Laboratoire national de métrologie et d'essais

Dr Jean-Rémy FILTZ



LNE

Sharing a passion for progress

Thermal and Optical Properties of Materials

Recent Developments at LNE in the field of Energy

Natural Gas
Development of a reference Calorimeter

LNE expert: Dr Frédérique HALOUA

Outline

- Background and objectives
- Calorimeter principle
- Gross calorific value determination
- Modelling
- Calorimeter description - Details
- Experimental results - Perspectives
- Conclusions

Background

SIMPOSIO Metrología 2008

Natural Gas Market; Key dates

Who can choose the supplier ?

August 2000	August 2003	July 2004	July 2007
20%	**37%**	**70%**	**100%**
Industrials **Very High Consumers**	Industrials > 83 GWh	Professionals Enterprises Local Communities	**All**

Europe, France,
the market is now fully open

Background

GrDF
GAZ RÉSEAU DISTRIBUTION FRANCE

ALTERGAZ
Naturellement économique

Today

2008

eRDF
ÉLECTRICITÉ RÉSEAU DISTRIBUTION FRANCE

POWEO

Metrology & Natural Gas:

What does it mean in Europe and in France ?

- **Opening of the natural gas market in Europe**
  - **Non constant natural gas composition flowing in the pipes**
  - **Accurate energy measurements * needed**

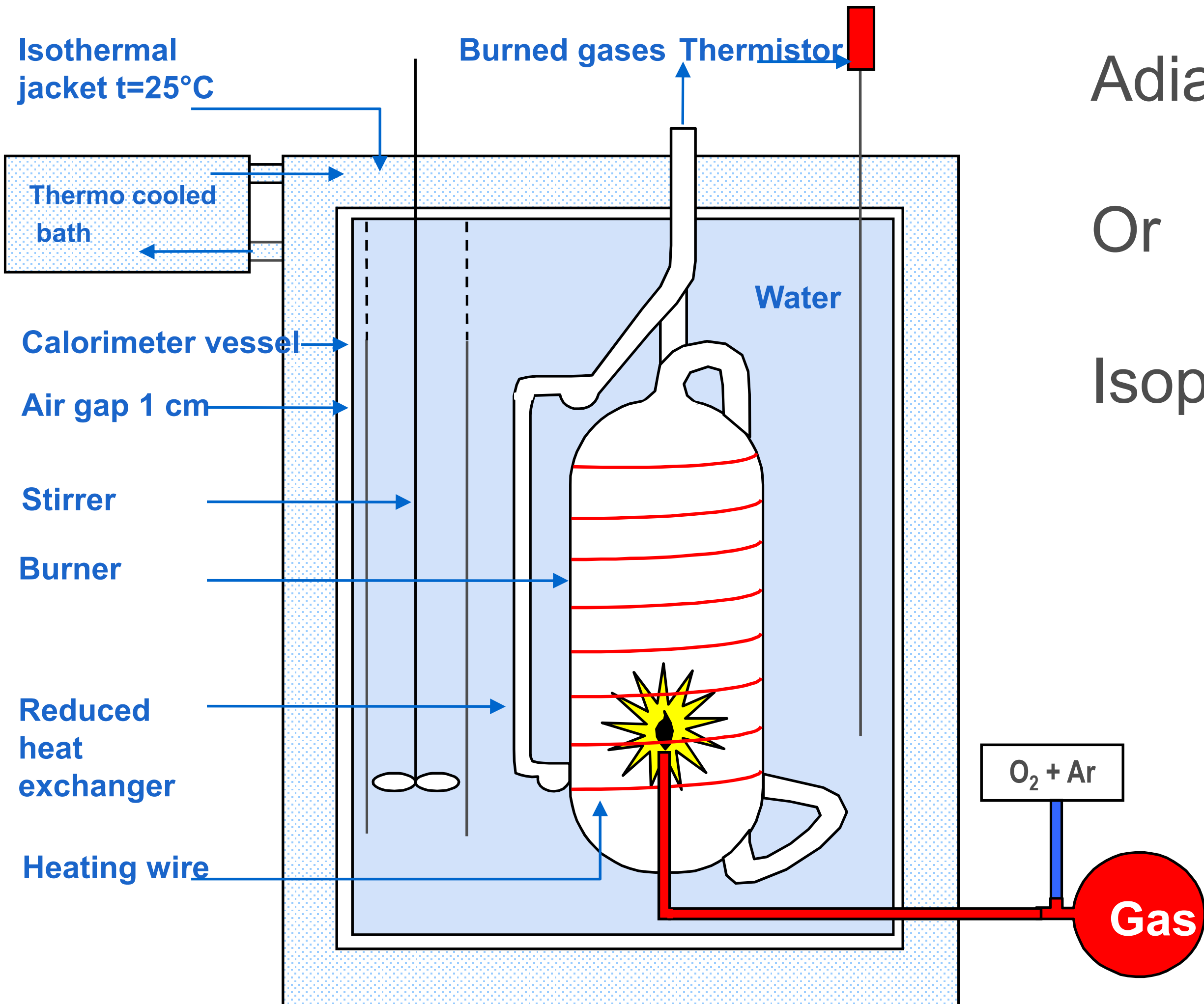
- **Improvement of the transported and distributed gas transactions by more accurate measurement of natural gas gross calorific value (GCV)**

•GCV = Quantity of heat released by complete combustion of a specified gas quantity

Objectives

- Redefinition of the values of the ISO 6976 standard
- Calibration of calorimeters and chromatographs
- Participation to the determination of energetic characteristics of sustainable energy products (natural gas, and also biofuels, biogases)
- Strengthening the metrological reference infrastructure in calorimetry in Europe (Germany, France, at least) and also in Russia, Ukraine…

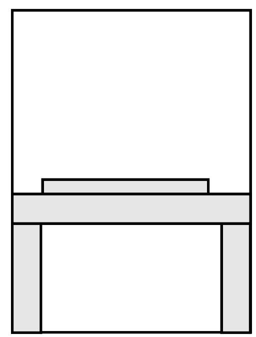
Calorimeter Principle



Adiabatic Calorimeter ?

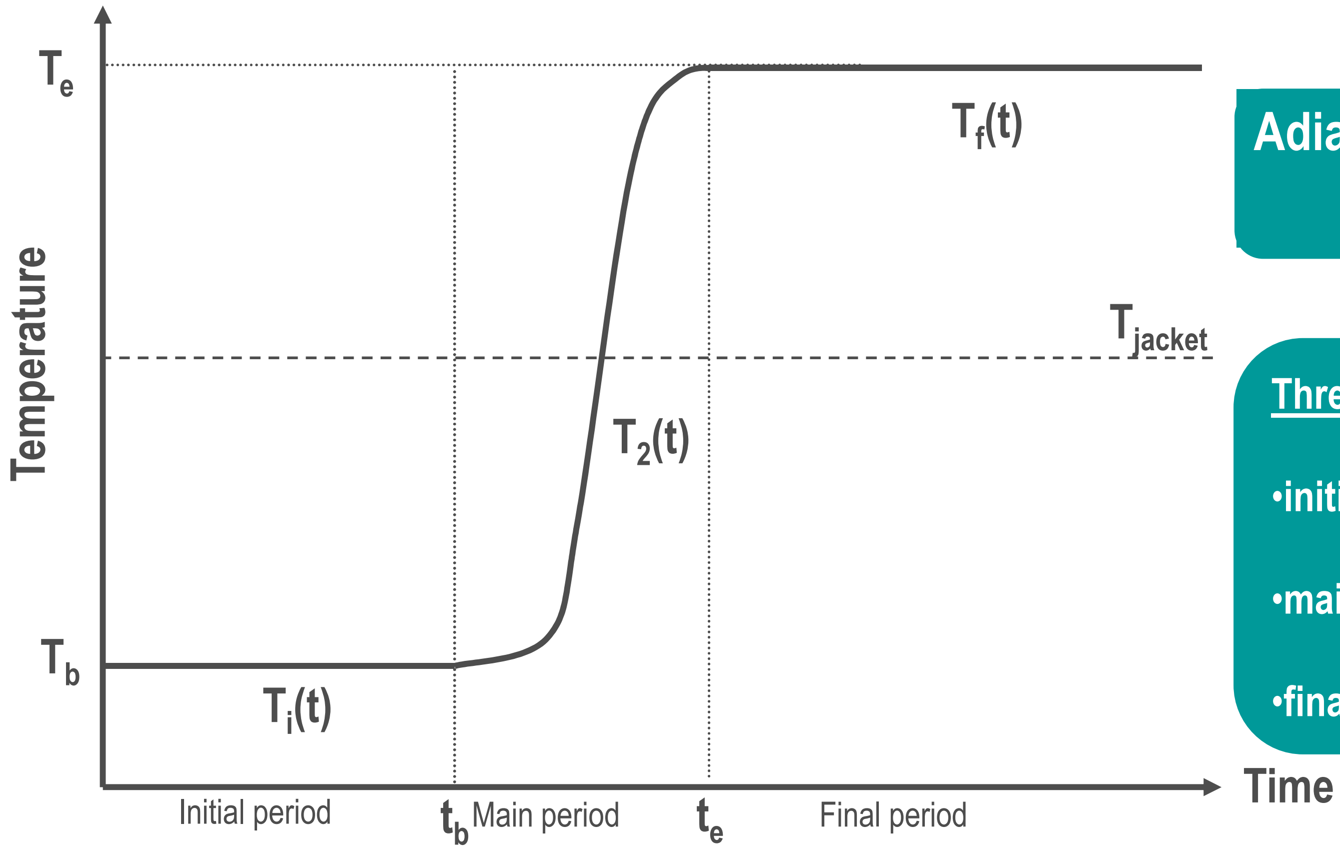
Or

Isoperibolic Calorimeter ?



Calorimeter Principle

Standard temperature curve of the water bath during heat release process



Adiabatic calorimeter

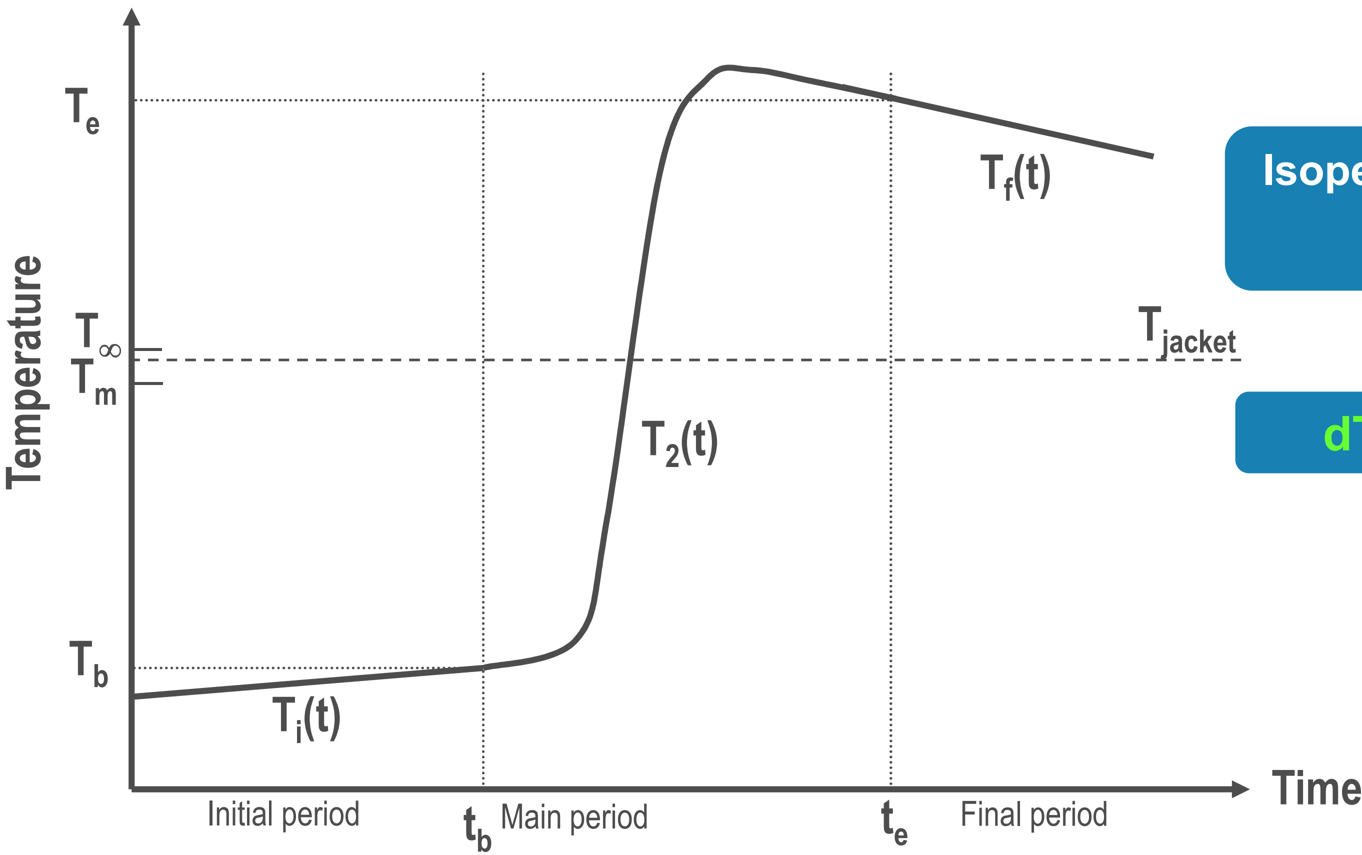
$$\Delta T_{ad} = T_e - T_b$$

Three phases:

- initial period
- main or heat release period
- final period

Calorimeter Principle

Standard temperature curve of the water bath during heat release process



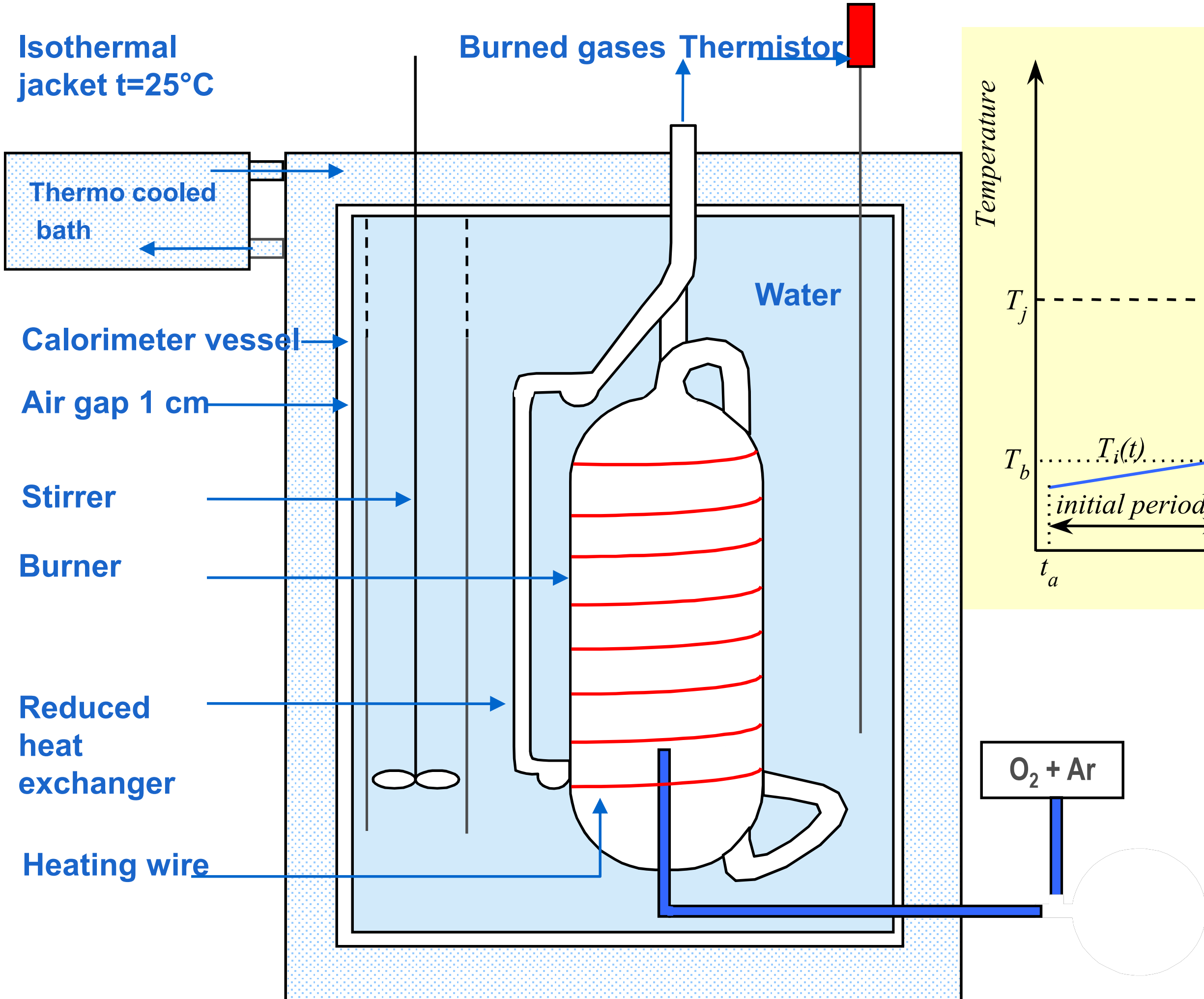
Isoperibolic Calorimeter

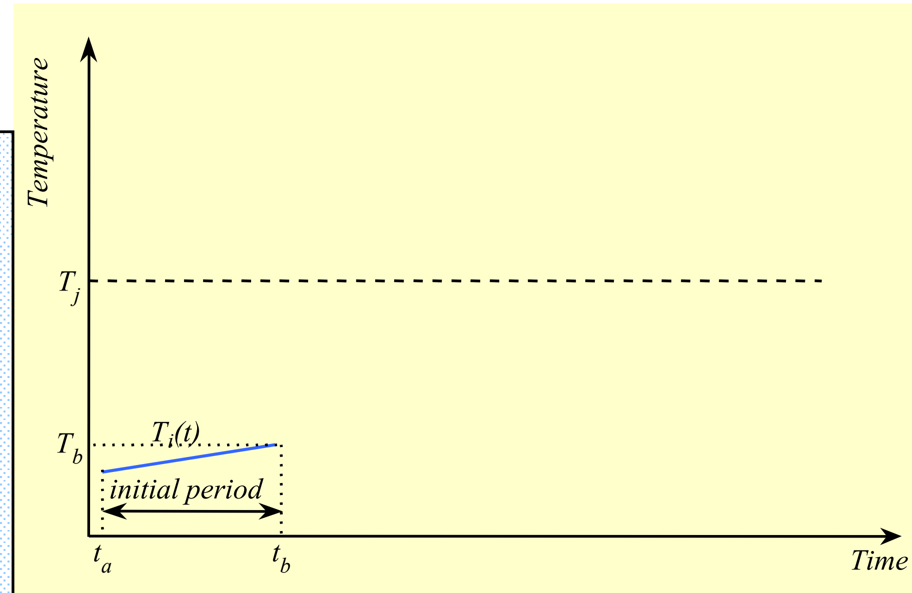
$$\Delta T_{ad} = T_e - T_b - dT$$

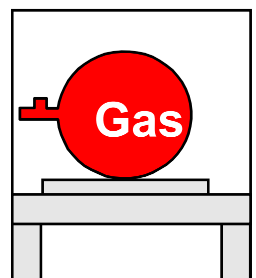
$$dT = k(T_\infty - T_m)(t_e - t_b)$$

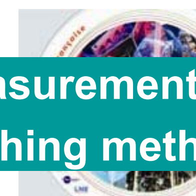
LNE reference calorimeter:

Principle





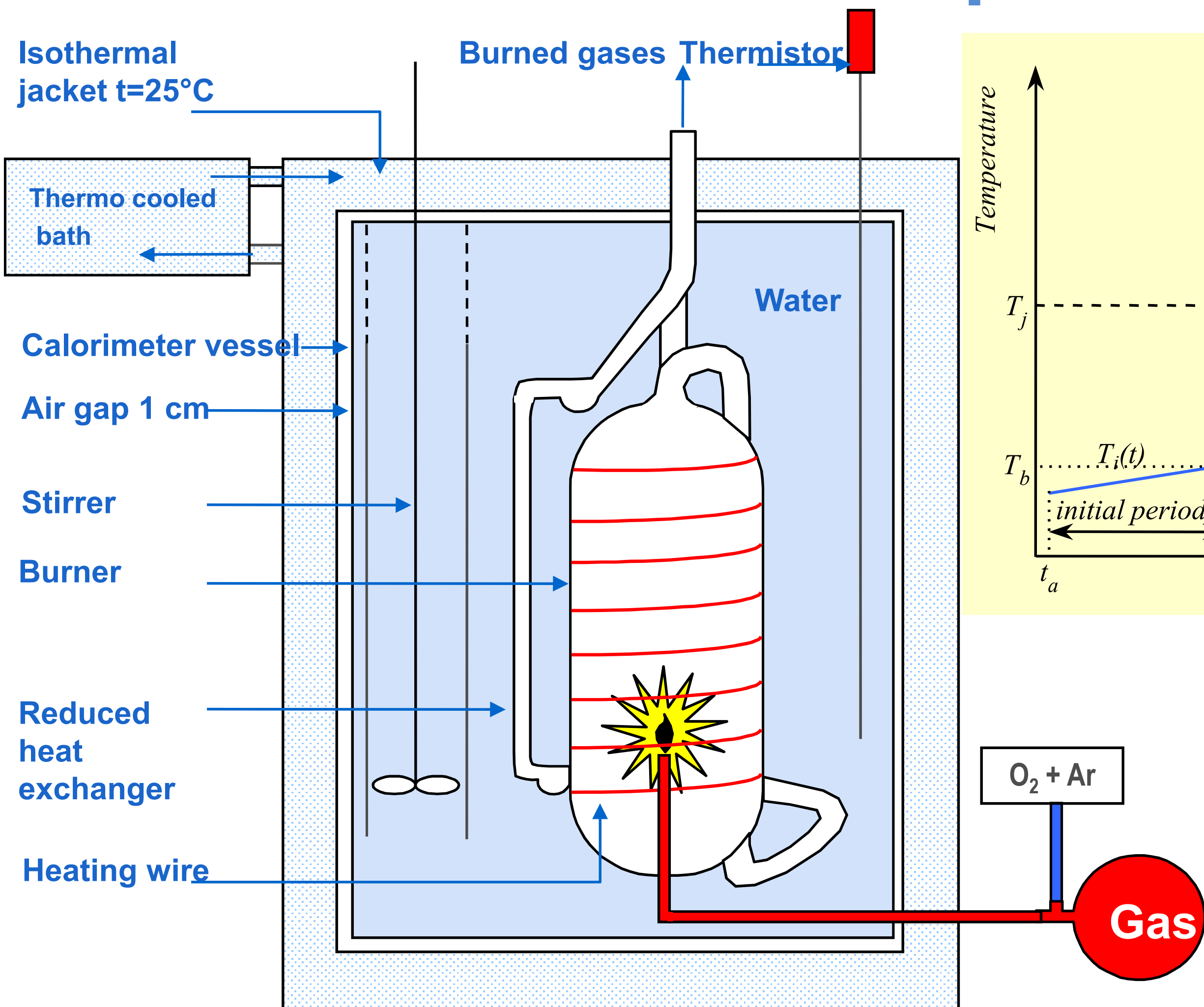


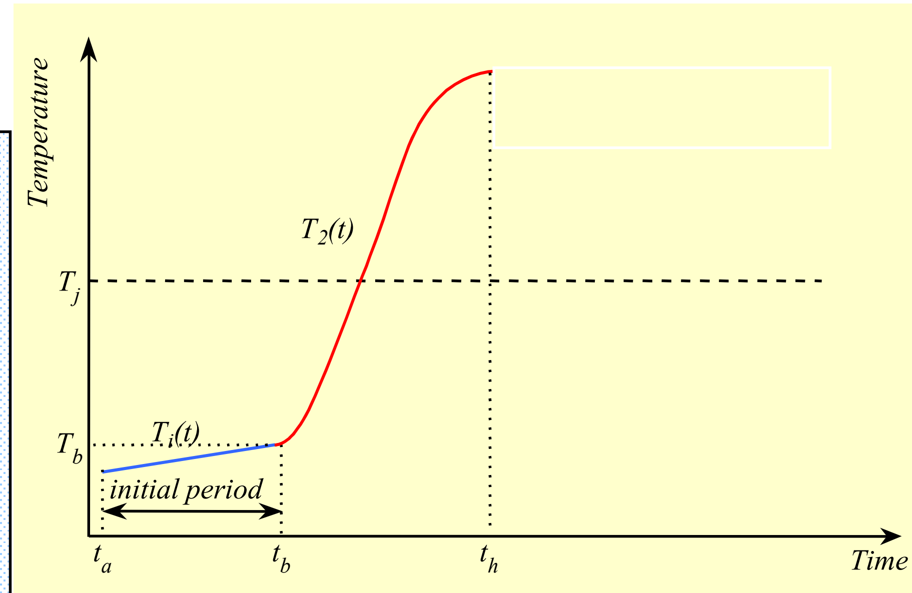


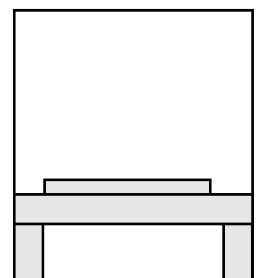
Gas mass measurement with double weighing method

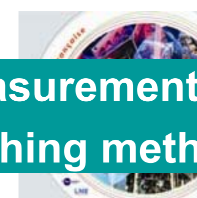
LNE reference calorimeter:

Principle





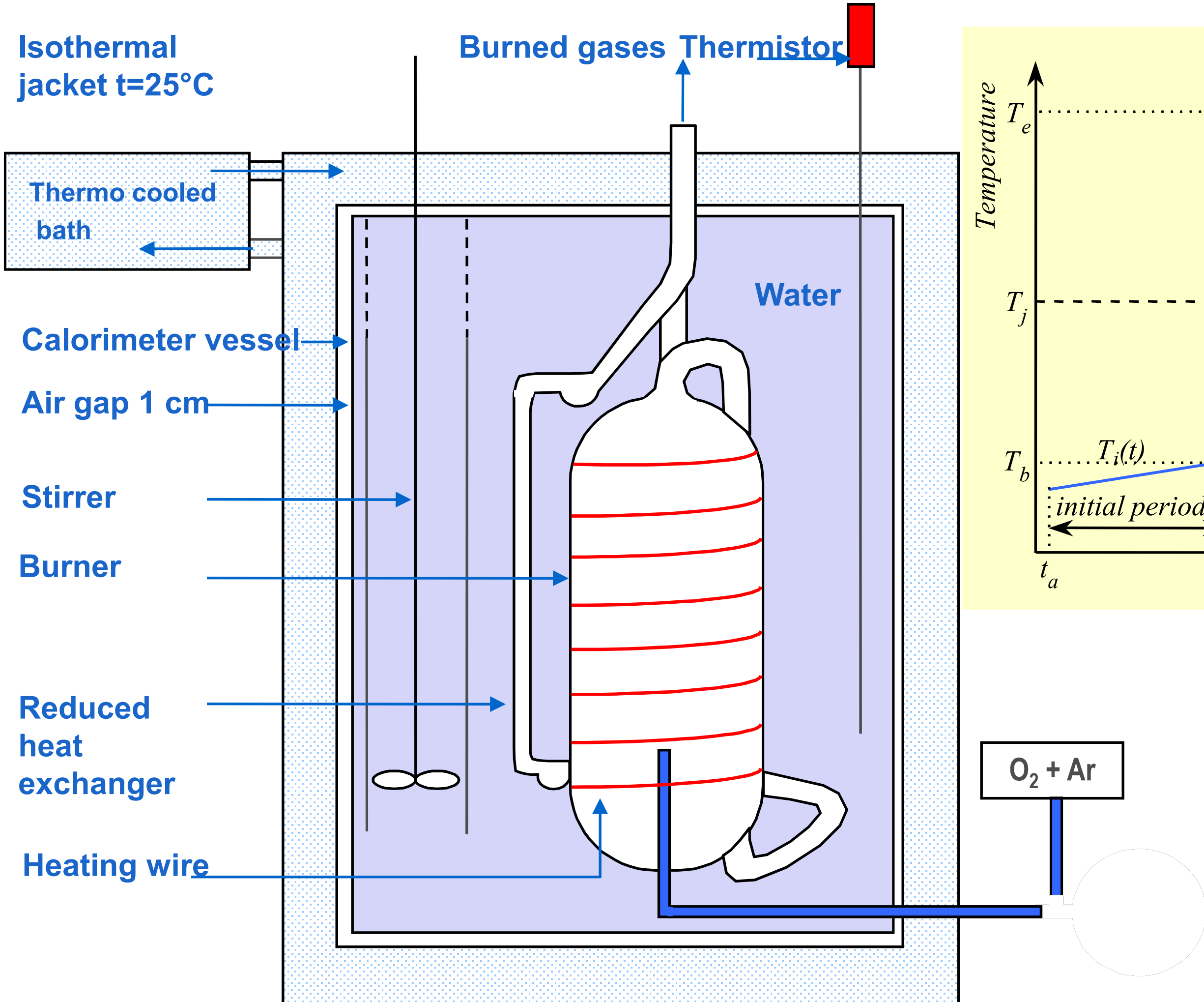


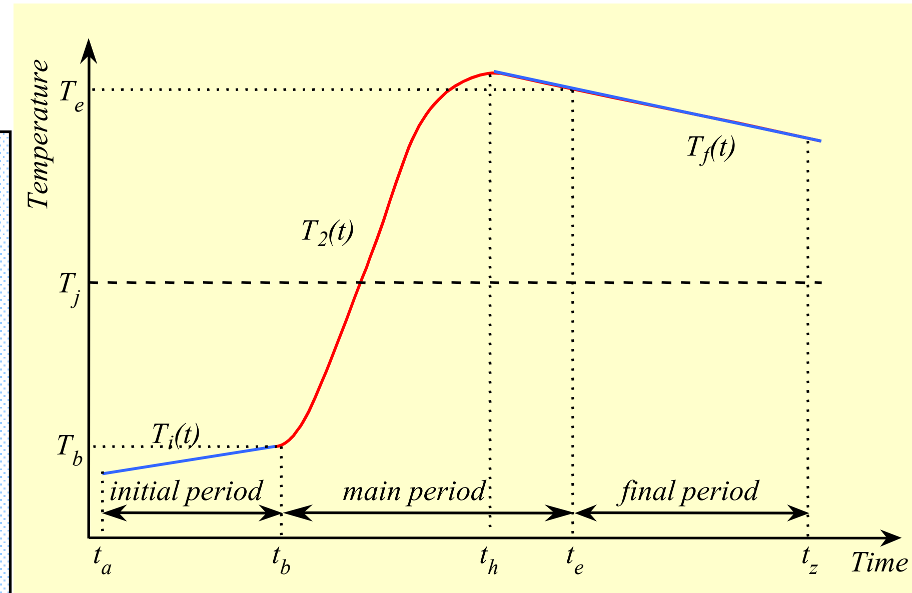


Gas mass measurement with double weighing method

LNE reference calorimeter:

Principle

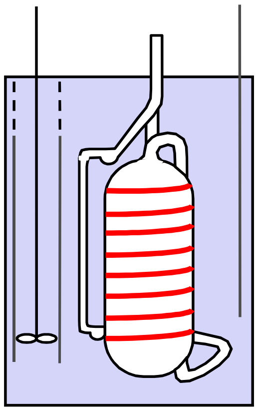




Gas mass measurement with double weighing method

Gross Calorific Value determination

$$C_{cal} = \frac{\sum_i U_{heat\,i}\, U_{ref\,i}\, t_i}{R_{ref}\ \Delta T_{cal,ad}}$$



$$\Delta T_{comb,ad} = T_e - T_b - k\left(T_\infty - T_m\right)\left(t_e - t_b\right)$$

Depends on:
- **temperature-time curve treatment**

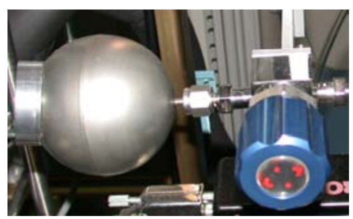
$$K = E_w + E_g - E_i$$

Depends on:
- **electrical ignition energy *Ei***
- **energy due to water leaving the calorimeter during the experiment *Ew***
- **energy traducing the difference of the in and out flowing gases temperatures *Eg***

$$GCV = \frac{C_{cal}\ \Delta T_{comb,ad} + K}{m_{gas}}$$

Depends on:
- **heating wire voltage**
- **standard resistor (voltage and value)**
- **adiabatic temperature rise from calibration run**

$$m_{gas} = M_{post-comb} - M_{fore-comb}$$



Depends on:
- **calibrated masses,**
- **density (air and calibrated masses)**
- **volume of calibrated masses**

Gross Calorific Value determination

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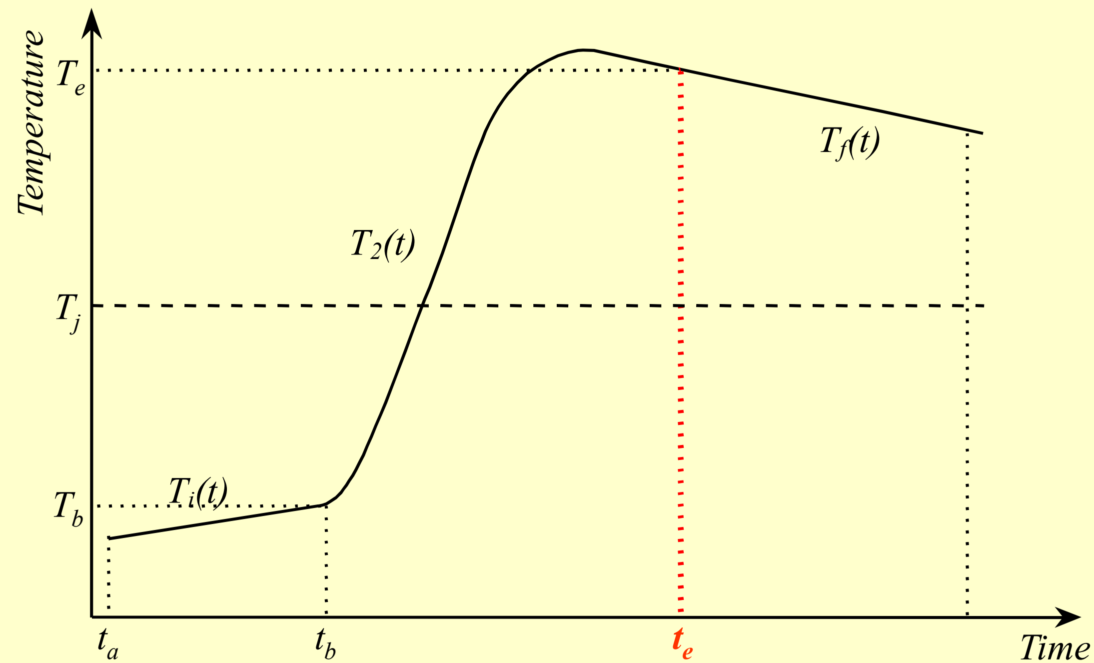
General equation

$$\Delta T_{comb,ad} = T_e - T_b - k\left(T_\infty - T_m\right)\left(t_e - t_b\right)$$

Chronological calculation steps for the determination of ΔT_{ad}

- **Determination of t_e**



Gross Calorific Value determination

General equation

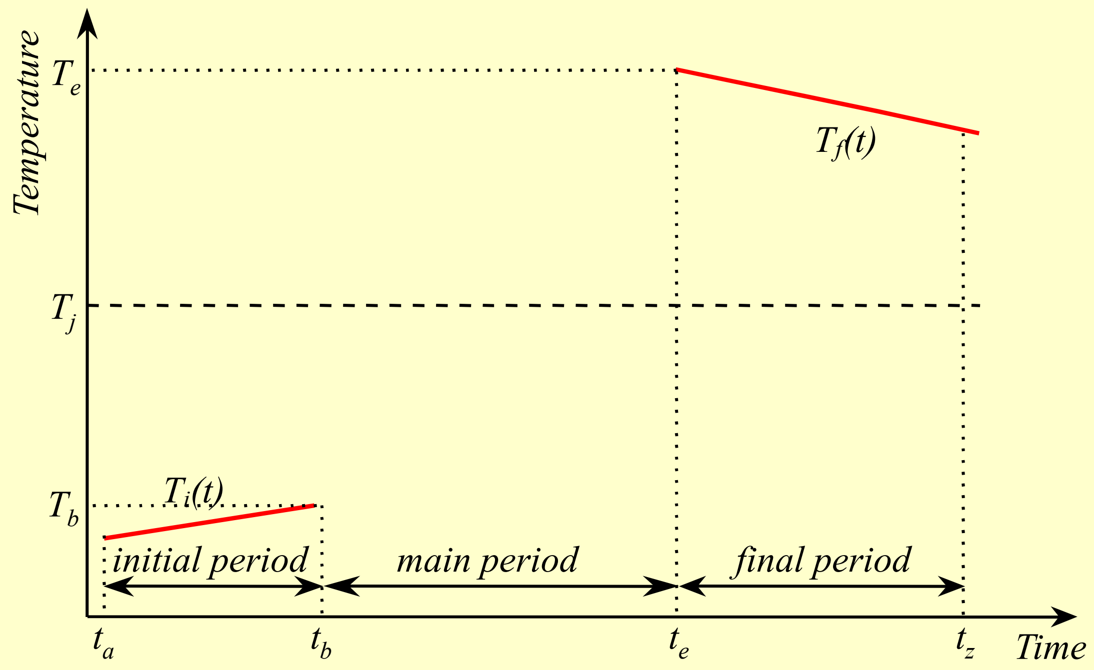
$$\Delta T_{comb,ad} = T_e - T_b - k\left(T_\infty - T_m\right)\left(t_e - t_b\right)$$

Chronological calculation steps for the determination of ΔT_{ad}

- Determination of t_e
- **Exponential simultaneous regression of the initial and final periods**

$$T(t) = T_\infty - \left[T_\infty - \left((1-y)T_b + yT_e\right)\right]\exp(-k\tau)$$

Calculation of T_e, T_b, k and T_∞



Gross Calorific Value determination

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Chronological calculation steps for the determination of ΔT_{ad}

- Determination of t_e
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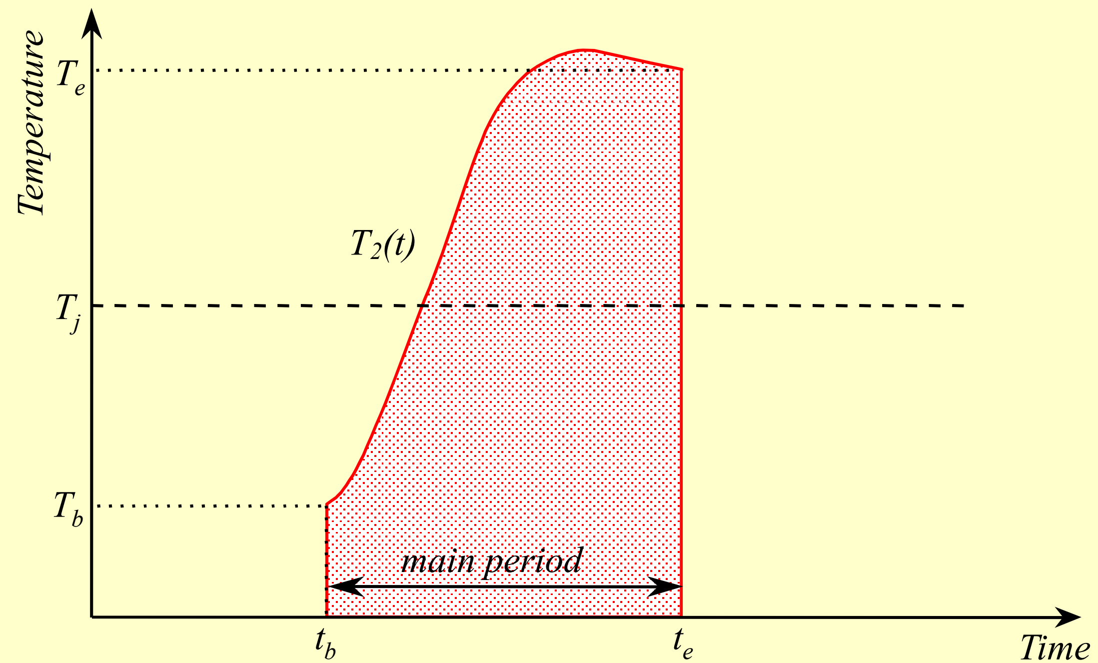
$$T(t) = T_\infty - \left[T_\infty - \left((1-y)T_b + yT_e\right)\right]\exp(-k\tau)$$

Calculation of T_e, T_b, k and T_∞

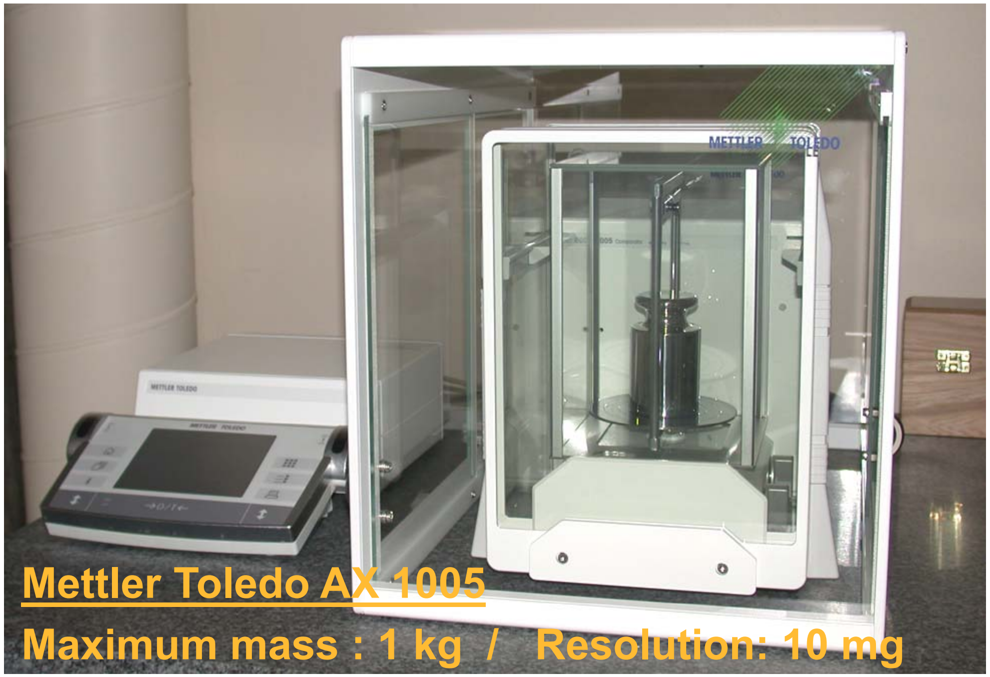
- Calculation of $T_m = \frac{1}{t_e - t_b}\int_{tb}^{te} T_2(t)\,dt$ by the trapezoidal method
- Calculation of $dT = k\left(T_\infty - T_m\right)\left(t_e - t_b\right)$
- Calculation of $\Delta T_{ad} = T_e - T_b - dT$



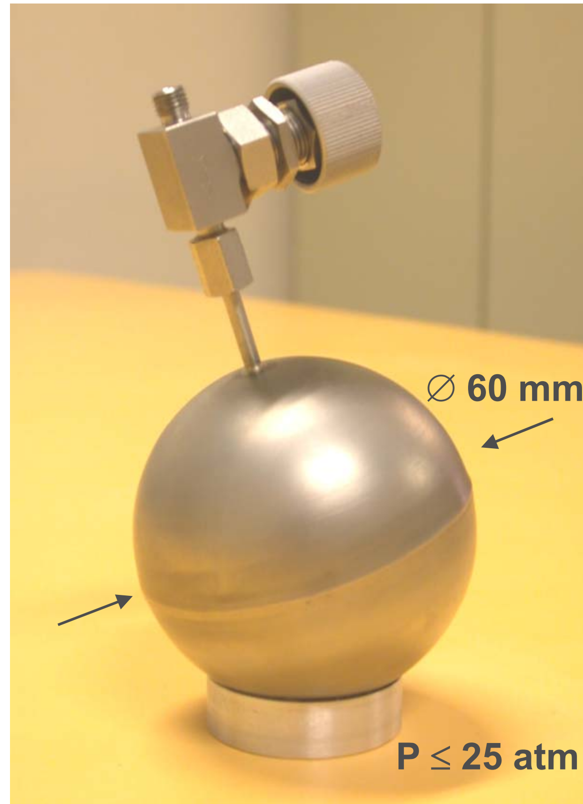
Calorimeter description

Gas weighing system

Mass comparator

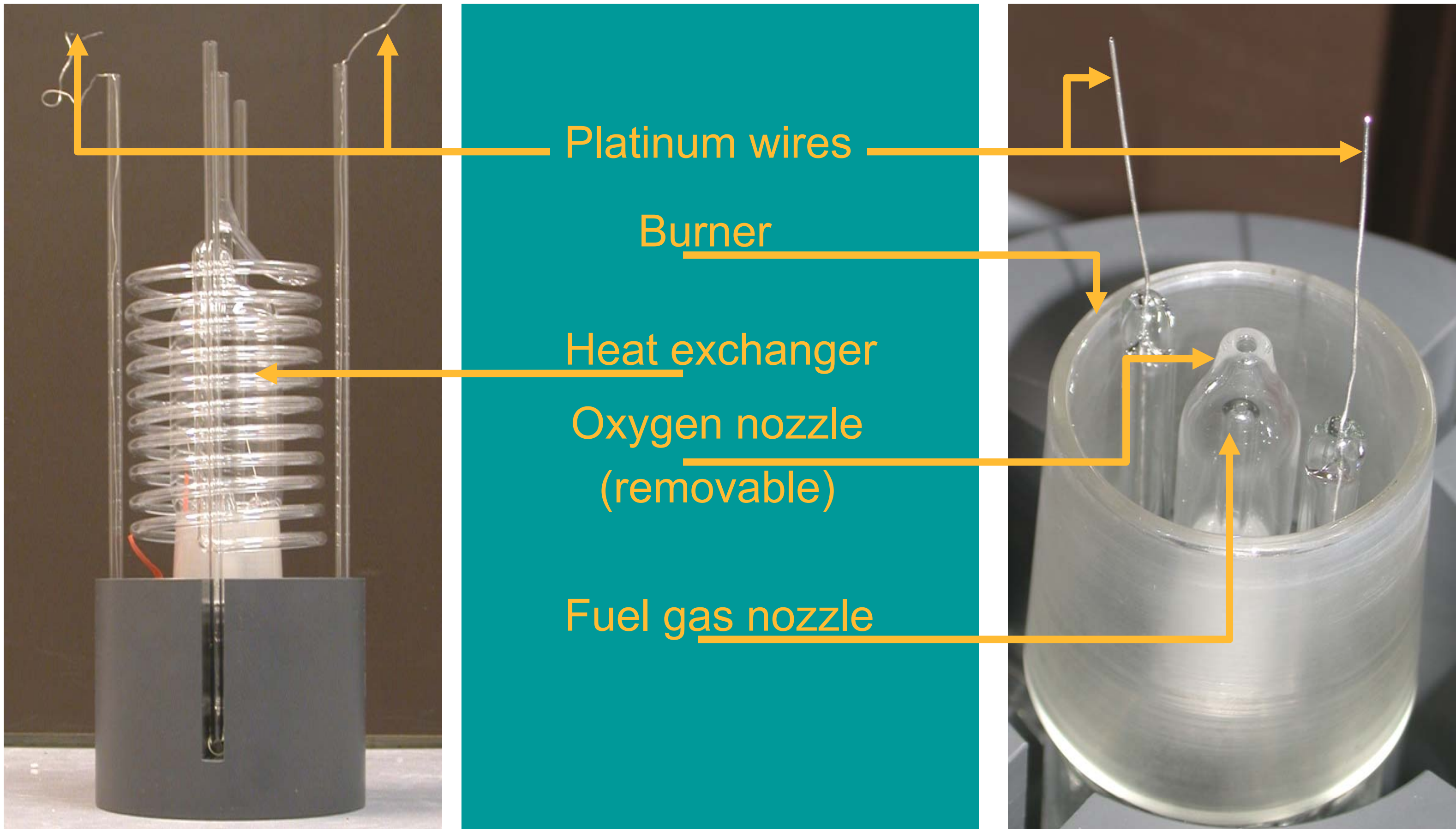


Sphere



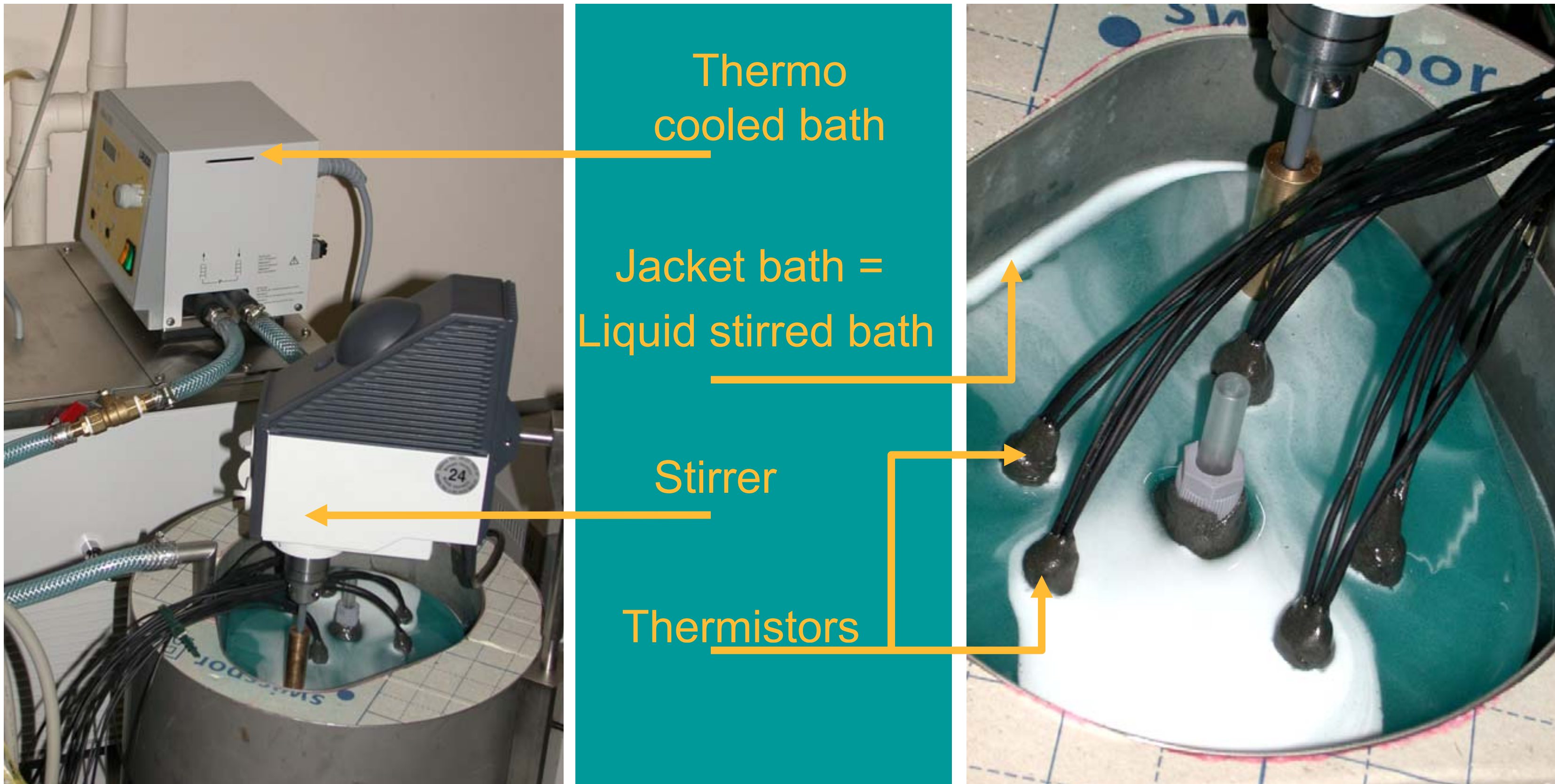
Calorimeter description

Combustion Chamber and Burner

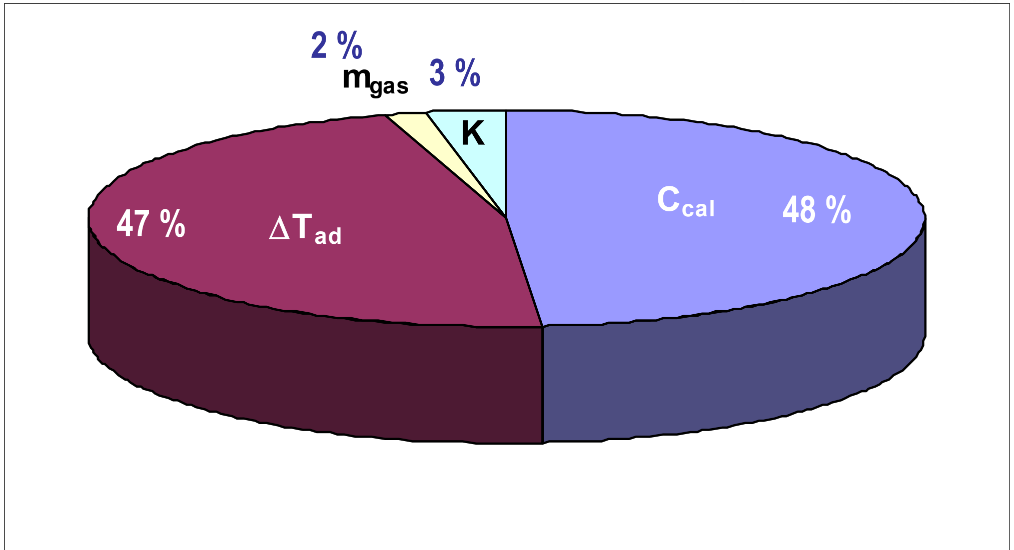


Calorimeter description

Calorimetric Vessels



Uncertainty contributions



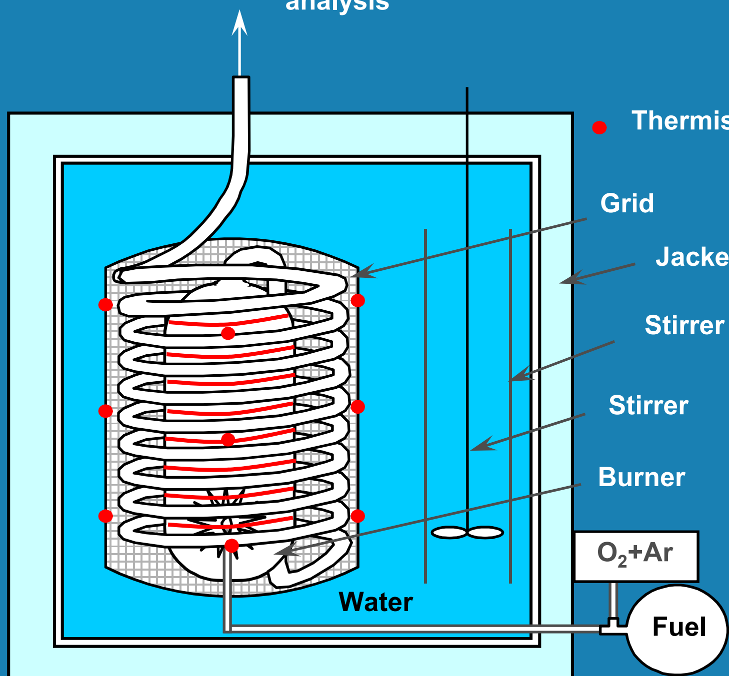
$$GCV = \frac{C_{cal}.\Delta T_{ad} + K}{m_{gas}}$$

$U(GCV) \leq 0{,}05\%$

- ✓ C_{cal}: heat capacity of the calorimeter
- ✓ ΔT_{ad}: adiabatic temperature rise
- ✓ K: energetic correction factor
- ✓ m_{gas}: mass of fuel gas

Preliminary measurements

Experimental data obtained by electrical dissipation



- **Electrical energy dissipation in the bath during 20 minutes with a heating coil located around the burner**

- **Temperature rise measurements with 9 thermistors immersed in the water bath**

Thermistors characteristics

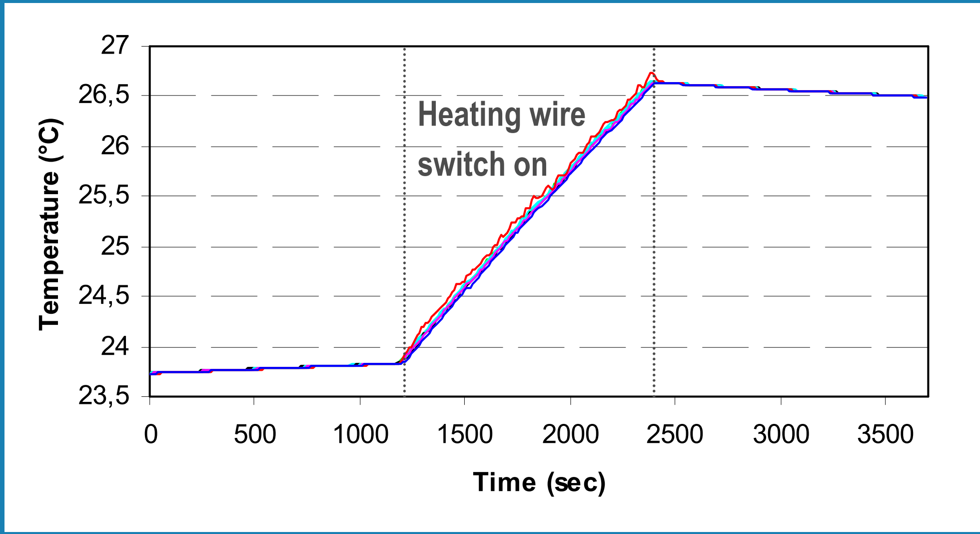
- **Sensitivity:** 430 W/°C
- **Small geometry:** glass bead probes of ~∅ 1 mm
- **Fast response time:** 1.5 sec in an oil stirred bath

Preliminary measurements

Experimental data obtained by electrical dissipation

Input parameters:

- T_{jacket} = 25°C
- Stirrer speed = 600 rpm
  - Water velocity in the outflow of the stirrer channel: 30 cm/s
  - $P_{stirrer}$: 0,39 W
- P_{heater} = 50 W



Experimental temperature rise	2.7713 K	
Standard deviation due to non homogeneity in the water bath	1.4 mK in the stable periods (initial and final periods)	Each period: 20 minutes
	32.3 mK in the dynamic regime (heat release period)	

Input parameters have been optimised operating a modelling

Thermal heat transfer modelling in the calorimeter

- Inventory of all the heat transfer types in the calorimeter
  - ➡ Importance of heat transfer by radiation

- Quantitative estimate of these heat transfers given by:
  - ➡ Mass and geometry (thickness, ρ, m)
  - ➡ Materials (λ, C_p, ε)
  - ➡ Temperature levels and total released power
  - ➡ Observed water flow in the bath

Overall validation of the numerical model

- Overall validation of the numerical model under the following conditions:
  - ✓ Maximal heat transfer from the burner to the water bath
  - ✓ Minimal heat loss to the jacket

- Recommendation for the 3D simulation implementation
  - ✓ to measure the water speed at the exit of the stirrer channel to identify the water flow regime: laminar or turbulent
  - ✓ to consider as stagnant the air between the inner and the outer vessels
  - ✓ to activate a radiative numerical model for combustion tests

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CFD 3D numerical model

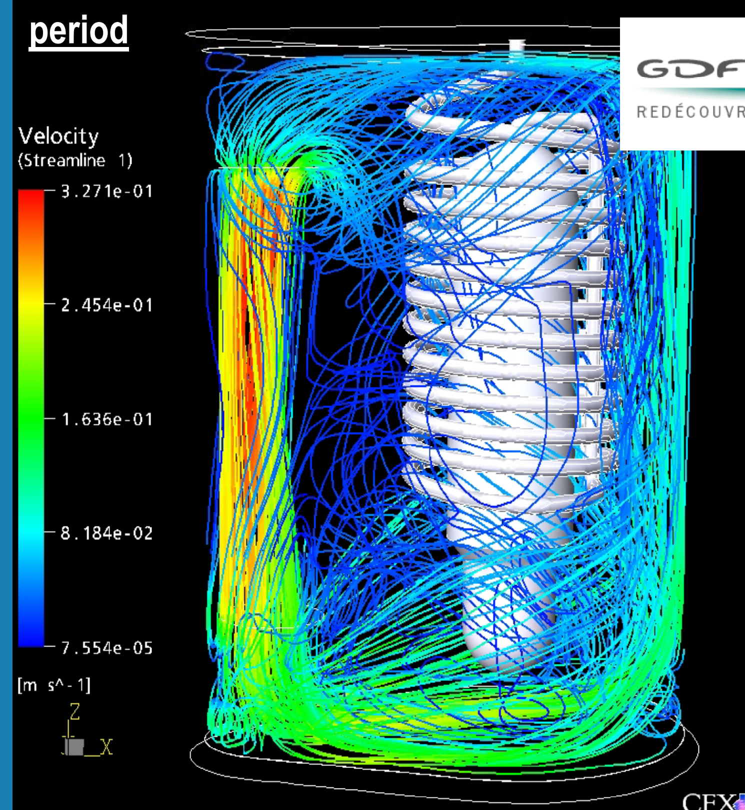
Input parameters:

- No heating
- Water velocity in the outflow of the stirrer channel: 30 cm/s
- $P_{stirrer}$: 0,39 W
- T_{jacket} : 27 °C
- $T_{calorimeter\ bath}$: 22 °C

Large exterior circulation loop creates almost stagnant regions between:

- burner and heat exchanger coil
- stirrer channel and burner

Stream lines of the water flow in the initial period



GDF SUEZ
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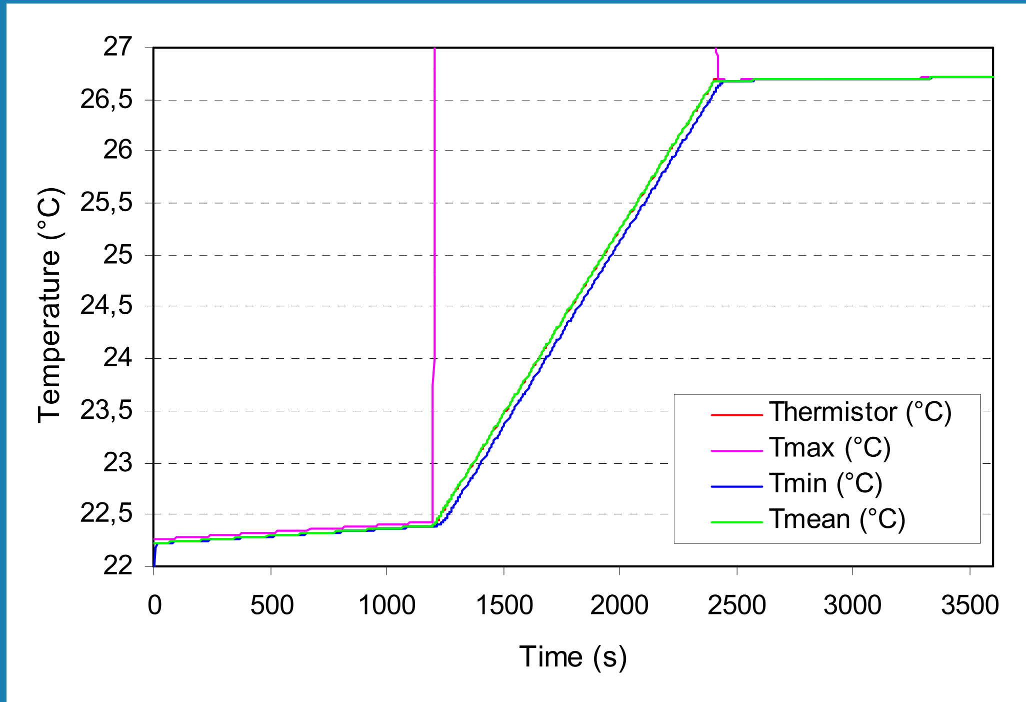
CFD 3D numerical model: Electrical dissipation

Input parameters:

- Convective heat flux applied uniformly over 10 cm height on the burner
- No heat transfer by radiation
- Water velocity in the outflow of the stirrer channel: 30 cm/s
- $P_{stirrer}$: 0,39 W
- T_{jacket} : 27 °C
- P_{heater} : approx. 60 W



- Good homogeneity in the bath during the power release
- Validation of thermistor location

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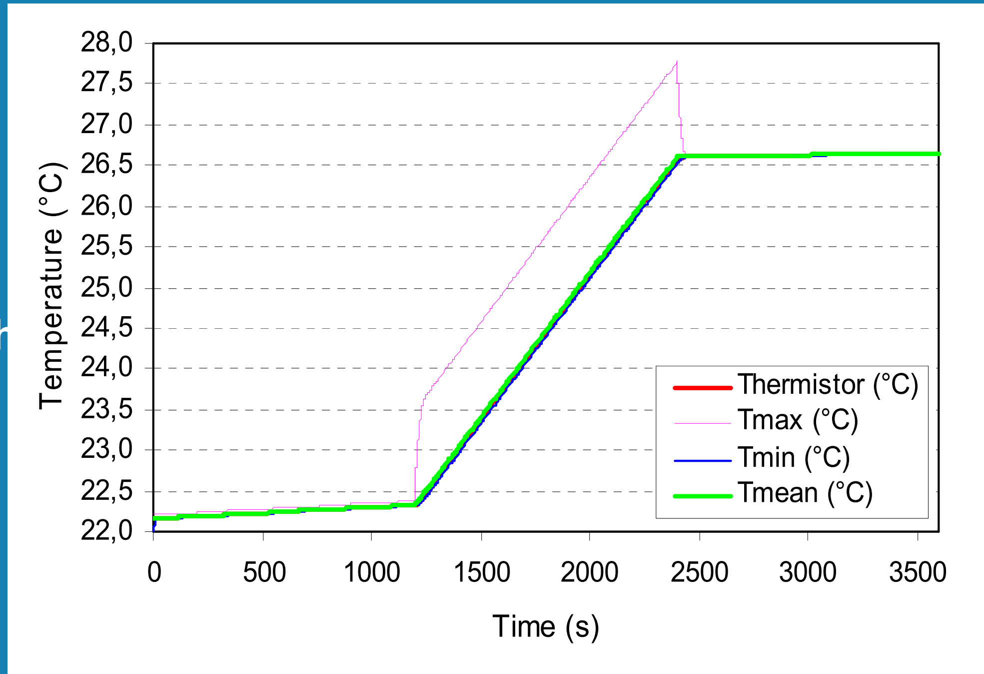
CFD 3D numerical model: Combustion heating

Input parameters:

- Pure radiative heat flux applied uniformly over 10 cm height on the burner
- Water velocity in the outflow of th stirrer channel: 30 cm/s
- $P_{stirrer}$: 0,39 W
- T_{jacket} : 27 °C
- P_{heater} : approx. 60 W



- Same general thermal behaviour as in the convective heat flux
- Validation of thermistor location
- The only difference concerns maximum temperature evolution

Modelling, Dimensioning the device

Comparison of the two theoretical heating cases

	T_{max}-T_{mean} (K)	T_{mean}-T_{min} (K)
Pure convective heating	1.17	8.54
Pure radiative heating	0.08	0.13

Modelling, Dimensioning the device

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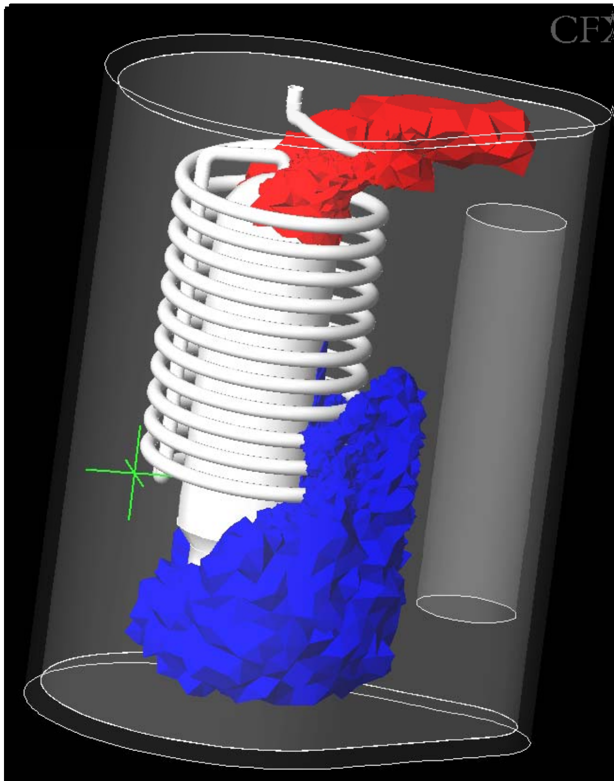
CFD 3D numerical model

Temperature evolution in the bath during heat release



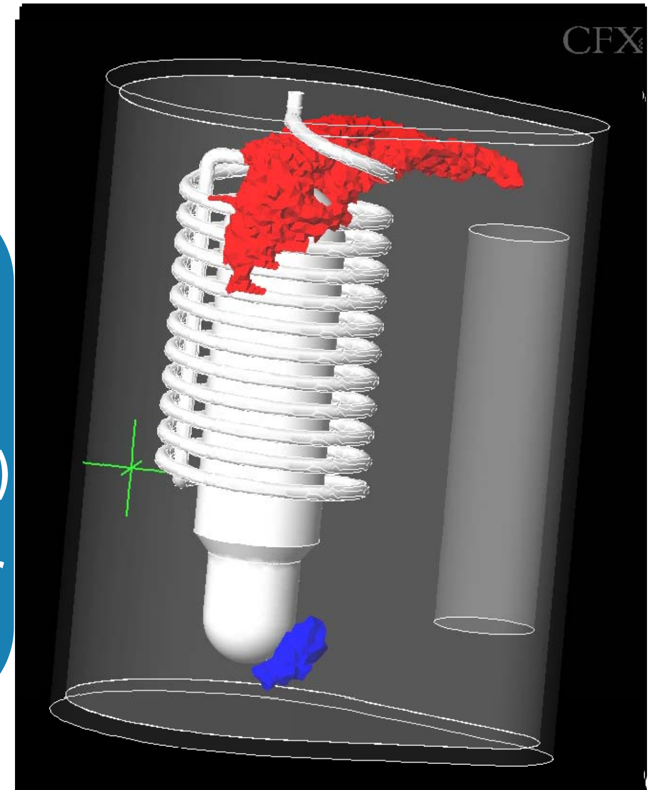
Convective power release (electrical calibration)

t = 2410 s

Volume of water where

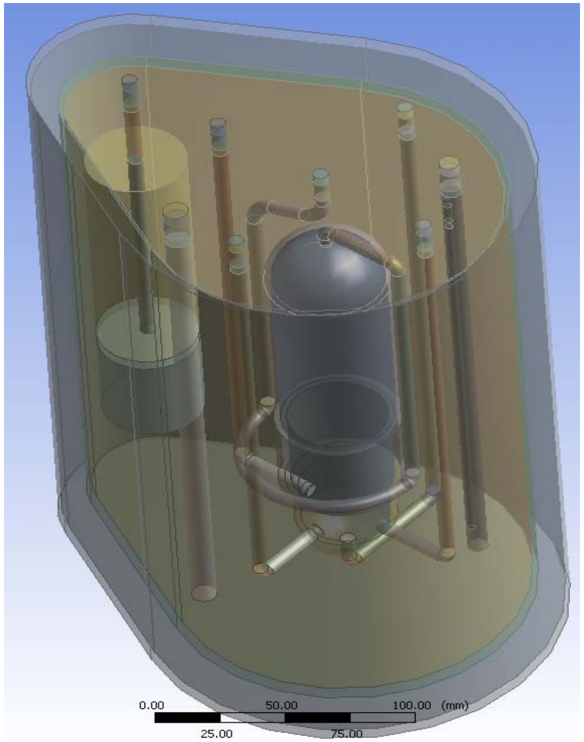
$T \geq T_{mean}$ + 50 mK (in red)
$T \leq T_{mean}$ – 50 mK (in blue)

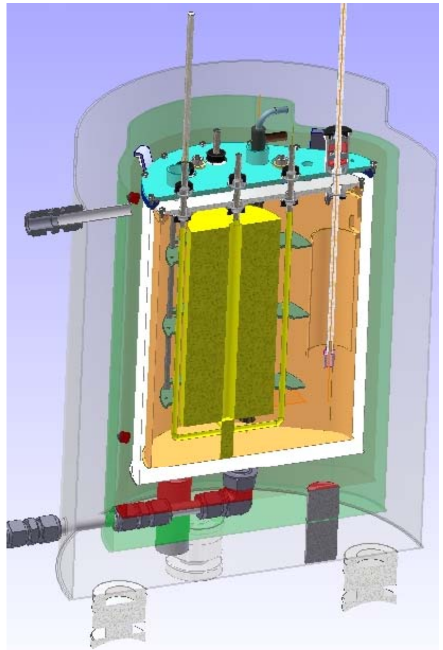
The location of the thermistor probe is critical



Radiative power release

Modelling, Dimensioning the device



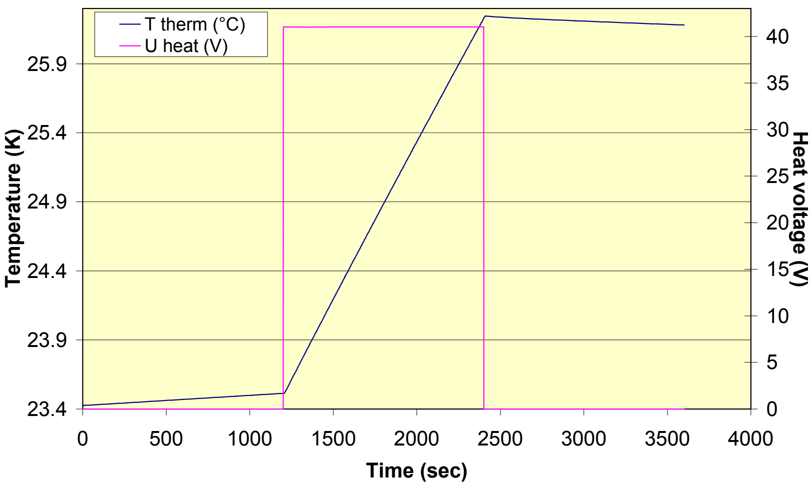


- Realization of the final version of the calorimeter
  - New internal and external electro polished vessels
  - Modification of the tightness system of the vessels
  - Implementation of an optical flame detector

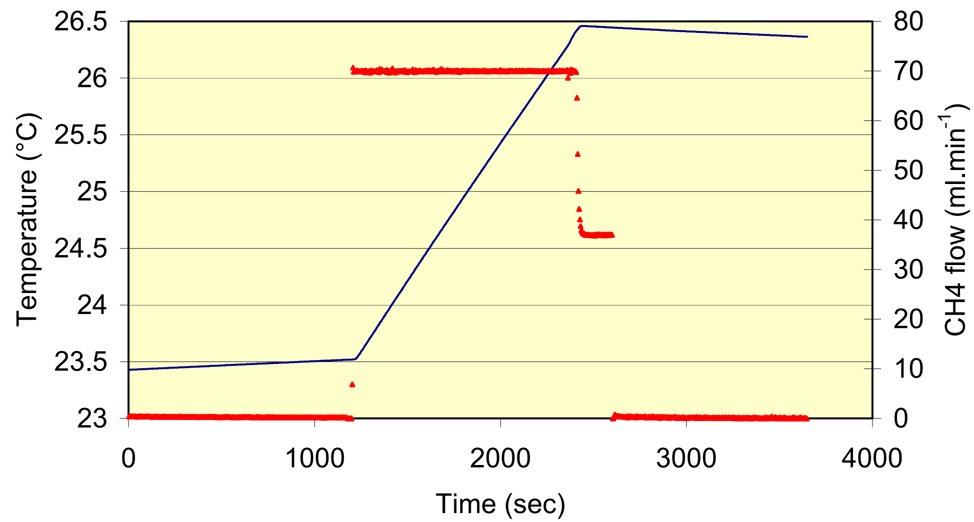
Experimental results

Two experiments → One GCV calculation

Calibration



Combustion



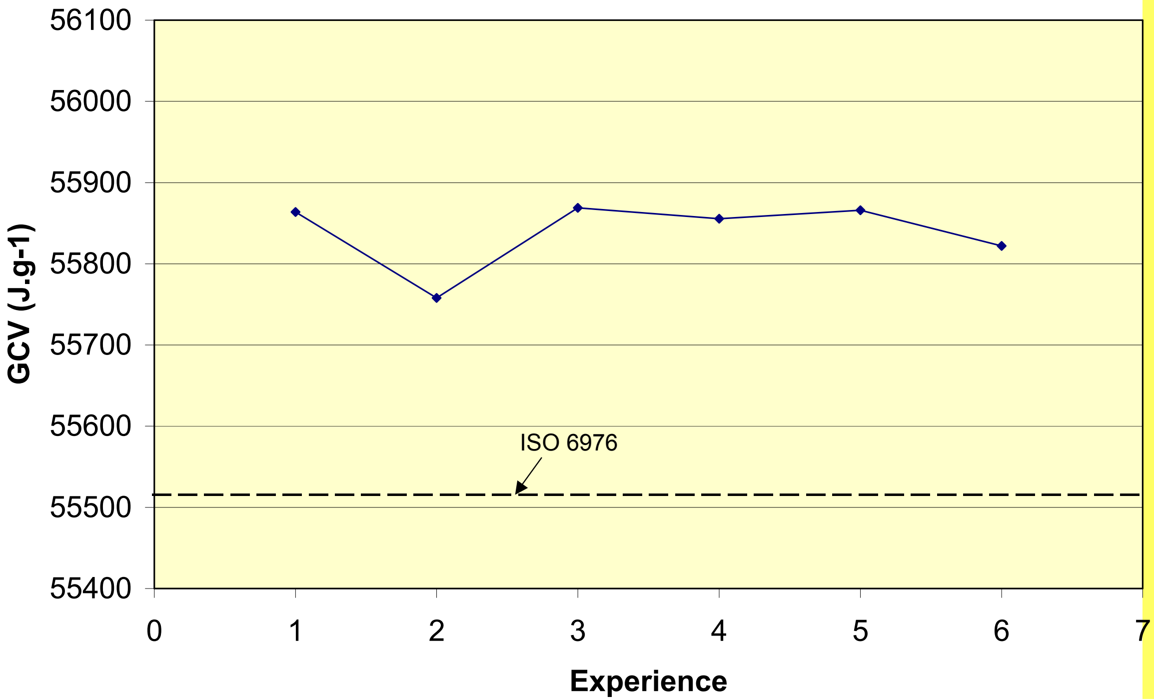
$$\Delta T_{cal,ad} = T_e - T_b - k\left(T_\infty - T_m\right)\left(t_e - t_b\right)$$

$$\Delta T_{comb,ad} = T_e - T_b - k\left(T_\infty - T_m\right)\left(t_e - t_b\right)$$

$$C_{cal} = \frac{\sum_i U_{heat\,i}\, U_{ref\,i}\, t_i}{R_{ref}\ \Delta T_{cal,ad}}$$

$$GCV = \frac{C_{cal}\ \Delta T_{comb,ad} + K}{m_{gas}}$$

Experimental results, Perspectives



Repeatability measurements of GCV with the prototype version of the calorimeter

On 6 experiments

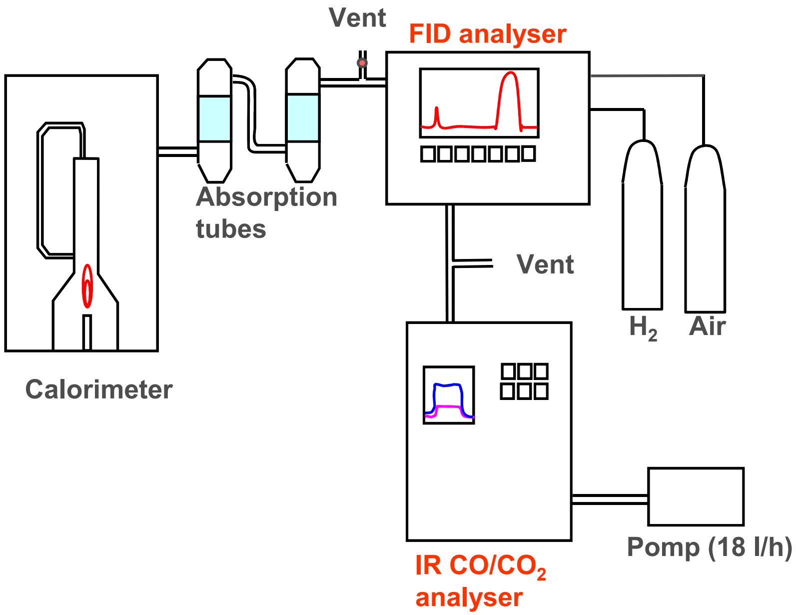
- **Mean value = 55839 $J.g^{-1}$**
- **Standard deviation = 0.077 % (0.16% on 11 experiments)**
- **Relative deviation between the experimental mean and normalised value given by ISO 6976 of 0.58 %**

➢ **Reduction of unburned methane quantity**

➢ **Implementation of a non-calibrated hydrocarbon analyser (FID method)**

Experimental results, Perspectives

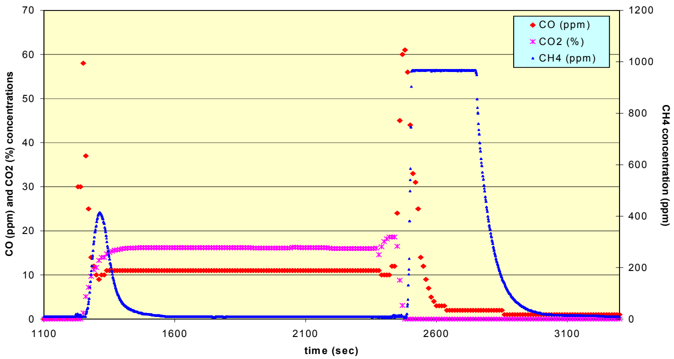
Unburned methane analysis



Implementation of a non-calibrated hydrocarbon analyser (FID method) in series with an infra-red CO / CO2 analyser

Continuous measurements of CH_4 concentration

Unburned methane analysis



Implementation of a non-calibrated hydrocarbon analyser (FID method) in series with an infra-red CO / CO2 analyser

Continuous measurements of CH_4 concentration

- **Total combustion *(except at ignition and extinction periods)***
- **Bad combustion at flame ignition and extinction**
  - **⇨ non-ideal mixture CH_4/O_2 and unstable inflow gases**
- **Time delay between CH_4 and CO picks**
  - **⇨ different analyser times response (FID and IR)**
- **Maximum CH_4 at flame extinction (saturation), lower at ignition**

Experimental results, Perspectives

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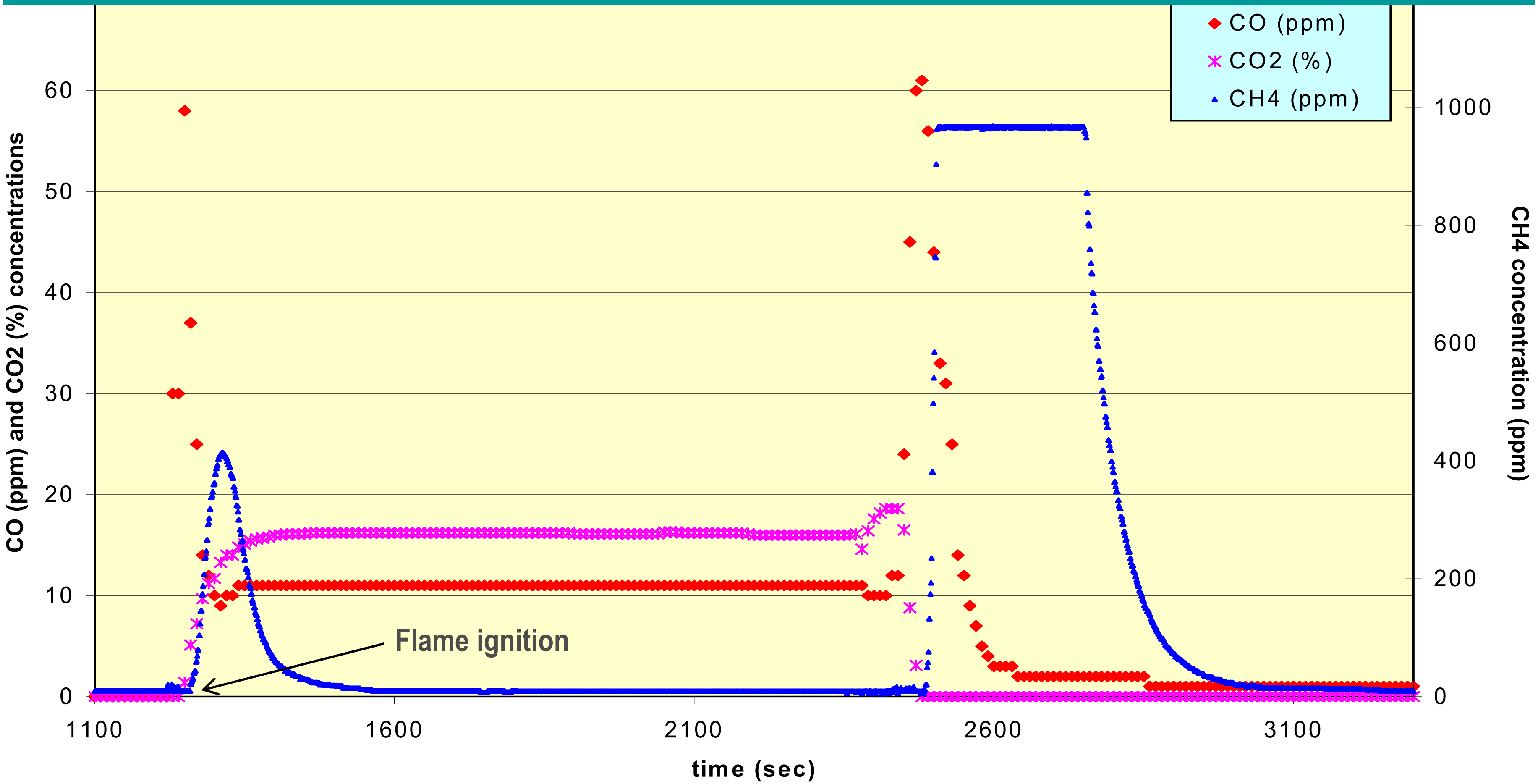
Unburned methane analysis



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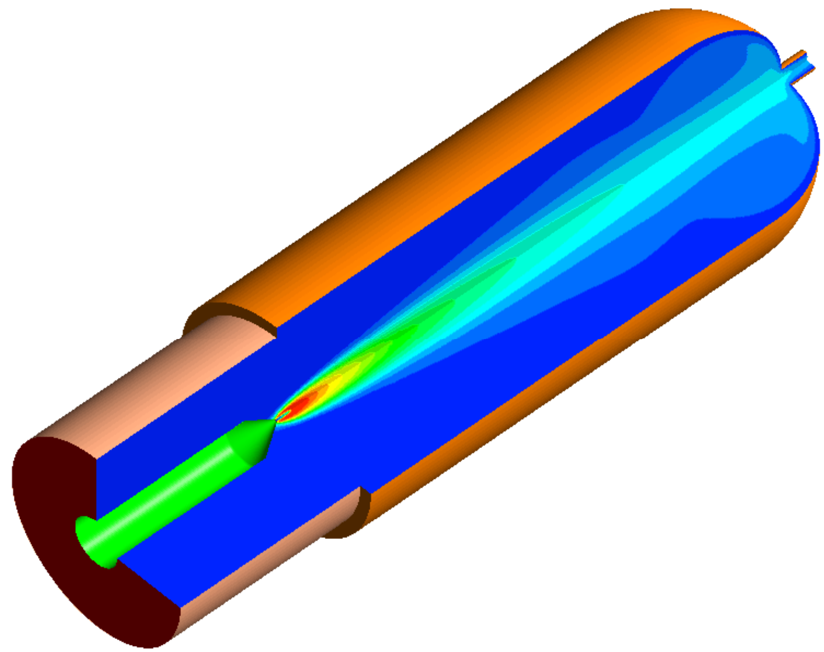
Improvement axes

- Flushing the methane pipes with Argon to help combustion at the end of the experiment

- Implementation of a chemical catalyser in the burner or in the heat exchanger to help combustion of the remaining methane

- Correct the GCV value by calculating the unburned methane concentration with the FID analyser



Conclusions

- Detailed calculation of the gross calorific value with a reference calorimeter
- First repeatability study
- Numerical simulations → optimised design geometry (burner, vessels, stirrer, location of the temperature sensor, …)
- Measurements with the improved calorimeter
- Measurement of homogeneity uncertainty of the water bath
- Inter-comparison with national metrology institutes on GCV of methane (CCT WG9)
- Application for biofuels ?

France, Reference Calorimetry

LNE, Sponsors and Partners

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Europe, Reference Calorimetry

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Laboratoire national de métrologie
et d'essais (LNE)

**Organisme de référence
pour la métrologie française
avec le concours de :**

3 autres laboratoires nationaux

- LNE-INM
  Conservatoire National des Arts et Métiers
- LNE-LNHB
  Commissariat à l'Energie Atomique
- LNE-SYRTE
  Observatoire de Paris

et 6 laboratoires associés

- Centre Technique des Industries Aérauliques et Thermiques (CETIAT)
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- Franche-Comté, Electronique, Mécanique, Thermique et Optique - Sciences et Technologies (FEMTO-ST)
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Thank you for your Attention

Gracias por su atención

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