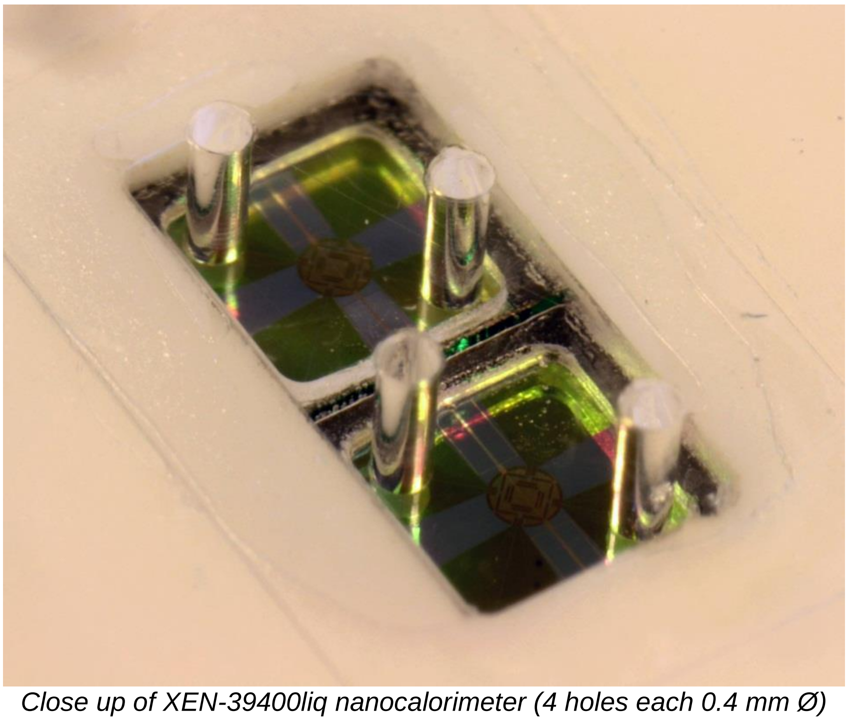
Liquid Nanocalorimeter

XEN-39400liq

Preliminary datasheet



Close up of XEN-39400liq nanocalorimeter (4 holes each 0.4 mm Ø)

Inhoud

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1 Introduction

1.1 About this Application Note

This Application Note is intended to help the users of Xensor Integration NanoCaloriMeters and interface electronics with the set-up and execution of their experiments. It will give some theoretical background information, practical guidelines, specific applications and references to the work of other users.
The Application Note is by no means exhaustive. This means, that if you miss something and have questions, or if you have useful information or interesting applications that you want to share, we highly appreciate your contribution to improving this note.

2 Short description

Introduction
There are several types of nanocalorimeter chips available from Xensor, based on thicker monocrystalline silicon membranes and based on thin silicon-nitride membranes.

The first types have low thermal isolation, but are very robust, they are well suited for use in liquid and slow applications (XEN-LCM2506, XEN-LCMquad, XEN-NCM9924).

The second type is fragile but very well isolated and fast, this is more suited for application in gaseous environments and for fast measurements, such as scanning calorimetry (XEN-TCG3880, XEN-3939?-series and XEN-39400 for the Flash DSC1 from Mettler-Toledo).

A new, third type, the XEN-39400liq, is now based on the fragile silicon-nitride membrane but still suitable for liquids. The XEN-39400liq will fit on the Flash DSC1 from Mettler-Toledo with very slight modifications.

This sensor is currently not supported by Mettler-Toledo.

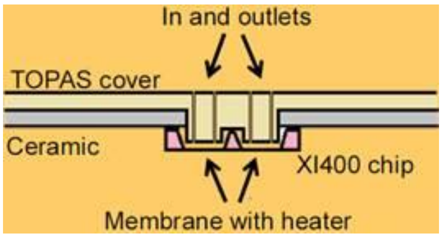
XEN-39400liq
The XEN-39400liq calorimeter is a dual-cell fast liquid differential scanning calorimeter chip (FLDSC chip). The chip is mounted on a standard ceramic plate with TOPAS® cover plate to enable differential scanning calorimetric measurements in liquids.
The chip is based on the standard FDSC chip used on the Flash DSC1 of Mettler-Toledo. For use on the Flash DSC1 a modified press-ceramic-down part is required.
The cover prevents evaporation of the liquid, which would give a very high interfering power signal, completely overshadowing any signals from interesting phenomena in the sample.
The cover also creates a very narrow gap of about 35 μm between the sensor's heated area and the cover itself, thus well defining the volume of liquid sample participating in the calorimetric measurement, which is about 15 nl. The narrow gap allows fast scanning rates in the liquid of up to 1000 K/s.

The sensor is suitable for use at room temperature.
For use at lower temperature, down to -100 °C, contact Xensor for special version.

Figure 1 Top view of FLDSC chip. The large square is the ceramic, the slightly smaller square is the plastic cover.

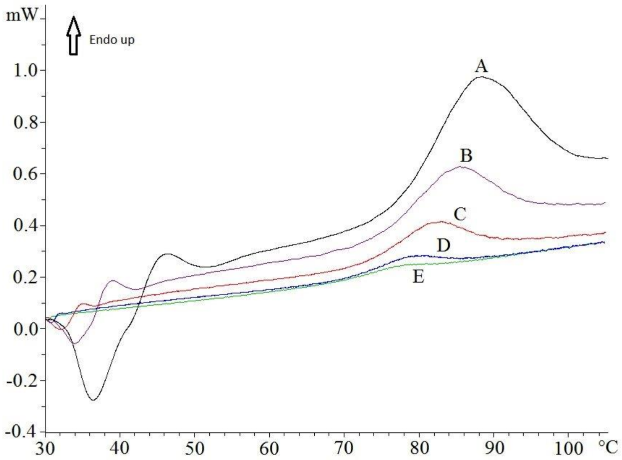
Figure 2 Close-up of the cavities and cover, showing the inlet and outlet holes for the liquid.

Figure 3 Schematic cross-section of the calorimeter.



In practical experiments where reversible and irreversible denaturation of proteins in water or in blood serum is measured, the best results were obtained with scanning rates of 20-500 K/s. The results obtained with the XEN-39400liq FLDSC chip are comparable to results obtained with standard DSC measurements at 1 K/min typical scanning rate. Thus, a measurement between 30 ºC and 105 ºC takes a few hours in DSC, but only some seconds in FLDSC, needing a µl of sample instead of ml's.

Figure 4 FLDSC measurements with XEN-39400liq of a 10% lysozyme solution at varying temperature scan rates, performed on the Flash DSC1 of Mettler-Toledo. Temperature scan rates: curve A: 200 °C/s, curve B: 100 °C/s, curve C: 50 °C/s, curve D: 20 °C/s and curve E: 10 °C/s.



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2.1 Applications

Below is a list of (known) applications of the nanocalorimeter sensors. For more on applications see the overview article in Thermochimica Acta (2005) in Section 4.6, available on www.xensor.nl.

application	*sensors*	*references [chap. 5]*
Fast scanning calorimetry	XEN-LCM2506, XEN-LCMquad, XEN-NCM9924, XEN-TCG3880, XEN-39400	Rostock, Inst. Analysentech.
Enzymatic blood analysis	XEN-LCM2506, XEN-LCMquad, XEN-NCM9924, XEN-39400liq	Ciba, Freiberg
Electronic nose	XEN-LCM2506, XEN-LCMquad, XEN-NCM9924	Freiberg
Liquid calorimetry	XEN-LCM2506, XEN-LCMquad, XEN-NCM9924, XEN-39400liq	Freiberg
Thermal analysis	XEN-LCM2506, XEN-LCMquad, XEN-NCM9924	Catalonia
Mixing reaction heat detection	XEN-LCM2506, XEN-NCM9924	

3 Technical data

3.1 Specifications of XEN-39400liq

Table 3.1 Specifications (typical parameters at ambient temperature 22 °C)

Parameter	*typ*		*unit*	*symbol*	*notes*
Dimensions					
housing size	24x24x2		mm^3		Including cover
chip dimensions	5x3.3		mm^2		
membrane size	1.6x1.6		mm^2		Per membrane
membrane thickness	2		µm		
heater area	0.5		mm		Diameter
sample height	0.03-0.04		mm		Gap between membrane and cover
heated sample volume	15		nl		
Output					
in air at 1013 mbar	13		V/W		With TOPAS cover (24 V/W without cover)
Filled with water	5.5		V/W		
Scan rate					
maximum	1000		K/s		In water
minimum	10		K/s		In water
Noise power					
Peak-to-peak noise	2		µW		At 10 000 samples/second (smoothing is recommended)
Thermopile					
resistance	13		kΩ	R_{tp}	
nominal sensitivity	2.4		mV/K	S_{tp}	
Heater					
Main resistance	5		kΩ	R_{main}	
Compensation resistance	4		kΩ	R_{comp}	
temperature coefficient	0.1		%/K		
Thermal resistance					
membrane	2		kK/W	R_{th}	In water
Sensor ambient temp					
typ	20		°C		
low temperature	-100		°C		Special version on request
Heater max temp	150		°C		In the absence of air bubbles

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4 Extended description and general notes on use

4.1 Nanocalorimeter operation principle

Why calorimeter chips
Calorimetry is the science of the measurement of thermal properties of materials, or the measurement of heat released or absorbed during reactions or phase changes. In traditional calorimeter instruments, crucibles, miniature ovens and thermocouples are put together by fine machining and assembly to manufacture the thermal measurement environment. This leads to certain characteristics of these instruments, certain time constants and minimum amounts of sample to perform the measurement.

In some cases, the physics or circumstances of real life demand that analyses be performed faster, or that smaller sample masses be analyzed. For this, calorimeter chips have been developed, which combine the functions of crucible, oven and thermocouple in a single chip of silicon with integrated circuits in it. This makes the calorimeter much smaller and faster, which allows for the analyzing of smaller samples with greater speed.

Passive and active measurement
There exist two types of thermal measurement, the passive type and the active type.
In the *passive type*, such as measuring material properties, energy has to be supplied to the material, after which the changes in the material can be observed.
In the *active type*, such as measuring chemical reactions, the chemical reaction supplies the energy for the measurement, and this measurement can be carried out without any biasing.

Calorimeter chips integrate the functions to carry out both types of measurements. A typical calorimeter chip consists of a thin membrane, suspended in a (0.5 mm) thick frame (the rim) of silicon. A thermopile integrated in or on top of the membrane measures the temperature increase of the center of the membrane with respect to the frame, and heaters in and around the center of the membrane are used to create the desired temperature (increase) in the center of the membrane, compared to the frame.

In general, calorimeter chips (or nanocalorimeter chips to indicate the minute amounts of heat and sample that can be measured) are used within a static isothermal environment.

For a *passive measurement*, the middle of the membrane, the active area, is varied in temperature –as measured with the thermopile- with the heaters to bring samples on the active area to the desired temperature, or to subject samples to a specific temperature profile (in a predetermined rate of temperature change), to observe the behavior of the sample with temperature (changes).
Two main techniques exist.
The *simple one* biases with a steadily rising amount of power, and measures the temperature profile. When a sample absorbs heat due to melting or another phase change, the temperature will lag behind, and this lag is a measure of the amount of heat absorbed.
The *more accurate one* uses feedback, and maintains a certain temperature profile by supplying the needed amount of power. Now, when the sample absorbs heat, this is seen as a temporary rise in the power needed to achieve the desired temperature profile. The excess energy supplied is now the direct amount of energy absorbed by the sample. This method is more accurate and direct, but more difficult to implement.

For an *active measurement* the output voltage of the thermopile is simply measured to give data on the heat output of the process. The heaters can now be used to advantage for a first order calibration of the transfer of the device, i.e., the output voltage obtained for a certain power supplied by the reaction. In general, corrections have to be made when the heating pattern by the reaction is not identical to that of the heating resistor. In that case, they will not give the same transfer in Volt/Watt. This especially applies to measurements in liquids and liquid flows. Prof. Torra from the Univ of Catalonia and Dr. Lerchner from the Freiberg Bergakademie (see References) have done a lot of work in this modeling.

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4.2 Types of calorimeter chips

Xensor Integration offers various types of calorimeter chips. One type is made with monocrystalline silicon membranes of 4-45 μm thickness. Other types have silicon-nitride/oxide membranes of in total about 1 μm thickness.

Silicon membrane liquid calorimeter chips
The silicon membrane chips are characterized by a low thermal resistance, a robust membrane, high sensitivity of the thermopile and larger time constant. And the membranes are generally fairly large, 4-8 mm in lateral size. They are especially well suited for use in liquids, since the liquid environment requires robust membranes that will not break when slight pressure or pressure shocks are present. Moreover, the liquid, especially in a flow-through analysis, strongly decreases the thermal resistance between center and edge of the membrane, even for the silicon membranes that already show a low thermal resistance. Measurements in liquids are usually performed in a constant temperature environment. The temperature range in which these sensors are operational is typically between -30 °C and 100 °C.

Silicon-nitride membrane calorimeter chips
The silicon-nitride membrane chips are characterized by a high thermal resistance to the ambient, a very small time constant and more fragile membranes. This makes these sensors particularly suited for measurements in gaseous environments on small samples with high temperature scanning rates. Temperature scan rates of up to 10 MK/sec have been obtained by Prof. Schick at Rostock University (see References), where traditional calorimetry instruments stop at 1 K/sec, or 10 K/sec for advanced models. Thus, in milliseconds, a complete measurement is carried out. Here typical temperature ranges are from 20 K up to 450 K for the frame, while the membrane center, with the sample, can go up to 800 K for very short periods of time. Calorimeter chips with high-temperature materials, such as gold for interconnections, can even measure up to 1250 K. Thus, the range of these sensors comes closer to that of basic calorimeter instruments.

Silicon-nitride membrane liquid calorimeter chip
New is the XEN-39400liq, which is a calorimeter chip based on a silicon-nitride membrane, but suitable for measurements with liquids. Because this chip is derived from the chip used for the Flash DSC1, it can be operated on this machine. But it can also be operated with a customer-made calorimeter set up.
While this chip is somewhat more fragile than liquid calorimeter chips with very thick silicon membranes, it can be used in practice rather well. And because of the very small volumes of sample being subjected to the temperature program, surprisingly high scanning rates of up to 1000 K/s are feasible without significant smearing of the peaks.

4.3 Handling of the XEN-39400liq

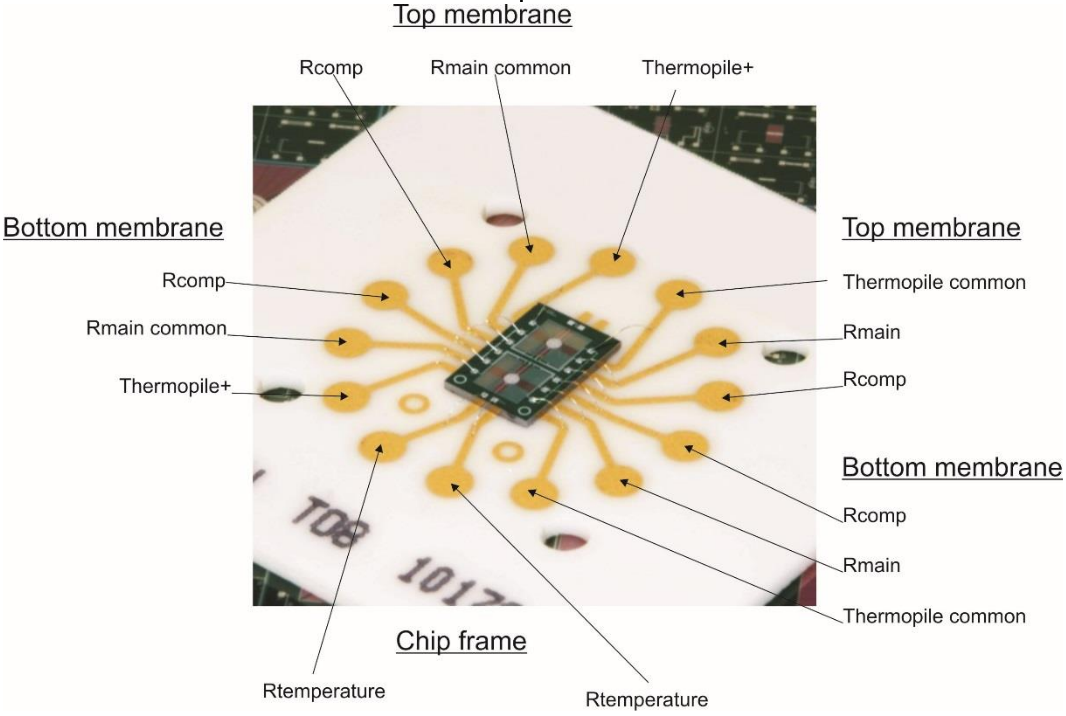
Feeding the liquid
Application of the liquid to the sensor is rather easy to do, feeding the liquid with a tube and needle into one of the holes in the cover, while the other hole serves to let out air.
Usually one cavity is used for the liquid sample, while the other is filled with a reference liquid. For water-based samples, this would be water, for buffer-based samples it would be buffer, etc.

Cleaning
Because of the fragility of the sensor, and the presence of a cover to prevent spurious signals by evaporation, cleaning of the chip is difficult in case of aggregation of proteins. Otherwise sensors can be reused after cleaning for a limited number of experiments.

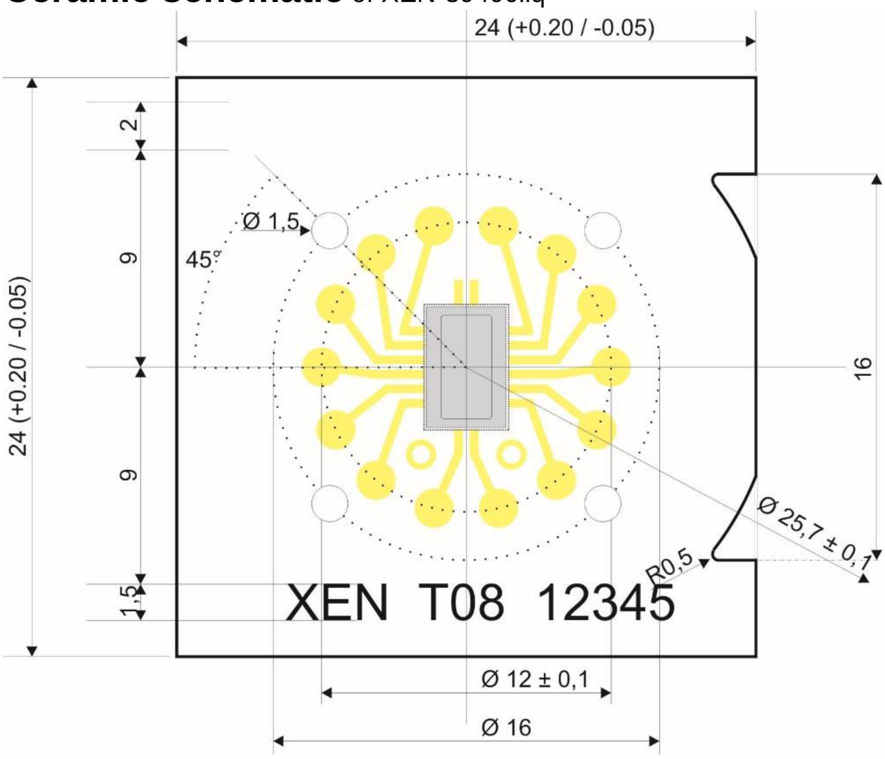
Air bubbles
The presence of air bubbles may influence the measurement, so that is to be avoided. In the absence of air bubbles, the heater may be heated up to a temperature of even 150 °C without boiling. If an air bubble is present, boiling may occur at such high temperatures and the membrane can rupture.

4.4 Description of the sensors

Pin out schematic of XEN-39400liq



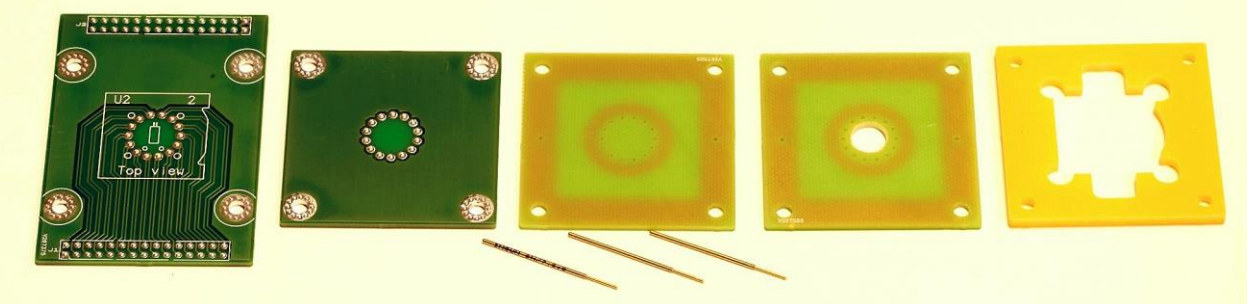
Ceramic schematic of XEN-39400liq



5 Holder for XEN-39400liq

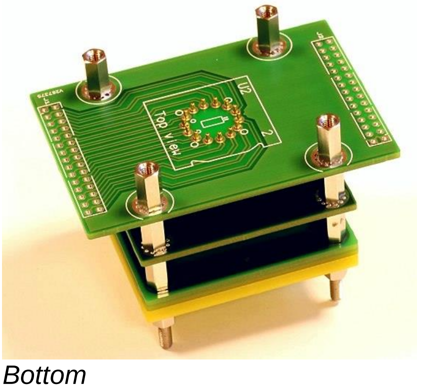
In case a Flash DSC1 from Mettler-Toledo is not available we can supply a holder (order code: XEN-86000). Supplied are 14 spring loaded contacts + 5 prints:

1. electronics connection print
2. guidance print
3. fine guidance print
4. fine guidance with hole print
5. ceramic alignment print

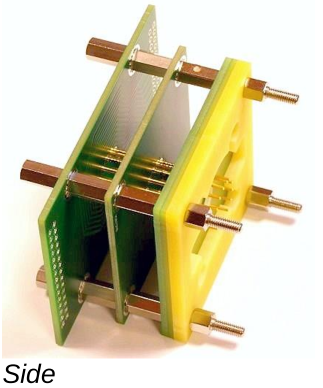


Prints: electronics connection + guidance + fine guidance + fine guidance with hole + ceramic alignment
Spring loaded contacts: 3x shown

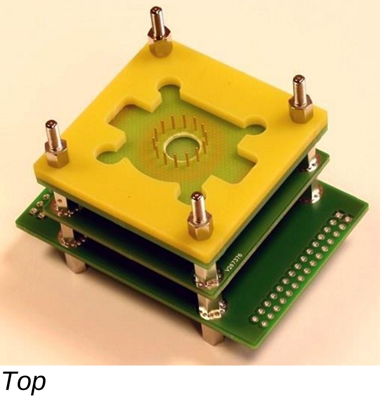
- Assembly has to be done by yourself. The spring loaded contacts should be about 2.5-3 mm above the surface of the fine guidance with hole print.
- Arrange pressing down of ceramic onto spring loaded contacts by yourself.
- 4 contacts to each pin.



Bottom



Side



Top

Top with XEN-39400liq mounted

6 Toolkit for XEN-39400liq

To bring in liquids in the sensor and to clean the sensor with air a toolkit (order code: XEN-86010) is available, consisting of:

XEN-86010: tool kit for XEN-39400liq

- 2x Syringes 5 cc.
  One for bringing in the reference material (for instance demi water or butanol), one for cleaning with air.
  Remark: the sample is brought in using a pipette. Xensor uses pipette tips of 2-200 microliter.
- 2x 30 cm silicon tubes, to be connected to the syringes.
- 6x needles, to be connected to the tubes.

Toolkit: parts

Toolkit: mounted

7 References

For articles on nanocalorimeters see our website:
www.xensor.nl/index.php/publications

In general for the work of the group of Prof. Schick, see their web site:
http://www.polymerphysik.uni-rostock.de/