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Scope

This Instruction covers the use of the Combustion Calorimeter that is used to measure the heat content and specific gravity of natural gas that is used in the Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF) Fire Research Laboratory (FRL) experiments.

Instrument Description

General

The purpose of the Combustion Calorimeter is to measure the calorific value and specific gravity of the natural gas entering the building. Figure 1 shows a photograph of the instrument.

The Combustion Calorimeter has a built in specific gravity measurement cell. Sample gas flows through the measuring chamber where a membrane vibrates at a constant frequency. Oscillations are transferred through the gas to a transducer. The amplitude of these oscillations is directly proportional to the density of the gas.

The calorific value is measured by way of a thermopile measuring system. Sample gas passes through a Wobbe range orifice and is burned at atmospheric pressure. The hot gases are mixed with a cooling

airflow and the temperature of the mix is measured by thermopile hot junctions. The cold junction of the

thermopile measures the temperature of the incoming cool air flow, which results in a pressure difference that is proportional to the Wobbe Index of the gas. To calculate the calorific value, the following relation is used by the Combustion Calorimeter:

$$\text{Calorific Value} = \text{Wobbe Index} \sqrt{\text{Specific Gravity}}$$

Figure 1: Combustion Calorimeter Mounted to Wall in 1 Megawatt Shed

System Components

The Major components of the Combustion Calorimeter include the following, as indicated in Figure 2:

1) Differential pressure for density cell (positive)
2) Differential pressure for density cell (negative)
3) Differential pressure for air (negative)
4) Differential pressure for air (positive)
5) Gas pressure at range orifice (Wobbe jet)
6) Power supply*
7) PC 104type processor circuit board*
8) Disk drive
9) Filter element for air supply*
10) Pt 100 temp correction
11) Pt 100 temp correction
12) Ignition electrode
13) Burner
14) Electrical noise filter
15) Air fan
16) Frequency controller for air fan
17) Discharge (exhaust) pipe
18) Solenoid valve for calibration gas
19) Solenoid valve for process gas
20) Specific gravity cell
21) Pressure regulator for process gas
22) Precision pressure regulator
23) Pressure regulator, specific gravity cell differential pressure
24) Range orifice (Wobbe jet) location
25) Primary air supply tube
26) E/A internal
27) Temperature sensor
28) Door switch
29) Terminal block for line power supply
30) Output signal PG cord connector
31) Line power PG cord connector
32) E/A Extern

* Items marked with "*" are not shown on the figure below; please see the Combustion Calorimeter user's manual for a diagram showing their location [1]
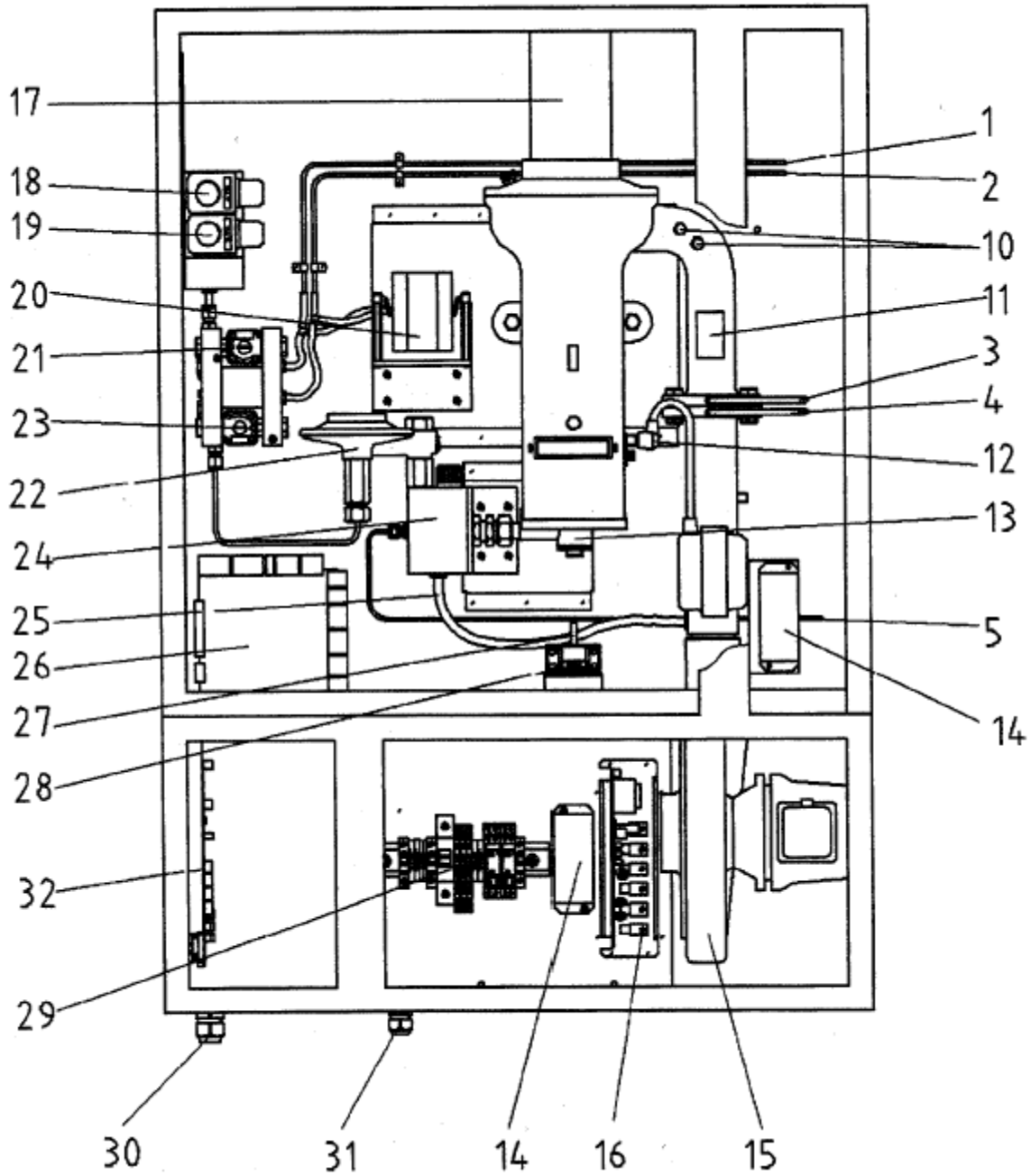
Figure 2: Inside View of CWD 2000 Combustion Calorimeter

FireToss Calculations

The Combustion Calorimeter can be used as a stand-alone instrument in FireTOSS. The parameters used for the Combustion Calorimeter are displayed in Table 1. The Combustion Calorimeter instrument in FireTOSS provides a data output of calorific value and specific gravity with respect to air. In addition, the instrument calculations compute the density and heat of combustion for the natural gas using Equations 1.1 and 1.2, respectively. The calculations also give minimum, maximum, and average values of these four sets of data.

Table 1: Combustion Calorimeter Data Acquisition Input Parameters

Parameter	Required	Input Method
Description	FALSE	User input
Bar Code	TRUE	User input from list
model number	TRUE	Automatically updated
manufacturer	TRUE	Automatically updated
serial number	TRUE	Automatically updated
Natural Gas Calorific Value Average	FALSE	Calculated after test
Natural Gas Specific Gravity Average	FALSE	Calculated after test
Natural Gas Calorific Value Max	FALSE	Calculated after test
Natural Gas Specific Gravity Max	FALSE	Calculated after test
Natural Gas Calorific Value Min	FALSE	Calculated after test
Natural Gas Specific Gravity Min	FALSE	Calculated after test
Natural Gas Density Average	FALSE	Calculated after test
Natural Gas Heat of Combustion Average	FALSE	Calculated after test
Natural Gas Density	FALSE	Calculated after test
Natural Gas Heat of Combustion	FALSE	Calculated after test
Natural Gas Specific Gravity	FALSE	Calculated after test
Natural Gas Calorific Value	FALSE	Calculated after test
Natural Gas Density Max	FALSE	Calculated after test
Natural Gas Density Min	FALSE	Calculated after test
Natural Gas Heat of Combustion Max	FALSE	Calculated after test
Natural Gas Heat of Combustion Min	FALSE	Calculated after test

$$\rho_{NG} = \rho_{Air} * SG_{NG} \qquad (1.1)$$

$$\Delta H_{c,gross} = \frac{C.V._{dry}}{\rho_{N.G.}} \qquad (1.2)$$

where

ρ_{NG} = density of natural gas in kg/m³

ρ_{Air} = density of ambient air in kg/m³

SG_{NG} = specific gravity of natural gas relative to air

$\Delta H_{c,gross}$ = gross heat of combustion of the gas mixture in MJ/kg

$C.V._{dry}$ = calorific value (dry) of natural gas in MJ/m³

For Equation 1.1, the density of ambient air is calculated using the FRL Laboratory Conditions measurements of ambient pressure and temperature [2]. Equation 1.2 yields a value in terms of the dry calorific value, which does not account for water vapor. To account for water vapor, a correlation from Bossel [3] was used to convert to the net heat of combustion. This correlation was empirically developed and is specific for natural gas.

$$\Delta H_{c,net} = \Delta H_{c,gross} * 0.896 \qquad (1.3)$$

Operating Instructions

Requirements

1. The assigned operator shall be qualified in accordance with laboratory proficiency requirements.
2. The instrument shall be calibrated in accordance with FRL calibration procedures.
3. If data acquisition is used, the data acquisition equipment shall be calibrated and be marked with the calibration status in accordance with FRL calibration procedures.

Procedure

The following is the general procedure that shall be followed. The operator shall also be properly trained on all appropriate procedures.

1. Set up
   1.1. The certification date on the calibration gas shall be checked to confirm that the gas certification has not expired.
       1.1.1. If the instrument is being powered up, a calibration shall be performed.
   1.2. The instrumentation shall be connected to the data acquisition hardware using the smallest voltage input range that will bound the output range of the instrument.
   1.3. Ensure that adequate fuel pressure is available.
2. Pre-Test
   2.1. The pilot flame shall be verified to be lit.
   2.2. All valves leading to the instrument shall be verified as "OPEN".
   2.3. It shall be verified that a calibration has been performed and the environmental temperature requirements have been met.
3. Test
   3.1. The display on the instrument shall show a stability reading ("STAB") of less than 0.15 to signify a stable reading.
4. The data shall be monitored to verify continuity.
   Post Test
   4.1. No action shall be taken other than to verify that the instrument is still yielding stable readings.
   4.2. The instrument shall be left in the "ON" position.

Uncertainty

When operated within the guidelines specified in this document and within the User's Manual [1], the Combustion Calorimeter functions within the following limits:

Accuracy: +/- 1.0% for CV or Wobbe Index

              +/- 0.8% for Specific Gravity

Linearity: +/- 0.2%

Repeatability: +/- 0.5%

In order to function within these limits the Combustion Calorimeter must be kept in an ambient temperature of between 10°C and 38°C with a rate of change of no more than +/- 2°C per hour. Further, the ambient temperature should be within +/-7°C of the temperature at which calibration was performed. This data is tracked and recorded using a temperature sensor connected to data acquisition. The data recorded is analyzed and the operator is alerted if the temperature trend is outside of tolerance.

The Combustion Calorimeter is used to calculate the density and heat of combustion of the natural gas. A standard uncertainty for these two values can be determined by the accuracy given by the User's Manual and a set of data taken from the Combustion Calorimeter. The uncertainty of these measurements was calculated using the guidelines of the National Institute of Standards and Technology (NIST) Technical Note 1297 [4], Special Publication 1007 [5] and the NIST Uncertainty Workshop [6], using the following equation:

$$u_C(y) = \sqrt{\sum s_i^2 u(x_i)^2} \qquad (1.4)$$

where:

$u_C(y)$ = Combined standard uncertainty of the quantity being calculated

$u(x_i)$ = Standard uncertainty of each component that is used in the calculation of y

s_i = Sensitivity coefficient $\left(\frac{\partial y}{\partial x_i} \right)$

Density

The combustion calorimeter measures the specific gravity of the process gas (natural gas) relative to air at ambient conditions. The uncertainty in the specific gravity measurement can be calculated based on the specifications of the instrument and an analysis of scatter in the data. In order to evaluate the natural gas density, Eqn 1.1 is used with ρ_{air} being calculated from the measured ambient conditions.

Applying Eq. 1.4 to Eq. 1.1 yields:

$$u_C(\rho_{NG}) = \sqrt{(SG_{NG})^2 \left(u(\rho_{air}) \right)^2 + (\rho_{air})^2 \left(u(SG_{NG}) \right)^2} \qquad (1.5)$$

The uncertainty of the specific gravity has two parts: the uncertainty of the combustion calorimeter and the fluctuations over time. The uncertainty in the combustion calorimeter is a function of the accuracy, linearity and repeatability of the instrument.

Union gives the accuracy of the combustion calorimeter specific gravity measurement as ± 0.8 % full scale [1], or 0.018 at the 0.2-2.2 range setting. The linearity is listed as ± 0.2 % full scale and the repeatability is listed as ± 0.5 % full scale. It can be assumed that these errors have a rectangular probability distribution, in which case the standard uncertainty is computed by dividing each component by $\sqrt{3}$ [4]. The standard uncertainties of these components are then, 0.01, 0.0025, and 0.0064, respectively.

The uncertainty over time can be calculated using a 30 day average standard deviation. NIST [4] states that for a sample of data, the uncertainty of the samples is:

$$U_s = {}^\sigma\!/_{\sqrt{n}} \qquad\qquad (1.6)$$

where:

U_S = Standard uncertainty of the samples

σ = Standard deviation of the samples

n = Number of samples

Using this formula, the uncertainty of the specific gravity samples can be determined. Over a sample of 30 data points, the standard deviation was 0.002, which yields 0.0004 as the standard uncertainty.

The uncertainty components can be combined in quadrature to estimate the combined uncertainty of the specific gravity measurement. The result is $u(SG_{NG})$ =0.012.

Air can be treated as an ideal gas, in which case the density is expressed as:

$$\rho = \frac{P}{RT} \qquad\qquad (1.7)$$

Where:

ρ = gas density (kg/m³)

P = gas pressure (kPa)

R = gas constant (0.287 kJ/kg/K for air)

T = gas temperature (K)

Uncertainty in the air density is a function of the Laboratory Conditions temperature and pressure measurements. Standard uncertainties for the temperature (0.59 °C) and pressure (0.16 kPa) were

computed based on an evaluation of the Lab Conditions measurements [2]. Uncertainty in the air density is calculated by applying Eq. 1.4 to Eq. 1.7.

$$u_C(\rho_{air}) = \sqrt{\left(\frac{1}{RT}\right)^2 (u(P))^2 + \left(\frac{P}{RT^2}\right)^2 (u(T))^2} \qquad (1.8)$$

From Equation 1.8, the uncertainty in the density of air is 0.003 kg/m³. Using Equation 1.5, the uncertainty in the natural gas density is then $u(\rho_{NG}) = \underline{0.015 \text{ kg/m}^3}$. This corresponds to a relative standard uncertainty of 2.5 % at the 30 day average specific gravity of 0.593.

Heat of Combustion

Substituting Eqs. 1.1 and 1.2 into Eq. 1.3 and applying Eq. 1.4 yields:

$$u_C(\Delta H_{c,net}) = \sqrt{\left(\frac{0.896}{\rho_{air}SG_{NG}}\right)^2 (u(C.V.))^2 + \left(\frac{-0.896\ C.V.}{\rho_{air}SG_{NG}^2}\right)^2 (u(SG_{NG}))^2 + \left(\frac{-0.896\ C.V.}{\rho_{air}^2 SG_{NG}}\right)^2 (u(\rho_{air}))^2} \qquad (1.9)$$

The uncertainty of the heat of combustion is a function of the uncertainty of both the specific gravity and calorific value measurements from the combustion calorimeter. The specific gravity uncertainty was calculated above. The calorific value uncertainty is comprised of two parts: the uncertainty of the combustion calorimeter and the variance over time. The uncertainty in the combustion calorimeter is a function of the accuracy, linearity and repeatability of the instrument.

Union gives the accuracy of the combustion calorimeter heating value measurement as 1% of full scale [1]. The linearity is listed as ± 0.2 % and the repeatability is listed as ± 0.5 %. It can be assumed that these errors have a rectangular probability distribution, in which case the standard uncertainty is computed by dividing each component by $\sqrt{3}$ [4]. At the 35-45 MJ/m³ range, the standard error

associated with the accuracy is 0.26 MJ/m³. The standard errors associated with the linearity and repeatability are calculated similarly to be 0.05 MJ/m³ and 0.13 MJ/m³, respectively.

The uncertainty over time can be calculated from Equation 1.4, using the 30 day average standard deviation. This yields a standard error of 0.028 for the variation of the measurement.

The uncertainty components can be combined in quadrature to estimate the combined uncertainty of the calorific value measurement. The result is $u(C.V.) = \underline{0.295\ \text{MJ/m}^3}$. This corresponds to a standard relative uncertainty in the calorific value of 0.8 % based on the 30 day average of 38.5 MJ/m³. From Equation 1.9, the combined standard uncertainty in the natural gas heat of combustion is then $u_c(\Delta H_{c,net}) = \underline{1.05\ \text{MJ/kg}}$.

References

For technical information regarding the theory behind the use of the Combustion Calorimeter please refer to the "Users Manual – CWD 2000 Combustion Calorimeter – For high speed measurement of fuel gases".

1. "Users Manual – CWD 2000 Combustion Calorimeter – For high speed measurement of fuel gases" Union, 2007.

2. ATF FRL Instruction, "Laboratory Instruction LI017: Laboratory Conditions.

3. Bossel, U., "Well-to-Wheel Studies, Heating Values, and the Energy Conservation Principle," Oberrohrdorf, Switzerland, 2003. http://www.efcf.com/reports/E10.pdf

4. Taylor, B. N., & Kuyatt, C. E., "NIST Technical Note 1297: Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," National Institute of Standards and Technology, Gaithersburg, MD 1993.

5. Bryant, A.R., Ohlemiller, T.J., Johnsson, E.L, Hamins, A., Grove, B.S., Guthrie, W.F., Maranghides, A., Mulholland, G.W., "Special Publication 1007," National Institute of Standards and Technology, Gaithersburg, MD 2003.

6. Guthrie, W. & Liu, H., "Hands-on Workshop on Estimating and Reporting Measurement Uncertainty," National Institute of Standards and Technology, Presentation given to CPSC, 2007.