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THE LIMIT OF DETECTION IN DIFFERENTIAL SCANNING CALORIMETRY*

S. Wies, A. Geyer and W. Eysel

MINERALOGISCH-PETROGRAPHISCHES INSTITUT, UNIVERSITÄT HEIDELBERG, F.R.G.

A procedure is described to determine the limit of detection of DSC instruments by using tiny signals from spontaneous polymorphic transitions of CsCl, $K_2Cr_2O_7$ and Na_2SO_4. It is shown how such signals can be found well-resolved in DSC diagrams of powder samples. To distinguish them from the baseline noise they should exhibit a height at least twice that of the baseline width. For the instrument employed the corresponding smallest amount of heat, i.e., the limit of detection, was found to be 0.1 mJ.

Keywords: DSC, limit of detection, polymorphic transitions

Introduction

For the determination of very small amounts of heat with DSC instruments, the following properties are of importance: the maximal sensitivity, the electronic noise and the limit of detection (LOD). The intention of this paper is to describe a procedure for the estimation of the LOD. This is done for a specific instrument, but the method can be applied also to others.

The sensitivity is the ratio between the instrumental response (DSC signal) to a given change of the measured property (heat, heat flux). Values may be given, for example, in μV/mW or cm/mW. The noise is the random short-time fluctuation of the baseline caused electronically, particularly by the amplifier. Comparisons of various DSC instruments [1] and fundamental

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details [2, 3] are given elsewhere. Sensitivity and noise give, however, no direct information on the LOD.

The LOD is defined as the smallest amount of heat, yet recognizable as DSC signal above the baseline. Therefore, the nature of the baseline is of significant importance. Due to the electronic noise the baseline exhibits a characteristic width which is able to mask small signals. Thus a major task is to find that signal height which defines the smallest recognizable signal. For the determination of this 'critical' height, broad signals are less suitable. The necessary sharp signals can be created as heat pulses in different ways: with electrical resistance heating as well as with spontaneous phase transitions or fast chemical reactions. Since not all DSC instruments allow for the electrical method, the second way is the more general. It is applied in this paper.

Experimental

The experimental investigations were carried out with a Du Pont 1090 Thermal Analyzer and the heat flux DSC cell 910 with the following features: maximal sensitivity 0.1 cm/μW (Du Pont gives the reciprocal value 10 μW/cm), heating rate 1 to 5 deg$\cdot$min^{-1}, sample pans Al, sample size 3 to 13 mg, purge gas 50 ml Ar/min, ΔT thermocouples Chromel/Constantan, evaluation program 'Interactive DSC V 2.0'.

The following sample materials were used: CsCl (Roth, puriss.), $K_2Cr_2O_7$ (Merck, p.a.), Na_2SO_4 (Merck, suprapur), KNO_3 (Merck, p.a.) and α–Al_2O_3 (Merck, p.a.).

Coarse crystalline material of the first three compounds was grown from aqueous solutions by evaporation. With these materials the necessary tiny DSC signals for the LOD estimation can not be obtained from individual single crystals, since these are too small to be handled. Therefore, such signals have to be selected from DSC runs of powder samples. The materials chosen here enable such selections in spite of the superposition of numerous signals, produced by the individual grains. Coarse powders with about 500 μm grain diameter were separated by sieving. Such samples usually contain some much smaller crystals which may cause tiny, resolved signals in the diagram. Another possibility is to use an unsieved powder sample and search for small resolved signals in the tails of the bulk signal. In both cases it is more promising to use cooling runs, because undercooling usually is more distinct than overheating.

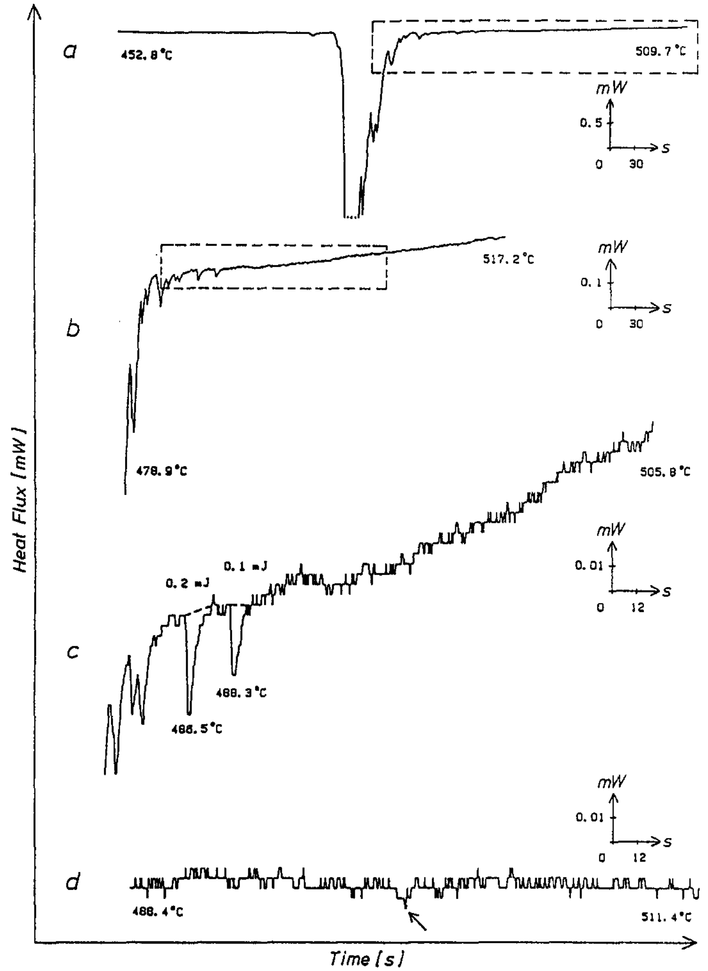

Fig. 1 a–c) Heating run of a CsCl sample with stepwise magnified sections. $\beta = 5$ deg·min^{-1}, sampling interval (S.I.) = 0.4 s/point. d) Section of the baseline of the empty DSC cell. $\beta = 5$ deg·min^{-1}, S.I. = 0.4 s/point. Endo = downwards, exo = upwards

Powder samples of KNO_3 were diluted with α-Al_2O_3 powder by mixing with a magnetic stirrer for at least 30 min. Samples down to a weight rations KNO_3:Al_2O_3 = 1:500 were prepared; the sample sizes were about 2 g, 10 mg of which were used for the DSC runs. A Sartorius balance with a sensitivity of 0.01 mg was used.

Some fundamental considerations

The determination of an amount of heat by DSC is based on the area of the corresponding DSC signal. This area is the result of two effects: the production or consumption of heat by the transition (which is responsible predominantly for the signal height) and the subsequent temperature equilibration (which is responsible predominantly for the signal breadth). The latter has no direct relation to the actual heat to be measured. The area has to be used, because both effects are always more or less superimposed due to kinetic reasons and can hardly be separated.

If the heat change would appear infinitely fast, the measurements could be carried out using only the signal height. Among the real effects these conditions are closely approached only by spontaneous transitions; this applies the more, the smaller the heat effect is.

Transitions may be particularly spontaneous if they can be strongly overheated (or undercooled) and show a very fast transition immediately after the nucleation. Typical examples are the polymorphic transformations of CsCl $\beta \Leftrightarrow \alpha$ (465 °C, $\Delta H = 2.90\,\mathrm{kJ \cdot mol^{-1}}$), $K_2Cr_2O_7$ $\beta \Leftrightarrow \alpha$ (243 °C, $1.54\,\mathrm{kJ \cdot mol^{-1}}$) and Na_2SO_4 II → III (231 °C, $2.0\,\mathrm{kJ \cdot mol^{-1}}$). Similar properties are observed for the crystallization of many metals from their undercooled melt as In, Sn, Pb, etc.

From these materials predominantly CsCl and $K_2Cr_2O_7$ turned out to be most suitable for the estimation of the LOD. Properties of these transitions were described recently [4–6].

Since heat and not temperature measurements are the aim of this paper, the following DSC diagrams are plotted as a function of time. Figures 1a–4a show characteristic parts of DSC diagrams of coarse powders ($\approx 500\,\mu\mathrm{m}$ grain diameter). The temperature ranges as well as some peak temperatures and transition heats are indicated. The strong undercooling or overheating of the individual crystals spread over extended time and temperature ranges, respectively. It should be mentioned that the best resolution of the single signals is obtained with small heating rates ($\leq 5\,\mathrm{deg \cdot min^{-1}}$). Powders with smaller grain sizes exhibit more continuous transition curves, since the signals are less resolved.

Estimation of the LOD

Figure 1d shows a typical segment of the baseline of the DSC cell used, recorded without sample and pans. The heating and cooling rates were 5 deg·min^{-1}, the sampling interval was 0.4 s/point. The tracing is plotted with the maximal sensitivity of the instrument of 10 μW/cm. It is evident that the electronic noise is ±5 μW as stated by the manufacturer. An exceptional deviation is indicated by an arrow.

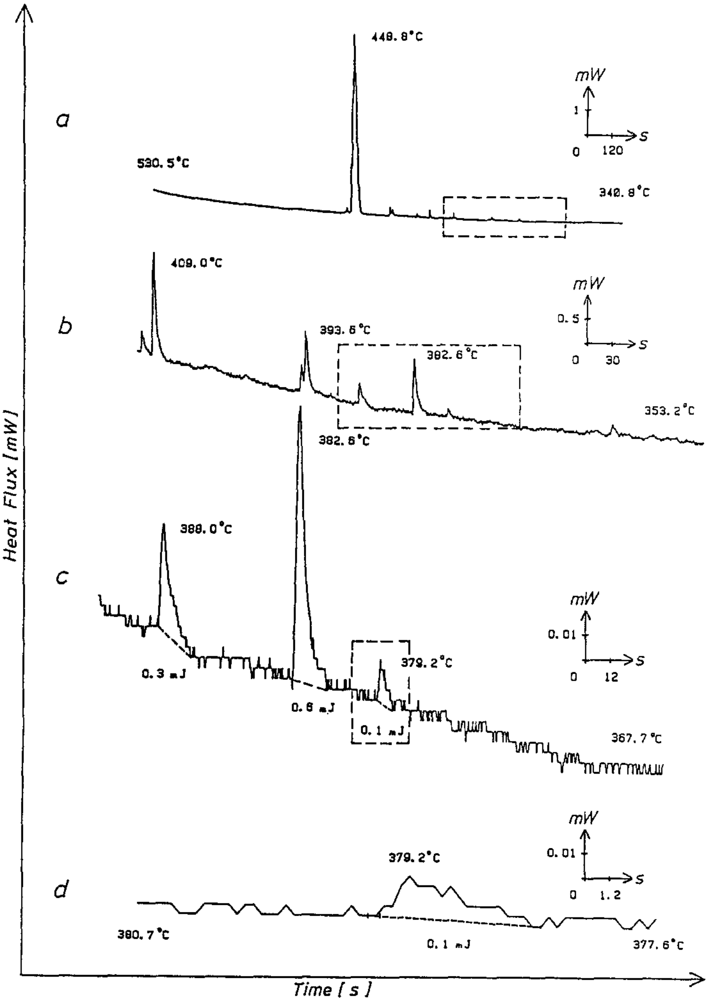

Fig. 2 a–c) Cooling run of CsCl with stepwise magnified sections. β = 5 deg·min^{-1}, S.I. = 0.4 s/point. d) Same as c), but with expanded time scale

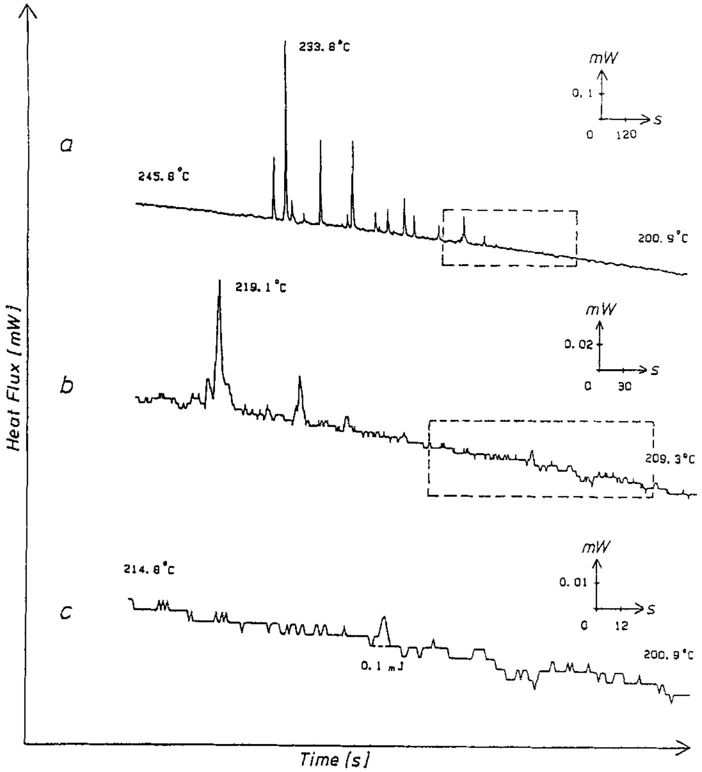

Fig. 3 Cooling run of $K_2Cr_2O_7$ with stepwise magnified sections. $\beta = 1$ deg·min^{-1}, S.I. = 1 s/point

Within the limits of error the same characteristics of the baseline have been found on heating and cooling for the whole temperature range of the cell. As shown below they apply also for runs with samples (Figs 1c–4c).

For the estimation of the LOD, sufficiently small transition signals have to be searched, i.e., resolved signals of extremely small crystals. The detection of such tiny signals, which are hardly visible in routine runs with common measuring ranges (Figs 1a–4a), affords maximal magnification of the heat flux scale. Typical examples are shown in Figs 1c to 4c. All these signals of spontaneous transitions exhibit a characteristic full width half maximum (FWHM) of about 5 s.

From these and many other investigated examples it is concluded that a deviation from the baseline is a true signal, if its height is at least twice that of the baseline width. One and a half times the width may still be significant, in particular if further indications exist such as the signal shape (FWHM) and the sign of the heat effect, provided these are evident from larger signals in the neighbourhood.

The visual recognition of such 'critical' signals in a diagram is easier if suitable scales are chosen. The small signal in Fig. 2c, e.g., is harder to identify with the ten times larger time scale in Fig. 2d.

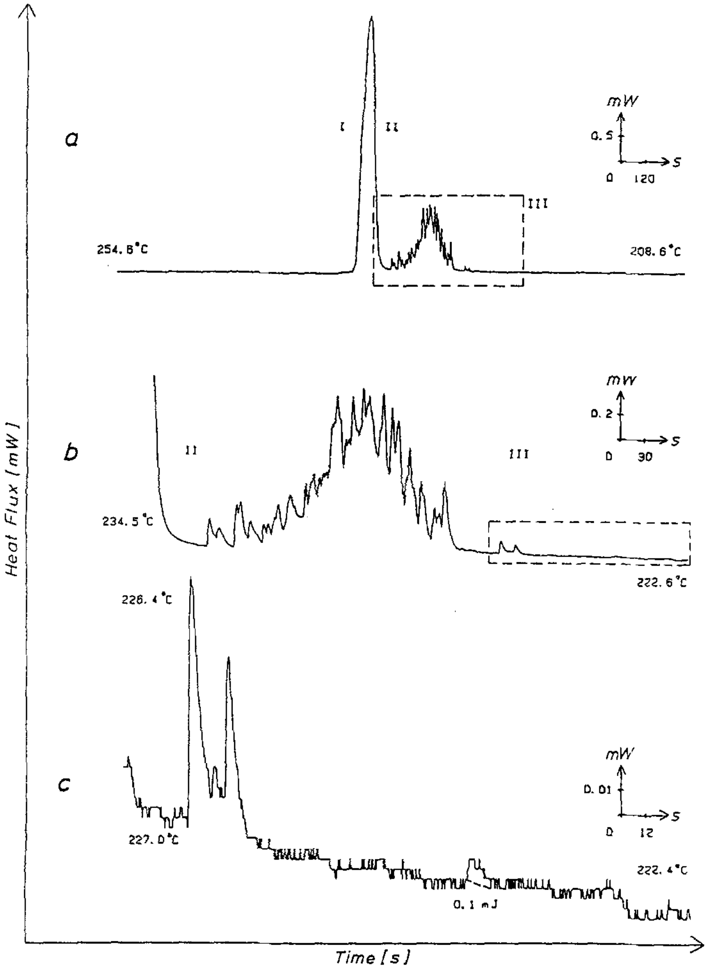

Fig. 4 Cooling run of the transitions I → II → III of Na_2SO_4 with stepwise magnified sections. $\beta = 1$ deg·min^{-1}, S.I. $= 0.4$ s/point

An important point is that the sampling interval allows to record the approximate signal shape. In Figs 1, 2 and 4 this is achieved by a sampling interval of 0.4 s/point. Already with 1 s/point the true signal shape is hardly recognizable (Fig. 3c). With still larger sampling intervals signals may even be missed completely. Smaller sampling intervals would afford larger computer storage capacity and plotting times.

If an analogue recorder is used, its settings (heat and time axis as well as time constant) have to be chosen correspondingly.

Table 1 Smallest detectable crystal masses and sizes for an LOD of 0.1 mJ

	Polymorphic transition	Mass / mg	Diameter / mm
CsCl	$\beta \leftrightarrow \alpha$	0.006	0.14
K2Cr2O7	$\beta \leftrightarrow \alpha$	0.015	0.22
Na2SO4	II $\leftrightarrow$ III	0.008	0.18

Whereas the existence of a signal is determined predominantly by its height, the heat content is derived from the area. For the smallest recognizable signals with heights twice the baseline width (Figs 1c–4c) an LOD of about 0.1 mJ was found as characteristic property of the applied instrument*.

From this amount of heat the smallest detectable single crystal masses and diameters for CsCl, $K_2Cr_2O_7$ and Na_2SO_4 were calculated (Table 1).

Influence of signal breadth

Among DSC effects sharp signals as used above for the LOD estimation are not the rule. Usually the signals are more or less broader. An example was investigated, using powders of KNO_3 diluted with α–Al_2O_3. The effect on the transition heat of the transformation $\alpha \rightarrow \beta$ of KNO_3 (128°C,

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* The software of the instrument does not allow for a heat determination with an accuracy less than one tenth (0.1 mJ). In addition, the area of very small signals, i.e., their transition heat, can be determined only approximately due to the few sampling points. Therefore, the same heat values are attributed to signals with similar, but recognizably different areas. For the rather rough estimation of the LOD, however, these uncertainties are without significance.

$\Delta H = 5.05 \mathrm{kJ \cdot mol^{-1}}$) for some of the prepared dilutions* are shown in Fig. 5. The linear relation between the content in KNO_3 and the corresponding amount of heat in Fig. 6 indicates that the dilutions were attained properly.

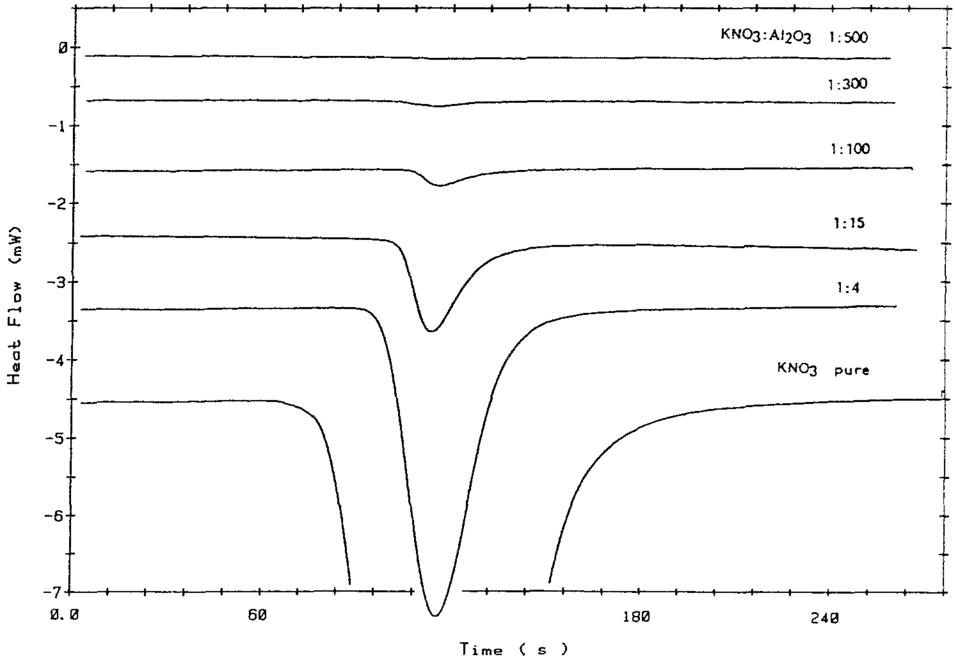

Fig. 5 Heating runs of the KNO_3 transition $\alpha - \beta$. Samples diluted with $\alpha - Al_2O_3$. β =5 deg·min^{-1}, S.I. =0.4 s/point

In Figs 7a and b the signals of the dilutions 1:500 and 1:300 in Fig. 5 are magnified, exhibiting an FWHM of about 15 s. They correspond to the two lowest points in Fig. 6. The existence of such broader signals is also proved by the ratio peak height/baseline width of 2, derived from the spontaneous transitions. Thus in Fig. 7a a signal with a height three times the baseline width is clearly recognizable. It exhibits 0.5 mJ, corresponding to 0.3 mJ for twice the baseline width. Thus the LOD = 0.1 mJ, as determined with spontaneous transitions (FWHM = 5 s) is not reached with broader signals. From

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* Similar dilutions were studied qualitatively with mixtures of $PbCO_3$ and Al_2O_3 [7].

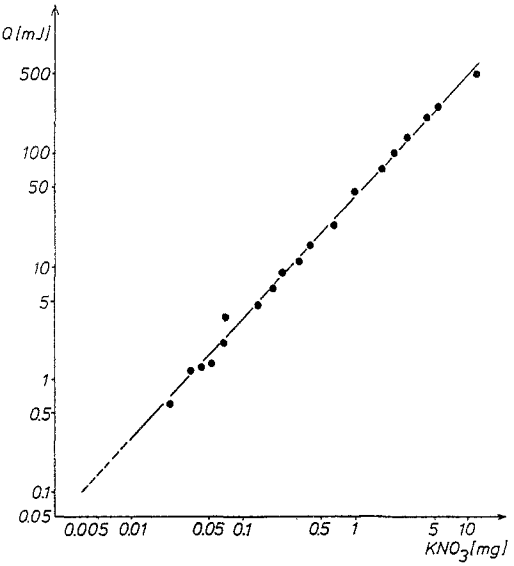

Fig. 6 Dependence of the transition heat of the diluted samples on the KNO$_3$ content (c.f. Fig. 5). Highest point = pure KNO$_3$. Logarithmic presentation

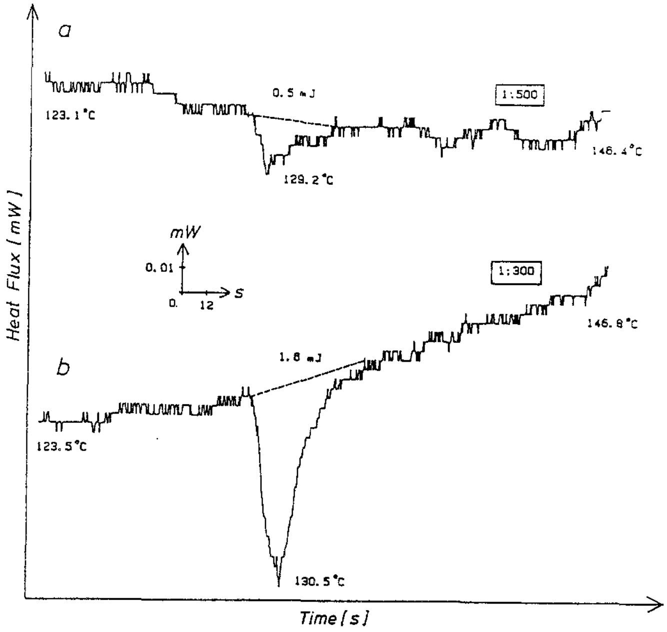

Fig. 7 Magnifications from Fig. 5 of the diluted samples KNO$_3$:Al$_2$O$_3$ = 1:500 (a) and 1:300 (b)

the experimental results a dependence of the minimal detectable heat on the FWHM can be estimated as $Q\,[\mathrm{mJ}] \approx 0.02\,\mathrm{FWHM}\,[\mathrm{s}]$.

Very broad signals may be hard to identify at all due to long range fluctuations of the baseline.

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Zusammenfassung — Anhand von sehr kleinen Signalen von spontanen polymorphen Übergängen bei CsCl, $K_2Cr_2O_7$ und Na_2SO_4 wird ein Verfahren zur Bestimmung der Nachweisgrenze von DSC-Geräten beschrieben. Es wird gezeigt, wie derartige Signale gut aufgelöst in DSC-Diagrammen von Pulverproben erhalten werden können. Um sie vom Rauschen der Basislinie zu unterscheiden, sollten sie eine Höhe von mindestens dem Doppelten der Basislinienbreite aufweisen. Für das angewendete Gerät beträgt die entsprechende geringste Wärmemenge, d.h. die Nachweisgrenze 0.1 mJ.