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A FLAMELESS CALORIMETER

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Abstract

This paper describes the design and operation of a new reference calorimeter based on a flameless combustion technique.
Within this technique, a mixture of (reference) gas and air is passed over a noble metal element that is electrically heated to a constant temperature. The gas is oxidized as it encounters the temperature of the noble metal element and rises above auto-ignition temperature within a small combustion cavity. The precise value of the electrical energy, required to heat the element, is stored.
The same procedure is again carried out with the (unknown sample) gas and the same air supply. The ratio of the value of the electrical energy now required to heat the element and the reference electrical energy, is inversely proportional to the ratio of the calorific values of the two gases.
The new instrument meets the ASTM 4891 standard and is designed to be integrated into a complete energy measurement system with an expected uncertainty in heating value of better than 0.25% and a repeatability better than 0.15%. The first test results of the instrument measuring low calorific- and high calorific gases are shown.

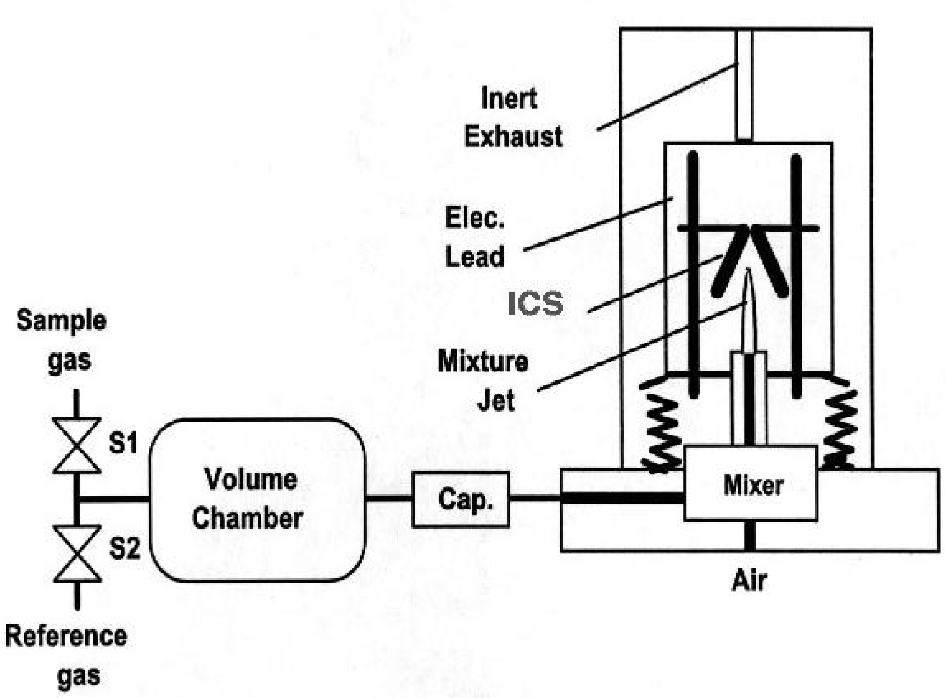
The Method

A method has been developed which directly and accurately measures the total calorific heat of combustion of combustible gases using an Inert Combustion Sensor (ICS) mounted in a small chamber. Within this small combustion chamber, at atmospheric pressure, a complete and rapid oxidation of all of the combustible gas molecules occurs, independently of the presence of water and inert gas molecules.

This physical method of oxidation used is related to the process that is generally employed in heaters that both utilize porous ceramic elements to moderate and enhance the combustion of gases and electrical heating power for start-up. The porous ceramic elements to provide this enhancement are also described as Porous Inert Media (‘PIM’). See Ref. 1

The Inert Combustion Sensor (ICS) and the small combustion chamber have the same physical functionality of the PIM by creating gas flow and heat transfer functions identical to those in the interstitial space (the tiny spaces between portions of ceramic) of the porous elements.
In addition to this a method has been developed to measure the amount of energy generated within the device, as a result of the oxidation of the combustible gas molecules.

Figure 1 shows the block diagram of the flameless calorimeter, with the location of the ICS.



The entire system is designed to both precisely generate the oxidation and simultaneously precisely measure the energy contribution of the sample and reference gases, alternatively and separately.

Electrical energy is used to bring the combustion chamber to the precisely defined operating temperature. Then the gas is brought into the ICS along with more air than is required for balanced combustion. In this mode, the heat of combustion produced is solely a function of the heat of oxidation of each mole of the combustible gas, times the number of moles of combustible gas introduced, whereby a subsystem within the apparatus is precisely measuring the number of moles.

As the amount of heat of oxidation increases, the amount of electricity required to maintain the precise operating temperature is decreased. A dedicated microcomputer system is measuring all of the electrical power required in all modes of operation. Because the decrease of the required electrical power is proportional to the heat of oxidation of the gas, the fundamentals are created to measure directly the calorific value of combustible gases.

The Technology

In the course of the research, numerous designs, including catalysts were investigated. While a measurement system based on this type of combustion was achieved, it could not be ensured that its implementation as a product could be expected to provide a long life span in the field, where aggressive agents in trace amounts might exist. Also it was observed that small and gradual erosion of the catalyst could easily occur during normal operation under certain circumstances. Therefore a non-catalytic sensor design was chosen.

The only materials being entirely inert against the gases and water in the sample are noble metals and ceramics. Using only these, a ICS (Inert Combustion Sensor) has been build that has been in operation for more than a year, including repeated start-stop cycles, with no apparent degradation at all, right down to the measurement accuracy of our system as a whole.

The main design problem of the ICS was concentrated on the uniformly distribution of the total combustion energy to the thermal system of the ICS. The different types of combustible gas molecules (C1-C6) have different ignition/flash temperature. The design of the ICS is such that all these molecules are oxidized at the same highest-temperature point within the ICS (about 850 °C), to ensure that the different types of the molecules are oxidized within a few milliseconds.

All the other critical components of the new calorimeter are entirely solid state, beyond the small electrical gas valves that select between sample gas and a reference gas. The oxidation is generated and measured through small passive components, beyond the electrical power input required to simply provide ohmic heating to raise the temperature of the gas to be oxidized.

Striving for 0.1 % measurement accuracy requires resolution that is both sensitive and accurate enough to measure other physical effects resulting from several of the gas properties other than calorific value (Ref. 2, Ref. 3). These other physical effects give rise to unwanted but measurable manifestations due to the physical aspects of the ICS. These manifestations can be resolved out of the data derived from the ICS by dedicated computer processing of this data.

The Product

The method has been developed and refined to yield a product we call the TruTherm II.

This device delivers accurate gas measurement in less than a minute, on a continual basis of fully automated successive measurements.

The initial cost of the device is below the most competitive prices found in the realm of chromatography.

Beyond initial installation, all of the TruTherm II's functions including calibration, are fully automated and require no operator monitoring or intervention. The calibration gas can be simple pure Methane, or any combustible gas having a certifiable known CV value. Multiple gas components in the calibration gas are not required, since the measurement method does not differentiate measurements between gas components. The rate of calibration gas consumption is only about 60 cc per hour.

The measurement and reporting resolution is better than .025%. The system is designed for automatic calibration, both at initial start-up of the system, and thereafter at intervals of significant change to the physical environment of the system (ambient temperature and pressure). For the past fifteen years certain methods of automatic and unattended self-calibration and also internal self-detection of measurement validity have been used. All this experience is implemented in this system as a whole.
The general approach is to use an internal dedicated microcomputer to sense, determine and implement all of the general logic required to have accurate precise measured parameter values for the reference gas at all times. Therefore while the sample gas is being sensed, those parameter values are taken as numeric pairs with the same parameter values for the reference gas. The internal computer then displays only the paired results of the measurements, and only after multiplication by the published calorific value of the reference gas.

At the .1% level virtually everything in the physical environment of the system is measured by the system. The system is therefore designed to sufficiently isolate our system from the physical environment well enough allow our total system to function within the published error specifications for the entire time between measurements of the reference gas.

The total cost of ownership of the TruTherm II is very small due to this low cost calibration gas and also completely unattended operation over the long term.

The product also implements all of the functions of display, communications and data logging in use in its predecessor the TruTherm H, which has been field proven in markets around the world over the past six years.

The Application

The calorific value measured by the TruTherm II, in combination with the measured flow at a site, can allow calculation of total energy flow through proper implementation of the attendant required flow measurement device (orifice plate, turbine meter, rotary meter, ultrasonic), and attendant required volume flow correction sensing and/or calculation.

The measurement accuracy, together with the continual internal self-checks provided by the final TruTherm II product, is intended to meet the requirements for Custody Transfer.

Its predecessor, the TruTherm H, achieved this quality of performance years ago, as certified by Federal Governments, and governing bodies within each geographic region.
We will provide the same measurement quality in the TruTherm II.

Current State of the Work

The TruTherm II product is in pilot production. The pilot product has been operated in a series of single-cycle tests.

We have measured and correlated the effects of varying ambient conditions in conjunction with the unit's precise internal operation, without any reference gas re-calibration during the test interval, which spanned a period of four days.
In summary of the series of single-cycle tests, four gases were measured two times each, with the results being within +3.69 to –2.94 BTU accuracy over the entire set of eight measurements.
We acquired two sets of data. The second set of data (B) was taken four days after the first set (A) was taken. In the interim, the equipment was powered down for two days, and then powered back up. This places the unit in worst-case accuracy vulnerability from all sources.
A measurement for each gas, relative to the methane gas that was measured in just the first set of data, was calculated and recorded. In this way the measurement of the methane calibration gas in the second test battery was not used as a reference gas, but the measurement of it was also treated as a sample gas.
The only link between the two sets of data was the measurement of ambient temperature and pressure. No other relative correction factors were applied.

The results were: (in BTU)

Test Battery	A	A	A	A	B	B	B	B
Gas Identity	B3M	IGM	B3H	B3L	B3M	IGM	B3H	B3L
Measured Error (BTU)	0	-3.69	+1.81	-2.62	+1.85	+2.94	+2.06	-1.42

Specified Gas Properties :

Gas	BTU	SGV	Main components
B3M	1013.1	0.5525	Methane
IGM	1014.5	0.5980	Ethane, Heavies, Nitrogen
B3H	1128.5	0.6284	Ethane, Methane
B3L	942.1	0.5838	Methane, Nitrogen

The same tests are currently in process for continuous operation for an extended period of time, including the internal computer programming for its entire self-management, as we achieved with its predecessor, the TruTherm H, seven years ago.

References

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