Isoperibol gas calorimeter with a stirred water bath – uncertainty contributions of temperature inhomogeneities

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A new Rossini–type calorimeter [1-3] was developed and built at PTB in order to perform high-accuracy measurements of the superior calorific value (SCV) of natural gas components, in particular methane, ethane, propane and other hydrocarbons. The aim is to establish a new collection of SCV reference data with the best possible and well-established uncertainty. Such new reference data would significantly improve the calculation of the SCV of natural gas from composition according to the International Standard ISO 6976 [4].

The Rossini-type calorimeter is an isoperibol gas calorimeter with a stirred water bath where approximately 1 g of gas is burnt in an open flame and a temperature rise of approximately 3 K is recorded. The calorimeter is calibrated with an electrical heater and the adiabatic temperature rise represents the total amount of the energy produced by combustion or during calibration. The SCV is the ratio of the energy released by the combustion and the gravimetrically determined mass of the burnt gas.

Uncertainty calculations of the SCV showed an enormous influence of the adiabatic temperature rise, its share being between 60 and 70%. Hässelbarth et al. [5] identified the deviation of the sampled temperature from the bath average as one of main contributions to the uncertainty of the adiabatic temperature rise.

During combustion or electrical calibration, where the energy produced is released into a stirred water bath, the difference between the recorded and the mean temperature of the water bath is caused by the position of the temperature sensor. The stirrer is not able to instantaneously create a homogeneous distribution of the energy released. Additionally, the positions are different where the energies of combustion and electrical heater are produced. These two effects lead to temporal and local inhomogeneous temperature distributions and, therefore, the adiabatic temperature rise depends on the position of the temperature sensor inside the stirred water bath.

In this contribution, an investigation of the mentioned temperature inhomogeneities is introduced. For this purpose, another calorimeter with similar design was built with a network of thermistors inside the water bath in order to measure the temporal and local distribution of temperature during combustion or electrical calibration. With these measurements it is possible to identify a location of the temperature sensor inside the water bath of the reference gas calorimeter where the determination of the adiabatic temperature rise is affected to a minimum by the temperature inhomogeneities.

[1] Rossini FD. The heat of formation of water. Bur Stand J Res. 1931;6:1–35.
[2] Rossini FD. The heats of combustion of methane and carbon monoxide. Bur Stand J Res. 1931;6:37–49.
[3] Rossini FD. The heat of formation of water and the heats of combustion of methane and carbon monoxide. A Correction. Bur Stand J Res. 1931;7:329–30.
[4] ISO 6976. Natural gas—calculation of calorific value, density, relative density and Wobbe index from composition (2nd ed. 1995-12, corrected and reprinted 1996-01; currently under revision); 1995.
[5] Hässelbarth W.; Rauch J.; Sarge S. M. Uncertainty evaluation for the adiabatic temperature rise in isoperibol calorimetry; Journal of Thermal Analysis and Calorimetry (2012)