.1 mols were N_2, 12.2 mols of C must have united with

12.2 mols of O_2 to form 12.2 mols of CO2 leaving 8.7 mols of O_2 which united with H_2 to form 17.4 mols of H_2O if no O_2 was indicated in the Orsat analyses. Multiplying the number of mols of C by its molecular weight (12.2 x 12 = 146.4) and the number of mols of H_2 by its molecular weight (17.4 x 2 = 34.8) and adding 146.4 + 34.8 = 181.2 pounds hydrocarbon combining with 100 mols of air. Of this 181.2 pounds of hydrocarbon 146.4 ÷ 181.2 = .808 or 80.8% is C and 34.8 ÷ 181.2 = .192 or 19.2% is H_2. Table VI gives the Orsat analysis from which figure 2 was plotted.

The chemical analysis of Albuquerque natural gas varied because it was not all from the same field. Analyses made during the summer of 1937 were: C--77.1%; H_2--22.9%; N_2--trace, but C--80.8%; H_2--19.2%; N--trace, seemed to be the average analyses during the winter months when this work was done.

APPENDIX C

CALCULATION OF H_2 AND C FROM FLUE GAS ANALYSIS

The results in tables II and III were calculated as follows:

CO_2 was the contraction in volume after the sample of flue gas had been passed through the KOH solution until a constant volume was obtained.

O_2 was the difference in volume between CO_2 and reading after passing gas through the pyrogallic acid solution to a constant volume. CO was the difference in reading after pyrogallic acid solution and after passing the sample through the cuprous chloride solution to a constant volume.

Free H_2 was two thirds of the contraction in volume which took place when the residue gas from the above absorptions was mixed with about 10 c.c. of pure O_2 and passed through the heated platinized silica gel tube to a constant volume.

Combined C was the amount of CO_2 remaining in the sample after the mixture of O_2 and gas had been passed through the slow combustion pipette to a constant volume.

Combined H_2 was twice the amount of O_2 difference between amount of O_2 put in and the amount taken by free H_2 plus amount used for combine C plus O_2 left in residue after final CO_2 determination.

ACKNOWLEDGEMENTS

The writer desires to express his thanks to Dr. Eric Therkelson and Dr. B. L. Johnson for their assistance and encouragement; to Dr. Henry Ward for assistance and use of Chemical Engineering Department equipment; and to Dr. John D. Clark and Dean M. E. Farris of the University of New Mexico, for their assistance and use of equipment.

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