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FRAUNHOFER-INSTITUT FÜR CHEMISCHE TECHNOLOGIE ICT

REACTION CALORIMETRY IN MICROREACTORS

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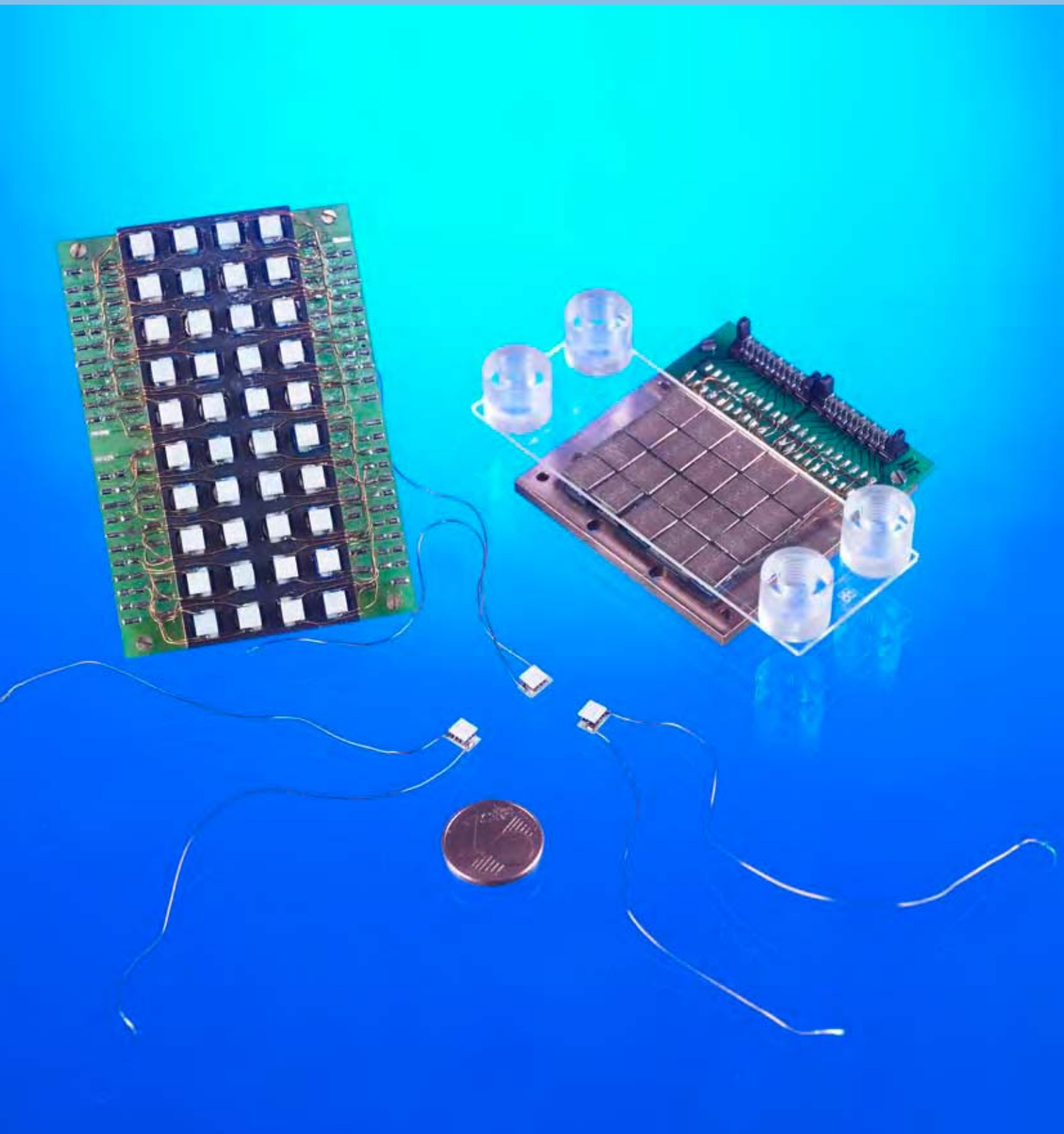


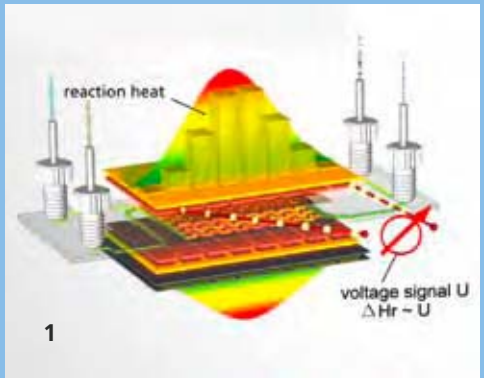
A POWERFUL TOOL FOR PROCESS DEVELOPMENT AND PROCESS OPTIMISATION

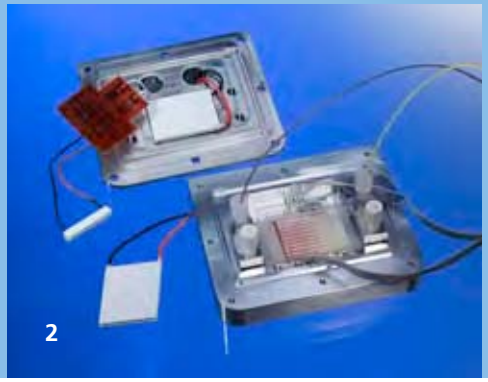
Together with ensuring safe process control, the energy efficient design and optimisation of chemical processes to minimise resource consumption is one of the fundamental demands of modern process design. Yet this requires knowledge of the thermodynamic and kinetic parameters, which in turn provide an in-depth understanding of the process and allow the definition of safe process conditions. Investigative measures, which provide a high level of information while simultaneously keeping experimentation times short are essential for the implementation of effective process design. The combination of microreaction technology with calorimetric measurement technology offers extremely promising methodical approaches in this field.

CALORIMETRY AS A UNIVERSAL METHOD OF ANALYSIS

The classical application of reaction calorimetry is the measurement of key data for evaluating the thermal process safety of chemical reactions. However, the range of potential applications for calorimetry is far wider as every chemical and physical process is characterised by the change of its energetic state. Calorimetry is therefore a universal analytical method for investigating thermal effects resulting from chemical or biochemical reactions and/or changes in physical states. Calorimetric measurements make it possible not only to make direct statements about thermodynamics but also about kinetics and physical constitutions. Knowing the heat flows that occur in a reaction therefore provides crucial information for the successful design and development of new chemical processes as well as for optimising existing processes. Measurement of heat flows is therefore an attractive methodical approach for developing new and rapid in-process analysis techniques.

Sensor arrays with up to 40 miniaturised Seebeck elements for spatially resolved, real-time measurement of heat flows. The sensor array can be adjusted to the dimensions of the microfluidic component being used.



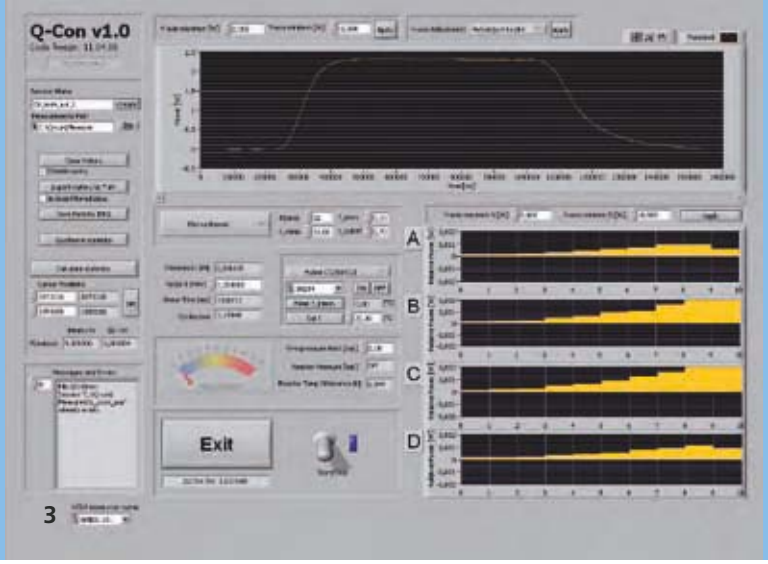


REACTION SCREENING IN MICROREACTORS

1 Measuring principle of "concal": spatially resolved measurement of heat flows.
2 Calorimetric cell with microreactor for liquid/liquid reactions.

In order to keep "time-to-market" as short as possible, it is important to have a detailed knowledge of the chemical reaction system even at an early stage of the process development in order to be able to make reliable decisions regarding synthesis and process management. Conventional reaction calorimeters have a relatively large reaction volume, which makes the subsequent processing of the reaction system very time- and cost-intensive. Due to the long thermal response time of the measurement systems, it is not possible to achieve an isothermic operation for strongly exothermic reactions. Furthermore, in the early stages of process development there are usually only small amounts of test substances available. Consequently, rapid screening of relevant process parameters cannot be performed in conventional reaction calorimeters.

To solve this problem, the Fraunhofer ICT has developed the "concal" measurement system – a small-volume, continuously operated µL-calorimeter based on microreactors, which permits rapid screening of thermokinetic key data. At the heart of the "concal" calorimeter are sensor arrays based on miniaturised Seebeck elements for the localised, quantitative characterisation of heat flows. The sensor arrays consist of up to 40 individual sensors, which can collect data concerning the reaction heat generated in a microreactor with a high degree of temporal and spatial resolution. Due to the large surface-to-volume ratio of microfluidic components and the resulting small time constants of just a few seconds, it is also possible to perform isothermal calorimetric measurements for rapid exothermic reactions. Even targeted investigations and quantitative analysis of the energetic potential of critical processing conditions (worst case scenarios) can be conducted safely. The test volume is extremely small (< 100 µL), which enables the consumption of materials to be reduced to a minimum, especially in the case of expensive chemicals.



The modular design of "concal" makes it possible to adapt the sensor arrays to different microreactors with differing dimensions and applications. A selection of processes that have already been analysed using "concal" shows the broad applicability of the measurement system for the calorimetric characterisation of chemical reactions in microreactors:

– Nitration of aromatics and alkylated ureas
– Lithiation and alkylation of aromatic compounds
– Polymerisation reactions based on acrylic acid
– Ozonisation reactions of cyclic alkenes
– Determination of mixing enthalpies
– and many more.

As well as being used for analysis of strongly exothermic reactions, the highly sensitive sensors also permit calorimetric observation of processes with low reaction heat as well as of endothermic processes.

The measurement software, based on LabVIEW, for controlling the measurement system and visualisation of the measured values is simple and intuitive to operate. During parameter screenings, the influence of individual process parameters (e. g. concentration, stoichiometry, use of alternative reactants, temperature, residence time, etc.) directly on the altered heat signal can be followed and quantified graphically on the screen. The measurement of the heat flows is in real-time; time-consuming calibrations for the heat transfer are not required.

The combination of continuous microreaction technology and efficient heat flow sensors based on miniaturised Seebeck elements thus opens the way to rapid and extremely efficient screening of reaction and safety-related parameters as well as the collection of thermokinetic key data for chemical processes.

3 *The clear layout of the "concal" measurement software interface allows operators to use the software easily and intuitively. The measured heat flows for the individual Seebeck elements are displayed graphically in real-time on the screen.*

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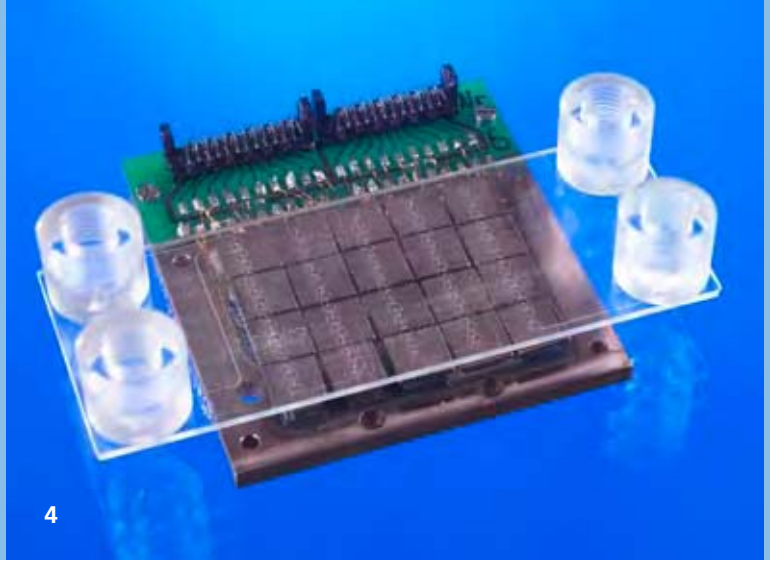

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IMPORTANT ADVANTAGES AT A GLANCE

- Reaction calorimetry in real-time
- Determination of thermokinetic and safety-relevant key data
- Rapid screening of reaction and process conditions
- Isothermal measurements even for rapid, strongly exothermic processes
- Minimisation of transport processes: determination of microkinetics
- No costly and time-intensive calibrations, simple to operate
- Small test volumes (<100 µL): minimal substance consumption
- Safe analysis of potentially dangerous reactions, even critical process conditions can be investigated
- The measurement principle can be adapted to a wide range of reactors and process components

OUR PRODUCTS AND SERVICES

We provide our customers and project partners with reaction calorimetry solutions based on microreactor technology for investigation and analysis of their chemical processes. We determine the thermokinetic parameters for your reactions and test the behaviour of your reaction systems under critical process conditions. Using parameter screenings, we determine relevant process parameters for process design and optimisation.

We supply the "concal" measurement system with the requested specifications and equipment to enable our customers to perform their own research. For special reaction processes and new areas of application, we develop customer-specific solutions on basis of the "concal" system. The spatial and temporal resolution of the heat flow measurement can be adapted to suit the intended application.

In addition, we offer a broad portfolio of other calorimetric measurement techniques as well as extensive R&D services in the areas of chemical process development, process optimisation and safety technology.

4 *Sensor array with 20 Seebeck elements for the two-dimensional calorimetric monitoring of the reaction progress in microreactors.*

PHOTO LEFT
Reaction calorimetry for real-time measurement of heat flows in a falling film microreactor for gas/liquid reactions. The sensor array makes it possible to make spatially resolved measurements of the heat flows within the falling film microreactor. The measurement software, based on LabVIEW, provides graphic visualisation of the measured heat flows.

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Fraunhofer-Institut für
Chemische Technologie ICT

Joseph-von-Fraunhofer-Strasse 7
76327 Pfinztal (Berghausen), Germany

Director:
Prof. Dr.-Ing. Peter Elsner
Phone +49 721 4640-0

Contact

Jürgen Antes
Phone +49 721 4640-340
Fax +49 721 4640-441
juergen.antes@ict.fraunhofer.de
www.ict.fraunhofer.de

For more information on microreaction technology at the Fraunhofer ICT, please visit:
www.microreaction-technology.info