CHEMICAL ENGINEERING TRANSACTIONS

VOL. 31, 2013

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

Guest Editors: Eddy De Rademaeker, Bruno Fabiano, Simberto Senni Buratti
Copyright © 2013, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-22-8; **ISSN** 1974-9791

DOI: 10.3303/CET1331150

Heat Exchange Elements in Sample Cells for Thermal Analysis

Georg W. Suter*, Volker Stocks, Carl Gwerder, Manfred Eiche

Swissi Process Safety GmbH, Schwarzwaldallee 215, CH-4002 Basle (Switzerland)
Georg.suter@swissi.ch

It is a basic assumption of micro calorimetric DTA and DSC tests that the temperature is homogeneous in the entire sample volume during the test. When using high heating rates or when investigating highly exothermic processes with high activation energy (highly energetic materials) this assumption may not be correct.

This paper deals with the elimination of temperature inhomogeneity in DTA and DSC sample cells by using heat exchange elements inside the cell. With this principle the thermal kinetics can be recorded even for highly exothermic processes with high activation energy, without signal distortion.

1. Introduction

In calorimetric measurements, in particular Differential Thermal Analysis and Differential Scanning Calorimetry, heat production rates are basically derived from measurements of temperature differences. Typically the difference between the sample temperature and some reference temperature (ΔT) is recorded, and – by using appropriate calibration factors – the heat production rate is derived from these values.

Basic Assumption

In isoperibolic, isothermal and dynamic testing modes of small scale (up to a few millilitres) testing equipment, it is assumed that

a) the relevant temperature difference is small
b) the temperature of the sample is homogeneous
such that data are representative for behaviour of the entire sample at the reference temperature.

The following effects have to be considered related to the ΔT values.

Design of the instrument and the sample container.

A high thermal resistance between the instrument and the sample (e.g. insulating layers, air gaps etc.) will increase the ΔT values, which means that even small heat production rates can precisely be detected. On the other hand, an instrument design optimized for low ΔT values will have a lower sensitivity than if higher ΔT values are achieved.

Heating rate

In dynamic test modes high heating rates increase ΔT values between that sample and the heating elements of the instrument, and – in case of exothermic processes in the sample – also between the sample and the reference temperature (Roduit, 2010)

Temperature inhomogeneity

Heating a sample, intrinsically is related to some temperature gradients inside the sample. The increase with increasing heating rate and are particularly relevant in dynamic testing modes. In addition, exothermic processes in the sample may lead to a non-homogeneous temperature distribution in the sample.

This paper deals with the reduction of the temperature inhomogeneity sample cells for DTA and DSC tests by using heat exchange elements inside the cell.

Please cite this article as: Suter G., Stocks V., Gwerder C. and Eiche M., 2013, Heat exchange elements in sample cells for thermal analysis, Chemical Engineering Transactions, 31, 895-900 DOI: 10.3303/CET1331150

2. The relevance of the basic assumption

2.1 Temperature differences between sample and reference

Significant temperature differences between sample and reference may occur e.g. in dynamic thermal analysis tests as a result of

- High heat capacity of the sample (cell)
- High heating rates
- High thermal resistance between the instrument (heating) and the sample

If in such cases the ∆T signal (or the power signal derived from it) is plotted against the reference temperature without without appropriate correction, exothermic signal show up at an apparently higher temperature (Figure 1).

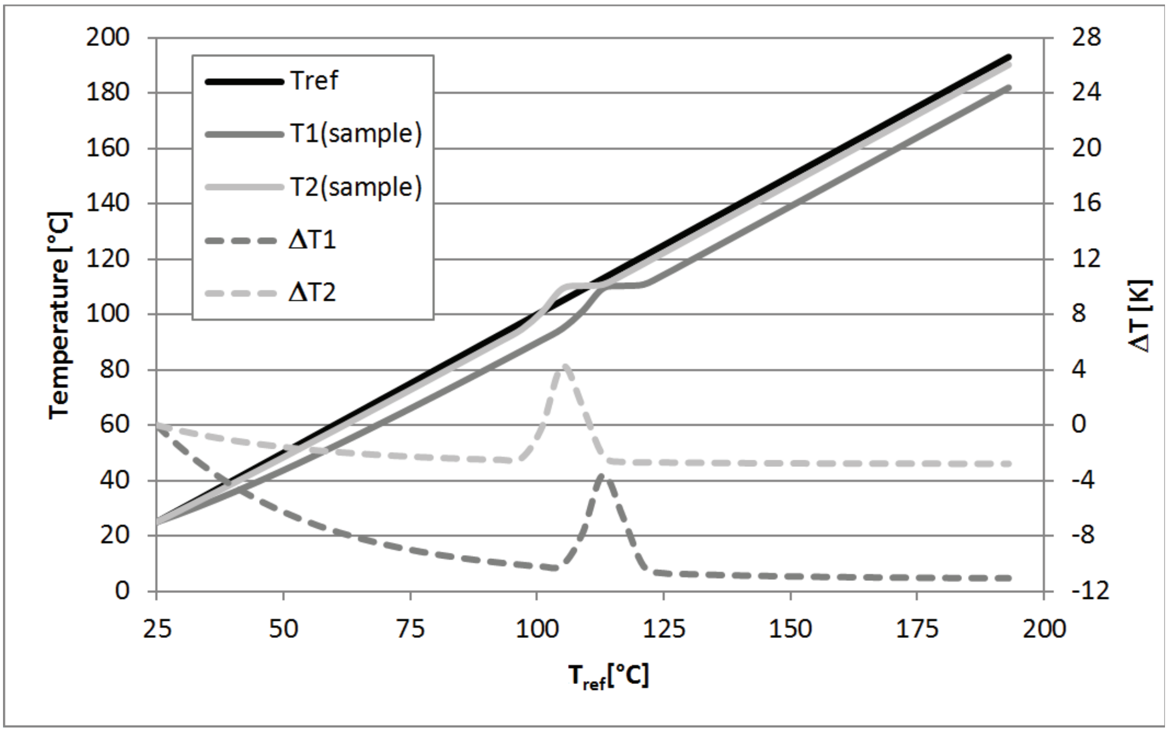

Figure 1: Effect of large ∆T values on the graphic representation of exothermic signals, if these are plotted against T_{ref}, without appropriate correction.

2.2 Non-homogeneous sample temperature due to external heating

During the heating process, the temperature inside the sample will not be homogeneous. Temperatures at the periphery of the sample will be higher than in the centre. (Figure 2a) shows the temperature distribution inside a cylindrical sample cell made of steel (diameter 1cm), filled with an organic powder, and heated from outside with a heating rate of 2 K/min.

The non-homogeneity increases with heating rate, increasing sample size and increasing thermal resistance within the sample.

Samples undergoing reactions, which have a reaction rate that depends strongly on temperature i.e. reactions with a high activation energy will behave differently in the centre of the sample (slow reaction) than outside. This will lead to a broadening of the DTA signals.

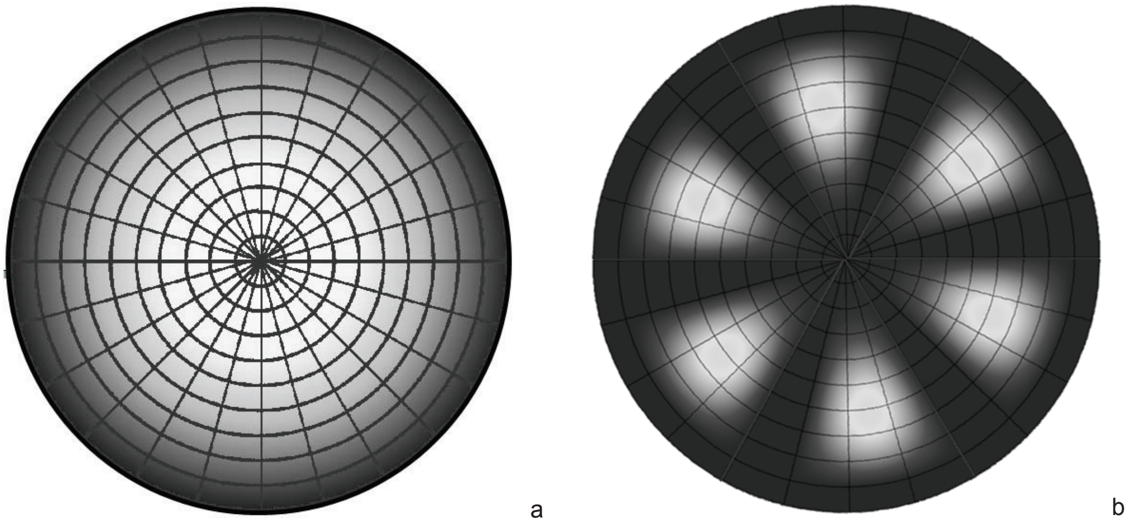

Figure 2: Calculated temperature distribution inside a steel sample tube (diameter 1cm, wall thickness 0.5mm) containing a solid powder heated from outside (Starting conditions at t=0sec: Sample temperature 25°C, outside temperature 120°C) The figures show the situation after 25 sec.
a) Standard sample tube: The temperature in the centre is still 25°C; b) Sample tube with six heat exchange fins; the minimum temperature is 70°C.

2.3 Non-homogeneous sample temperature due to exothermic reactions

Exothermic reactions may also lead to non-homogeneous temperature fields inside a sample., in particular, if the reaction rate and the reaction energy are high and the heat conductivity of the sample is small, i.e. typically for solid powders. In the extreme, even a thermal explosion may occur in a sample cell due to heat accumulation, as shown in Figure 3.

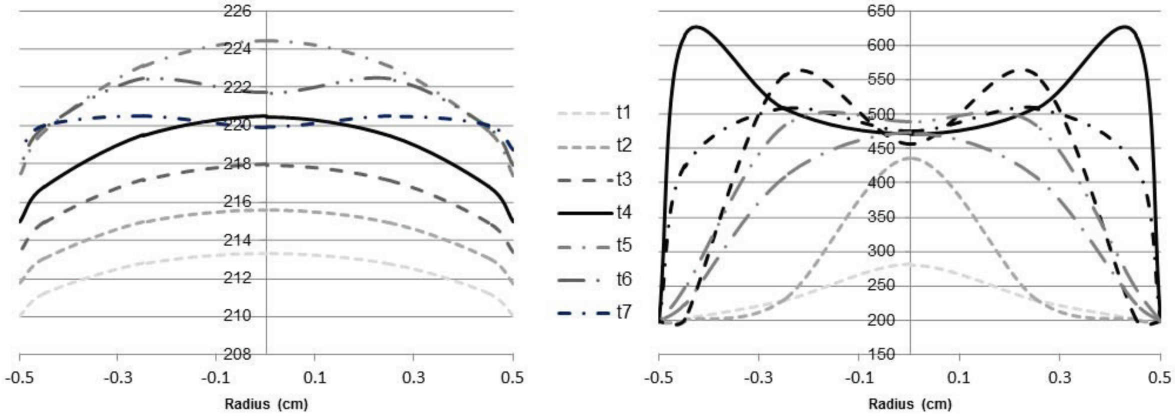

Figure 3: Temperature distribution inside a steel sample tube containing a solid powder undergoing an exothermic reaction at around 210°C. Cylindrical sample, diameter 1cm, Radius = 0.0 = center of the sample. t1 to t7 indicate temperature distributions in a sequence of time intervals. The left figure shows a subcritical situation (slow reaction, low reaction energy). At the right, a hot spot is formed in the center of the sample by a fast, highly energetic reaction. The reaction propagates from the center towards the wall of the sample cell (see curves at times t2, t3 and t4). Notice the different temperature scales!

2.4 Short summary of thermal explosion theory

In general such phenomena are analysed with the Franck-Kamenetzkii model, which describes the dependence of the critical heat production rate on the geometrical dimension of the container:

$$q'(T_{0,crit}) = \delta_c \times \frac{\lambda \times R \times T_{0,crit}^2}{\rho \times r^2 \times E_a} \tag{1}$$

The maximum temperature difference between the center of the container and the surrounding which does not lead to a thermal run away in the container is then given by:

$$(T_I - T_0)_{max} = \phi \times \frac{R \times T_{0,crit}^2}{E_a} \tag{2}$$

where

$q'(T_{0,crit})$	Specific heat production rate at T_0 [W kg^{-1}]
λ	Thermal conductivity [typically 0.1 W m^{-1} K^{-1}]
ρ	Bulk density [typically 400 - 700 kg m^{-3}]
E_a	Activation Energy [typically 100000 J mol^{-1}]
R	Gas Constant [8.31 J mol^{-1} K^{-1}]
$T_{0,crit}$	Critical temperature of the environment [K]
T_I, T_0	Temperature in the center of the container and of the environment [K]
δ_c, ϕ	Dimensionless parameters depending on the shape of the bulk material [-]
r	Dimension of the bulk material [m]

Sphere:	r = Radius	$\delta_c = 3.32$	$\phi = 1.60$
Layer, insulated on one side:	r = Thickness	$\delta_c = 0.88$	$\phi = 1.19$

The theory of thermal explosions is well established and frequently applied for the assessment of storage stabilities or processes involving large containers such as drums, bins and silos with reactive substances at elevated temperature (e.g. after unloading from a dryer).

However, it has been shown, that the same effects may appear in micro-scale, e.g. in micro reactors and DTA sample cells (Klais et al., 2010). Table 1 shows typical values for q' and the maximum temperature gradient in the sample as a function of the sample dimension r and the activation energy E_a. From these examples it can be concluded, that the situation might become critical in the millilitre/gram scale only for reactions with a high activation energy.

Table 1: Typical values for criticality (spherical approximation)

	E_a = 50'000 J mol^{-1}		E_a = 200'000 J mol^{-1}	
r [m]	q' [W/g]	$(T_I-T_0)_{max}$ [K]	q' [W/g]	$(T_I-T_0)_{max}$ [K]
0.100	0.017	41.6	0.004	10.4
0.030	0.192	41.6	0.048	10.4
0.010	1.727	41.6	0.432	10.4
0.003	19.194	41.6	4.799	10.4
0.001	172.746	41.6	43.187	10.4

Figure 4: Sample cells for the SETARAM C80 twin calorimeter: In the middle: conventional "beaker type" sample cell. Right: cell with six heat exchange fins- Left: cell 37 micro tubes.

3. The Effect of Heat Exchange Elements

In order to reduce the inhomogeneity of the temperature inside a sample, the simplest approach is to reduce the sample size. However this has two disadvantages. First, it decreases the thermal signal, i.e. it decreases the sensitivity, and second it increases the problem with non-homogeneous samples.

The approach presented here consists of inserting heat exchange elements with high heat conductivity into the sample cell. The comparison of figure 2a and 2b shows clearly the effect of six steel fins inside a cylindrical sample cell on the temperature distribution. Heat exchange elements divide the sample volume and thereby reduce the dimensions in the sub-compartments, which reduces temperature gradients and criticality. Notice the dependence of the critical heat production rate q' on the sample dimension r, equation (1).

4. Examples

Figure 5 shows the effect of heat exchange fins in a 100µl cell on dynamic DSC curves: The exothermic signal in the cell with heat exchange element appears at somewhat lower temperature. Without heat exchangers the reaction in the cell leads to a run away: The temperature difference to the reference becomes very high and the reference temperature is no longer representative for the conditions in the sample, as can be seen from the strong distortion of the signal, when plotting it against the sample temperature (dashed curves). This effect is clearly smaller in the cell with heat exchangers.

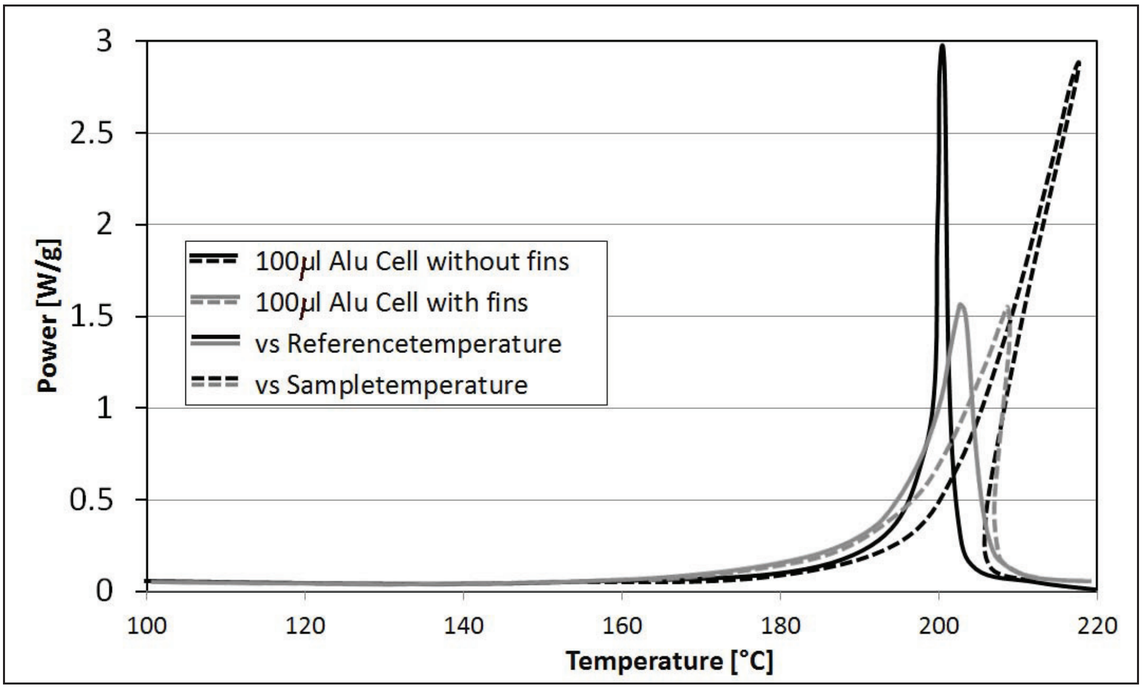

Figure 5: Effect of Heat Exchange Fins on the DSC Signal in a 100µl Aluminum cell (Heating rate 4K/min)

An even better improvement was observed when using micro-tube cells (Figure 4) in a SETARAM C80 experiment (Figure 6). The heat production curve in both cell types was identical up to 205°C. At this temperature, a spontaneous reaction occurred in the standard cell. The heat production increased immediately and exceeded the detection range of the instrument. An integration of the curve was not possible. In the micro-tube cell the reaction remained under control.

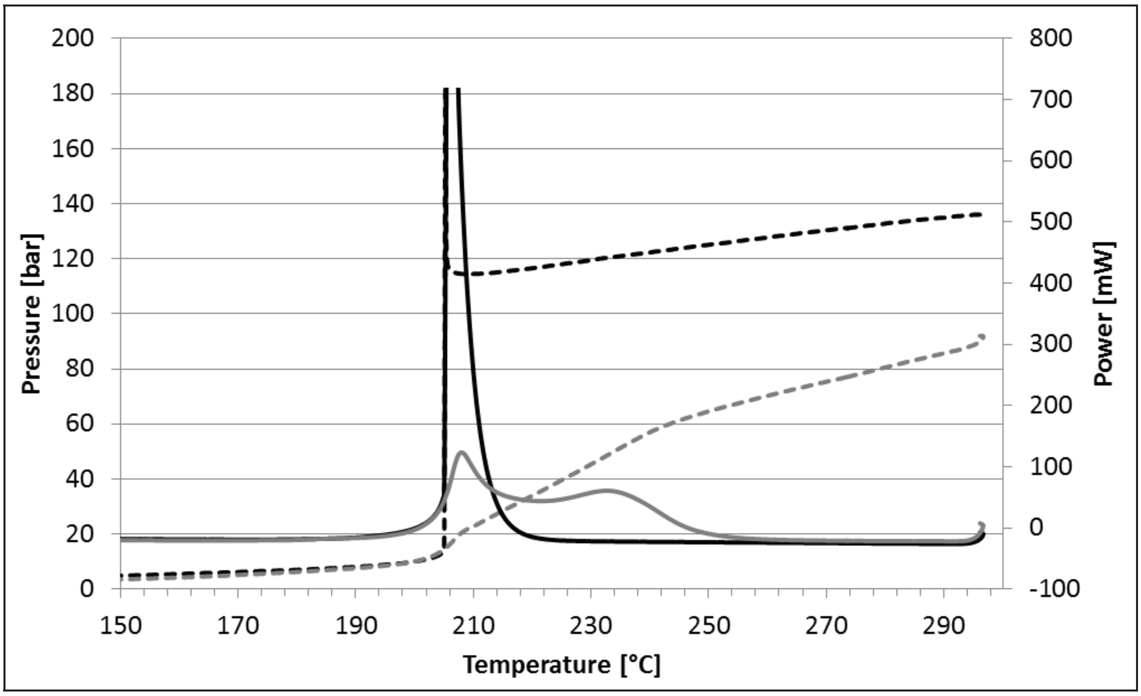

Figure 6: Dynamic test of a highly reactive material in a SETARAM C80 calorimeter. Black: standard cell; grey: micro-tube cell. Notice that the reaction gets out of control in the standard cell and a thermal explosion occurs, which exceeds the detection range of the instrument. The pressure curves (dashed) are also different: While the decomposition gases are produced almost instantaneously in the standard cell, they are formed gradually with the progress of the decomposition in the micro-tube cell. The difference in the final pressure is mostly due to the difference in the free volume, which is 1.00ml in the standard cell and 0.52ml in the micro-tube cell. (Sample mass: 226mg; Heating rate 0.5K/min)

5. Conclusions

It has been shown that highly energetic exothermic reactions may lead to run-away reactions even in very small sample cells resulting in strongly non-homogeneous temperatures in the sample. In such situations, a conventional evaluation of the data, e.g. integration or used for kinetic modelling is not possible

This effect is prominent if the heat conductivity in the sample is small and if there is no heat transfer by convection.

By using of sample cells with heat exchange elements such effects can be reduced or even eliminated.

In the field of determination of safety relevant data, it is very important to eliminate non-homogeneous temperatures in samples, in particular if the data are used for multiple regression analysis (Roduit, 2008).

References

Klais O., Köper O., Vollbrecht B., 2010, Safety Considerations for Implementation of Micro-designed Equipment, Proceedings of the 13th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Volume 2, 295, Brugge, Belgium, June 6-9.

Roduit B., Folly P., Berger B., Mathieu J., Sarbach A., Andres H., Ramin M. and Vogelsanger B., J. Therm. Anal. Cal., 93 (2008) 153.

Roduit B., Xia L., Folly P., Berger B., Mathieu J., Sarbach A., Andres H., Ramin M., Vogelsanger B., Spitzer D., Moulard H. and Dilhan D., J. Therm. Anal. Cal., 93 (2008) 143.

Roduit B., Dermaut W., Lunghi A., Folly P., Berger B. and Sarbach A., J. Therm. Anal. Cal., 93 (2008) 163.

Roduit B., 2010, Problem related to self-heating during DSC experiments, AKTS Technical Note 2010-08-24