

Gas Appliance Engineers Handbook

SECTION 3 — FLUE GAS ANALYSIS

FLUE GAS ANALYSIS

by Andrew A. Mitchell — Central Chapter

NATIONAL GAES AWARD — 1965

FLUE GASES

It is important to determine what is meant by "Flue Gases" and probably the best description is that flue gases are the final product of a combustion process. The common fuels consist primarily of carbon and hydrogen with their compounds and the flue gases resulting from combustion contain oxides of these elements and those of the impurities together with any excess air and, under some conditions, other substances evolved from the heated material.

An analysis of the flue gases gives evidence of efficiency of combustion and is a prime factor in controlling the operation for maximum results and in arriving at improvements in design. Flue gas analysis indicates the air-fuel ratio. Good or poor mixing of the air and fuel determines the significance of the flue gas analysis to a considerable extent. This is shown by the curves given in Exhibit 1. If the mixing is poor, an excess of air must be supplied to make sure that every particle of fuel will contact some air and burn.

Before dealing with the analysis of the flue gases, consideration should be given to the products of combustion. It is often desirable to predict the quantity and analysis of the products of combustion to determine flue sizes and furnace pressure, and to predict the magnitude of stack or flue gas losses. Exhibit 2 lists the products resulting from perfect combustion and Exhibit 3 gives equations to permit calculation of the quantities of gases in the combustion products of gaseous fuels either by volume or by weight. The percentages to be submitted in all of these equations are percentages by volume. For cases in which an excess of air is supplied, it is necessary only to add the weight or volume of the excess nitrogen and excess oxygen to the other combustion products. When there is a deficiency of air, it is difficult to predict the volume or the analysis of the combustion products, but the total weight of the products is equal to the weight of the fuel plus the weight of the air supplied.

SIGNIFICANCE OF PERCENT CARBON DIOXIDE

With good gas/air mixing, perfect combustion is obtained when the flue gas analysis shows no CO, H₂ or O₂ and when the percentage CO₂ is at a maximum. The theoretical maximum percent CO₂ in the dry flue gases is termed the ultimate percent CO₂. If the air-fuel ratio is adjusted until the maximum percent CO₂ is obtained, then the furnace is operating very close to the point of greatest thermal efficiency. This permits the approximate setting of the air-fuel ratio without metering the fuel and the air flow.

With poor mixing, the manner in which the flue gas analysis varies with changes in the air-fuel ratio is a function of the physical arrangements of the burner and combustion chamber. The following is the percent CO₂ readings which should be obtained with perfect mixing of various amounts of air with natural gas, propane and butane.

Effect of Excess Air on CO₂ in Combustion Products

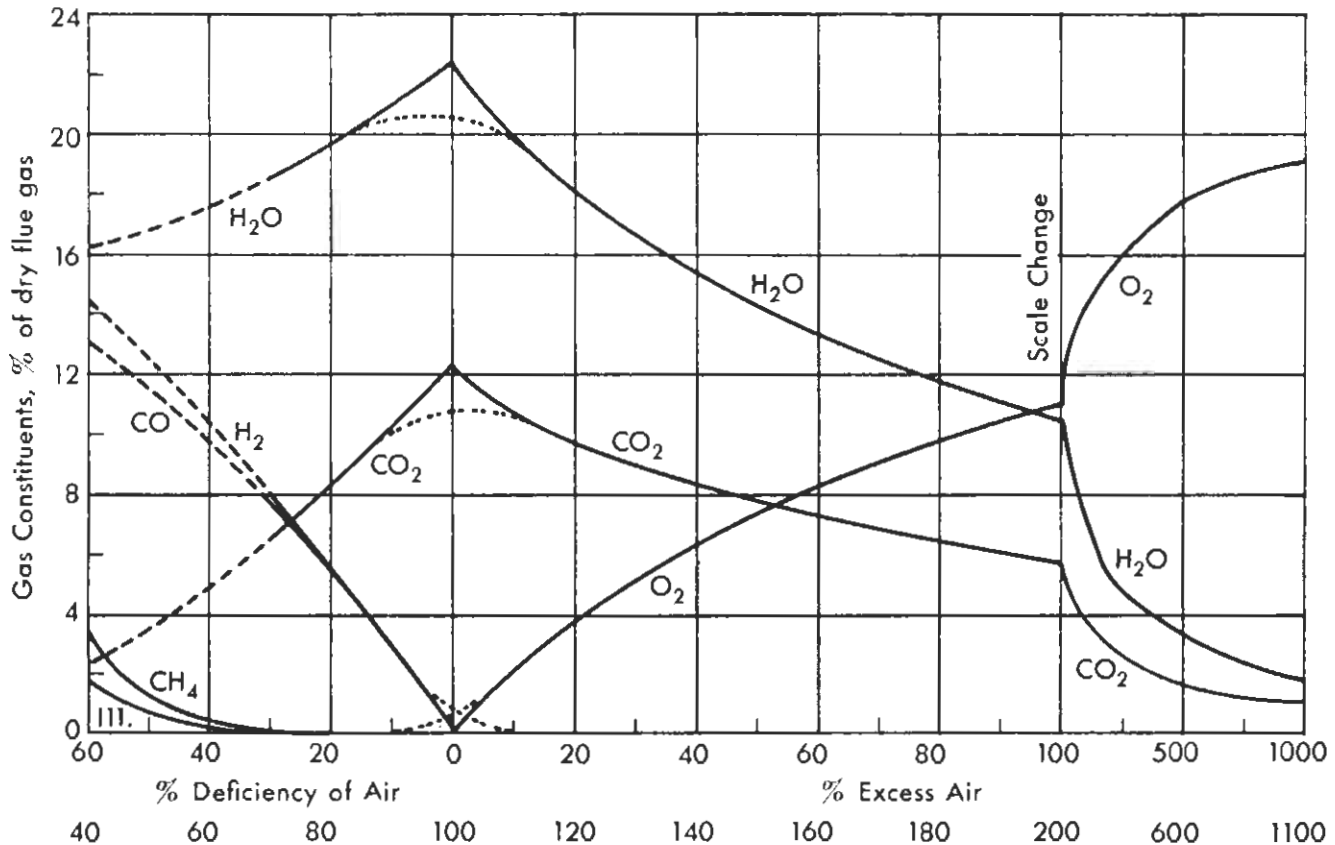
Fuel Gas	Excess Air, Per Cent	Theoretical Air, Per Cent	CO ₂ , Per Cent	Cubic Foot Air Per Cubic Foot Gas
Natural (1,000 Btu per cubic foot, specific gravity 0.6)	0	100	12.1	9.4
	10	110	10.8	10.3
	20	120	9.8	11.3
	40	140	8.4	13.2
	60	160	7.3	15.0
	80	180	6.5	16.9
	100	200	5.8	18.8
Propane (2,529 Btu per cubic foot, specific gravity 1.55) — Pure measured at 60F, 30 inches mercury pressure saturated. Commercial propane has a heating value from 2,250 to 2,450 Btu per cubic foot and a gravity about 1.53.	150	250	5.0	23.5
	200	300	3.8	28.2
	0	100	14.0	23.9
	10	110	12.5	26.3
	20	120	11.4	28.7
	40	140	9.7	33.4
	60	160	8.4	38.2
Butane (3,333 Btu per cubic foot, specific gravity 2.00) — Pure measured at 60F, 30 inches mercury pressure saturated. Commercial grades have heating values of 3,150 to 3,250 Btu per cubic foot.	80	180	7.5	43.0
	100	200	6.6	47.8
	150	250	5.3	59.7
	200	300	4.4	71.7
	0	100	14.1	31.1
	10	110	12.7	34.2
	20	120	11.6	37.3
	40	140	9.8	43.5
	60	160	8.5	49.7
	80	180	7.5	55.9
	100	200	6.7	62.1
	150	250	5.4	77.6
	200	300	4.5	93.2

Gas Appliance Engineers Handbook

EXHIBIT 1

Flue gas analyses are used to indicate the air-fuel ratio and to indicate the degree of completeness of combustion. If the mixing is poor, an

excess of air must be supplied so that every particle of fuel will contact some air and burn. Exhibit 1 shows the effects of good or poor mixing.



Effect of Fuel/Air Ratio on Flue Gas Analysis for 1108 Btu/cu ft natural gas (0.63 gas gravity) containing 83% CH₄ and 16% C₂H₆. Values for rich mixtures depend somewhat on combustion chamber design. The average values shown are within ½% of correct for H₂, CO, and CO₂, but may be as much as 2% low for other constituents. Some external heat is usually required for mixtures with less than 70% aeration (dotted lines). Dashed lines show the trends with poor mixing. Gas constituent percentages

are on a dry basis to allow comparison with of gas analyzers, which measure the gas volumes after water vapor has condensed out of the sample. With correct ratio, this gas produces 2.11 cu ft H₂O, 1.152 cu ft CO₂, 8.38 cu ft N₂; so % CO₂ = $100 \times \frac{1.152}{2.11 + 1.152 + 8.38}$ = 12.08%.

Information came from The North American Mfg. Co.'s Combustion Handbook

The following table indicates the Carbon Dioxide produced in the products of combustion of commonly-used domestic appliances, on the dry basis —

Ranges	from 2 to 5 per cent
Water Heaters	6 to 10 per cent
Room Heaters	3 to 10 per cent
Refrigerators	4 to 7 per cent
Central Heating furnaces and boilers	6 to 11 per cent

TRACE PRODUCTS

Trace products of combustion of fuel gas include oxides of nitrogen, aldehydes, organic acids and, if sulphur compounds exist in the fuel, oxides of sulphur. These trace products are in such small

amounts that a delicate chemical analysis is necessary to determine their presence. It is impossible to detect them by normal flue gas analysis. However, the presence of oxides of nitrogen and sulfur has been called to the attention of the gas industry in the investigation relating to smog control in the city of Los Angeles. The sharp, penetrating odor which usually accompanies and serves to identify partially-burned fuel gases is commonly attributed to the products of incomplete combustion, chiefly aldehydes. The presence of aldehydes is recognized as an indication of incomplete combustion. When adjusting appliances, no tests for traces of Carbon Monoxide are made until such odors have been eliminated. The supply of adequate air for combustion will not always correct

Gas Appliance Engineers Handbook

EXHIBIT 2

Combustion Characteristics of Chemical Compounds

Fuel	Specific gravity relative to air	Specific volume cu ft/lb	Theoretical air required		Gross Btu per cu ft std air	Ultimate percent CO ₂	Products of perfect combustion ^a				
			cu ft/cu ft	cu ft/lb			CO ₂	H ₂ O	N ₂	SO ₂	Total
Carbon (C)				151.3	93.0	20.9	3.67	0	8.85	0	12.52
Hydrogen (H ₂)	0.070	187.7	2.39	453	135.0		0	1.00	1.89	0	2.89
Sulfur (S)				56.7	70.3		0	0	3.32	2.00	5.32
Carbon monoxide (CO)	0.969	13.51	2.39	32.5	133.7	34.6	1.00	0	1.89	0	2.89
Hydrogen sulfide (H ₂ S)	1.194	10.98	7.17	78.5	95.3		1.57	0	1.90	0	3.47
							0	1.00	5.67	1.00	7.67
							0	0.53	4.68	1.88	7.09
Methane (CH ₄)	0.555	23.61	9.56	226.5	105.4	11.68	1.00	2.00	7.56	0	10.56
							2.75	2.25	13.28	0	18.28
Ethane (C ₂ H ₆)	1.048	12.50	16.72	212.0	105.2	13.15	2.00	3.00	13.22	0	18.22
							2.96	1.80	12.40	0	17.16
Propane (C ₃ H ₈)	1.551	8.45	23.9	206.5	104.9	13.70	3.00	4.00	18.90	0	25.90
							3.00	1.64	12.07	0	16.71
Butane (C ₄ H ₁₀)	2.082	6.29	31.1	203.5	104.7	14.00	4.00	5.00	24.60	0	33.60
							3.04	1.55	11.90	0	16.49
Octane (C ₈ H ₁₈)				199.0	103.5	14.42	3.09	1.42	11.67	0	16.18
Acetylene (C ₂ H ₂)	0.901	14.54	11.95	176.7	122.1	17.46	2.00	1.00	9.45	0	12.45
							3.38	0.69	10.22	0	14.29

^a Boldface figures are in cu ft/cu ft of fuel; lightface figures are in lb/lb of fuel.

Information came from
The North American Mfg. Co.'s Combustion Handbook

this condition, because unbalanced and uneven distribution of this air and impingement of the burner flames may be occasioned by burner or appliance design, permitting incomplete combustion to occur in some part of the flame.

FLUE GAS ANALYSIS — GENERAL METHODS

Methods for determining flue gas composition can be divided into three general categories, namely, Chemical, Instrumental and Trace Analysis. The latter involves special techniques which may be either chemical or instrumental and which usually require the services of a trained chemist or chemical technologist.

In all cases methods for taking the sample are most important and will be discussed briefly. No attempt is made here to describe specific apparatus for sampling or analysis. A bibliography is appended from which detailed information can be derived.

SAMPLING

Samples are taken by means of a tube and an aspirator bulb being drawn either directly into the analyzer or stored in glass sampling tubes for analysis at a later date. Sample tubes must be made of a gas-tight material and the kind of tube

Gas Appliance Engineers Handbook

EXHIBIT 3

Equations for Determining Products of Combustion of Gaseous Fuels (all percentages are percents by volume)

$$\frac{\text{lb comb prod}}{\text{cu ft fuel}} = \%CO \times 0.00256 + \%H_2 \times 0.001873 + \%CH_4 \times 0.00772 + \%C_2H_6 \times 0.01356 + \%C_3H_8 \times 0.0194 + \%C_4H_{10} \times 0.0261 + \%CO_2 \times 0.001164 + \%N_2 \times 0.00074 + \%H_2O \times 0.000476 - \%O_2 \times 0.0028$$

$$\frac{\text{lb } CO_2}{\text{cu ft fuel}} = \%CO \times 0.001165 + \%CH_4 \times 0.001165 + \%C_2H_6 \times 0.00230 + \%C_3H_8 \times 0.00349 + \%C_4H_{10} \times 0.00465 + \%CO_2 \times 0.001164$$

$$\frac{\text{lb } H_2O}{\text{cu ft fuel}} = \%H_2 \times 0.000476 + \%CH_4 \times 0.000951 + \%C_2H_6 \times 0.00143 + \%C_3H_8 \times 0.001905 + \%C_4H_{10} \times 0.00238 + \%H_2O \times 0.000476$$

$$\frac{\text{lb } N_2}{\text{cu ft fuel}} = \%CO \times 0.001398 + \%H_2 \times 0.001398 + \%CH_4 \times 0.00561 + \%C_2H_6 \times 0.00980 + \%C_3H_8 \times 0.01398 + \%C_4H_{10} \times 0.01821 + \%N_2 \times 0.00074 - \%O_2 \times 0.0028$$

$$\frac{\text{cu ft comb prod}}{\text{cu ft fuel}} = \%CO \times 0.0289 + \%H_2 \times 0.0289 + \%CH_4 \times 0.1056 + \%C_2H_6 \times 0.1824 + \%C_3H_8 \times 0.2590 + \%C_4H_{10} \times 0.3360 + \% \text{ inerts} \times 0.01 - \%O_2 \times 0.0378$$

$$\frac{\text{cu ft dry comb prod}}{\text{cu ft fuel}} = \%CO \times 0.0289 + \%H_2 \times 0.0189 + \%CH_4 \times 0.0856 + \%C_2H_6 \times 0.1524 + \%C_3H_8 \times 0.2190 + \%C_4H_{10} \times 0.2860 + \% \text{ inerts} \times 0.01 - \%O_2 \times 0.0378$$

$$\frac{\text{cu ft } CO_2}{\text{cu ft fuel}} = \%CO \times 0.01 + \%CH_4 \times 0.01 + \%C_2H_6 \times 0.02 + \%C_3H_8 \times 0.03 + \%C_4H_{10} \times 0.04 + \%CO_2 \times 0.01$$

$$\%CO_2 \text{ in dry flue gases} = 100 \times \frac{\text{cu ft } CO_2}{\text{cu ft fuel}} + \frac{\text{cu ft dry comb prod}}{\text{cu ft fuel}}$$

$$\frac{\text{cu ft } H_2O}{\text{cu ft fuel}} = \%H_2 \times 0.01 + \%CH_4 \times 0.02 + \%C_2H_6 \times 0.03 + \%C_3H_8 \times 0.04 + \%C_4H_{10} \times 0.05 + \%H_2O \times 0.01$$

$$\frac{\text{cu ft } N_2}{\text{cu ft fuel}} = \%CO \times 0.0189 + \%H_2 \times 0.0189 + \%CH_4 \times 0.0756 + \%C_2H_6 \times 0.1324 + \%C_3H_8 \times 0.1890 + \%C_4H_{10} \times 0.2460 + \%N_2 \times 0.01 - \%O_2 \times 0.0378$$

Information came from
The North American Mfg. Co.'s Combustion Handbook

Gas Appliance Engineers Handbook

used depends upon the temperature of the flue being sampled. Here is a general guide—

	Temperature
Uncooled Metal Tubes	up to 250 C (482 F)
Combustion Glass	up to 500 C (932 F)
Water Cooled Metal Tubes	above 500 C

Uncooled metal tubes (iron for instance) at high temperatures not only remove oxygen through the formation of iron oxide but also may reduce CO₂ to CO and produce H₂ by reaction with water vapour.

Stainless steel tubes are satisfactory for sampling domestic gas appliances.

Great care must be taken in choosing a location that will give a truly representative sample of the flue products being tested. Sampling at a position where the flue products being tested have been diluted with air, drawn in through faulty brick work or through openings in metal ducts, can give very misleading information. Gases should not be kept in sample tubes for longer than necessary particularly where moisture is present since differential absorption of the various constituent gases may occur.

A. CHEMICAL METHODS

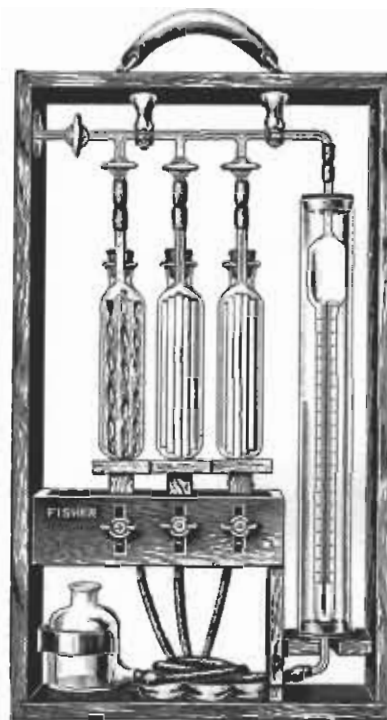
Chemical methods are the original and perhaps best known of all methods of flue gas analysis and are applicable to most gases with the exception of nitrogen, argon, etc. which are chemically inert.

Flue gases resulting from incomplete combustion also contain methane, hydrogen, carbon monoxide and traces of aldehydes, etc. Determination of such gases other than CO requires additions to the ordinary Orsat apparatus. They are not normally determined in field testing except as combustible components (see instrumental methods).

The standard apparatus for analyzing flue gases is known as the Orsat and many types of Orsat are available. For field work very simplified forms are available for doing a single gas such as CO₂ or oxygen. For example, the Fyrite Tester is one such device used for testing for carbon dioxide. Caustic potash solution is used to absorb carbon dioxide contained in the flue gas sample, and this results in a slight vacuum which can be measured with a gage. The temperature of the flue gas sample may affect the result, and the apparatus must be completely tight to secure reasonably accurate results.

Basically an Orsat type apparatus consists of an accurately calibrated measuring tube (burette) attached by means of a glass manifold to a succession of absorbing tubes or scrubbers known as pipettes (See Exhibit 4). There are many designs of pipettes on the market but all have the same purpose, namely to bring the gas sample into intimate contact with a chemical reagent so that a specific component of the flue gas is absorbed by the chemical as rapidly and completely as possible.

EXHIBIT 4



Technical Orsat Assembly
(Courtesy Fisher Scientific Co.)

In doing an analysis the sample volume (usually 100 ml.) is measured in the burette before and after absorption. The difference in the two readings is taken as the volume of component absorbed.

Carbon dioxide and oxygen are very soluble in water. A 1 per cent solution of sulfuric acid in distilled water decreases the solubilities of these gases in water so that it may be used as the confining fluid in all but the most accurate Orsat analysis. A permanent acid, one with a very low vapor pressure, is preferred. A nearly saturated acid solution of sodium chloride (salt) may be used but this may lead to difficulties in manipulation under conditions of use where a slight lowering of temperature occurs. It is convenient to color these solutions red with a very small amount of

Gas Appliance Engineers Handbook

powdered methyl orange for ease of reading and the methyl orange also acts as an indication that the solution is always acid.

The burette is enclosed in a water jacket to help maintain a constant temperature during analysis. Errors due to temperature change and variations in barometric pressure are normally minimal during the time needed to complete an analysis. However in flue gas analysis hot samples are normally obtained. These samples must be cooled to the temperature of the water jacket of the burette or room temperature before it enters the Orsat. If the sample is measured and analyzed above this temperature, each 5F the sample is above jacket temperature results in an apparent 1 per cent increase in carbon dioxide percentage due to the contraction of the sample during the analysis.

The accuracy of the burette readings are in the range of 0.2% of the scale reading. It should be noted that the pipettes are arranged on the manifold in such a way that no reagent will remove more than one constituent gas. Alkaline pyrogallol, for instance, will absorb both CO₂ and O₂ and hence must not be used before the CO₂ has been removed by the potassium hydroxide pipette. The following reagents are used in Orsat type apparatus for determining the components in flue gases:

For absorbing CO₂ — 60 per cent potassium hydroxide.

For absorbing O₂ — alkaline pyrogallol or chromous chloride.

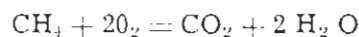
For absorbing CO — when the concentration is over 1/2 per cent acid cuprous chloride or cuprous sulfate-beta naphol solution may be used for absorbing carbon monoxide. In the concentrations that carbon monoxide occur in flue products (usually under .04 per cent) the Orsat apparatus cannot be used.

COMBUSTION METHODS

Orsat apparatus used for laboratory and more detailed testing can in addition to the above determine the amount of hydrogen and unburnt hydrocarbons. These tests are not often made in a routine flue gas analysis but when required they can be done chemically as follows:

Methane — determined by explosion or slow combustion with a measured volume of O₂ and

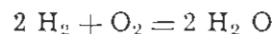
determination of the CO₂ and volume contraction due to water vapour. Ignition takes place either by means of a spark in the explosion method or over a hot platinum wire in the combustion method. Combustion of the hydrocarbon over a catalyst is also used.



Volumes

1 2 1 2

Hydrogen — determined by oxidation over hot copper oxide or platinum catalyst, and determination of volume contraction due to water formed.



ETHANE, PROPANE AND HIGHER HYDROCARBONS

Only two hydrocarbons such as methane can be determined in a single mixture by chemical combustion. Total amount of each is calculated from the CO₂ and water formed by using equations with two unknowns. Instrumental methods have largely displaced chemical application in this. (See Table in Exhibit 5)

B. INSTRUMENTAL METHODS

Instrumental methods of flue gas analysis range from portable instruments designed to determine CO₂ and/or O₂ to complicated electronic assemblies for completely analyzing a flue gas. Two standard methods of analysis are being used to an ever-greater degree for the latter purpose.

(1) GAS — LIQUID CHROMATOGRAPHY

Gas Chromatography is a comparatively new technique with a wide field of applications. Briefly it consists of the separation of the constituents of a flue gas by absorption on a packed column from a moving stream of a carrier gas (usually helium). The length of time each constituent gas is retained on a specific column is constant under given conditions. It is known as the retention time and it depends upon the temperature, flow rate of the carrier gas, size of column and molecular structure of the gas. Not all gases can be separated on the same column and the following are typical columns and instrument parameters for separating the constituents of flue gases.

Gas Appliance Engineers Handbook

EXHIBIT 5

FORMULAS FOR COMBUSTION ANALYSIS CALCULATIONS

Mixture	w	x	y	z
Carbon monoxide } Methane } Ethane }	$\frac{a}{3} + \frac{4b}{3} - c$	0	$\frac{5a}{3} - \frac{b}{3} - c = b - (w + 2z)$	$c - a$
Carbon monoxide } Hydrogen } Ethane }	$\frac{a}{3} + \frac{4b}{3} - c$	$\frac{5a}{6} - \frac{b}{6} - \frac{c}{2}$	0	$\frac{c}{2} - \frac{a}{6} - \frac{6}{b}$
Carbon monoxide } Hydrogen } Methane }	$\frac{a}{3} + \frac{4b}{3} - c$	$a - c$	$c - \frac{a}{3} - \frac{b}{3} = b - w$	0
Methane } Ethane }	0	0	$\frac{4a}{3} - \frac{5b}{3} = b - 2z$	$\frac{4b}{3} - \frac{2a}{3}$
Hydrogen } Methane }	0	$\frac{2a}{3} - \frac{4b}{3}$	b	0
Carbon monoxide } Methane }	$\frac{4b}{3} - \frac{2a}{3}$	0	$\frac{2a}{3} - \frac{b}{3} = b - w$	0
Carbon monoxide } Hydrogen }	b	$\frac{2a}{3} - \frac{b}{3}$	0	0

a = mols volume contraction; b = mols carbon dioxide produced; c = mols oxygen consumed; w, x, y and z = mols in original sample of carbon monoxide, hydrogen, methane, and ethane, respectively.
Table from *Gas Analysis—Testing of Gaseous Materials*, Published by American Gas Association.

FOR SEPARATING OXYGEN, NITROGEN AND METHANE

Column Material	Linde Molecular Sieve Type 5A.
Column Length	2 Meters
Operating Temperature	40 C.
Helium Flow	50 ml/min.
Sample Size	1 ml.

AIR, METHANE, ETHANE, CO₂ AND PROPANE

Column Material	Silica Gel.
Column Length	2 Meters
Operating Temperature	40 C.
Helium Flow	50 ml./min.
Sample Size	1 ml.

After separation on the column the individual components are moved by the carrier gas into a detector cell connected to an electronic recorder. There are several forms of detector cells. The one most commonly used for flue gas analysis is the thermal conductivity cell in which the resistance of a thermistor bead or platinum wire varies with temperature. This cell operates in much the same manner as the indicator circuit of a combustible gas indicator.

For determining very small percentages of compounds other types of cells are used. Ionization detectors such as the flame and Beta ray are among the more common.

In the gas chromatograph the electronic impulse emitted by the detector cell is transmitted to a moving chart by means of a standard electronic recorder. The position, height and area under the curve drawn by the recorder bears a definite relationship to the amount and type of each gas separated by the column.

In doing a quantitative analysis of a flue gas, the succession of curves drawn by a given volume of the sample put into the chromatograph are compared to a similar set of curves drawn by an equivalent sample of a standard gas. The constituents of the standard gas are accurately known. If a standard gas is not available air may be used as a standard when doing nitrogen and oxygen in a flue gas. Pure CO₂ and air may also be used provided the amount used as a standard is within 25% of the mass of CO₂ in the sample being tested. The volume of any pure gas varies directly as the height of the curve for that gas.

Once set up gas chromatographs are easy to operate but the standardization, and interpretation of chromatograms should be under the supervision of a well trained technologist.

This method is satisfactory for separating and determining different fuel gas components, but is

Gas Appliance Engineers Handbook

not accurate enough for the small amounts of carbon monoxide usually found in appliance flue products.

(2) MASS SPECTROSCOPY

Mass spectroscopy is primarily a laboratory technique requiring rather more expensive equipment than does gas chromatography.

In this procedure the molecular species making up a gaseous mixture are ionized and dissociated by electron bombardment, the resulting positive ions of different masses are then accelerated in an electric field and separated magnetically. A spectrogram is obtained showing the mass of each constituent and this is compared to a similar spectrogram for a known mixture.

Instrumentation for mass spectroscopy is considerably more expensive than that required for gas chromatography. It also requires the attention of a highly skilled operator.

PORTABLE INSTRUMENTS FOR FIELD TESTING OF FLUE GASES

There are a number of equally good Combustion Analysers on the market for determining the CO_2 and O_2 content of flue gases. They all operate on the same general principles and determine the amount of O_2 and combustibles. Using the percent oxygen and curves supplied with the instruments the percent CO_2 and the amount of excess air in the flue gas can be determined.

The principle of operation is catalytic combustion. The combustibles are detected by burning them with air on a detecting filament (again similar method to the combustible gas indicator). The O_2 is determined in a similar manner by burning it in a stream of a combustible gas, usually propane.

As in all instrumentation an operator is required who is fully conversant with the analyzer he is using and in the interpretation of results, for example: The O_2 is limited to a maximum of 21%. The Combustibles indication will not be usable above a fixed concentration of combustibles. Dilution with air is the limiting factor. When the Combustibles concentration goes above the value where enough O_2 is present the instrument is liable to give a low reading.

C. TRACE COMPONENTS

Of the trace components in flue gases carbon monoxide, nitric oxide and sulphur trioxide are the most important.

CARBON MONOXIDE

This is the most important of the minor constituents and certainly the most dangerous. It is not normally detected in regular Orsat analysis. The following methods are used for detecting carbon monoxide in trace amounts:

Hoolamite Iodine Pentoxide Indicator—for 0.1 per cent or more in contaminated atmospheres.

Iodine Pentoxide Apparatus—for trace amounts with precision and accuracy, but this method is long and arduous.

Pyrotannic Acid Method—for determining CO in the blood. Fresh blood samples are needed when used on flue gas samples. Range of method is 0.01 to 0.2 per cent, with accuracy of 0.01 per cent.

Hopcalite Cell—Fairly accurate method. Difficult to maintain and manipulate. Of historical interest at present.

Infra-Red Absorption—Specific absorption of infra-red radiation by CO is a distinctive physical property, which provides a rapid accurate method when a standard reference sample is available for comparison. Used at A.G.A. and C.G.A. Laboratories, its accuracy is 0.001 per cent.

Colorimetric Tubes—A 60 ml. rubber aspirating bulb is used to draw a sample through a 15 mm. long yellow indicator gel between white guard gel sections 15 and 45 mm. long. The yellow gel section is composed of a sulfuric acid solution of ammonium molybdate and palladous sulfate. The yellow gel changes shade uniformly from yellow to shades of green. The test color intensity is a function of the product of carbon monoxide concentration and time. The range of concentration for which this bulb is useful is from 0.001 to 0.1 per cent. Other reducing gases also cause this change in color. Better results are obtained with these tubes when a filter made up of potassium dichromate crystals is used between the sample and the indicating tube.

Length of Stain Indicators—A new tube has recently been placed on the market in which the carbon monoxide percentage is indicated by the length of stain instead of the change in color. Preliminary experi-

Gas Appliance Engineers Handbook

ence with these tubes have indicated good accuracy.

Nitric oxide and sulphur trioxide in trace amounts are only determined in special cases. When needed their accurate determination requires rather elaborate equipment and is a job for the professional chemist.

Water vapour might also be considered as a minor component. Here once again sampling is most important and the flue gas must reach the instrument at a temperature above the dew point of the gas being tested.

Dew point determinations are only made for specific purposes since a great deal of work has been done and curves exist from which the dew point can be obtained when excess air, gas temperature, etc. are known.

One of the simplest and most effective instruments for determining flue gas dew points is known as the Alnor Dew Pointer. Its operation is based on the rapid expansion of compressed gas into a sealed chamber containing a very low emission radioactive source. The rapid expansion of the sample into the chamber causes a temperature drop. When this drop is sufficient to lower the gas temperature below the dew point a fog is visible in the chamber. A calculator is supplied from which the pressure differential causing a minimum amount of fog can be converted into dew point.

The dew point may also be determined by wet and dry bulb thermometers and cooled cup hygrometers. In the latter device a sample of flue gas is aspirated across the outer surface of a highly polished metal cup in which is placed a cooling mixture such as ice and alcohol.

WATER VAPOUR IN FLUE GASES

Water vapour plays a significant role in gas burning problems. Important points to consider are:

- (1) Heat loss due to water vapour can be calculated at 50.3 Btu per cu. ft. of water vapour produced (on 60 F., 30 in. Hg. basis).
- (2) Dew point of the flue gases. This is most marked in the case of domestic appliances where the moisture may be undesirable or may be the carrier for corrosive sulphur acids. It is also important in certain industrial furnace atmospheres.
- (3) Radiation from water vapour. Water vapour and carbon possess considerable radiating power in the infra-red end of the spectrum. Thus, they contribute heavily

to the radiant heat transmitted from non-luminous flames.

The dew point is of particular importance. It can be defined as the temperature at which the vapour phase is in equilibrium with a minute quantity of liquid phase in any system. More simply it is the temperature at which condensation begins to occur. To minimize corrosion from gases containing sulphur oxides and water vapour, it is customary to maintain the temperature higher than the dew point of the gas. A chart to determine the dew point of the combustion products of natural gas is given in Exhibit 6. The set of curves gives the expected dew point of the combustion products when the amount of excess air and the dew point of the air used for combustion are both known. An example is inserted on the graph—a burner with 300% theoretical air and with the dew point of the combustion air at 60 F. gives the dew point of the combustion product as 107 F. With natural gas, most furnace dew points run between 125 F and 135 F.

APPLICATIONS OF FLUE GAS ANALYSIS

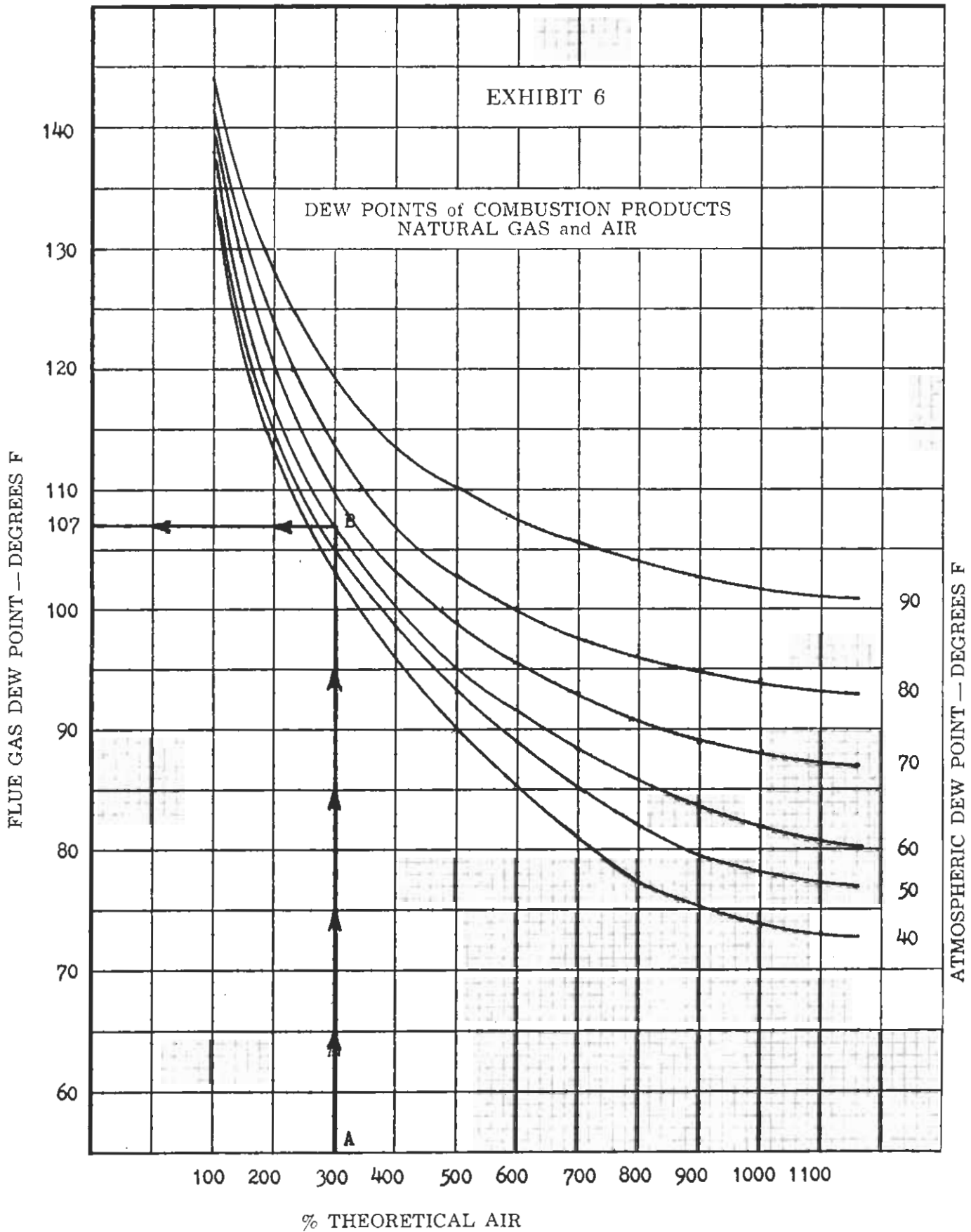
Since the flue gases consist of the end products of a combustion heating process, their composition is of interest and importance, chiefly from the viewpoint of (1) safety; (2) efficiency; and (3) computation of specific values pertaining to either or both.

Safety operation requires the elimination, within reason, of all hazards which might affect the continuity of the process. In combustion processes the common personnel hazard is carbon monoxide which can result from incomplete combustion. An operational hazard can be the formation of an explosive mixture. This hazard can be present wherever combustible gases or vapours are in contact with a substance which will support combustion and the properties are in the explosive range. Flue gas analysis can be used to detect and/or to confirm and locate suspected conditions of this nature.

The uses of gas analysis to promote efficiency are many and varied. Each installation gives rise to considerations peculiar to itself. Efficiency and economy do not necessarily imply the most complete oxidation of the fuel with the least amount of oxygen or air. In metal heating, scaling loss is frequently more important economically than fuel conservation.

In each installation there are specific considerations which are represented by values reflecting

Gas Appliance Engineers Handbook



Developed by J. C. Clark, Consumers' Gas Co., Toronto

Gas Appliance Engineers Handbook

either safety, operating efficiency, or both. These act as criteria by which the engineer judges and controls his operations. In most plants, safety and efficiency are not necessarily separate considerations. Flue gas analysis is the means by which the goals for good utilization can be reached —

- (1) for gas appliances to operate safely without liberating injurious quantities of toxic gases.

- (2) for gas appliances to operate near optimum efficiency.

Exhibit 7 gives an easy formula, sufficiently accurate, to calculate excess air in a combustion process, also an alignment chart to calculate percentage flue loss so that combustion efficiency may be known.

EXHIBIT 7

1. The following simple formula is useful in determining excess air:

$$E = \frac{(U - C) \times Q \times 100}{A \times C}$$

where E = percentage of excess air.

A = theoretical air required for complete combustion of 1 cu. ft. of gas.

Q = volume of theoretical flue products formed by combustion of 1 cu. ft. of gas.

C = % CO₂ in flue gas sample.

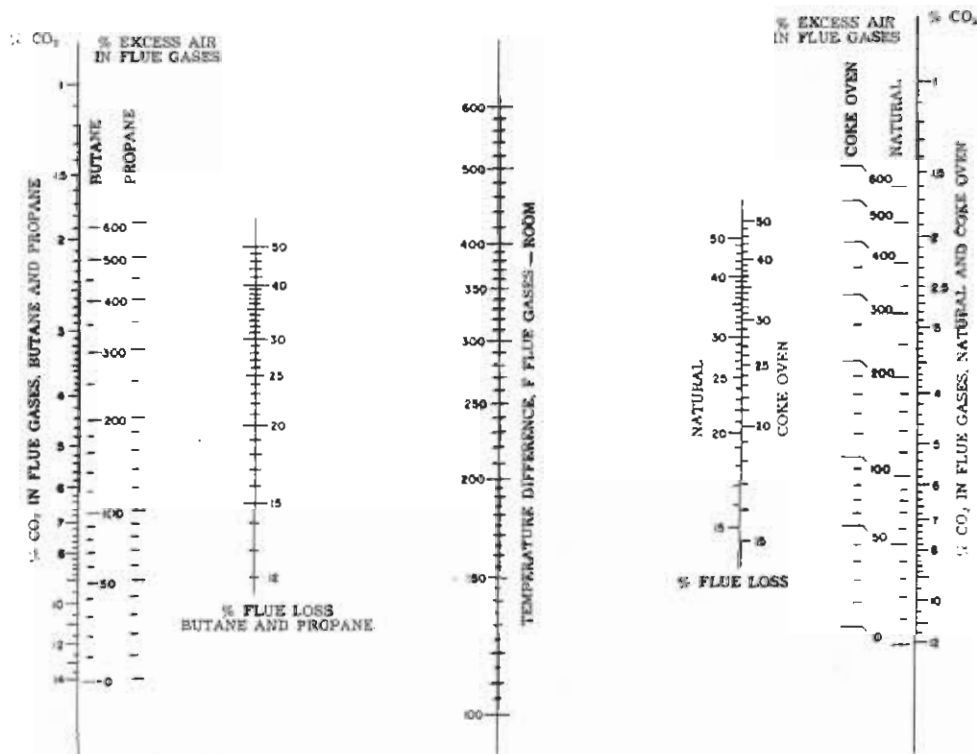
U = ultimate % CO₂ in flue gas.

Example: Suppose a natural gas sample is burned which requires 10 cu. ft. of air for complete combustion and this will develop 11 cu. ft. of flue products per cubic foot of gas having an ultimate CO₂ of 12.5%. The flue gas sample contains 10.5% CO₂.

What is the percentage of excess air?

$$\text{Excess air} = \frac{(12.5 - 10.5) \times 11 \times 100}{10 \times 10.5} = 21\%$$

2. When using an Orsat-type apparatus in the field, alignment charts are used to calculate percentage flue loss so that combustion efficiency may be known. The following chart is typical of the type used.



ALIGNMENT CHART FOR CALCULATION OF FLUE LOSSES FOR BUTANE, PROPANE, COKE OVEN AND NATURAL GASES

ADAPTED FROM AMERICAN GAS ASSOCIATION LABORATORIES FLUE LOSS CHARTS

Gas Appliance Engineers Handbook

BIBLIOGRAPHY

- "Products of Combustion of Gaseous Fuels"
by Edwin L. Hall
Director, A.G.A. Laboratories.
- "North American Combustion Handbook"
by The North American Manufacturing Co.
Cleveland, Ohio.
- "Gaseous Fuels"
An A.G.A. Publication
edited by Louis Schidman.
- "Gas Liquid Chromatography"
by Stephen Dal Wogare, Richard S. Juvety, Jr.
Interscience Publishers 1962.
- "Manual on Hydrocarbon Analysis."
First Edition — 1963
A.A.T.M. Special Technical Publications
No. 332.
- American Society for Testing and Materials.
1916 Race Street, Philadelphia 3.
- "Modern Gas Analysis"
by P. W. Mullen.
- "Gas Analysis — Testing of Gaseous Materials"
by V. J. Altieri, B.S. First Edition
Published by American Gas Association.