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Report

Report on the workshop “Nanocalorimetry”

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In the year 1997 the 12th Ulm-Freiberg Conference on calorimetry was concerned for the first time with current tendencies of the miniaturization of calorimeters in the context of a separate workshop. At that time by E. Gmelin in a review lecture [1] techniques, applications and limitations of the scanning thermal microscopy (SThM) were presented and discussed. First applications of silicon chip based calorimeters were demonstrated by G. Wolf. Since it is probably obvious the fact that it concerns topical developments, on the occasion of the 13th Ulm-Freiberg Conference in a similar workshop should be discussed, to what extent the tendencies determined at that time continued, whether there are new instrumentation concepts for miniaturized calorimeters, where their limitations lie, to what extent application fields resulted and/or whether the application of miniaturized calorimeters is supported sufficiently by commercial developments. Like already two years ago apart from the actual calorimetry in a part equal from the scope also features of SThM were discussed, since concerning the common basis measuring technique similar aspects are interesting.

The workshop was introduced by E. Gmelin with a short overview about the state-of-art. A relevant bibliography is available on request. In each case three short contributions were held on the topic ‘Miniaturized Calorimeters’ (Caspary, Weber, Zieren) and on the topic ‘Scanning Thermal Microscopy’ (zur

Mühlen, Breitenstein, Kessler). The discussion was moderated by J. Lerchner.

With the contribution of D. Caspary (Freiberg) about a silicon chip based flow-through calorimeter for the determination of heats of absorption of vapors at thin layers a basic discussion about goals and benefits of the miniaturization of calorimeters was initiated. With the described device amounts of heat of $1 \mu\text{J}$ can be determined with a resolution of approximately 60 nJ. On the other side, cantilever calorimeters (see i.e. [2]) are able to detect only a few nJ with a resolution in the pJ range. Does that mean a progress? Looking at the data in Table 1 it seems clear that it must be discussed more differentiated. Thus, one must ask the question, how it comes to such a high heat resolution, i.e. under which conditions this is reached, and to what extent this heat resolution is usable. Calorimeters constructed on the basis of thermopile chips and cantilevers are comparable, since both devices can be regarded as heat flow calorimeters. The calorimeter described by Lai [3] which is also specified in the table is a chip calorimeter too; however it operates likewise as an adiabatic one. Determining for the excellent heat resolution is its extremely low heat capacity. Basis values of the heat flow calorimeters are the heat power resolution data, which are not so different in both cases. Remarkable differences in heat resolution of some orders result because the width of the input heat power pulses can be much lower in the case of the cantilever calorimeters due to their time constant of only 0.5 ms. If the pulse width is considerably lower than the thermal

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Table 1
Typical parameters of miniaturized calorimeters

	Chip calorimeter adiabatic [3]	Chip calorimeter heat flow [4]	Cantilever calorimeter heat flow [2]
Heat power resolution σ_p		0.27 (0.038) ^a μW	0.3 μW
Typical heat value q	39 nJ	1 μJ	3 nJ
Heat resolution σ_q	0.2 nJ	0.45 (0.062) μJ	0.5 nJ
Typical sample mass m	2.3 ng	150 μg	40 pg
Active area A	4 mm^2	16 mm^2	3.3 10^{-3} mm^2
Mass specific heat resolution σ_q/m	90 mJ g^{-1}	3.0 (0.4) mJ g^{-1}	12.5 J g^{-1}
Area specific heat resolution σ_q/A	0.05 nJ mm^{-2}	27.6 (3.8) nJ mm^{-2}	151 nJ mm^{-2}
Heat capacity C	6 10^{-4} mJ K^{-1}	1.3 mJ K^{-1}	4.9 10^{-6} mJ K^{-1}
Time constant τ		30 ms	0.5 ms
Typical pulse width Δt	2 ms	2 s	1 ms

^a Data in parenthesis correspond to 100 fold accumulation.

time constant of the device, the heat power resolution worsens linearly with the time constant. Further, the ratio of heat or heat power resolution and the usable sample mass is of substantial interest. The limited heat power density of the process leads to the decrease of the measurable total power with due to a reduction of the sample mass. In general this cannot be over-compensated by the increase of the measurement resolution as shown in the table and consequently a decrease of the signal-to-noise ratio results. As conclusion one can state that miniaturized calorimeters should be applied if it requires the sample size and if the inevitable loss of accuracy is tolerable. Advantages over conventional devices result particularly if short heat power pulses are to be measured. Main restrictions are due to the limited heat power density of the processes under investigation.

For the first time calorimeters for liquid fluids, also miniaturized, played a larger role in this conference. M. Zieren (Jena) presented an interesting overview about technological possibilities of the design of multi-chip flow-through calorimeters. The design combines a free-standing membrane within a silicon frame and a glass chip with wet-etched reaction channel connected by glue-bonding. BiSb/Sb-thermocouples in series are deposited by electron beam evaporation and photographically pattern. The heat power resolution is in the region of 1 μW at flow rates of 30 $\mu\text{l min}^{-1}$. As pointed out by A. Weber (Freiberg) the residence time and the degrees of mixing evolve as crucial parameters of miniaturized flow-through calorimeters. Because of the laminar flow mixing is only possible by diffusion, and further, the low volume

of the reaction chamber decreases the residence time which is especially disadvantageous in the case of kinetically controlled reactions. It appears, that for chemical reactions with low rate constants the modular arrangement of a highly efficient micromixer with a miniaturized flow-through calorimeter results in optimal operation conditions (M. Zieren). Nevertheless, calorimeters of this kind will not be applicable for thermo-chemical tasks. But they should have some potentials for flow injection analysis as A. Weber has shown. Using a miniaturized flow-through calorimeter as sensing device, mixtures can be analyzed by sequential combining with different reagent flows (i.e. enzyme solutions) and processing of the measured heat power pulse sequence (sequential flow injection analysis).

The main contribution of the second part of the workshop came from E. Zur Mühlen (Alzenau). He presented the first commercially available instrument for scanning thermal microscopy (μTA 2990 Micro-Thermal Analyzer). The μTA 2990 system consists of an AFM head with thermal probe, electronics control unit, and controller with data acquisition and analysis software. The thermal probe is scanned over the surface of the sample, simultaneously acquiring topography, thermal conductivity and thermal diffusivity images. Due to the applied modulated temperature technology the μTA 2990 system also provides depth profiling capability. Spatial and thermal resolution are in the range of a few μm and mK, respectively. A technology for scanning thermal microscopy with a temperature resolution of 10 μK but a spatial resolution of 100 μm was described by O. Breitenstein

(Halle). The score of the system is a temperature measuring bridge with a thermistor probe and applied lock-in technique.

That silicon thermopile chips can also be used for contactless thermal imaging, this was the message of the last contribution of the workshop (E. Kessler, Jena), opens up some new possibilities for an easy screening of i.e. the activity of catalyst samples.

All in all, it can be stated that the workshop witnessed a rising interest in miniaturized calorimeters and related techniques. This field is in its infancy and has not yet reached its full potential. It

is expected to grow rapidly in the area of new device design and novel applications.

References

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