greenTEG

gSKIN® Application Note: Calorimetry

Fast and precise calorimetric measurements with the gSKIN® Sensor

The gSKIN® Sensor enables fast and highly precise measurements of heat flows in a variety of applications, including calorimetry. Calorimetric measurements are of paramount importance in the field of chemical engineering, physical chemistry, materials science and biology.

No additional equipment needed
"Thanks to the heat flow based measurement, you do not need an isolated reaction chamber. For many measurements, you don't even need a thermometer."

Easy to use
"The small size and robust packaging allows for a simple application on virtually all surfaces. Just apply the sensor with a film adhesive and you are ready to go."

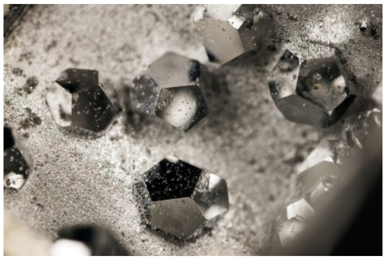
Wide range of sample volumes
"Use the same sensor for the analysis of samples volumes ranging from cubic millimeters to cubic meters."

High sensitivity
"Measure heat energies of less than one millijoule on an assay of just one cm^3. Explore the thermal behavior of matter beyond your imagination!"

Applications

The fields of application of the gSKIN® Sensor are numerous and vast as the field of calorimetry itself. The small standardized sensors are ideal for routine measurements in research and development as well as in an educational context. In cooperation with manufacturers of chemical lab equipment, the gSKIN® Sensor can also be tailored and built in as an integral part of high-end chemical synthesis systems.

- **Chemical engineering**
  Calorimetric data is essential for process safety control. The heat release rate of novel chemical reactions must be known in order to design the cooling and heating systems for large scale synthesis. With the help of our sensing solutions, chemical engineers can provide this information already in the research lab while working on small reaction volumes.



- **Material science**
  The engineering of energetic materials like phase change materials for latent heat energy storage relies on precise calorimetric measurements. The same applies for many analytical techniques in materials science like the measurement of heat capacities or the investigation of microstructural changes.

- **Biology**
  Calorimetry is used for non-invasive measurements of metabolic activities of biological systems, from cell cultures up to athletes. Gain insights into the energy balance of living systems!

- **Education**
  Illustrate and explain the concepts of exergonic and endergonic reactions, enthalpy, heat capacity etc. with live measurements of the heat flows.

Measurement Setup

Figure 1 shows the overview of a simple calorimetric measurement of a liquid solution using the gSKIN® Sensor. The individual parts of the setup and the measurement principle are described in the following.

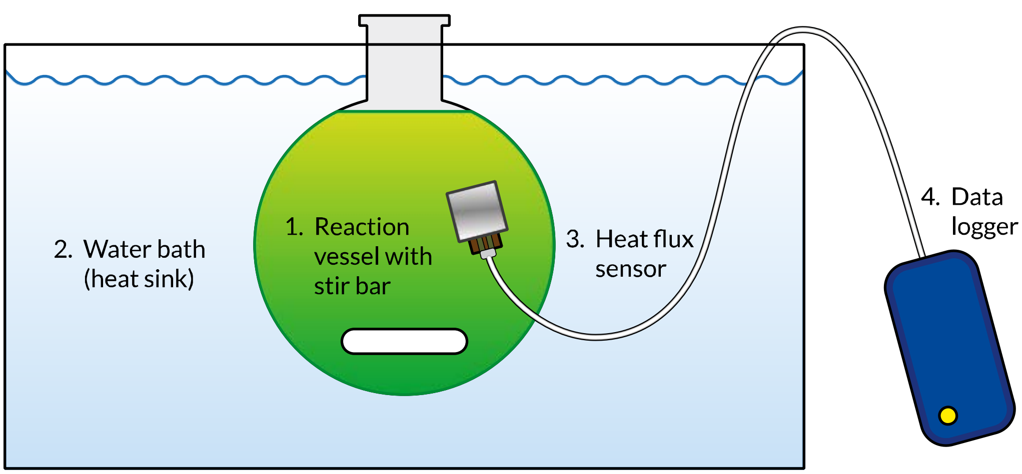


Figure 1: Simple calorimetric measurement setup for liquid solutions. The setup consists of a reaction vessel of Pyrex glass, a heat flux sensor and a water bath acting as a heat sink. The heat sink / water bath may be heated to the desired reaction temperature.

1. **Reaction vessel:**
The global heat transfer through the reaction vessel is extrapolated from the local probing of the heat flux sensor. In order to get accurate results, your vessel needs to fulfill some requirements with respect to geometric and thermal uniformity:

    - A stir bar is recommended for reaching a uniform distribution of the reactants and of the heat inside the reaction vessel.
    - In order to guarantee a uniform heat flux distribution, the shape of the vessel should be close to spherical. Cylindrical vessels work as well as they have rotational symmetry. Cubic or prismatic vessels will only provide accurate results if you include a setup correction factor (see appendix 2 of this document for details). Avoid vessels with conical shape or complex geometries and recessions.
    - Avoid exceedingly thermally conductive or insulating vessel materials. Glassware with uniform wall thickness around 1mm will work best.

2. **Water bath / heat sink**
The heat generated during the reaction must be carried away by a heat sink in order to be measured by the sensor. Water will work well since it has a large heat capacity. Use at least 10x more water than the volume of your reaction vessel. Make sure to cover the bath during the measurement as evaporating water may alter the result. The temperature of the heat sink must stay constant during measurement but must not necessarily be at room temperature.

3. **gSKIN® sensor:**
gSKIN® sensors transform the heat power flowing through the reaction vessel into an analog voltage. In most applications, the voltage signal is in the range of a few mV. Customization options with respect to sensitivity, shape and wiring are described in appendix 3 and 4.

    Correct mounting of the sensor to the reaction vessel is of paramount importance for getting precise and reproducible measurements. The methods listed in Table 1 provide a good thermal integration of the sensor into your system.

Option	Description/Instruction
Double-sided adhesive tape	Adhesive tapes offer average thermal coupling and reasonable mechanical stability. The measurements may not be as reproducible as with other mounting methods. In return, the sensor can be repositioned at will and transferred to other surfaces.
Thermal paste	Thermal pastes offer good thermal contact when applied appropriately. Pastes are also suitable for filling up recessions or compensate for curvatures of the reaction vessel. The mechanical stability of such a bond however is generally weak and requires special attention.
Thermally conductive epoxy adhesive	Thermoset adhesives offer the best performance with respect to mechanical stability and reproducibility of the measurements. However, this is a permanent bond and the sensor cannot be repositioned.
Silicone mold	More advanced permanent and repositionable sensing solutions can be designed with elastomeric molds. Contact us for more information.

Table 1: Mounting options for the gSKIN® sensor.

4. **Read-out electronics:**
The output signal of gSKIN® sensors is an analog voltage response. Silver-plated copper wires are used as electrical connection cables.

For read-out of the analog voltage signals, you can use your electronics, greenTEG electronics or a simple multimeter. For optimal results, a data logger with a measurement frequency of 1Hz or better is strongly recommended.

The resolution of the measurement depends on the resolution of the read-out electronics. To resolve the complete power spectrum, the read-out solution should have a voltage resolution of 1 µV. Table 2 compares the three read-out options.

Option	Description
Your read-out electronics	For integration in final products (*i.e.* calorimeters, synthesis stations), the combination with specifically adapted electronics is inevitable. The adaption to your system strongly depends on your overall design.
greenTEG electronics	We provide custom fabricated electronics to measure calorimetric power in the µW to W range. Contact us for more information.
Multimeter	Optimal solution for infrequent usage, especially for testing. Depending on your needs, a multimeter with data transmission via USB or Bluetooth might be applied.

Table 2: Options for electronic read-out of power measurement.

Working principle:

In the absence of endothermic or exothermic reactions in the reaction vessel, the temperatures of the reaction vessel and of the heat sink are the same. There is no heat flow between the two reservoirs and therefore no signal is recorded.

As soon as heat energy is released or absorbed in the reaction vessel, there will be a net heat flow through the sensor. When the reaction ends and thermal equilibrium is reached the heat flow will be equal to zero again.
By measuring the heat flow over a certain time, one can derive the energy difference between the two states.

The sensor output voltage V_{out} is proportional to the heat flux q. The heat flux q is measured in the dimension of W/m^2. In order to get the amount of heat energy ΔE crossing the vessel surface, the heat flux must be multiplied by the measurement time Δt in seconds and by the outer surface A of the reaction vessel in square meters. A calibration constant S_C (unit $V/(W/m^2)$) is further needed to establish the proportionality between voltage and heat flux (See formula below).

$$\Delta E = q \cdot A \cdot \Delta t = (V_{out} / S_C) \cdot A \cdot \Delta t \quad [J]$$

ΔE: energy change [J], q: heat flux [W/m^2], A: vessel surface [m^2]
Δt: measurement time [s], V_{out}: voltage output of the sensor [V]
S_C: calibration constant [$V/(W/m^2)$]

V_{out} is the output of the sensor of the gSKIN® sensor in Volts. The calibration constant S_C is a unique value provided in the documentation of the sensor.

If you need to calculate the molar energy ΔE_{mol} of your reaction, you further need to multiply the energy ΔE by the molar mass and divide by the mass of your substance:

$\Delta E_{mol} = \Delta E \cdot M/m$	[J/mol]	ΔE_{mol}: molar energy change [J/mol] M: molar mass [g/mol], m: mass [g]

Please refer to appendix 1 of this document for a step by step tutorial of a simple calorimetric measurement.

Appendix 1: Tutorial: A measurement with the gSKIN® sensor

Goal: To measure the molar enthalpy of dissolution of a salt in water. 10 g of a salt with a molar Mass of 100 g/mol will be dissolved in 100 ml Water in a vessel with an outer surface of 104 cm2.

You need: A setup as shown in figure 1 and the substance to be tested.

Make sure that all components involved in the measurement are at room temperature. The ambient temperature must not fluctuate during the measurement. Isolate your setup from direct air currents. If you use water as the heat sink, make sure to cover it in order to avoid artifacts due to evaporation.

1. Connect the readout data logger to the sensor. Set the measurement rate of the data logger to 1Hz = 1 data point per second (faster rates are possible but rarely necessary).

2. Before starting the reaction, check the output value of the sensor. The output signal should be very close to zero. If this is not the case, wait for the system to equilibrate. There may also be a problem with the accuracy of the readout device[1].

3. Start the data logger.

4. Put the salt into the reaction vessel.

5. Wait for the salt do dissolve and let the system some time to reach thermal equilibrium. This may between 5 to 60 minutes, depending on the volume of your sample.

6. Load the measurement data into a spreadsheet. The picture below shows an example of a measurement over 20 minutes (1200 data points) using the greenTEG data logger.

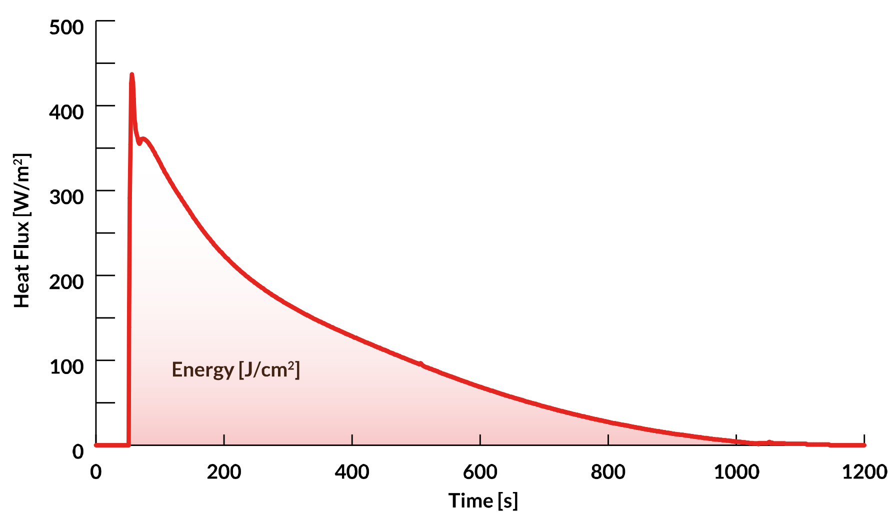


Figure 2: Typical measurement curve as recorded with the greenTEG data logger. The shaded area included by the curve is proportional to the reaction energy.

7. Convert all measurement values ($q_1, q_2, \dots q_n$) into the unit W/m2. If you are using the greenTEG data logger, the output is already converted to W/m2. If you are using a voltmeter, convert the values using the relation $q = V_{out} / S_C$

[1] If you have a small constant offset, you may just substract it from the measurement signal.

8. Calculate the total energy released ΔE. You need to summate all measurement points (q_1, q_2, … q_n), correct for the measurement rate f (usually f = 1 Hz) and multiply by the outer vessel surface A according to the following formula:

$\Delta E = (q_1+q_2+...+q_n) \cdot 1/f \cdot A$	[J]	ΔE: energy change [J], q: heat flux [W/m^2] f: measurement frequency [Hz], A: vessel surface [m^2]

9. The molar enthalpy of dissolution can be derived as follows from the molar Mass M and the mass of the dissolved salt:

$\Delta H_S = \Delta E \cdot M/m$	[J/mol]	ΔH_S: molar enthalpy of dissolution [J/mol] M: molar mass [g/mol], m: mass [g]

A short video on Youtube (http://www.youtube.com/watch?v=UWksEiJAaLk) shows an example of a calorimetric measurement.

Appendix 2: Setup correction factor

Every sensor is carefully calibrated by greenTEG using a standard procedure. However, once the sensor is integrated into a custom setup, the sole calibration constant may not prove satisfactory due to the unique thermal boundary conditions of the system. These influences can be compensated by introducing a setup correction factor X_{corr}.
The correction factor of any self-made measurement setup can be easily derived with the help of hot water and a temperature sensor. The combined heat flux/temperature data logger provided by greenTEG will work best for this task. How to proceed:

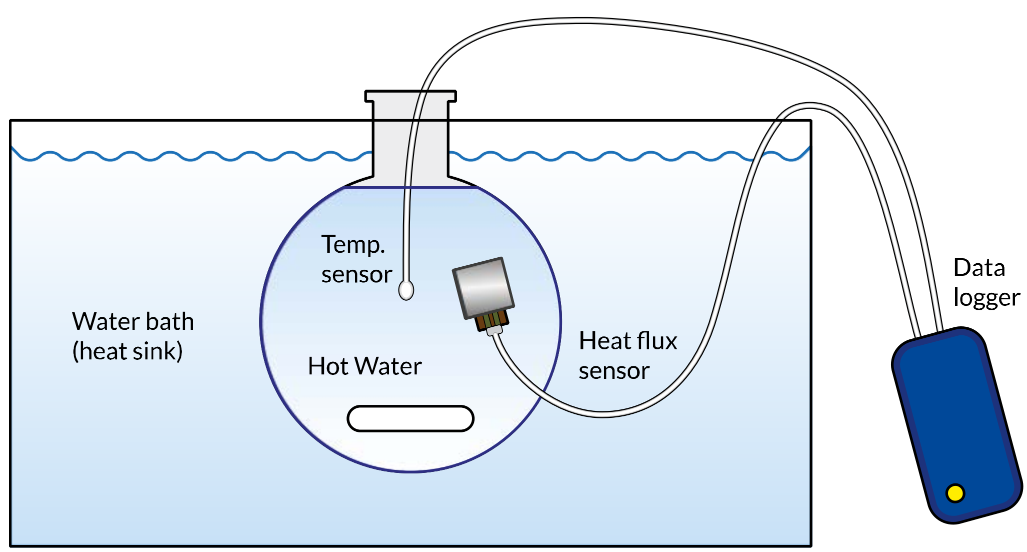


Figure 3: How to calibrate your system with hot water.

1. Set up your experiment as shown in figure 4.
2. Pour an exact amount of hot water into the reaction vessel. Choose water temperature slightly above your expected experimental conditions.
3. Wait 1 minute for the system to equilibrate.
4. Start data logger and record contemporaneously both heat flux and water temperature until the water temperature has reached room temperature.
5. Select a temperature range ΔT that best represents your experimental conditions (e.g 40 - 30 °C).
6. Calculate the energy released while the temperature was in that temperature range (see Figure 5). For data analysis, proceed as explained in appendix 1.
7. Divide the obtained molar energy by ΔT. This value corresponds to the heat capacity of water in this temperature range.
8. The correction factor X_{corr} is calculated by dividing the theoretical value by the measured value: $X_{corr} = c_p$ (theoretical)/c_p (measured).
9. Multiply all your future measurement values with X_{corr} to correct them.

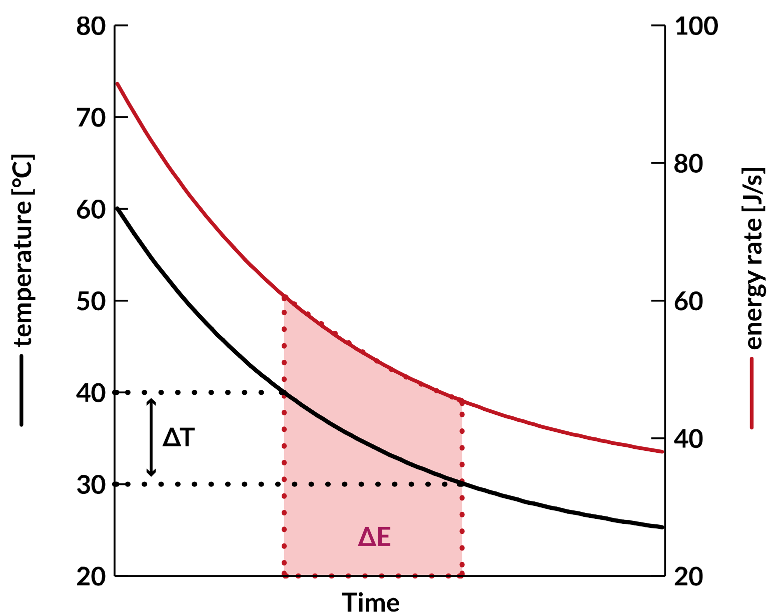


Figure 4: Schematic of a setup calibration as described in the main text. As the water cools from 40°C to 30 °C it releases heat energy. The amount of energy released during that time corresponds to the (known) heat capacity of water between 30 °C and 40 °C.

Appendix 3: Sensor specifications

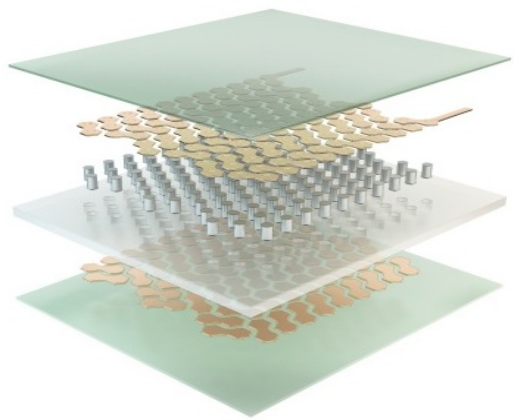


Figure 5: Explosion view of a standard gSKIN® sensor.

Figure 2 illustrates schematically the structure of the gSKIN® sensor.

The thermal sensor consists of axially aligned semiconductor thermocouples connected in series. These thermocouples are embedded in a polymer matrix (transparent in Figure 2).

The sensor is electrically insulated with a layer of epoxy (green in Figure 2). This layer also ensures that the sensor is shielded from environmental influences such as moisture and oxidation.

Many properties of the sensor can be customized to your specific system and application requirements. Appendix 5 gives an overview of customization options.

	gSKIN®-XE 23 9C	**gSKIN® sensors portfolio**
Surface type	Aluminum	Various material and coating options on request
Dimensions[2] [mm x mm]	8.5 mm x 8.5 mm	3 mm x 3 mm to 40 mm x 40 mm (shape customizable)
Thickness [mm]	0.4	
Sensor Output Signal	Bipolar voltage output	
Electrical Resistance [Ω] at 25 °C	<5	
Operating Temperature Range Min / Max [°C]	-50 °C / 200 °C	
Sensitivity [µV/(W/m²)]	~1 .9	Up to 50
Read out electronics	Voltmeter and data logger (not included)	greenTEG read-out electronics
Minimum Power Resolution [J/s]	2µ	
Response Time (0-95%) [s]	0.8 s	0.1 s
Calibration Accuracy [3] [%]	+/- 5 %	

Table 3: Specifications of gSKIN® thermal sensors.

[2] The sensor dimensions correspond to the active area.
[3] The accuracy of the sensor may not be directly applicable to your calorimetric system. It is strongly recommended to determine the correction factor of sour setup as described in appendix 2.

Appendix 4: Customization options

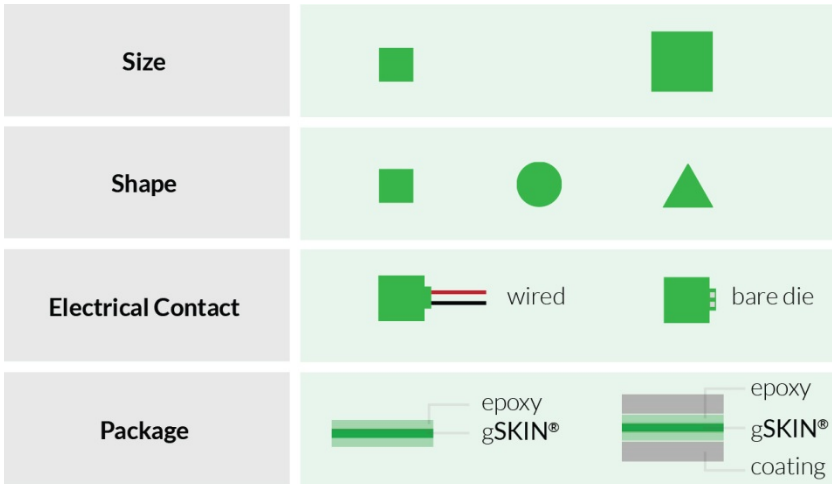


Figure 6: Customization options of size, shape, electrical contact and package.

Document information

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Pictures by greenTEG AG and Flickr
Video Calorimetry: http://www.youtube.com/watch?v=UWksEiJAaLk