A COMPARATIVE TEST OF DIFFERENTIAL SCANNING CALORIMETERS

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Abstract

The Dutch Society for Thermal Analysis has developed tests to measure the resolution and the sensitivity of Differential Scanning Calorimeters. For this test the substance 4,4′-azoxyanisole is used. This substance shows two transitions: a solid to liquid crystal transition at about 117°C ($\Delta H \approx 120$ J g^{-1}) and a liquid crystal to isotropic liquid transition at about 134°C ($\Delta H \approx 2$ J g^{-1}). The resolution test is performed using an amount of 5 mg substance and a high heating rate of 20°C min^{-1}. The resolution is evaluated by measuring how well the two peaks are separated. An amount of 0.25 mg substance and a low heating rate of 0.1°C min^{-1} is used for the sensitivity test. The sensitivity is evaluated as the ratio of the peak height of the LC-transition and the top-top noise level.

Members of the TAWN were asked to participate in the test. Each participant was provided with an amount of sample and a test procedure. 47 Contributions were received and these results are presented.

Keywords: DSC, resolution, sensitivity, test

Introduction

Among the most important properties of DSCs are the resolution (the ability to observe two effects, which are close to one another, separated) and the sensitivity (throughout this paper the property "sensitivity" indicates the ability to measure very small effects; it is not interpreted as the physical definition, i.e. the size of the measured signal divided by the causing physical property). As far as we know, an independent investigation with the purpose to compare these properties for a large number of commercially available instruments, has not been performed before. Therefore the board of the Dutch Society for Thermal Analysis (TAWN) decided to

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set up a committee with the assignment to develop tests to quantitatively measure the resolution and the sensitivity of a DSC. The members of the TAWN were invited to participate in the investigation by performing the tests on their own equipment, and to report the results to the committee. After evaluation of the results obtained (47 persons participated in the tests), the committee presented the results on a meeting of the TAWN in Apeldoorn, The Netherlands. Because of the great success of this meeting, it was decided to present the tests and the results also internationally on the 11th ICTAC. This paper may be regarded as a written report of the findings of the committee. It should clearly be stressed that the total quality of a DSC can not be determined from the results of the test, because of the fact that resolution and sensitivity, although important, are only two out of a large number of properties which, all together and depending on the wishes of the user, determine the total quality of a DSC.

Disclaimer

Although the committee and the board of the TAWN have exercised much care at the formulation of the tests and at the evaluation of the results obtained, no responsibility is assumed, concerning content or otherwise, for the use of the tests and for the correctness of the results presented.

Description of the tests

For the tests to be developed, an a priori requirement was that the tests are easy to perform, so that as many persons as possible could participate. This practically limited the sample(s) to be used to non-volatile solids (because liquids are more difficult to handle and because of problems with most so-called hermetically sealed sample containers). After considering several alternatives, the committee finally presented two tests with different amounts of the same substance: 4,4′-azoxyanisole. This substance shows two transitions:

- a solid to liquid crystal transition at about 117°C (390 K) ($\Delta H\approx 120$ J g^{-1});
- a liquid crystal to isotropic liquid transition at about 134°C (407 K) ($\Delta H\approx 2$ J g^{-1}).

The tests developed, which are presented in the following sections, should be addressed to as: "TAWN tests for measuring resolution and sensitivity of DSCs".

The members of the TAWN who participated in the tests were provided with an amount of test substance from a batch which was obtained from Janssen Chimica Belgium (purity: better than 98%); this assured that all experiments were performed with the same batch of test substance.

The resolution test

Because the two transitions in 4,4′-azoxyanisole are only 17°C apart, the degree of separation of the two transition peaks is used to quantify the resolution of the instrument. The experiment to measure the resolution is to be performed using the following prescriptions:

Sample mass:	(5.0±0.1) mg.
Sample container:	not prescribed; the type and mass should, however, be indicated.
Reference:	empty sample container or a carefully weighed amount of inert material; material and mass should be indicated.
Pre-treatment:	5 min at 145°C (418 K); successively cooling down to 30°C (303 K), preferably using a programmed cooling rate of 20°C min^{-1}.
Purge gas:	nitrogen; any discrepancies should be indicated accurately.
Temperature program:	heating from 30 to 165°C (303–438 K) with a heating rate of 20°C min^{-1} and a sampling rate of 10 data points per second (i.e. sampling time 0.1 s).

If an instrument does not perform well on the resolution test, the experiment may be repeated with a heating rate of 10°C min^{-1} and a sampling rate of 5 data points per second (i.e. sampling time 0.2 s); however, an experiment performed using the latter conditions can in no way be compared to the other experiments.

The sensitivity test

Because the liquid crystal to isotropic liquid transition at about 134°C (407 K) is small ($\Delta H \approx 2$ J g^{-1}) and reversible, this transition may be used to quantify the sensitivity of the instrument on heating as well as on cooling if a small sample mass and a low heating or cooling rate is used for the experiment. The experiment to measure the sensitivity is to be performed using the following prescriptions:

Sample mass:	(0.25±0.02) mg.
Sample container:	see resolution test.
Reference:	see resolution test.
Pre-treatment:	5 min at 130°C (403 K).
Purge gas:	no purge gas is to be used; perform the experiment in a static air atmosphere.
Temperature program:	heating from 130 to 140°C (403–413 K) with a heating rate of 0.1°C min^{-1} and a sampling rate of 1 data point per 10 s (i.e. sampling time 10 s); cooling from 140 to 130°C (413–403 K) with a cooling rate of 0.1°C min^{-1} and a sampling rate of 1 data point per second (i.e. sampling time 1 s).

If an instrument does not perform well on the sensitivity test, the experiment may be repeated with a heating/cooling rate of 1°C min^{-1} and a sampling rate of 1 data point per second; however, an experiment performed using the latter conditions can in no way be compared to the other experiments.

Presentation of the results of the tests

It is important that no mathematical operations on the curves obtained are performed. Especially smoothing or filtering is not allowed. It is allowed, however, to perform a linear base line correction, because this operation does not alter the results of the test.

Resolution test

The results of the resolution test are to be plotted in two plots as follows:

Plot 1:	horizontal axis:	temperature from 60 to 160°C.
	vertical axis:	heat flow; 60 mW full scale (for experiments at 10°C min^{-1}: 30 mW full scale).
Plot 2:	horizontal axis:	temperature from 100 to 150°C.
	vertical axis:	heat flow; 10 mW full scale (for experiments at 10°C min^{-1}: 5 mW full scale).

In plot 1 as well as in plot 2 linear base lines are drawn between 100 and 150°C. In plot 1 the extrapolated onset temperatures and the peak temperatures are indicated as well as the peak heights relative to the linear base line. In plot 2 the peak height (again relative to the drawn linear base line) of the liquid crystal to isotropic liquid transition and the minimum distance between the recorded curve and the linear base line between the two transitions (as well as the temperature at which this minimum distance occurs) are indicated (Fig. 1, distances b and a, respectively). The resolution is calculated as distance a divided by distance b. This implies that a smaller number indicates a better resolution!

Sensitivity test

The results of the sensitivity test are to be plotted as follows:

Heating curve:	horizontal axis:	temperature from 132 to 136°C (for experiments at 1°C min^{-1}: 132–137°C).
	vertical axis:	heat flow; 15 μW full scale (for experiments at 1°C min^{-1}: 150 mW full scale).
Cooling curve:	horizontal axis:	temperature from 136 to 132°C (for experiments at –1°C min^{-1}: 137–132°C).
	vertical axis:	heat flow; 15 μW full scale (for experiments at –1°C min^{-1}: 150 μW full scale).

Note: for best interpretation it is desired that the base line is horizontal; therefore a linear base line correction may be applied such that in the temperature range 132 to 134°C the base line is horizontal.

In both plots, in the temperature range 132–134°C, a linear line is drawn which represents the mean base line. This line is extrapolated into the transition region. Parallel to this line two other lines are drawn such that all recorded data points are

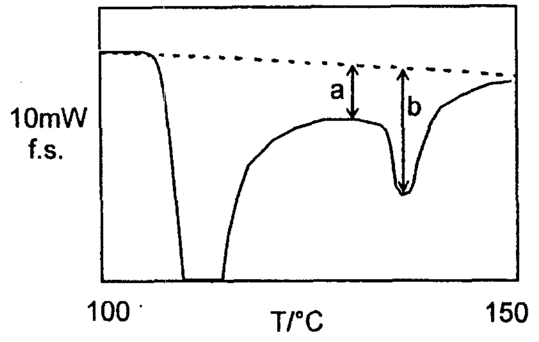

Fig. 1 Distances to be measured for calculating the resolution. The resolution is given by the quotient a/b

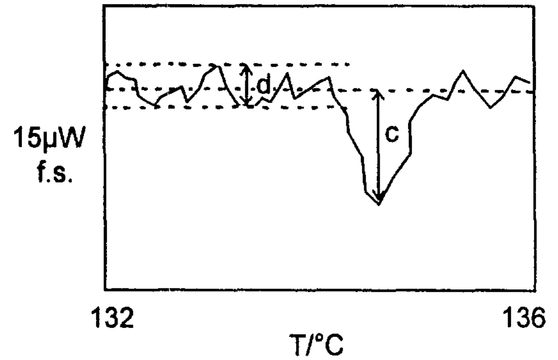

Fig. 2 Distances to be measured for calculating the sensitivity. The sensitivity is given by the quotient c/d

trapped between these two lines. The vertical distance between the last two lines (the top to top noise) is indicated together with the distance between the mean base line and the peak of the transition (Fig. 2, distances d and c, respectively). The sensitivity is calculated as distance c divided by distance d. This implies that a larger number indicates a better sensitivity!

Results of the tests

47 Members of the TAWN, from The Netherlands and from Belgium, participated in the tests. 22 Different models of DSCs of in total 8 manufacturers were included in the results. Because of incorrect interpretation of the results, however, the committee had to correct more than half of the contributions. Mistakes which were commonly observed include drawing an incorrect base line for the resolution test and an erroneous calculation of the top to top noise for the sensitivity test.

Results of the resolution test

The results of the resolution test are presented in Table 1. Some participants used helium as a purge gas, instead of nitrogen, which was recommended. That results with helium as purge gas can not be compared to results which were obtained with nitrogen (or air) as purge gas, was demonstrated by a participant, who performed experiments with helium, nitrogen and air. Results obtained with nitrogen did not deviate significantly from results obtained with air (Table 1, Shimadzu DSC 50). Another participant demonstrated the influence of the type and/or mass of the sample container on the resolution: a – considerable – larger mass of the sample container has a bad influence on the resolution (Table 1, first two rows of the Seiko DSC 220 (C)).

Table 1 Results of the resolution test. The last two columns indicate the resolution at 20°C min^{-1} and at 10°C min^{-1}, respectively. Note that values obtained with different crucibles or different purge gases can not be compared

DSC	Crucible	Purge gas	R(20)	R(10)
DuPont 910	Al; 23 mg	nitrogen	0.22	–
	Al; 23 mg	nitrogen	0.33	0.15
	Al; 23 mg	nitrogen	0.27	0.12
Mettler DSC 12 E	Al; 25 mg	nitrogen	0.22	–
	Al; 51 mg	nitrogen	0.33	0.15
Mettler DSC 20	Al; 52 mg	nitrogen	0.64	–
	Al; 50 mg	none	0.19	0.09
Mettler DSC 27HP	Al; 49 mg	nitrogen	0.22	–
Mettler DSC 30	Al; 49 mg	nitrogen	0.54	0.26
	Al; 50 mg	nitrogen	0.66	0.22
	Al; 49 mg	?	–	0.25
(ceramic sensor)	Al; 49 mg	nitrogen	0.19	–
Mettler DSC 820	Al; 50 mg	?	0.18	–
Netzsch DSC 200	Al closed	nitrogen	0.36	–
Netzsch DSC 404	Pt; 250 mg	argon	0.73	–
Perkin Elmer DSC 6	Al; 26 mg	nitrogen	0.19	–
	Al; 26 mg	nitrogen	0.19	–
Perkin Elmer DSC 7	Al; 25 mg	nitrogen	0.18	–
	Al; 29 mg	nitrogen	0.14	–
	Al; 26 mg	nitrogen	0.13	–
	Al; 26 mg	nitrogen	0.17	–
	Al; 27 mg	nitrogen	0.16	–
	Al; 40 μl	nitrogen	0.17	–
	Al; 27 mg	nitrogen	0.13	–
	Al; 24 mg	nitrogen	0.11	–
	Al; 55 mg	none	0.18	–

Table 1 Continued

DSC	Crucible	Purge gas	R(20)	R(10)
Perkin Elmer DSC 7	Al; 55 mg	none	0.18	–
	Al; 26 mg	nitrogen	0.13	–
	Al; 45 mg	nitrogen	0.12	–
	Al; 24 mg	nitrogen	0.10	–
	Al; 35 mg	nitrogen	0.17	–
	Al; 26 mg	nitrogen	0.12	–
	Al; 25 mg	?	0.16	0.09
	Al; 25 mg	?	0.10	–
	Al; 54 mg	nitrogen	0.21	–
	Al; 54 mg	nitrogen	0.18	–
	Al; 25 mg	nitrogen	0.14	0.08
Rheometrics Gold Cell	Al; 36 mg	nitrogen	0.45	–
Rheometrics DSC-SP	Al; 31 mg	nitrogen	0.26	–
Seiko DSC 120	Al; 23 mg	nitrogen	–	0.62
	Al; 206 mg	nitrogen	–	0.65
	Al; 23 mg	none	–	0.23
	Al; 400 mg	nitrogen	0.73	0.57
Seiko DSC 220 (C)	Al; 208 mg	argon	–	0.87
	Al; 23 mg	argon	0.36	0.16
	Al; 24 mg	nitrogen	0.35	–
	Al; 23 mg	nitrogen	0.42	–
Seiko TG-DTA 320	Al; 23 mg	argon	–	1.00
Setaram DSC 111	Al; 240 mg	none	0.91	0.66
Setaram DSC 141	Al; 30 μl	?	0.20	0.09
Setaram TAG 24	Pt; 175 mg	helium	0.56	–
Setaram TG-DSC 111	Al	none	–	0.92
Shimadzu DSC 50	Al; 25 mg	none (air)	0.81	0.29
	Al; 25 mg	nitrogen	0.84	–
	Al; 25 mg	helium	0.26	0.11
TA Instr. DSC 10	Al; 23 mg	argon	0.55	–
	Al; 23 mg	argon	0.46	–
TA Instr. TA 2010	Al; 23 mg	nitrogen	0.26	–
TA Instr. TA 2920	Al; 58 mg	nitrogen	0.35	–
	Al; 24 mg	helium	0.15	–
	Al; 24 mg	helium	0.12	–
	Al; 25 μl	nitrogen?	0.18	–
	Al; 22 mg	nitrogen	0.25	–

Results of the sensitivity test

The results of the sensitivity test are presented in Table 2. Here too, the influence of the type and/or mass of the sample container was demonstrated (Fig. 2, first two rows of the Seiko DSC 220 (C)): a – considerable – larger mass of the sample container decreases the sensitivity. The influence on sensitivity, however, is probably less extreme than the influence on resolution. Furthermore, for instruments for which more participants have sent results (e.g. Perkin Elmer DSC 7), it is observed that there is a large spreading in the reported values of the sensitivity. It is our experience that, for a particular instrument, the reproducibility is good. Because it is known that the sensitivity (especially noise level and base line stability) is influ-

Table 2 Results of the sensitivity test. The last two columns indicate the sensitivity at 0.1°C min^{-1} and at 1.0°C min^{-1}, respectively. Only the sensitivity on heating is presented in this table. ND stands for: Not detected

DSC	Crucible	Purge gas	S(0.1)	S(1.0)
DuPont 910	Al; 23 mg	none?	–	2.35
	Al; 23 mg	none?	–	7.00
	Al; 23 mg	none?	–	ND
Mettler DSC 12 E	Al; 25 mg	none	1.80	–
	Al; 51 mg	none	–	1.84
Mettler DSC 20	Al; 52 mg	none	ND	–
	Al; 50 mg	none	ND	2.52
	Al; 40 μl	none	–	2.34
Mettler DSC 27HP	Al; 49 mg	none	–	4.06
Mettler DSC 30	Al; 49 mg	none	ND	3.00
	Al; 50 mg	none	–	ND
	Al; 49 mg	?	ND	ND
(ceramic sensor)	Al; 49 mg	none	ND	1.71
Mettler DSC 820	Al; 50 mg	?	3.70	–
	Al; 50 mg	?	16.00	70.00
Netzsch DSC 200	Al closed	none	2.35	8.10
Netzsch DSC 404	Pt; 250 mg	?	–	ND
Perkin Elmer DSC 6	Al; 26 mg	none	1.78	–
	Al; 26 mg	none	2.12	–
Perkin Elmer DSC 7	Al; 25 mg	none	1.07	3.47
	Al; 29 mg	none	–	12.20
	Al; 26 mg	none	1.23	–
	Al; 26 mg	none	–	4.33
	Al; 27 mg	nitrogen	–	8.25
	Al; 40 μl	none	–	8.79

Table 2 Continued

DSC	Crucible	Purge gas	S(0.1)	S(1.0)
Perkin Elmer DSC 7	Al; 27 mg	?	–	12.50
	Al; 24 mg	none	ND	4.61
	Al; 55 mg	none	ND	–
	Al; 26 mg	none	2.40	–
	Al; 45 mg	–	1.40	16.60
	Al; 24 mg	none	–	2.69
	Al; 35 mg	none	1.00	4.30
	Al; 26 mg	none	9.00	–
	Al; 25 mg	none	ND	2.54
	Al; 25 mg	none	ND	3.79
	Al; 54 mg	none	1.36	–
	Al; 54 mg	none	2.90	27.00
	Al; 25 mg	none	ND	3.90
Rheometrics Gold Cell	Al; 36 mg	none	–	1.79
Rheometrics DSC-SP	Al; 31 mg	none	1.00	9.70
Seiko DSC 120	Al; 23 mg	none	2.30	8.75
	Al; 206 mg	none	7.00	–
	Al; 23 mg	none	13.50	89.00
	Al; 400 mg	none	4.40	17.60
Seiko DSC 220 (C)	Al; 208 mg	none	1.90	4.06
	Al; 23 mg	none	3.40	10.90
	Al; 24 mg	none	1.31	–
	Al; 23 mg	none	3.27	–
Seiko TG-DTA 320	Al; 23 mg	none	–	4.00
Setaram DSC 111	Al; 240 mg	none	ND	3.80
Setaram DSC 141	Al; 30 μl	none	ND	4.60
Setaram TAG 24	Pt; 175 mg	none	–	ND
Setaram TG-DSC 111	Al	none	–	ND
Shimadzu DSC 50	Al; 25 mg	none	3.00	–
TA Instr. DSC 10	Al; 23 mg	none	ND	ND
	Al; 23 mg	none	1.00	ND
TA Instr. TA 2010	Al; 23 mg	none	3.44	–
TA Instr. TA 2920	Al; 58 mg	none	2.47	–
	Al; 24 mg	none	4.79	–
	Al; 24 mg	none	5.55	–
	Al; 25 μl	none	5.60	–
	Al; 22 mg	none	1.50	–

enced by contamination of the DSC-cell, probably a number of participants worked with contaminated instruments. Another explanation may be that there possibly may be a considerable difference in sensitivity between different instruments of the same model.

It is possible that some participants did not detect the small transition in the sensitivity test because of a calibration error at this unusual low heating rate: if the error is more than two degrees, the effect to be observed is not within the measuring and/or plotting range.

Conclusion

If the prescribed experimental conditions are followed precisely (i.e. nitrogen purge gas for the resolution test, no purge gas for the sensitivity test and no use of smoothing or filtering), than the presented tests may be very useful to compare different DSCs concerning resolution and sensitivity objectively. Manufacturers are advised to add the results of these tests to the technical specifications of their instruments.

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All members of the TAWN who participated in the tests are thanked for their contributions.