

NEW ASPECTS OF THERMAL ANALYSIS

Part I. Resolution of DSC and means for its optimization

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Abstract

The definitions of the temperature resolution, the so-called resolution of DSC instruments given in literature are discussed. A new definition of the resolution for DSC instruments is presented and outlined. The main characteristic introduced in this new definition is a minimum between two caloric events as a prerequisite of an existing resolution. Possible candidates of test substances have been evaluated. The oligomer *n*-hexatriacontane is revealing an interesting phenomenon, namely a lambda transition which is in the peak temperature only 2 K lower than the melting temperature of 76°C. The substance was selected as an ideal test substance for the quantification of the resolution of DSC instruments. The lambda transition is a second order process which may reach under certain conditions the saturation of the occurring molecular dislocation within 0.2 K, and after saturation the heat flow rate drops sharply down.

Investigations concerning the main characteristics of *n*-hexatriacontane in respect to the temperatures of transition (lambda transition and melting), to the involved enthalpies, and to the resolution factors were performed as functions of the sample mass and the heating rate.

The importance of relevant evaluation procedures increasing the resolution factors of DSC curves are discussed and these procedures are integrated into the testing of the resolution. The necessity for widening the experimental scope from instruments to evaluation procedures is forced by the existence of instruments with built-in signal treatments based on electronic devices and software procedures. A comparison with literature data is outlined for all of the mentioned characteristic values of *n*-hexatriacontane.

Keywords: lambda transition, *n*-hexatriacontane, resolution of DSC, resolution factor, temperatures and enthalpies of lambda transition

Introduction

Each of the existing differential scanning calorimeters (DSC) has certain attributes and quite a number of given specifications that cannot be altered. One has to accept most of these characteristics; however, operational conditions may be selected in a certain frame appropriate to the instrument used and to the sample under investiga-

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tion. The best results for a given sample may be finally obtained by a procedure based on experience. There are no clear rules existing how much theoretical and experimental know-how is afforded to find an unknown characteristic of a given material or a given substance or to find experimental conditions, which allow a meaningful and straightforward analytical process control. On the other hand it is also not known at the beginning of an investigation, if the search for a procedure of analysis could by chance also lead to a new discovery and if the surprisingly found properties are of any further and general value. In pure science, a new property for a material or substance is pre-eminent for the enlargement of the knowledge. Such a new discovery could give rise in applied science and in industry to solve a problem in the development or in the production of chemical substance or materials. Additionally, a new unknown behavior or a new generated chemical entity or a new phase could also lead to an invention. Marti *et al.* comprised some of the fine-tuning necessary for a laboratory to perform thermoanalytical experiments on a state-of-the-art level in 'Thermoanalytical Characterization of Pharmaceuticals' in 2000 [1].

The attributes and the parameters of a DSC instrument are varying from type to type, however, some of these characteristics are basic ones and the variations possible are within a certain frame. Certain parameters can be selected in the laboratory and the available range and their limits are also a characteristic part of any DSC instrument. According to the given statements such a list is a rather heterogeneous one:

- Sample pans or several sets of pans (volume, mass, material, geometry, contact area)
- Sample volume, sample mass, and sample area in contact to the heating and cooling platform and with the surroundings
- Thermal resistance of the instrument
- Thermal resistance of the sample material including the sample pan in use
- Thermal relaxation time of the instrument (time constant)
- Thermal relaxation time of the instrument including the sample material and the pan in use
- Range of temperature without and with cooling devices
- Heating and cooling rates under controlled conditions
- Temperature and caloric accuracy
- Noise, short-time noise
- Repeatability and linearity
- Sensitivity
- Resolution

The presented investigations are concerned with the resolution of DSC instruments. The resolution of DSC instruments will be discussed and a caloric characterization for a new test substance was executed. The substance *n*-hexatriacontane has been selected as the new test substance because of the existing thermal behavior. Resolution factors were defined for the new test substance for a quantification of the resolution. Additional measurements were performed with 4,4'-azoxyanisole. Van Ekeren *et al.* introduced the substance in 1997 [2] for DSC experiments to determine the resolution and the sensitivity. A round robin test in a

great number of laboratories using a considerable number of different types of instruments was initiated under the guidance of the board of the Dutch Society for Thermal Analysis (TAWN) and the results published in [2].

Our investigations were performed in the Netzsch application laboratory in Selb. The DSC 204 Phoenix[®] equipped with the μ -sensor was used, and for the two test substances experimental conditions and parameters were changed. These conditions and parameters changed are the sample mass, the sample pans, and the heating rates. In literature, the resolution and the sensitivity are discussed only on the basis of the definitions; so far the reported practical investigations by van Ekeren have a position of exclusiveness. Furthermore, the resolution as the temperature separation of two caloric phenomena in a narrow temperature region by a DSC instrument was only discussed in literature explicitly in respect to the uncorrected curves. Nowadays, the evaluation procedures are playing an important role in the elucidation of measured data. Certain instruments are only presenting data, which are already treated with some algorithms, based on additionally obtained data, measured during preceding DSC scans. Therefore, it seems obvious to discuss the resolution not only on the basis of uncorrected curves, however, also on data obtained after a treatment with appropriate evaluation procedures. Two important parameters mentioned above have a strong influence on the resolution of a DSC, namely the thermal resistance of the instrument and under certain conditions also the thermal resistance of the sample material including the sample pan in use. The whole subject has to be considered under the aspects of instrument- or sample- limited conditions. The sum of these two parameters is approximated and taken into account by software programs making a correction for the thermal resistance and thermal relaxation time (time constant).

In this paper we evaluated the resolution of the DSC instrumentation not only by the uncorrected curves, however, also after the treatment of the curves for the correction of the thermal resistance as well as with the peak separation procedure.

The definition of the resolution and the sensitivity for a DSC instrument is given in [3]:

- The resolution of a DSC measuring system describes its ability to clearly identify overlapping thermal events (peaks) as separate ones.
- The sensitivity of a measuring system is defined as the ratio between the change of the measurement signal and the change of the measured quantity that creates the signal. For the DSC system the measured quantity is the heat flow rate, and the signal output is an electric voltage, thus the ratio yields the sensitivity given in V/W.

A new definition for the resolution is presented here:

- The resolution of a DSC instrument describes its ability to identify overlapping caloric events by the existence of a minimum between the peaks. The minimum can be observed for uncorrected curves or only after an evaluation procedure has been executed.

A general definition for the resolution of a DSC instrument should already incorporate the concept of a quantitative realization. Furthermore, the definition should not be understood only by an additional interpretation.

The quantification of the resolution is executed by a resolution factor defined as

$$R_{\text{MKE}} = \frac{h_{\text{peak}}}{h_{\text{min}}} \quad (\text{MKE: Marti, Kaisersberger, Emmerich}) \quad (1)$$

The definitions for the sensitivity and the resolution stated in [2] are not definitions in a theoretical and basic sense, however, guidelines for a quantitative procedure. In this publication the resolution and sensitivity tests are defined for the test substance 4,4'-azoxyanisole. The melting behavior of this substance forming liquid crystals is shown in Fig. 1. The first transition from the solid phase into a nematic liquid crystalline phase is at $T_{\text{trs}}=118^\circ\text{C}$ with an enthalpy of transition of $\Delta_{\text{trs}}H=31.0 \text{ kJ mol}^{-1}$ (120 J g^{-1}). The second transition from the liquid crystal phase into the isotropic liquid is at a temperature of $T_{\text{trs}}=136^\circ\text{C}$ with a rather low enthalpy change of only $\Delta_{\text{trs}}H=0.52 \text{ kJ mol}^{-1}$ (2 J g^{-1}). The DSC curve measured for 4,4'-azoxyanisole with the Netzsch DSC 204 Phoenix[®] with a μ -sensor as well as the evaluation of the 'resolution' is presented for a thermal corrected curve in Fig. 1.

The conditions applied were proposed by van Ekeren *et al.* for the resolution test. These conditions are the following: 5 mg sample mass of 4,4'-azoxyanisole, heating rate preferably 20 or 10 K min^{-1} , premelting cycle with a temperature interval of 5 min at 145°C , cooling to 30°C , preferably with a cooling rate of 20 K min^{-1} , purge gas is nitrogen, temperature interval from 30 to 165°C , sampling rate 10 data points per s.

The insert of the Fig. 1 shows the evaluation of the 'resolution' according to [2] as the quotient of the height of the minimum between the two caloric events and the peak height of the second transition at 136°C . The 'resolution' has been calculated for the curve in Fig. 1 as

$$R_{\text{vEK}} = \frac{a}{b} = 0.08 \quad (\text{vEK: van Ekeren } et al.)$$

According to the definition of the resolution factor in Eq. (1) the inverse value to R_{vEK} is obtained for $R_{\text{MKE}}=12.5$.

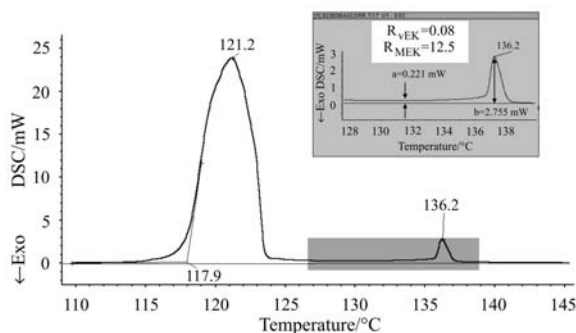


Fig. 1 Resolution test experimentally performed according to van Ekeren *et al.* [2]: DSC curve of 5.12 mg 4, 4'-azoxyanisole, aluminum crucible with pierced lid, heating rate 10 K min^{-1} , nitrogen flow. Resolution determined after the treatment of the DSC curve with 'Correction for the Thermal Resistance' [1]

Figure 2 contains 4 different cases of overlapping and resolved DSC curves. The part 2.1 presents a case where clearly overlapping phenomena are visible, however, a procedure for a quantitative value of the resolution would have to be formulated first. Such a DSC curve with overlapping events without a minimum in between is preferably treated for an improved resolution with a software program 'Peak Separation'. In a second step the quantitative determination of the resolution factor according to Eq. (1) may be possible. The case 2.1 is rather common in experiments through following phenomena: mixtures of substances or polymorphs with rather narrow melting points, impurities, mainly solvents or small molecules, which evaporate on melting of the main component of the sample.

The cases 2.2 to 2.4 can be quantitatively described with our resolution factor R_{MKE} . The case 2.2 gives resolution factor $R_{MKE}=1$, the case 2.3 greater than 1 and for 2.4 the value is infinite.

The upper and the lower limit of the 'resolution' R_{VEK} by van Ekeren *et al.* is given by following values which are based on the special way of definition. The upper limit for two caloric events with a disappearing minimum in between, Fig. 2.2, is approaching the highest value for the quotient $R_{VEK}=1$, which means the lower limit of the resolution is reached. In case the two peaks or thermal events are completely separated (Fig. 2.4), what means $a=0$, yields the lower limit, namely $R_{VEK}=0$. In these limits of 0 and 1 the 'resolution' is approaching the value zero for an ideal resolution, and a disappearing resolution for $R_{VEK}=1$. In approaching zero the quotient is getting insensitive for high resolutions. Of course from a mathematical point of view van Ekeren's quotient is absolutely correct. However, direct proportional relationships are much easier in handling and understanding than inverse ones.

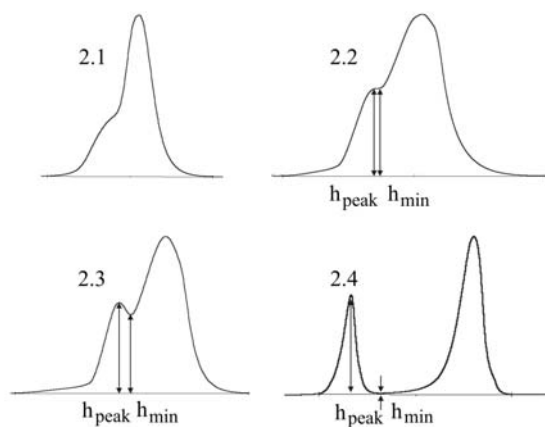


Fig. 2 Visual description of the DSC resolution according to van Ekeren *et al.* (R_{VEK}) and of this paper assigned as R_{MKE} ; selection of different cases: 2.1 clearly identified overlapping events, however no resolution; 2.2 disappearing minimum: $R_{VEK}=h_{min}/h_{peak}=1$, $R_{MKE}=(h_{peak}/h_{min})=1$; 2.3 partially separated peaks with minimum: $R_{VEK}=a/b=h_{min}/h_{peak}<1$, $R_{MKE}=h_{peak}/h_{min}>1$; 2.4 ideal resolution of the peaks: $R_{VEK}=h_{min}/h_{peak}=0$, $R_{MKE}=(h_{peak}/h_{min})=\infty$

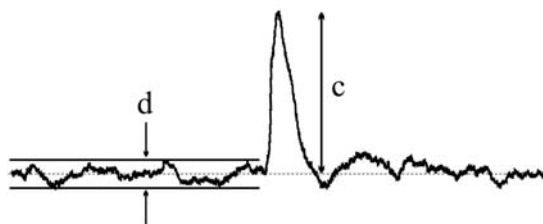


Fig. 3 Sensitivity defined as quotient of the peak height for the nematic-isotropic transition of 4,4'-azoxyanisole and the peak to peak noise before this transition

The 'sensitivity' is given by van Ekeren *et al.* as the quotient of the peak height for the second transition of 4,4'-azoxyanisole, assigned with c , and the peak-to-peak noise directly before the second transition, defined as d , Fig. 3. The 'sensitivity' is therefore given as

$$S_{\text{VEK}} = \frac{c}{d}$$

The 'sensitivity' S_{VEK} according to [2] is in contrary to the 'resolution' in a direct linear relationship, Fig. 3. Therefore, the higher sensitivity is proportional to the value of the quotient called 'sensitivity'. Also in a different approach to Höhne [3] the 'sensitivity' by van Ekeren is a signal to noise (pp) relationship (Fig. 3). However, the sensitivity given by [3] is defined as a transfer function typical for any DSC as a ratio for the output signal in Volt to the input of the sample or the electrical calibration device through the measured heat flow from or into the sample in Watt.

Selection of test substances

The selection of test substances for a determination of the resolution of DSC instruments of a broad variety of characteristic parameters is not done with a straightforward procedure. Two facts have to be taken into consideration, namely that the resolution of the DSC instrumentation has been gradually improved and will become even better in the future. Additionally, the measured data of DSC instruments are improved by built-in devices (electronics and physical mathematics) as well as by evaluation procedures applied in a consecutive step. The basic resolution of an instrument may be strongly influenced by the two different pathways mentioned above. Therefore we propose here, as a new approach, to regard also the resolution factors achieved either by the built-in devices or by the computational procedures as DSC quality criteria.

Let us discuss substances representing different groups of possible test systems. These substances are the following ones:

- 4,4'-azoxyanisole
- cimetidine, mixture of the crystal modifications A and D

- *n*-tricosane C₂₃H₄₈
- *n*-hexatriacontane C₃₆H₇₄

The comparison of the transitions of these four substances is presented in Table 1.

Comparing the four substances from Table 1 it seems obvious, that cimetidine is not recommendable as a test substance for the evaluation of the resolution for DSC instruments. First, test substances in form of a physical mixture are not very practicable, and second, a mixture of two crystal modifications could create additional problems in their stability. The temperature difference for the two crystal modifications of only 0.35 K could be a value for a test substance of the resolution for instruments and evaluation procedures of the next decades.

4,4'-azoxyanisole as test substance for the resolution is revealing on the other hand for many DSC instruments, which are today on the market a rather weak test. The main reason for this handicap is the rather large temperature difference of the two caloric events of about 18 K. The temperature difference for the neighboring peaks of 4,4'-azoxyanisole is even for uncorrected curves and for heating rates below 20 K min⁻¹ too large for most of the today existing DSC instruments. The situation is getting even worse, if in addition the influence of evaluation procedures should be tested. Under this latter aspect, the differentiation in respect to the resolution is practically lost.

The possible test substance *n*-tricosane is revealing an interesting solid-state behavior with a λ -transition for the temperature of 41°C and a melting temperature of 48°C. The temperature difference between the two transitions of 7 K is certainly better for the discrimination of the resolution, compared with the value of 18 K for 4,4'-azoxyanisole.

The melting process is certainly influenced by the purity of the normal alkanes therefore substances of a high purity are afforded. Furthermore the temperature difference between the lambda transition and the melting temperature is a strong function of the number of C atoms within these alkanes [8].

n-hexatriacontane enables a critical resolution test because of the temperature difference for the two caloric phenomena of only 2 K. Also the improvements of the resolution achieved by instrument internal or external evaluation procedures should give a rather significant test. Our results on *n*-hexatriacontane presented in the following should underlay our statement. The two phenomena causing the transitions in *n*-hexatriacontane, an oligomer with the formula C₃₆H₇₄ are a lambda transition at a temperature of 74°C and the melting at 76°C. The lambda transition is defined as a second order transition revealing a rather sharp change of the heat capacity. This phenomenon is observed for hydrocarbons with a chain length between C₁₇ and C₃₆. A consideration about the entropy of the lambda transition into two parts, namely an entropy of the volume change and a part for the configuration change brought Stuart [9] to the explanation as a co-operative phenomenon of a stiff rotation of the molecules from one rotational segment position to the next. This dynamic dislocation mobility is reaching extremely fast a new energetic level within the quasi-solid-state caused by a saturation effect for this molecular rotation. After reaching the peak value, the heat capacity drops sharply. The thermal resistance of the instrument and additionally the thermal resis-

Table 1 Characterization of substances as candidates for a resolution test

Substance	$T_{\text{fus},1}/^{\circ}\text{C}$	$T_{\text{fus},11}/^{\circ}\text{C}$	$\Delta T_{\text{fus},11}/^{\circ}\text{C}$	$\Delta_{\text{fus},1}H/\text{kJ mol}^{-1}$	$\Delta_{\text{fus},11}H/\text{kJ mol}^{-1}$	$\Delta_{\text{fus},1}H+\Delta_{\text{fus},11}H/\text{kJ mol}^{-1}$
4,4'-azoxyanisole	117 [2]	134 [2]	17	0.52	31	31.5
	118 [4]	136 [4]	18			
Cimetidine [5]	$T_{\text{fus},A}$ 140.30±0.03	$T_{\text{fus},D}$ 140.65±0.03	0.35±0.06	39.7±0.5	41.0±0.5	40.4 ¹
<i>n</i> -tricosane [6]	40.5	47.5	7.0	21.8	54.0	75.8
<i>n</i> -tricosane (1 K min ⁻¹) this paper	40.3	47.9	7.6	23.9	52.4	76.3
<i>n</i> -hexatriacontane [7]	T_A 74.0	T_{fus} 76.0	2.0	31	89	120
	73.0	75.4	2.4	40	82	122

¹as a mixture of 50 to 50% in weight²data given for: sample mass 41 μg, heating rate 10 K min⁻¹, 2nd heating, curve treated with the software 'Peak Separation'

tance of the sample material have a considerable influence on the resolution of a DSC instrument. It is obvious, that physically regarded always the total thermal resistance will be representative for the characteristic of the substance under investigation. However, there are two regimes possible, namely the instrument-limited condition and the sample-limited one. Only the thermal resistance of the instrument has to be taken into consideration in case of the instrument-limited conditions. The two extreme conditions are only approached; the reality lies normally in between these two regimes. To get a good approximation of the instrument-limited regime it is only necessary to make the thermal resistance of the instrument rather high and the sample masses rather small. However, resolution and sensitivity of a heat flow DSC are incompatible characteristics because a good temperature resolution affords a low thermal resistance, in contrary the sensitivity demands a rather high one. This statement supports the concept of a rather high thermal resistance selected for a heat flow DSC and taking into account a certain loss on resolution for uncorrected curves. This concept diminishes the influence of the sample resistance and increases the sensitivity, a situation that is from an experimental point of view very well accepted. Two experimental procedures are advisable in this case, namely to increase the resolution by a small sample mass and to get an additional improvement of the temperature resolution by applying a software program for the correction of the thermal resistance.

An experimental fact which has some general consequences is the instability of crystalline and amorphous substances as well as polymers in respect to a first heating especially over a first or second order transition such as the melting point or the glass transition. The instability could be of a chemical nature; here we are concerned about the physical phenomena. An example is the recrystallization of a substance after melting. There is no straightforward procedure to overcome this problem; it must be solved in consideration of the substance under investigation and the specific data one would like to achieve. Normally, you observe in the first scan a temperature distortion of the caloric effect that is decreasing strongly or even is not existing at the second heating and in consecutive ones. The situation is easily understood for a crystalline substance. The sample in form of a crystalline powder and with a typical bulk density which incorporates gas atmospheres with a relative volume of a range of 20 to 80% collapses on melting, forming a liquid film and on cooling small crystals are growing or an amorphous film could also be formed. The newly formed crystals have a much higher bulk density. Both of the cooled systems, the crystalline and the amorphous one reveal a much higher surface contact and also the thermal resistance of the sample is strongly reduced.

A completely different pathway than performed with the instrument-limited conditions is presented by Sørensen and Rouquerol with a publication on 'Sample Controlled Thermal Analysis' [10]. The method reacts in a sample-limited regime on the behavior of the sample by an appropriate change of the experimental conditions.

Materials and methods

The two substances used in our investigation were 4,4'-azoxyanisole and *n*-hexatriacontane. 4,4'-azoxyanisole ($C_{14}H_{14}N_2O_3$) with a molar mass of 258.27 was obtained from Aldrich (A 97009). The purity is 98% and the melting region is indi-

cated with 118–121°C. The *n*-hexatriacontane (C₃₆H₇₄) with the molar mass of 506.97 is declared as purum from Fluka (52920) with a purity according to GC of higher than 96%. The melting range is indicated with 74–76°C.

The instrument used for all the measurements was the DSC 204 Phoenix[®] (Netzsch-Gerätebau GmbH) equipped with the μ -sensor.

The sample masses were measured with a microbalance CP2P from Sartorius.

The evaluation procedures applied for the elucidation of appropriate data from the measured DSC curves were the following ones [1]:

- Netzsch Proteus[®] software
- ‘Correction for Thermal Resistance’
- ‘Peak Separation’

Definition of the resolution factors for the test substance *n*-hexatriacontane

The substance *n*-hexatriacontane is proposed in this paper as new test substance for the determination of the resolution of DSC instruments for uncorrected curves. Several sets of experiments were performed and also the influence on the resolution through the application of the evaluation procedures in respect to the correction of the thermal resistance and in treating the uncorrected curves with the software for peak separation was elucidated. Additionally, in consecutive evaluation procedures the curves were submitted first to the correction of the thermal resistance and secondly to the peak separation method. The thermodynamic characterization of this test substance was carefully investigated.

In a further investigation, the two physical transitions observed for *n*-hexatriacontane – the lambda transition and the melting – have been studied in their interrelation. The thermodynamic behavior of *n*-hexatriacontane in the melting region is as basic characterization for the use as a test substance for the elucidation of the resolution extremely important.

Let us go back to the definition given in this paper for the resolution of DSC instruments. We introduced a new criterion for the resolution, namely the existence of a minimum between two caloric events. This minimum leads us straightforward to a quantification of the resolution by the definition of a resolution factor (Eq. (1)).

We define for *n*-hexatriacontane two resolution factors, one for the lambda transition and one for the melting.

The resolution factor is defined in respect to the lambda transition of *n*-hexatriacontane:

$$R_{\lambda} = \frac{h_{\lambda}}{h_{\min}} \quad (2)$$

with h_{λ} the peak height for the lambda transition in W g⁻¹ or in kW mol⁻¹, and with h_{\min} the height of the minimum of the DSC curve in between the two peaks measured in respect to the base line. The dimensions for the minimum are the identical ones as for the lambda peak height.

The resolution factor for DSC instruments is also defined in respect to the melting process of *n*-hexatriacontane:

$$R_{\text{fus}} = \frac{h_{\text{fus}}}{h_{\text{min}}} \quad (3)$$

The peak height h_{fus} for the melting process has also the dimensions W g^{-1} or kW mol^{-1} . The height of the minimum of the DSC curve h_{min} is the same as in the Eq. (2).

The resolution factors are increasing for a better resolution and are therefore inverse to the 'resolution' given in [2] by van Ekeren *et al.*

The resolution factors according to the Eqs (2) and (3) have the following limiting values:

- $R_{\lambda}=R_{\text{fus}}=\text{infinity}$ in case the two transition peaks are separated by a minimum touching the baseline, which means $h_{\text{min}}=0$
- $R_{\lambda}=R_{\text{fus}}=1$ if a disappearing minimum is existing between the two transition peaks.

Experiments and results

Azoxyanisole

The experiments with 4,4'-azoxyanisole were performed with the DSC 204 Phoenix[®] equipped with the μ -sensor and with four samples of a sample mass of about 5 mg. The samples were enclosed in aluminum crucibles with pierced lids. Two of these samples were put into sample crucibles with the cover in an inverse position. The heating rates applied were 20 and 10 K min^{-1} . The instrument was purged with N_2 using a flow rate of 20 mL min^{-1} . The DSC curve of 4,4'-azoxyanisole with a sample mass of 5.12 mg and treated with the software 'Correction for Thermal Resistance' is presented in Fig. 1.

The conditions and results of the DSC curves for 4,4'-azoxyanisole are comprised in Table 2.1 for uncorrected curves and in Table 2.2 for curves which were treated with the software program 'Correction for Thermal Resistance'. The resolution factors R_{fus} according to our definition as well as the 'resolution' R_{vEK} were calculated and the influence of the experimental conditions on the resolution are elucidated.

Hexatriacontane

The determination of the resolution was performed with the DSC 204 Phoenix[®] installed with the μ -sensor. Four samples of *n*-hexatriacontane in the sample mass range of 2 μg to 5 mg were put into aluminum crucibles with pierced lids and the instrument was flushed with a nitrogen flow rate of 20 mL min^{-1} . The samples were heated from room temperature to 85°C with a heating rate of 10 K min^{-1} . The samples were cooled with 10 K min^{-1} to 30°C and heated for a second time with 10 K min^{-1} to 85°C. The sample masses selected for *n*-hexatriacontane were in micrograms 5097, 787, 41, and for the lowest value the mass was estimated as about 4 μg . The lowest

Table 2.1 Resolution of the DSC 204 Phoenix[®] equipped with the μ -sensor determined with 4,4'-azoxyanisole based on the experimental conditions of [2]. Results for uncorrected curves

Sample pan	Sample mass/mg	Heating rate/K min ⁻¹	Resolution factor/ R_{MKE} ^a	Relative resolution factor/% for R_{MKE}	"Resolution" R_{VEK}
Al crucible pierced lid	5.16	20	2.7±0.02	100	0.37
Al crucible pierced lid, cover inverse position	5.14	20	3.6±0.03	133	0.28
Al crucible pierced lid	5.12	10	6.5±0.1	100	0.15
Al crucible pierced lid, cover inverse position	5.03	10	7.4±0.03	114	0.14

^a R_{MKE} (Eq. (1)), mean value of three scans. The first scan to 145°C has been regarded as a premelting process, reported are the 2nd, 3rd and 4th scan

Table 2.2 Resolution of the DSC 204 Phoenix[®] equipped with the μ -sensor determined with 4,4'-azoxyanisole based on the experimental conditions of [2]. Results for curves which were treated with the procedure 'Correction for Thermal Resistance'

Sample pan	Sample mass/mg	Heating rate/K min ⁻¹	Resolution factor/ R_{MKE} ^a	Relative resolution factor/% for R_{MKE}	Resolution R_{VEK}
Al crucible pierced lid	5.16	20	7.6	100	0.13
Al crucible pierced lid, cover inverse position	5.14	20	12.2	161	0.08
Al crucible pierced lid	5.12	10	12.6	100	0.08
Al crucible pierced lid, cover inverse position	5.03	10	17.6	140	0.06

^a R_{MKE} (Eq. (1)). The first scan to 145 °C has been regarded as a premelting process, reported is the 2nd scan

sample mass was of a poor accuracy, because the mass resolution for the microbalance was about 1 μ g. The estimated mass of 4 μ g was corrected by taking the literature value for the total enthalpy of transitions from [7] as $\Delta_{trs,I} H + \Delta_{trs,II} H = 120$ kJ mol⁻¹ and comparing this value with the measured enthalpy of 69.9 kJ mol⁻¹. The lowest sample mass was then determined over a measurement of the enthalpies of transition with 2.3±0.2 μ g.

The DSC curves observed for these samples of *n*-hexatriacontane are presented for the first scan in Fig. 4 and for the second scan in Fig. 5.

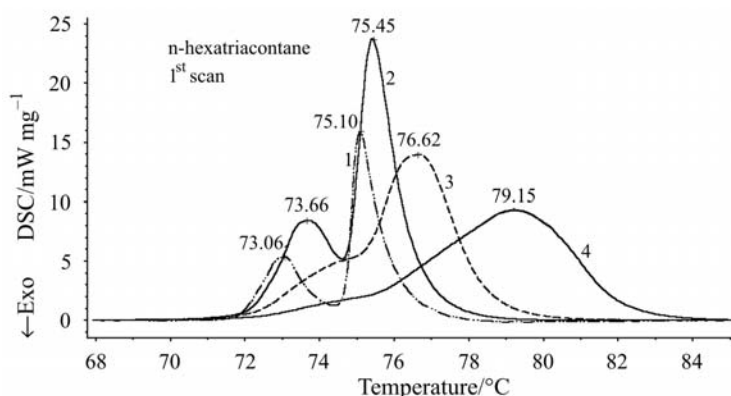


Fig. 4 Dependence of the resolution on sample mass for *n*-hexatriacontane, DSC curves, first scan, measured with a DSC 204 Phoenix[®] equipped with the μ -sensor, heating rate 10 K min⁻¹

Number of curve	Sample mass/ μ g	Total enthalpy	
		J g ⁻¹	kJ mol ⁻¹
1	2.3	236	120
2	41	248	126
3	787	261	132
4	5097	259	131

An inspection of the two sets of curves leads to the following qualitative findings. The samples of *n*-hexatriacontane reveal for the first heating (Fig. 4) only peaks with a minimum in between for the mass of 2.3 and 41 μ g. The curves for the two higher sample masses show a clear overlapping of the two calorific phenomena. However, in the second heating presented in Fig. 5 for all samples clear minima are existing. This fact stresses the importance of the thermal resistance of a crystalline powder with a considerable amount of gas (normally nitrogen or air) incorporated between the crystals. The measured curves were evaluated by applying several software procedures, namely with the Netzsch Proteus[®] software described in [1]. The following data were obtained for all measured curves:

- Peak temperatures for the lambda transition and the temperature of melting
- Enthalpies for the lambda transition and the enthalpies of fusion and their sum
- Resolution in respect to the lambda transition and in respect to the melting peak.

Additionally, the curves were treated with the evaluation procedures ‘Correction for the Thermal Resistance’ and ‘Peak Separation Software’ [1].

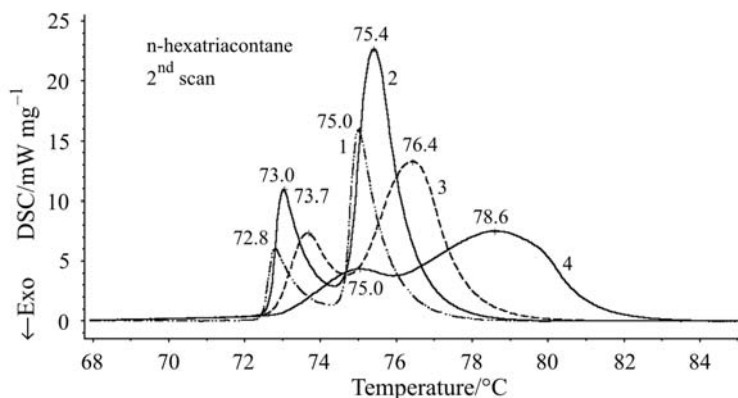


Fig. 5 Dependence of the resolution on sample mass for *n*-hexatriacontane, DSC curves, second scan, measured with a DSC 204 Phoenix[®] equipped with the μ -sensor, heating rate 10 K min⁻¹

Number of curve	Sample mass/ μ g	Total enthalpy	
		J g ⁻¹	kJ mol ⁻¹
1	2.3	236	120
2	41	248	126
3	787	236	119
4	5097	239	121

The transition temperatures, namely the lambda transition temperatures and the melting temperatures for these samples of *n*-hexatriacontane are collected for the uncorrected curves in Table 3. The similar data after a curve treatment with the procedure 'Correction for the Thermal Resistance' are found in Table 4. The data obtained after the procedure 'Peak Separation' are seen in Table 5.

The enthalpies of transitions for the curves measured and evaluated for the samples of *n*-hexatriacontane are comprised in Table 6. The enthalpies are related to the lambda transition and to the melting of this substance. These values were calculated after a treatment of the curves with the software 'Peak Separation'. In case that no minimum between the two peaks was observed for the peak-separated-curves, the enthalpies of transition are reported only as the sum of both of the phenomena. A comparison with literature values is integrated. The results for the first heating are presented in Table 6 and the data for the second heating in Table 7.

The resolution factors for the lambda transitions as well as for the melting peaks are collected for the two sets, namely for the first and second heating of the indicated samples of *n*-hexatriacontane in Tables 8.1 to 8.4. The visual image of the resolution for the uncorrected curves using a DSC 204 with the μ -sensor can be inspected in Figs 4 and 5. All results are given for the first and second heating for all of the samples. Furthermore, the resolution factors are calculated for the curves corrected for

Table 3 Temperatures for the two transitions of *n*-hexatriacontane and their temperature differences for the uncorrected curves. Measurements with the DSC 204 Phoenix[®] equipped with the μ -sensor, for the first and second heating with a heating rate of 10 K min⁻¹

Evolution procedure literature data	Sample mass/ μg	T_{λ} 1 st scan/ $^{\circ}\text{C}$	T_{fus} 1 st scan/ $^{\circ}\text{C}$	$\Delta T_{\text{fus}-\lambda}$ 1 st scan/ K	T_{λ} 2 nd scan/ $^{\circ}\text{C}$	T_{fus} 2 nd scan/ $^{\circ}\text{C}$	$\Delta T_{\text{fus}-\lambda}$ 2 nd scan/ K
Original curves	2.3	73.1	75.1	2.0	72.8	75.0	2.2
Original curves	41	73.7	75.4	1.7	73.0	75.4	2.4
Original curves	787	–	76.7	–	73.7	76.4	2.7
Original curves	5097	–	79.2	–	75.0	78.6	3.6
Reference [7]	–	74.0	76.0	2.0	–	–	–

Table 4 Temperatures for the two transitions of *n*-hexatriacontane and their temperature differences for the curves measured with the DSC 204 Phoenix[®] equipped with the μ -sensor, in applying for the first and second heating a heating rate of 10 K min⁻¹. The curves were treated with the 'Correction for the Thermal Resistance'

Evaluation procedure literature data	Sample mass/ μg	T_{λ} 1 st scan/ $^{\circ}\text{C}$	T_{fus} 1 st scan/ $^{\circ}\text{C}$	$\Delta T_{\text{fus-}\lambda}$ 1 st scan/ K	T_{λ} 2 nd scan/ $^{\circ}\text{C}$	T_{fus} 2 nd scan/ $^{\circ}\text{C}$	$\Delta T_{\text{fus-}\lambda}$ 2 nd scan/ K
Correction of the thermal resistance	2.3	72.7	74.9	2.2	72.7	74.9	2.2
Correction of the thermal resistance	41	73.2	75.2	2.0	72.9	75.1	2.2
Correction of the thermal resistance	787	74.5	76.0	1.5	73.3	75.8	2.5
Correction of the thermal resistance	5097	–	–	–	74.5	78.0	3.5
Reference [7]	–	74.0	76.0	2.0	–	–	–

Table 5 Temperatures for the two transitions of *n*-hexatriacontane and their temperature differences for the curves measured with the DSC 204 Phoenix[®] equipped with the μ -sensor, in applying for the first and second heating a heating rate of 10 K min⁻¹. The curves were treated with the software ‘Peak Separation’

Sample mass/ μ g	T_{λ} 1 st scan/ $^{\circ}$ C	T_{fus} 1 st scan/ $^{\circ}$ C	$\Delta T_{\text{fus-}\lambda}$ 1 st scan/K	T_{λ} 2 nd scan/ $^{\circ}$ C	T_{fus} 2 nd scan/ $^{\circ}$ C	$\Delta T_{\text{fus-}\lambda}$ 2 nd scan/K
2.3	73.0	75.1	2.1	72.8	75.0	2.2
41	73.8	75.5	1.7	73.0	75.4	2.4
787	74.2	76.6	2.2	73.7	76.4	2.7
5097	74.1	79.3	5.2	74.7	78.6	3.9

Table 6 Enthalpies for the transition of *n*-hexatriacontane were measured with the DSC 204 Phoenix[®] equipped with a μ -sensor and presented for the first heating. The heating rate was 10 K min⁻¹. The curves were evaluated with the software ‘Peak Separation’. The relative values of the enthalpies of transition are calculated by taking the sum of both of these enthalpies of transition as 100%

Evaluation procedure literature data	Sample mass/ μ g	$\Delta_{\lambda}H + \Delta_{\text{fus}}H/$ kJ mol ⁻¹	$\Delta_{\lambda}H/$ kJ mol ⁻¹	$\Delta_{\text{fus}}H/$ kJ mol ⁻¹	$\Delta_{\lambda}H_{\text{rel}}/$ %	$\Delta_{\text{fus}}H_{\text{rel}}/$ %
Peak separation	2.3	–	–	–	34	66
Peak separation	41	137	51	86	37	63
Peak separation	787	130	23	107	8	82
Peak separation	5097	129	2	127	1.7	98.3
Reference [7]	–	120	31	89	26	74

Table 7 Enthalpies for the transition of *n*-hexatriacontane were measured with the DSC 204 Phoenix[®] equipped with the μ -sensor and presented for the second heating. The heating rate was 10 K min⁻¹. The curves were evaluated with the software ‘Peak Separation’. The relative values of the enthalpies of transition are calculated by taking the sum of both of these enthalpies of transition as 100%

Evaluation procedure literature data	Sample mass/ μ g	$\Delta_{\lambda}H + \Delta_{\text{fus}}H/$ kJ mol ⁻¹	$\Delta_{\lambda}H/$ kJ mol ⁻¹	$\Delta_{\text{fus}}H/$ kJ mol ⁻¹	$\Delta_{\lambda}H_{\text{rel}}/$ %	$\Delta_{\text{fus}}H_{\text{rel}}/$ %
Peak separation	2.3	–	–	–	34	66
Peak separation	41	122	40	82	33	67
Peak separation	787	115	28	87	24	76
Peak separation	5097	118	23	94	20	78
Reference [7]	–	120	31	89	26	74

the ‘Thermal Resistance’ and also for the curves treated with the software ‘Peak Separation’. Finally, the resolution factors are integrated in the Table 8.4 for curves of *n*-hexatriacontane which were first corrected for the thermal resistance and in a second step with the ‘Peak Separation’ program.

Table 8.1 Resolution factor according to the definition of this paper for *n*-hexatriacontane for uncorrected curves measured with a Netzsch DSC 204 Phoenix[®] equipped with the μ -sensor with a heating rate of 10 K min⁻¹

Sample mass / μ g	R_λ 1 st scan	R_{fus} 1 st scan	R_λ 2 nd scan	R_{fus} 2 nd scan
2.3	4.1	12.5	4.8	13.0
41	1.6	4.7	3.8	7.8
787	0	0	1.9	3.5
5097	0	0	1.2	2.0

Table 8.2 Resolution factor according to the definition of this paper for *n*-hexatriacontane for curves measured with DSC instruments with a heating rate of 10 K min⁻¹. The curves were measured with a Netzsch DSC 204 Phoenix[®] equipped with the μ -sensor and in an additional step treated with the software 'Correction for Thermal Resistance'

Sample mass/ μ g	R_λ 1 st scan	R_{fus} 1 st scan	R_λ 2 nd scan	R_{fus} 2 nd scan
2.3	∞	∞	∞	∞
41	10	37.6	∞	∞
787	1	3.2	14.0	19.0
5097	–	–	1.7	2.6

Table 8.3 Resolution factor according to the definition of this paper for *n*-hexatriacontane for curves measured with DSC instruments with a heating rate of 10 K min⁻¹. The curves were measured with a Netzsch DSC 204 Phoenix[®] equipped with the μ -sensor and in an additional step treated with the software 'Peak Separation'

Sample mass/ μ g	R_λ 1 st scan	R_{fus} 1 st scan	R_λ 2 nd scan	R_{fus} 2 nd scan
2.3	7.9	23.3	6.0	15.6
41	2.4	5.4	6.5	11.7
787	1.5	5.6	4.1	7.7
5097	–	–	1.7	3.8

Table 8.4 Resolution factor according to the definition of this paper for *n*-hexatriacontane for curves measured with DSC instruments with a heating rate of 10 K min⁻¹. The curves were measured with a Netzsch DSC 204 Phoenix[®] equipped with the μ -sensor. The curves were treated in two additional steps with the software 'Correction for Thermal Resistance' and with the 'Peak Separation'

Sample mass/ μ g	R_λ 1 st scan	R_{fus} 1 st scan	R_λ 2 nd scan	R_{fus} 2 nd scan
2.3	∞	∞	∞	∞
41	14.1	59.0	6.5	∞
787	2.0	6.7	18.9	24.7
5097	–	–	1.7	4.3

The data presented in the Tables 8.1 to 8.4 shall be restricted to the second scan for the further evaluations. The first scan is regarded as a premelting, namely a physical process which is concomitant with a drastic change of the thermal resistance of the sample in respect to the instrument. The following equations are applied for the mathematical representation of the dependence for the resolution factor of the λ -transition and the melting peak.

$$R_{\lambda} = -a_{\lambda} \cdot \log m_s \quad (4)$$

$$R_{\text{fus}} = -a_{\text{fus}} \cdot \log m_s \quad (5)$$

with a_{λ} and a_{fus} as coefficients for the dependence of the resolution factors with the sample mass m_s . The coefficients of the transition curves of *n*-hexatriacontane according to the Eqs (4) and (5) are collected in Table 9.

Table 9 Coefficients for the dependence of the resolution factors with the sample mass for *n*-hexatriacontane according to the Eqs (4) and (5) calculated as regression lines for the resolution factors obtained from the curves of the second heating from the data of the Tables 8.1 to 8.4

Evaluation procedure	a_{λ}	a_{fus}
Original curves	1.1	3.3
Peak separation	1.9	3.5

The dependence of the transition temperatures, namely for the lambda transition and the melting, as well as the enthalpies related to these transitions were investigated in respect to the heating rate using a DSC 204 Phoenix[®] equipped with the μ -sensor. The same set of curves was evaluated for the resolution factor. The experiments have been performed with three samples of rather identical masses of *n*-hexatriacontane.

Aluminum crucibles with pierced lids in inverse position were used and the instrument was flushed during the experiments with a nitrogen flow of 20 mL min⁻¹. The *n*-hexatriacontane with the sample mass 796 μg was heated for the heating rates 2.5 to 20 K min⁻¹ from 20 to 90°C. For the heating rate 40 K min⁻¹ the upper temperature limit was 100°C. The cooling rate was throughout 20 K min⁻¹. These samples were exposed for each of the heating rates to four consecutive scans. The measurements with the sample mass 786 μg were repeated only 3 times. The very first scan for the three samples were regarded as a preheating and therefore no data were evaluated for these two curves. Only the mean values for the temperatures of the λ -transition as well as the melting temperatures of *n*-hexatriacontane and additionally the temperature differences of these two transitions are collected for all of the mentioned heating rates in Table 10. The transition temperatures and their differences are reported for selected heating rates with errors of the mean values on 95% confidence limits.

The enthalpies of transitions in dependence of the heating rates were calculated after a treatment of the uncorrected curves with the software 'Peak Separation'. The three curves for the second sample of *n*-hexatriacontane with a mass of 786 μg and measured with a heating rate of 3 K min⁻¹ – the first scan is regarded as a premelting

Table 10 Mean values for the transition temperatures and their temperature differences for the λ -transition and melting for *n*-hexatriacontane in relation to the applied heating rates. Errors of the mean values are given for selected samples on 95% confidence limits. The measurements were made with a DSC 204 Phoenix[®] equipped with the μ -sensor and the data presented are calculated from the uncorrected curves. Aluminum crucibles with pierced lids in inverse position were used

Heating rate/K min ⁻¹	Sample mass/ μ g	$\bar{T}_{\lambda}/^{\circ}\text{C}$	$\bar{T}_{\text{fus}}/^{\circ}\text{C}$	$\bar{\Delta}T_{\text{fus-}\lambda}/\text{K}$
40	796	76.04 \pm 0.06	79.26 \pm 0.06	3.22 \pm 0.12
20	796	75.04	77.85	2.81
10	796	74.53	77.10	2.57
5	796	74.24	76.68	2.44
4	786	74.32	76.74	2.42
3	786	74.12 \pm 0.03	76.50 \pm 0.03	2.38 \pm 0.06
2.5	796	74.02	76.37	2.35
1	786	73.89	76.15	2.26
0.5	786	73.80	76.01	2.21
0.25	792	73.76	75.91	2.15
0.1	792	73.70 \pm 0.03	75.84 \pm 0.03	2.14 \pm 0.06
0.05	792	73.71	75.81	2.10

– were used for an evaluation of the error limits of the calculated enthalpies. The error limits for these enthalpies obtained for the selected experimental conditions can be regarded as a good estimation for all the other heating rates. The results shown in Table 11 are the enthalpies of the lambda transition and the enthalpies of fusion only for one of the repeated curves, however selected as the representative one. Also the sum of both of these enthalpies is included.

Finally, the relative values of these enthalpies, taking the sum of both as 100%, are listed. A comparison with the data published by Domalski and Hearing [7] is included in Table 11.

The resolution observed with a DSC 204 using the μ -sensor was elucidated from the above defined samples of *n*-hexatriacontane and under the above explained experimental conditions. The resolution factors were calculated from the uncorrected curves according to the definitions of this paper (Eqs (2) and (3)) and are mean values of three or four consecutive heating cycles. The data set is contracted in Table 12.

The results of the resolution factors from Table 12 are presented in Fig. 6 as a logarithmic function of the heating rate.

Two selected examples of the DSC measurements with *n*-hexatriacontane of 796 μ g sample mass are shown in Fig. 7 for 2.5 and 40 K min⁻¹.

Table 11 Mean values of the enthalpies of transitions and the sum as well as the relative values are collected for the measurements with three samples of practically identical sample masses of 800 μg of *n*-hexatriacontane. The data are shown for heating rates between 40 and 0.05 K min^{-1} . The curves were measured with a DSC 204 Phoenix[®] equipped with the μ -sensor. The enthalpies are determined after the treatment of the curves with the software 'Peak Separation'. A comparison with a literature value from reference [7] is made

Heating rate/ K min^{-1}	Sample mass/ μg	$\Delta_\lambda H + \Delta_{\text{fus}} H /$ kJ mol^{-1}	$\Delta_\lambda H /$ kJ mol^{-1}	$\Delta_{\text{fus}} H /$ kJ mol^{-1}	$\Delta_\lambda H_{\text{rel}} /$ $\% ^2$	$\Delta_{\text{fus}} H_{\text{rel}} /$ $\% ^2$
40	796	117 ± 2.3	17 ± 1.2	100 ± 1.1	15 ± 1.4	85 ± 0.5
20	796	117	26	91	22	78
10	796	115	27	88	23	77
5	796	113	31	82	27	73
4	786	112	32	80	29	71
3	786	109 ± 2.6	31 ± 2.4	78 ± 0.2	28 ± 1.6	72 ± 0.6
2.5	796	109	30	79	28	72
1	786	110	29	81	26	74
0.5	786	111	29	82	26	74
0.25	792	114	29	85	25	75
0.1	792	111 ± 2.3	27 ± 1.5	84 ± 0.8	25 ± 0.7	75 ± 0.3
0.05	792	114	29	85	25	75
⁻¹	–	120	31	89	26	74

Table 12 Mean values of the resolution factors R_λ and R_{fus} for *n*-hexatriacontane in respect to the lambda transition and the melting process evaluated for uncorrected curves in dependence of the heating rates. The instrument used was a DSC 204 Phoenix[®] equipped with the μ -sensor and the mass of the three samples was about 800 μg . The first heating of each of the samples was not taken into account

Heating rate/ K min^{-1}	Sample mass/ μg	R_λ	R_{fus}
40	796	1.1	2.5
20	796	1.3	2.8
10	796	2.1	3.8
5	796	4.7	8.2
3	786	10.3	16.2
2.5	796	12.3	21
1	786	63	99
0.5	786	120	196
0.25	792	∞	∞
0.1	792	∞	∞
0.05	792	∞	∞

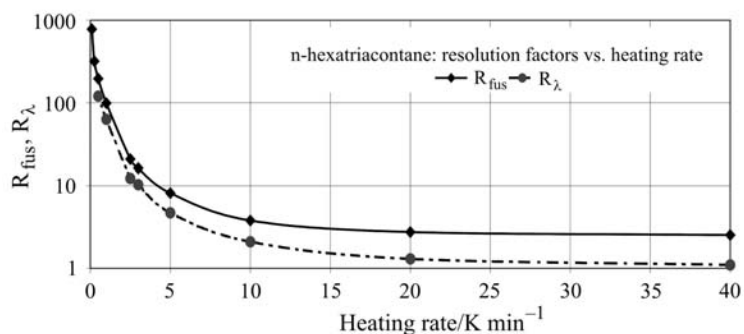


Fig. 6 Dependence of the resolution factors R_λ and R_{fus} (in logarithmic scale) on heating rate for *n*-hexatriacontane

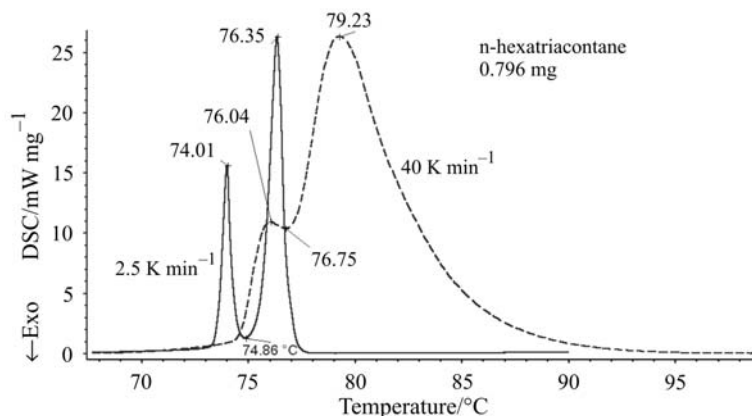


Fig. 7 *n*-hexatriacontane: Improvement of DSC resolution (uncorrected curves, relative scaling at *Y*-axis) through reduction of heating rate

Discussion

Resolution and sensitivity are decisive qualities of DSC instruments. The temperature resolution, assigned normally as resolution, is the ability of a DSC to separate calorific processes which are occurring in neighboring temperature intervals. The sensitivity of a DSC instrument is defined as the ratio between the change of the signal measured to the change of the enthalpy liberated or taken up by the sample. The sensitivity is in a technical expression given by the electric voltage created in the DSC instrument on the base of heat production or heat consumption rate produced in the sample in μV per μW .

Neighboring processes, at least two or more than two processes, could be based on physical or chemical changes of the sample substance or the sample material. Such processes may overlap each other and therefore a temperature indication may become impossible for the different events. Additionally, the calorimetric resolution

from the overall curve into clearly separated single effects could become questionable or even end up as an impossible task. Between the ideal resolved caloric events and completely overlapping processes, which may then occur under the image of a single event, is a large range of overlapping DSC curves of a rather different overlapping quality. The question is simple: one has to construct DSC instruments with a perfect resolution and as a consequence the overlapping caloric phenomena are reduced to a rather small number of cases. However, the heat flux DSC instruments combine on the basis of the measuring principle resolution and sensitivity. The above demanded perfect resolution decreases the sensitivity to zero. Resolution and sensitivity are incompatible and therefore the DSC instruments and their measuring devices must be constructed with the goal of a more or less ideal balance of temperature resolution and sensitivity.

The definition of the resolution of DSC instruments can not be solved in a straightforward experimental procedure with the statement 'clearly identified overlapping thermal events as separate ones' [3]. This definition is leaving the question open, namely what is the meaning of the statement. Additional interpretation is afforded to obtain a practical guideline. Therefore, we introduced in this paper a new definition for the resolution with a new approach and in addition with an enlargement of definition 'instrument'.

The resolution of a DSC instrument according to our definition describes its ability to identify overlapping caloric events by the existence of a minimum between the peaks. The minimum can be observed for uncorrected curves or only after an evaluation procedure has been executed.

The differentiation procedure of two caloric events with the feature of a minimum is an unambiguous approach. Furthermore the definition for the resolution incorporates for the first time also appropriate evaluation procedures for an improvement of the resolution in comparison with the uncorrected curves. This enlargement is a necessity and opens the possibility for a comparison of instruments with built-in signal treatment based on electronic devices and software procedures.

A different approach for the resolution and the sensitivity of DSC instruments was published in 1997 by van Ekeren *et al.* [2]. The 'sensitivity' is given in [2] for the substance 4,4'-azoxyanisole as the quotient of the peak height for the transition from the nematic into the isotropic liquid phase at 136°C and the peak-to-peak noise in the nematic phase. A higher value of the quotient corresponds to a better sensitivity. The 'resolution' of DSC instruments is given in the same publication as the quotient for the value of the heat flow at minimum within the nematic phase to the peak height for the transition out of the nematic phase into the isotropic liquid phase. An ideal resolution gives a quotient R_{VEK} which approaches practically a height of the minimum equal to zero. In reality, the nematic phase reveals as seen in Fig. 1 a higher heat capacity than the crystalline phase of 4,4'-azoxyanisole below the melting temperature and also a higher value than the isotropic liquid. Therefore, the heat flow at minimum is also for an ideal resolution, an endothermic baseline deviation. Additionally the differentiation for high resolution values is rather insensitive.

Therefore, the lower the quotient R_{VEK} is the better the resolution, which has a lack on practicability. Therefore we introduced a new quantification of the resolution by the so-called resolution factor which corresponds to our definition, namely to an existing minimum between two caloric events. The resolution factor given in Eq. (1) is generally applicable and not restricted to a specific test substance. The minimum demands also two peaks and therefore any of the investigated substance reveals two resolution factors namely in respect to the first or in respect to the second peak. Additionally, the higher the value of the resolution factor R_{MKE} is the better the resolution.

In an attempt to select and to characterize further test substances for the evaluation of the today existing instrumentation, we collected thermal data for some candidates. The caloric phenomena which are related to these substances are the following:

Substance	phenomena
4,4'-azoxyanisole	liquide crytal, nematic phase
Cimetidine	polymorphism
<i>n</i> -tricosane, <i>n</i> -hexatriacontane	lambda transition and melting

4,4'-azoxyanisole confirmed already the validity as test substance by van Ekeren *et al.* The handicap is the large temperature difference of about 18 K between the two physico-chemical transitions. The state-of-the-art instrumentation with improved sensitivity and resolution and with sophisticated evaluation procedures require test substances allowing a better discrimination of the resolution.

The two monotropic crystal modifications A and D of cimetidine have two melting peaks with a temperature difference of 0.35 ± 0.06 K [5]. A physical mixture of these two crystal modifications of cimetidine in a ratio of 50 to 50% gave in one DSC measurement a temperature difference of the two melting points independent from a temperature calibration and independent from all errors which occur from one sample to the next of

$$\Delta T_{\text{fus}} = T_{\text{fus, D}} - T_{\text{fus, A}} = 0.36 \pm 0.01 \text{ K.}$$

The two values for the temperature difference are in an excellent agreement and the fact of an existing minimum between the peaks is a prerequisite of a test substance. The many existing polymorphs of cimetidine could create difficulties in the preparation of a 50 to 50% mixture of the pure crystal polymorphs A and D. By the way, any physical mixtures of crystal modifications are problematic in their production and their homogeneity. Cimetidine has been disregarded on the basis of these facts as a possible test substance.

The lambda transition occurring for oligomers of a chain length of C_{17} to C_{36} is a scientifically interesting phenomenon. The temperature difference between this second order transition and the melting temperature is a complex function of the chain length. The oligomers with an even number of C atoms have rather small temperature differences between the two transitions, the odd numbers reveal for C_{17} a temperature

difference of 11 K and for the *n*-tricosane with C_{23} 7 K and *n*-hexatriacontane with a chain of C_{36} has a temperature difference of 2 K. The selection of *n*-hexatriacontane as test substance was rather obvious, based on the small temperature difference of the transitions of about 2 K, on the absolute temperature of the melting point of 76°C, and on the sharp lambda transition which is a prerequisite of a minimum between the two transitions.

Two evaluation procedures are extremely important in relation to the resolution of the applied instrument. The thermal resistance from the instrument to the upper surface of the sample in the sample pan causes a temperature shift to higher values. This temperature shift is influenced in quite different relationships by the heating rate, by the sample mass and by the absolute value of the heat flow. All these parameters are in a direct relationship to this temperature shift.

The resolution of the DSC 204 Phoenix[®] equipped with the μ -sensor is presented in Table 2.1 for samples of 4,4'-azoxyanisole with sample masses of about 5 mg. Two parameters were changed in these experiments, namely the heating rate and the cover of the aluminum crucible with pierced lid. To press the cover in the normal and in the inverse position to the bottom part of the pan is changing the resolution factor R_{MKE} for both of the heating rates. The influence is for a heating rate of 20 K min⁻¹ an improvement of the resolution factor of 33% for the inverse cover. The increase of the resolution factor with only 14% for the crucible with the inverse cover is observed for the lower heating rate of 10 K min⁻¹. The explanation for the increase of the resolution factors are given by the better thermal contact to the measuring device of the DSC. The dependence upon the heating rate is that the higher this rate the more decisive is the thermal resistance. The mean values of the resolution factor R_{MKE} are given with error limits for three consecutive scans. These limits reveal the excellent reproducibility of the DSC curves by the high accuracy demonstrated for the resolution factors. In Table 2.2 are results of the resolution factors presented for curves treated with the mathematical algorithm 'Correction for Thermal Resistance'. Clearly demonstrated is the influence of the thermal resistance and the time constant for the resolution factors which are about three times higher for a heating rate of 20 K min⁻¹ and for 10 K min⁻¹ about a factor of two compared to the values obtained from the uncorrected curves.

The relationship in respect to the sample mass for *n*-hexatriacontane is demonstrated in the Figs 4 and 5 for the constant heating rate of 10 K min⁻¹ and with a variation of the sample mass from 5097 to 2.3 μ g. In Fig. 4 for the first heating of the samples *n*-hexatriacontane we observe for the sample masses of 787 and 5097 μ g examples for general case 1 in Fig. 2. We see clearly identified overlapping events not resolved because of the lack of a minimum. The samples with the masses of 41 and 2.3 μ g separate already at the first heating the lambda transition from the melting peak (case 3 in Fig. 2).

The DSC curves of *n*-hexatriacontane in Fig. 5 show a clear minimum for all of the sample masses investigated corresponding also to the case 3 in Fig. 2. The visual inspection of the transition peaks for the first and the second heating indicates the influence of the sample mass in respect to the resolution as well as the drastic change of

Table 13 Influence of mathematical procedures applied on DSC curves for correction of the thermal resistance and for peak separation on the half width of the λ -peak of *n*-hexatriacontane, curves measured with a DSC 204 Phoenix[®] equipped with the μ -sensor, heatin rate 10 K min⁻¹

Sample mass/ μg	Half width for the λ -peak of <i>n</i> -hexatriacontane in K					
	Uncorrected curves		Curves corrected for thermal resistance		Curves treated with peak separation	
	1 st scan	2 nd scan	1 st scan	2 nd scan	1 st scan	2 nd scan
2.3	1.3	0.74	0.91	0.20	1.4	0.86
41	1.7	0.80	1.2	0.29	1.9	1.0
787	–	1.3	–	0.8	1.8	1.2
5097	–	2.5	–	2.2	–	2.1

the thermal resistance of the samples. The influence of the thermal resistance of the sample is remarkable even for rather low sample masses. The half width of the uncorrected curves of the lambda transition shown in Figs 4 and 5 are collected in the following. The values for the curves corrected for thermal resistance, and for curves evaluated with the ‘Peak Separation’ software are integrated in the Table 13.

The half width for the peak of the lambda transition of *n*-hexatriacontane for a heating rate of 10 K min⁻¹ gives a quantification of the influence of the sample resistance, which is caused by the geometrical dimensions of the crystals within the samples. In the first scan the starting bulk density of the sample becomes effective, which is followed by the change of the sample profile after the melting to a thin layer and recrystallization to a crystal layer with the formation of an intimate contact to the sample pan. A similar relationship of the half width could be observed for the melting peak. The influence of the thermal resistance is also represented in comparison of the half width for the second heating for all of the sample masses evaluated for uncorrected curves and for curves corrected for thermal resistance. The half width is decreasing by a factor of 3 for uncorrected curves comparing the samples of 5097 and 2.3 μg . The factor is even 11 for curves corrected for thermal resistance and for the equal sample masses as above. The influence of the ‘Peak Separation’ software is a minor one, because no correction for the thermal resistance is made.

The peak temperatures of the transitions of *n*-hexatriacontane show a clear shift to lower values with decreasing sample masses (Tables 4 and 5). A minor shift is observed between the temperatures of the first and the second heating. The comparison with the literature values [7] is rather good with the exception of the sample with 5097 μg . A specific comparison was made for sample masses of about 780 μg in correspondence with our uncorrected curves using the DSC 204 and the uncorrected curve from DSC 2920 published in [11]. Also the transition temperatures measured with the Q 100, $T_{\text{zero}}^{\text{TM}}$ differ only 0.3°C from the values we obtained for similar sample masses.

A mean value of the temperature differences between these transition temperatures is calculated out of the 17 data reported in Tables 3 to 5, in omitting the data

with the highest sample mass. The calculation yields $\Delta T_{\text{fus}-\lambda} = T_{\text{fus}} - T_{\lambda} = 2.12 \pm 0.10$ K. The error limits are the standard deviation of the mean value. The literature value according to Domalski and Hearing [7] is $\Delta T_{\text{fus}-\lambda} = 2.0$ K.

The enthalpies of transition for the DSC curves of Tables 6 and 7 are calculated with the software 'Peak Separation'. The sum of the transition enthalpies is for the heating rate of 10 K min^{-1} and the second heating cycle $\Delta H = \Delta_{\lambda} H_{\lambda} + \Delta_{\text{fus}} H_{\text{fus}} = 118 \pm 2 \text{ kJ mol}^{-1}$. The agreement with the literature [7] is excellent with the reported value of 120 kJ mol^{-1} . The corresponding mean value for the first heating according to the measurements in this paper is 10% higher.

The relative fractions of the enthalpy for the lambda transition in respect to the sum of the enthalpies of transition indicate a strong dependence on the sample mass. The dependence upon the mass is shifting for the second heating from 20% for the $5097 \mu\text{g}$ to 34% for the 2.3 mg . The first heating, however, shows a much higher change from 2 to 34%. The first and the second heating integrate for sample masses above about $100 \mu\text{g}$, a part of the lambda transition into the melting peak. The DSC curves of the lower sample masses of 2.3 and $41 \mu\text{g}$ ψιελδ α ρελατιωε εντηαλπψ φορ τη λαμβδα τραν-σιτιον οφ 33% ανδ τη αβσολυτε παλυε ωασ χαλχυλατεδ φορ $41 \mu\text{g}$ ωιτη $40 \text{ κθ } \mu\text{ολ}^{-1}$. Domalski and Hearing reported in [7] corresponding values of 26% and 31 kJ mol^{-1} . The results of the enthalpy for the lambda transition for the first and the second heating with a heating rate of 10 K min^{-1} reveal the fact that the temperature gradients are rather small for sample masses below about $100 \mu\text{g}$.

The resolution factors for *n*-hexatriacontane R_{λ} and R_{fus} collected in Tables 8.1 to 8.4 reveal a significant decrease with increasing sample masses. Restricting the discussion to the sample mass of $787 \mu\text{g}$ and to the second scan, we observe the following resolution factors for the lambda transition starting with the value for uncorrected curves, the curves corrected for the thermal resistance, the curves treated with the software 'Peak Separation' and last with the sequence of curve treatments 'Correction for Thermal Resistance' and 'Peak Separation', the row is obtained 1.9, 14.0, 4.1, and 18.9. The software 'Peak Separation' improves the resolution factor for the given conditions by a factor of 2 compared with the untreated curves, and the improvement by thermal correction results in a factor of 7. The visual comparison of the DSC 204 with the DSC 2920 for practically equal sample masses yields rather identical resolution factors for uncorrected curves [11]. In contrary with the statement in [2], under certain restrictions, a correlation between the resolution factors and the sample mass is existing. The same statement holds for the dependence upon the heating rate (Fig. 6). The relations for the resolution factors of the lambda transition and the melting process are presented in Eqs (4) and (5) and constants are shown in Table 9.

The investigations of the transition temperatures for *n*-hexatriacontane and the corresponding differences as well as the involved enthalpy differences shall be discussed finally. The resolution factors are also obtained for three samples of a mass of about $790 \mu\text{g}$. The twelve heating rates selected varied from 40 to 0.05 K min^{-1} . Generally, the temperatures of transition decrease slightly with decreasing heating rates. Comparing values for two heating rates, namely for 3 and 0.1 K min^{-1} , we observe a drop from 74.12 ± 0.03 to $73.70 \pm 0.03^{\circ}\text{C}$ and for the corresponding melting tempera-

ture a drop from 76.50 ± 0.03 to 75.84 ± 0.03 °C. The differences of the transition temperatures are for the same two heating rates 2.38 ± 0.06 and 2.14 ± 0.06 K. The differences of the transition temperatures are in good agreement with the value we obtained for the investigations with changing the sample masses, namely 2.12 ± 0.10 K.

The enthalpies evaluated for the lambda transitions in function of the heating rate (Table 11) from DSC curves treated with the software 'Peak Separation' are of a rather weak variation. The relative enthalpies for 10 K min^{-1} are equal to the value obtained in the variation of the sample mass. The highest relative enthalpy for the lambda transition is observed for 4 K min^{-1} with a value of 29%. The different variations of the parameters, first the sample masses and second the heating rate may influence the rotation of the molecules within the saturation process of the lambda transition in the crystal domains with different interactions.

The resolution factors evaluated for the second and higher scans of untreated curves of *n*-hexatriacontane (Table 12, Fig. 6) demonstrate a strong dependence on the heating rate. The extreme values are $R_\lambda=1.1$ and $R_{\text{fus}}=2.5$ for 40 K min^{-1} and $R_\lambda=4.7$ and $R_{\text{fus}}=8.2$ for 5 K min^{-1} and reaching resolution factors of $R_\lambda=120$ and $R_{\text{fus}}=196$ for 0.5 K min^{-1} . The resolution factors for lower heating rates from 0.25 to 0.05 K min^{-1} are reaching infinity and therefore completely separated transition peaks are recorded.

Conclusions

The attempt for a selection and characterization of test substances which could be used in the evaluation of the temperature resolution of DSC instruments was undertaken. The investigations were started with measurements based on the publication of van Ekeren *et al.* [2] using the test substance 4,4'-azoxyanisole. A further consideration brought us to the possibility of mixtures of organic substances as test substances. Cimetidine with the two practically 'isoenergetic' crystal modifications A and D shows as 50 to 50 mixture melting without any transition from the stable into the instable crystal form in two separated melting points with the temperature difference of 0.36 K. The melting temperature of the modification with the slightly higher thermodynamic stability is $T_{\text{fus}}=140.65 \text{ K}$ [5]. The conclusion was made not to use a physical mixture as a test substance.

The test substance anticipated had to undergo physical changes or solid-state transition with a considerable amount of enthalpy change compared with the sum of both of the transitions. The second transition, most likely a melting of the substance should occur within a temperature difference of a few Kelvin. It is self-evident that the substance must be of a high eutectic purity. The first transition should also reveal a narrow half width. The lambda transition, as a second order solid-state transition, is caused by a molecular saturation effect. A certain group of alkanes reveal a so-called lambda transition which is caused by a sharp energy uptake.

The selected substance for the tests of the resolution for DSC instruments is *n*-hexatriacontane. The transition peaks are only separated by 2 K compared with the 18 K for 4,4'-azoxyanisole. The narrow temperature interval allows to discriminate

with significant resolution factors uncorrected DSC curves as well as curves treated with evaluation procedures. Additionally, the resolution for curves treated with a software for the elimination of the thermal resistance allows to compare the resolution obtained for instruments which have built-in algorithms and electronic devices so that uncorrected curves are not existing.

The presented definition for the resolution is based on a minimum between the two caloric events under inspection. The introduced resolution factor R_{MKE} is inverse in respect to the quotient defined by van Ekeren *et al.* The resolution factors for *n*-hexatriacontane increase with a better separation of the peaks by decreasing heating rates and the data we elucidated are presented in Fig. 6. This example can be regarded certainly as a general example for solving a resolution problem with a DSC.

The agreement of the thermodynamic data for *n*-hexatriacontane evaluated from our DSC curves with the literature values is rather good or even excellent.

The half width measured for *n*-hexatriacontane is sensitive to the sample mass and also to the heating rate. The influence from the first heating over the melting point is a question of the changing crystalline sample in respect to the grain size, the morphology and the contact area. The smallest half width measured is 0.2 K which is certainly close to the limiting value. The time interval necessary for passing at a given heating rate through the temperature difference of the half width is the time which allows the chains of $C_{36}H_{74}$ to reach the saturation of their rotational movement. The time interval is 0.3 s for a heating rate of 40 K min^{-1} . The fraction of the rotational molecular movement which is reached compared to the saturation within this time interval is evaluated from the enthalpy involved. The enthalpy uptake for a heating rate of 40 K min^{-1} is 17 kJ mol^{-1} , a value which gives 53% of the maximum reached. The time interval for a heating rate of 4 K min^{-1} is 3 s and the enthalpy of the lambda transition is determined with 32 kJ mol^{-1} or 29% of the sum of the two enthalpies of transition (lambda transition and melting).

A resolution test using *n*-hexatriacontane as the test substance could be easily formulated on the basis of the investigations performed and presented here.

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References

- 1 E. Marti, E. Kaisersberger, G. Kaiser and W.-Y. Ma, Netzsch Annual 2000 'Thermoanalytical Characterization of Pharmaceuticals' Netzsch-Gerätebau GmbH, D-95100 Selb/Bavaria.
- 2 P. J. van Ekeren, C. M. Holl and A. J. Witteveen, *J. Thermal Anal.*, 49 (1997) 1105.
- 3 G. W. H. Höhne, W. F. Hemminger and H.-J. Flammersheim, *Differential Scanning Calorimetry*, 2nd ed., Springer, Berlin 2003, p. 250.
- 4 Sigma-Aldrich, Product Description (www.sigmaaldrich.com).

- 5 A. Bauer-Brandl, E. Marti, A. Geoffroy, A. Poso, J. Suurkuusk, E. Wappler and K. H. Bauer, *J. Therm. Anal. Cal.* 57 (1999) 7.
- 6 E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data*, (1990) 881.
- 7 E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data*, 1 (1996).
- 8 A. A. Schaerer, C. J. Busso, A. E. Smith and L. B. Skinner, *J. Am. Chem. Soc.*, 77 (1955) 2017.
- 9 H. A. Stuart, *Die Physik der Hochpolymeren*, Bd. III, Springer, Berlin 1955, p. 450.
- 10 O. T. Sørensen and J. Rouquerol, *Sample Controlled Thermal Analysis*, Vol. 3 Series Ed., J. Simon, Kluwer Academic Publishers, Dordrecht, The Netherlands 2004.
- 11 G. W. H. Höhne und W. Kunze, *Laborpraxis*, Dezember 2001, 38.