Thermal and Optical Properties of Materials

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ABSTRACT

The priority actions at LNE affect currently the areas of sustainable development and some other strategic matters. In recent years, the works of the metrology laboratory devoted to thermal and optical properties of materials have been motivated by some key issues: the development of a high accurate calorimeter for measuring the gross calorific value of natural gas, the construction of reference experimental facilities for measuring the transport properties of solid materials and the measurement of spectral transmittivity of liquids for improving the traceability to SI in analytical laboratories. This article is intended to highlight with developments in progress, LNE R&D activities in the field of thermal and optical properties.

1. INTRODUCTION

The laboratory "thermal and optical properties of materials" is one of the major units of the division "thermal & optical metrology", itself being one part of the centre in charge of the Scientific and Industrial Metrology activities.

Its activities are growing at two levels; one hand basic and applied Research and secondly the dissemination of measurements or calibrations, as well as the knowledge transfer to serve Industry, Research and Society.

The main concerned actions today affect the areas of sustainable development (environment, energy, health care…) and any matter relating to the economy, the nation and citizen in accordance to the French government policy and to European directives. The studies in progress in the "thermal and optical properties of materials" laboratory have been motivated by the three following major issues:

- In Europe, the liberalization of the energy markets has generated greater competition between energy producers, distributors and service companies. This has led notably gas producers to seek to enhance their knowledge on the thermal properties of natural gas. To this end, the development of a high accurate calorimeter for measuring the Gross Calorific Value (GCV) of natural gas has been set up in close cooperation with key stakeholders and European metrology experts in that field. Today this facility, after designing a prototype based on numerical modelling, is being experimentally characterized for measuring the GCV of methane. The main other constituents of natural gas will be studied shortly.

- The Kyoto Protocol has generated a significant increase in activities in the field of energy and environment in France. For building applications, the goal is to lead to a better control of energy losses and of release of greenhouse gases in the atmosphere. The latest developments in progress concern the thermal conductivity measurement of materials covering the range up to 10 $W \cdot m^{-1} \cdot K^{-1}$ such as insulating materials, polymers, plastics, ceramics, composite materials, glasses… by applying the guarded hot plate technique. In addition, for solar or high-tech aerospace applications, control of radiative properties in energy balance calculations is quite crucial. In this context, LNE has developed a technical platform, which is composed of various advanced spectro-radiometric means in order to meet the most common configurations needing a low level of uncertainties (typically around 1 %).

- In the field of health, high stakes of the prevention, treatment, and management of disease is a key point. Ongoing projects refer to dedicated optimized spectrophotometers. They aimed at improving the traceability of measurements performed in analytical laboratories especially in Biology. The spectral transmittivity measurement on optical slabs constituted with many samples is one of the recent developments leads by the laboratory.

2. NATURAL GAS - A NEW REFERENCE CALORIMETRY FACILITY

The LNE is developing a reference isoperibolic calorimeter for measuring the gross calorific value (GCV) of natural gas.

2.1. Measurement Method

The calorimeter consists in a glass burner in which a given quantity of gas is burnt. The heat released during combustion is transmitted to a water volume surrounding the burner (Fig. 1).

The assembly is thermally uncoupled from outside by means of an enclosure (isothermal jacket) maintained a constant temperature that characterizes the isoperibolic aspect. The mass of gas is determined by double weighed before and after combustion. The burned gases circulate in a heat exchanger and go out from the upper of the calorimeter for analysis. These gases raise the temperature of the water in which the chamber is diving.

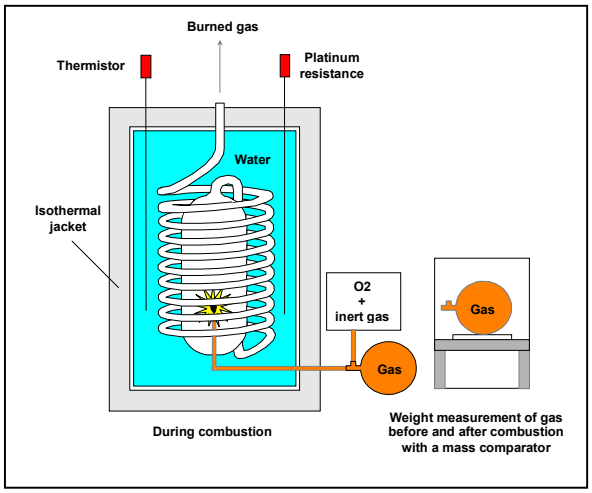

Fig. 1. Scheme of the isoperibolic calorimeter.

The calculation of the water temperature rise in an ideal adiabatic case ΔT allows an evaluation of GCV according to the following relationship:

$$GCV = \frac{C_{cal} . \Delta T}{m_{gas}}, \qquad (1)$$

where C_{cal} is the heat capacity of the calorimeter ($J.K^{-1}$) and m_{gas} is the mass of burned gas (kg).

The calibration of the calorimeter is required to determine its heat capacity C_{cal}. This calibration is done electrically with a resistance placed around the combustion chamber to reproduce as better as possible energy released during combustion.

2.2. Calorimeter Prototype

Measurements of gross calorific values (GCV) of methane have recently been performed with a calorimeter prototype built after an initial feasibility study. Meanwhile, through collaboration with Gaz de France, 3D transient simulations of speed and temperature fields in the calorimeter have been carried out to optimize the final design of the device [1, 2].

2.3. Repeatability Measurements of GCV - Preliminary Steps

A study of repeatability has been achieved with the prototype version of the calorimeter. Fig. 2 shows the GCV of methane (without taking into account all the correction factors) obtained over a dozen consecutive measurements. The dispersion of these GCV measurements is 0.1 %. In addition, the average is 55 807 $J.g^{-1}$ and the relative gap between this value and that shown in ISO 6976 (55 516 $J.g^{-1}$) is 0,52 %.

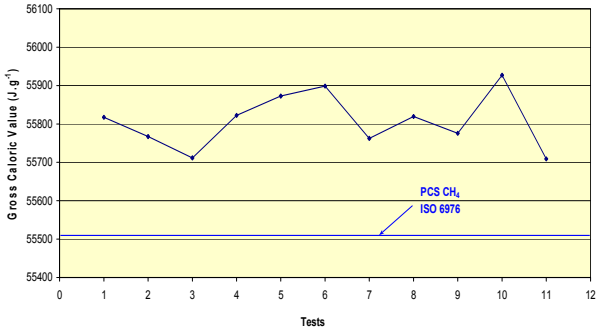

Fig. 2. GCV of methane measured with the LNE prototype calorimeter.

2.4. Reference Calorimeter

The manufacture of elements of the new calorimeter ended in 2008. Fig. 3 shows a picture of some elements, which are: internal and external electro-polished chambers, photodiode, and stirrer.

Fig. 3. Overview of the calorimeter elements.

This calorimeter integrates new sealing systems for both chambers (watertight for the internal one and "glycol-tight" for the external one). The development of the reference calorimeter is currently underway with integration of the detection system flame.

2.5. Modelling of Temperature Field in the Calorimeter under Unsteady Condition

The main modification performed on the burner after the first simulation concerns the reduction of the length of the heat exchanger burner to a half-lap. Following the recent simulations, further improvements were made to the model, by using combustion and radiation advanced models. The geometry and inertia of several elements (burner, thermistor, cooling finger, stirrer…) situated in the bath have been taken into account.

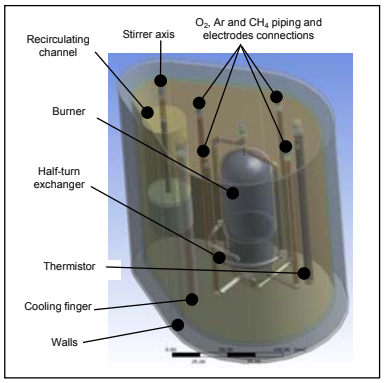

Fig. 4. New design of the LNE calorimeter.

In both modes, calibration (dissipation by Joule effect) and combustion, the released energy is splitted in three parts. Almost all of this energy is absorbed by the water bath (90 %), 9 % by the walls of the internal enclosure and the rest by the glass burner. These simulations have enabled to study the temperature fields in the water bath during combustion and calibration, and to validate the choice of the temperature of the isothermal jacket around 25 °C.

The new geometric model incorporating these improvements is presented Fig. 4.

2.6. Conclusion

Measurements of gross calorific values (GCV) of methane have been made with the prototype version of the calorimeter. The relative gap between this value and that given in ISO 6976 is around 0,5 % on eleven values (without taking into account all correction factors) and the repeatability is 0,1 %. Various actions have been undertaken to reduce the amount of unburned methane, produced particularly during the extinction of combustion.

The calorimeter in its final version was assembled and its development is underway [3]. The modelling results are broadly consistent with the thermal behaviour of the calorimeter observed during experiments, for the two modes of heating (combustion or electrical calibration).

3. INSULATION MATERIALS AND THERMAL CONDUCTIVITY MEASUREMENTS

One of the developments in progress, is the absolute measurement of thermal conductivity in the from 23 °C to 500 °C and in the thermal conductivity range 0.1 $W.m^{-1}.K^{-1}$ to 10 $W.m^{-1}.K^{-1}$. The goal is to measure thermal conductivity with a relative uncertainty from 1 % to 5 %.

3.1. Measurement Technique

The guarded hot plate technique [4] in steady temperature regime was selected because of its good metrological performance.

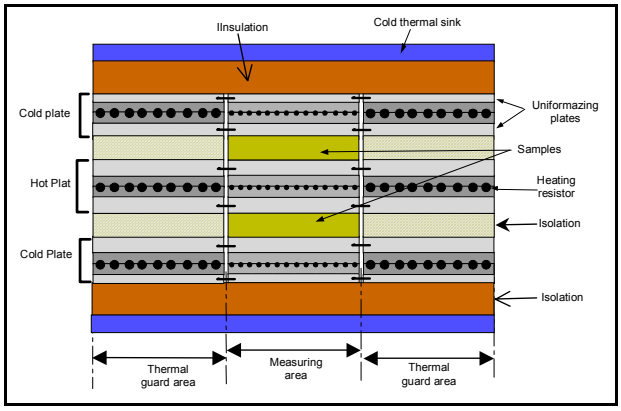

Fig. 5. Cross section view of the "stacking".

Fig. 5 shows a general cross-section view of the stacking. The hot plate and the two cold plates are heated electrically. Two plates cooled by water at ambient temperature and placed at the top and at the bottom of the "stacking", are used to stabilize the temperatures at the ends of the stacking. Those two cold plates are the "thermal wells" of the system. The use of two "cold plates" heated electrically allows getting high and stable temperatures much more easily than plates thermostated by a fluid.

3.2. Reference Set-Up

The heating plates are made of nickel 201 (Ni 99,2% Co 0,1 % Fe 0,3 %) to have a high thermal conductivity (about 70 $W.m^{-1}.K^{-1}$) and a good stability at high temperature.

Each heating plate is composed of a "measuring area" and of a "thermal guard area". The measuring area is square 100 mm wide. The "thermal guard" area surrounds the "measuring area" and is 104 mm wide. The gap between the two areas is 4 mm wide. Each area is heated independently, the measuring area is controlled in temperature and the "guard area" is controlled in temperature by reference to the temperature of the measuring area. A thermopile measure the difference of temperature between the two areas.

The hot and cold plates are heated by metal sheathed electrical heating elements embedded in grooves between two 8 mm thick nickel plates, Fig. 6. The depths of the grooves are adjusted in order to have a good thermal contact between the resistors and the plates.

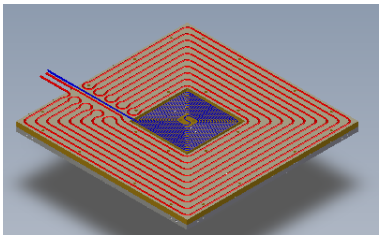

Fig. 6. Patterns of the heating resistors of the measuring area and the thermal guard ring

The two grooved plates maintaining the resistor are clamped between two 8 mm thick nickel plates called "uniformising plates". The "uniformising plates" are used to get uniform temperatures on each side of the samples. There are also used to maintain the temperature sensors and the thermopile. The "measuring area" of each heating plate is attached to the "thermal guard area" by 8 "stainless steel pins" with a low cross-section area.

Flatness of about 0,01 mm was obtained for the nickel plates constituting the central "measuring areas" (100 mm x 100 mm). For the guard rings the flatness is about 0,1 mm (320 mm x 320 mm). After final assembly, the flatnesses of the heating plates are about 0,02 mm for the surfaces in contact with the samples.

An insulating material, placed between each cold plate and each heat sink, ensures a transfer of heat. That transfer is required to allow the regulation of the temperatures of the "cold heating plates" but it should not be too high to avoid discrepancies of temperature of the surfaces in contact with the samples.

Fig. 7. General views of the LNE set-up and of the heating plates.

The facility (Fig. 7) is computer-controlled and is equipped with power supplies and control temperature systems. Each heating plate is suspended by cables with a system of counterweights to control the pressure generated by the heating plates on the two samples [3].

3.3. Procedure of Measurement

The measurement procedure should be quite similar to that of guarded hot plates used for conductivity measurements on insulating materials around ambient temperature. But for materials with a fairly high thermal conductivity, it will probably be preferable not to have "continuous" samples over the measuring area and the guard area. Indeed, for those materials an insulating gap of air around the samples will reduce significantly the perturbations of the heat flux due to a possible difference of temperature between the guard rings and the measuring areas. Moreover, it is preferable to use a compressible material between the guard rings to allow a good mechanical and thus a better thermal contact between the samples and the measuring plates.

For materials with a high conductivity, it will also be better to perform the temperature measurements

either directly in grooves machined at the surfaces of the samples or, better, inside the samples by embedding thermocouples in holes drilled in the sample. Thus, the thermal contact resistance between the heating plates and the samples will not be a direct source of error in the temperature gradient.

3.4. Progress

The elements have been fitted together. A set of type K thermocouples has been calibrated in-situ by using an aluminum thermal block heated between two heating plates. The parameters of the temperature controllers have been settled to get very steady temperatures.

Some materials have been calibrated in thermal conductivity using a very accurate guarded hot plate of LNE used for insulating materials around ambient temperature. Table 1 shows the thermal conductivity ranges of those materials (PVC and polymers) from 0,14 $W.m^{-1}.K^{-1}$ to 0,3 $W.m^{-1}.K^{-1}$ from 20 °C to 70 °C.

The calibrated samples will be used to check the bias of the instrument at low temperatures.

For higher temperatures the reference "Pyrex glass" CRM 039 (provided by the IRMM) and calibrated from -75 °C to +195 °C will be used to check the results for a "high" conductive material.

Table a. Materials used for checking.

Material	Specimen thickness	Temperature (°C)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Incertainty (k=2) ($W \cdot m^{-1} \cdot K^{-1}$)
Rubber	20 mm	20	0.2822	0.0068
		70	0.3168	0.0074
Silicone	10 mm	20	0.2211	0.0037
		70	0.2156	0.0035
PVC	20 mm	20	0.1403	0.0068
		70	0.1815	0.0074

4. HEALTH LABORATORY AND OPTICAL PROPERTIES OF LIQUIDS

The testing laboratories using optical instruments such as microplates readers for making biological and bacteriological analyses in the field of health, food or the environment need to be traceable to SI.

These readers are usually used as a biochemical technique in immunology to detect the presence of an antibody or antigen in a sample.

For quality assurance, the sets of filters fitted into quality control plates, used to check the accuracy of microplates readers, require calibration in spectral optical density.

The LNE has developed specific ways to calibrate in regular spectral transmittance the very small reference filters fitted in microplates. A selected commercial spectrophotometer operating in double beam configuration, and a set-up used to calibrate the spectral sensitivity of detectors have been characterized for those calibrations. The filters are calibrated between 300 nm and 800 nm.

4.1. Measurement Method

The measurement technique consists to measure directly the ratio between the incident flux and transmitted flux (Fig. 8).

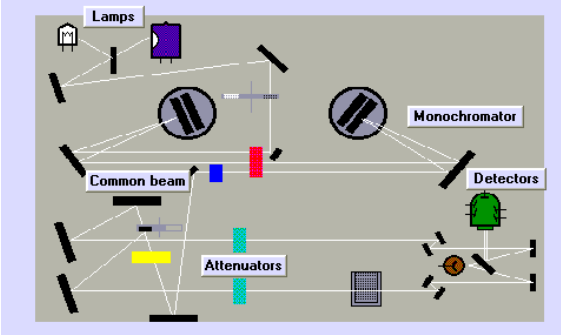

Fig. 8. Scheme of the spectrophotometer.

For a spectrophotometer operating in "double beam" mode the variations of the emission of the source and the variations of the transmission along the optical path (mainly atmosphere) are corrected automatically.

4.2. Uncertainties Assessment

A detailed analysis of the sources of uncertainties has been performed for each spectrophotometer [5]. The sources of uncertainties are: the noises on the signals, the errors of measurement due to multireflexions, the linearity defects, the error on the wavelength generated by the spectrophotometer. The errors due to linearity defects and to multireflexions are measured by calibrating the spectrophotometer with a set of calibrated reference filters with different level of transmittance. The noises are measured through repeatability and reproducibility. Other sources of uncertainty related to the object in calibration can occur such as the non-uniformity, they are considered specifically.

In the visible spectrum the combined standard uncertainty for the regular spectral transmittance is estimated between 0,000 4 and 0,003 depending on the transmittance.

The practice of testing laboratories is to use the optical spectral density instead of the transmittance. The optical spectral density is given by the Eq. (2):

$$D(\lambda) = -log_{10}(T(\lambda)) \quad ; \qquad (2)$$

and the uncertainty on the density is given by the Eq. (3):

$$u(D(\lambda)) = \frac{1}{\tau(\lambda) \,.\, \ln(10)} * u_c(\tau(\lambda)) \quad . \qquad (3)$$

Fig. 9 shows the enlarged uncertainty on the optical density.

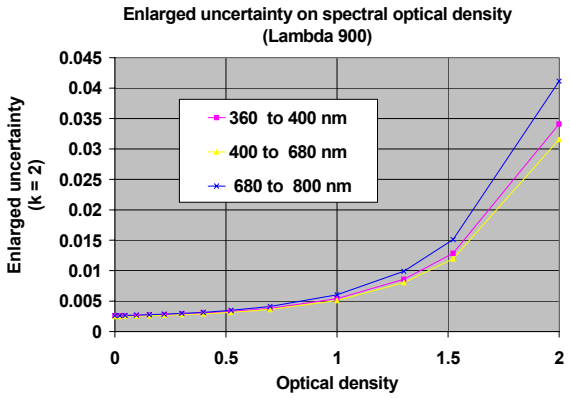

Fig. 9. Optical density - Enlarged uncertainty.

5. CONCLUSIONS

LNE has developed so far skills and facilities for measuring thermal and optical properties of materials. As stated in the different topics mentioned above and ongoing studies, interest in the properties of gas and liquid is a major thrust for development of the metrology laboratory.

These actions complete research activities in the field of metrology where the need for data of properties of materials validated is essential for improving the measurement uncertainties. Finally this article highlights the R&D activities in the field of thermal and optical properties being carried out by LNE in France, where International networking is becoming a priority to respond effectively to the expectations of the issues facing society today.

ACKNOWLEDGEMENTS

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