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RESULTS OF A ROUND ROBIN EXPERIMENT ON THE CALIBRATION OF DIFFERENTIAL SCANNING CALORIMETERS*

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ABSTRACT

Three substances (indium, rubidiumnitrate and lithiumsulfate) with five samples each were run on four scanning calorimeters of different type to measure the heat of five well defined transitions in the temperature range 150 - 580 °C. In order to avoid errors due to differences in composition and weighing, identical samples were measured on the different apparatus. The results of the two power compensated scanning calorimeters fit very well, but the heats measured on calorimeters of heat-flux type are systematically to small in cases of higher transition temperatures and large specific transition enthalpies. Explanation is possible by the theory of heat-flux calorimeters predicting such effects.

INTRODUCTION

The calibration of differential scanning calorimeters (DSC) requires standard reference substances both for temperature and heat (resp. heat-flux) and a sufficient knowledge of the respective calorimeter. Especially the dependence of the calibration factor on sample parameters as size, transition temperature, specific transition heat, heat conductivity of the sample etc. should be well known. Moreover, according to experience the statements of the manufacturers should not be taken as very trustworthy. Thus all experiments testing the calibration of calorimeters and the suitability of materials as standard reference substances are of high interest, including round robin experiments.

In this paper the results of testing two inorganic nonmetallic substances ($RbNO_3$ and Li_2SO_4) by a miniature round robin experiment on four different calorimeters are reported. Indium was added for the determination of the calibration-factor of the respective calorimeter. Certainly, it is not possible to draw definitive conclu-

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sions since the population of the test was rather limited. Nevertheless the results of this first attempt are valuable, in particular as a base for enlarged test series.

EXPERIMENTAL

Preceeding experiments showed,that the coincidence of the results got from metal-samples by different scanning calorimeters (compared with literature) was rather good (Ref.1,2,3), whereas the transition heat of inorganic salts determined with different apparatus fluctuate sligthly more. Thus, $RbNO_3$ with three well defined solid-solid transitions (at 166, 225 and 285 °C) and Li_2SO_4 with one at 580 °C were choosen for the round robin experiment.

Five samples each of about 10 mg mass were weighed on a high precision balance into sample containers (Du Pont Al-pans) suitable for all calorimeters under investigation. Five samples of Indium were added in order to control and compare the calibration of the equipment. To normalize the results we defined the melting heat of the Indium samples to be 3280 J/mol.

The fifteen samples were measured in scientific institutes with comparable high experience in precise scanning calorimetry. All samples were run applying a heating rate of 5 K/min. The calorimeters were calibrated with the individual method of the respective institute. The following calorimeters were used:

	Type	Investigators	University of
A	PERKIN ELMER DSC-2	Hohne,	Ulm
B	PERKIN ELMER DSC-2C	Wruck and Salje	Hannover
C	DUPONT TA 1090/910	Breuer and Eysel	Heidelberg
D	HERAEUS TA 500	Reichelt and Cammenga	Braunschweig
E	same as C but with other sample holder assembly		

(Type A,B: power compensated Type C,D,E: heat flux calorimeter)

Indeed there are much more types of scanning calorimeters in use, but we didn't succeed to hunt up scientists apploying them. May be this paper encourages one or other to contact us in order to participate in these experiments.

After the return of the samples from the round robin experiment they were run once more on the calorimeter A in order to test whether the samples remained unchanged. During transport and storage the samples were kept in dry atmosphere. All measurements were carried out within half a year, the control run after one year.

TABLE 1

Results of the round robin experiment on transition heat determination

Calorimeter Type	Heat of transition and standard deviation (kJ/mol) of				
	Indium	$RbNO_3$ I	II	III	Li_2SO_4
A (1.run)	3.280±.003	3.83± .01	3.16 ±.02	1.301±.015	24.8 ± .2
B	3.280±.006	3.850±.004	3.192±.008	1.31 ±.02	24.8 ± .3
C	3.28 ±.05	3.86 ± .04	3.19 ±.04	1.29 ±.01	23.9 ± .3
D	3.28 ±.06	3.82 ± .13	3.09 ±.10	1.21 ±.04	22.8 ± .5
E	3.28 ±.03	3.72 ± .03	3.02 ±.03	1.235±.006	22.1±1.3
A (2.run)	3.280±.004	3.81 ± .02	3.10 ±.04	1.28 ±.01	24.5 ± .4

RESULTS

The experimenters reported the heat and the temperature of the onset and of the maximum of the five transitions in question. As expected the onset temperatures of the transition peaks fit rather well on all calorimeters. Temperature calibration, however, is not considered in this paper.

The transition heat obtained from the indium samples was used to calculate a normalization factor (defining the true melting heat as 3280 J/mol). All results of the respective calorimeter were multiplied with this factor to get comparable data. Table 1 includes the results of the round robin experiment, i.e. the average and the random uncertainty of the five samples as well. As can be seem the results of the two power compensated calorimeters fit rather well, whereas the calorimeters of heat flux type yielded more diverging results in the case of higher transition temperature and larger specific heats of transition. Table 2 includes the deviation of the observed heats from the average of the two power compensated calorimeters.

TABLE 2

Difference between the heats measured on heat flux calorimeters and the average measured on power compensated calorimeters.

Calorimeter	Difference from average value of calorimeter A and B			
Type	$RbNO_3$ I	$RbNO_3$ II	$RbNO_3$ III	Li_2SO_4 (percent)
C	0.5	- 0.4	- 1.2	- 3.6
D	0.6	- 2.7	- 7.3	- 8.2
E	- 3.2	- 4.9	- 5.4	-11.0

DISCUSSION

As can be seen from the standard deviations in Table 1 the 'quality' of the four calorimeters differs. Moreover, there seem to be systematic errors in the temperature dependence of the calibration factor of calorimeters D and E. For calorimeter E the replacement of the sample holder assembly obviously has altered the calibration factor versus temperature function to differ from unity, a fact rather unknown for this type of calorimeter.

Another phenomenon was found for the third transition of $RbNO_3$ (at 285 °C) Here the curves of the peak of calorimeters of heat flux type showed a clear larger step change in the baseline (Fig.1) than that of the curves of power compensated calorimeters (for theory see Ref.4,5). Different methods of determining the peak area (Ref.5) lead to results varying up to three percent. The method of straight-line baseline correction applied in this case yields an area systematically too small. This deviation is considerably larger for the heat flux calorimeters.

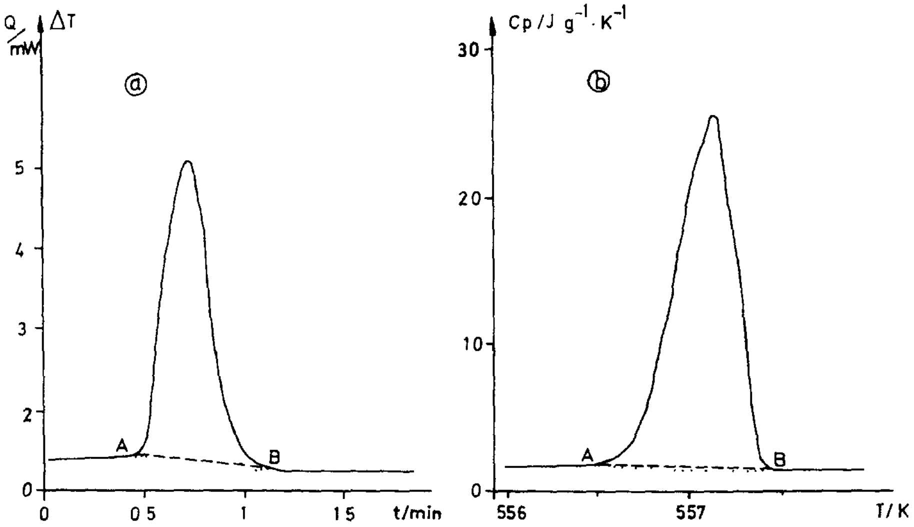

Fig.1: Plots of $RbNO_3$ transition at 285 °C measured
a) by a heat flux calorimeter (Du-Pont TA 1090/910)
b) by a power compensated calorimeter (Perkin-Elmer DSC-2)
of the same sample. The left curve shows a larger baseline shift than the right one caused by the heat flux method.
---- straight-line baseline ..... 'true' baseline

Furthermore the measuring method of calorimeters of the heat flux type involves sources of errors (Ref.4) leading to a dependence of the calibration factor on sample parameters as mass, heat conductivity, specific heat of transition etc. The very deviation between the transition heat of Li_2SO_4 measured by means of the calorimeters C,D and E and that measured by power compensated calorimeters seems to be caused by this fact. The transition heat of this material is about eight times larger than that of the other transitions.

SUMMARY

The round robin experiment has to be evaluated with great precautions because of its limited number of participants, instruments and test materials. Nevertheless some conclusions can be drawn which are also based on previous experiences of the authors (Ref.1 - 5) and other literature data.

All results indicate a slight better reproducibility of the power compensated instruments. Moreover, the heat flux instruments need an excellent set of standards for heat calibration covering its full temperature range. Such standards are not yet available. A major task for the near future should be their development and international recommendation. At the moment the quality of calibration of heat flux calorimeters depends on expense of time and cleverness of the respective experimenter. Only by great care and permanent calibration control it is possible to obtain and maintain results comparable to those of a power compensated DSC. On the one hand the calibration factor may alter by aging (oxidation) of the differential temperature probe and the heat conducting material, on the other hand theoretical (Ref.4) and experimental results indicate, that the calibration factor depends to a certain extent on the combination of the quantity of transition heat and the temperature of the transition in question.

Nevertheless the heat flux DSC can be recommended in case the pretensions in repeatability and accuracy are slightly reduced. The major advantage is its close relation to the DTA method leading to a less sensitive electronic measurement equipment at a lower price. For that reason it is easy to include a DSC module in a thermal analysis system with very low costs, whereas the power compensated scanning calorimeter is available only as a complete system so far.

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