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RESULTS OF A JOINT TRIAL ON THE METHOD OF THE DIFFERENTIAL THERMAL ANALYSIS IN THE TEMPERATURE RANGE FROM 25 TO 1000°C*

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ABSTRACT

For settling the question to what degree standardization of differential thermal analysis (DTA) is feasible by a joint trial of different laboratories, DTA-measurements on temperature-standard-substances have been carried out. The results are comparable with those obtained on identical substances by the International Confederation for Thermal Analysis and the National Bureau of Standards. A statistic evaluation of the DTA-procedures of the individual laboratories shows that the preponderant number of laboratories is achieving data which could be considered to belong to the same basic set. As a common standard deviation of the procedure of differential thermal analysis in the temperature interval of 25 to 1000°C a value of 3.6 K has been ascertained.

1. INTRODUCTION

The labor committee B6b "Thermoanalyse" of the "Fachnormenausschuss Materialprüfung im Deutschen Normenausschuss (DNA)" intended to clarify through a joint trial how far differential thermal analysis (DTA) could be normalized. There should participate experts from as many as possible branches of science and technique on this joint effort, whose problems are to be treated thermoanalytically in the temperature range from 25 to 1000°C.

2. TEST SUBSTANCE

The test substances have been chosen and supported by similar trials of the International Confederation for Thermal Analysis (ICTA) with respect to substances showing a first order transition in the temperature range mentioned. The following aspects have been taken into account:

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The substance should display enough chemical stability and undergo no changes on storage.

The substance should be inert against the materials of the DTA-measuring heads.

The equilibrium change temperature of the crystal change should be known.

Other thermal effects should not take place in the temperature range of the crystal transition.

Preheating of the substances should not be necessary.

The substances should endure heating in a normal atmosphere without showing secondary effects.

The materials should be commercially obtainable in high purity.

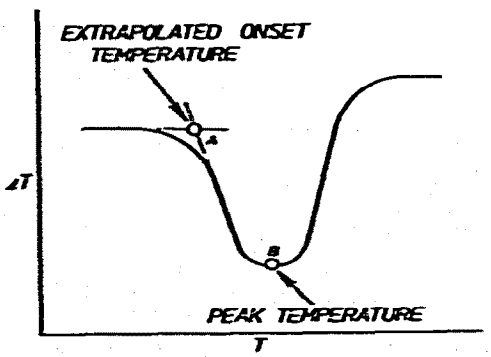
These criteria are met by the following chemicals (with few limitations):

Substance	T_u (°C)
KNO_3	127.7
$KClO_4$	299.5
Ag_2SO_4	430
K_2SO_4	583
$BaCO_3$	810
$SrCO_3$	925

whose equilibrium temperatures T_u of the transition effect are also indicated.

All these substances have been investigated from 1966 to 1972 by the Committee for Standardization of ICTA in cooperation with the National Bureau of Standards by a bigger international association of scientists. The evaluation took place outlining the extrapolated onset temperature T_o and the peak temperature T_p which are characterized more closely in Fig. 1. The results of these round robin have been published[1, 2] and may be summarized as follows:

The values established with different DTA-equipment show a distinct dependency of the extrapolated onset temperatures and the peak temperatures upon the geometry of the sample holder. The influence of the position of the ΔT couple and the calibration are undetectable. The rate of heating has a minor but significant



influence on the peak temperature. The extrapolated onset temperatures were marginally above the equilibrium temperatures. The standard deviations of the measured values were in the order of 5 to 8 K.

3. CONDITIONS OF THE COMMON TRIAL

12 scientists placed themselves at the disposal for the common trial which will be discussed in the following; some could not supply measuring values. As others have been carrying out measurements with different equipment a total of 12 measuring series could be evaluated. When the evaluation took place details on the measuring method, the quantity of the sample, the manner of reference, the weight of the reference sample, the sample- and reference receptacle, their volumes, the atmosphere and pressure, the temperature range, the kind of thermocouples, the heating rate, the DTA measuring interval and the paper feed were known.

4. EVALUATION OF RESULTS

The evaluation of the results of the working group of the Technical Standard Committee was first undertaken in analogy with the international evaluation. For

TABLE 1

RESULTS OF THE JOINTLY PERFORMED TRIAL OF JUDGING THE TEST SUBSTANCE

Compound	T_u (°C)	*Heating rate* (K min^{-1})	*n*	*Outlier 90%*	T_{onset} (°C) $\bar{x}$	T_{onset} (°C) s	*n*	*Outlier 90%*	T_{peak} (°C) $\bar{x}$	T_{peak} (°C) s
KNO_3	127.7	5	11	1	128	2.2	12	0	135	4.6
		16	11	0	130	5.5	11	0	138	4.6
$KClO_4$	299.5	5	10	1	299	5.1	10	1	306	4.8
		10	10	0	301	7.5	8	2	307	3.5
Ag_2SO_4	430	5	11	1	423	4.1	11	1	430	5.2
		10	9	2	425	3.5	10	1	434	5.7
K_2SO_4	583	5	8	0	578	7.3	8	0	584	5.8
		10	6	1	581	4.1	6	1	589	3.9
$BaCO_3$	810	5	9	1	806	5.5	9	1	815	5.9
		10	8	1	808	5.3	8	1	821	3.9
$SrCO_4$	925	5	8	0	923	6.6	8	0	933	6.3
		10	7	0	925	6.2	7	0	938	7.2

T_u = equilibrium temperature; n = number of measuring values taken into account; $\bar{x}$ = mean value; s = standard deviation.

every substance and every heating rate the mean value and the standard deviation have been ascertained and in addition outliers have been established with a statistic confidence level of 90%. The results (Table 1) correspond with the international trials, i.e., standard deviations of up to 7 K have been found. The mean values of the extra-polated onset temperatures were close to the equilibrium temperatures.

From this evaluation it becomes evident that the trials come close to the international trials, but they only give information on the usability of the test substances. As the questioning of the working group was not for test substances but for DTA equipment including their evaluation of results, statistical evaluations of the DTA-procedures of the individual laboratories have been carried out further on. The evaluation of a procedure is feasible with a model analysis. The principle consists in assigning to a certain amount of preset values — in the case described here to the equilibrium temperatures — an equivalent number of measuring values. The deviations between the given and the measured values form the basis of the statistical procedure.

In connection with the literature[3] a calculating program for this statistical procedure has been developed characterizing the quality of the DTA-method (equipment and evaluation) on the strength of the calculated standard deviations[4].

In order to obtain a sufficient number of measuring data for the statistical evaluation, the measuring results of the trials with heating rates of 5 and 10 K min^{-1} have been considered belonging to a basic set. This is necessary as the high temperature measurements with some DTA-equipment could not be carried out.

Since the onset temperatures come closer to the equilibrium temperatures the statistical calculations have been performed only with T_e and not with T_p.

In Table 2 the results of this evaluation are compiled in such a manner that the measuring series performed in the individual laboratories are assigned to the corre-

TABLE 2

RESULTS OF THE JOINTLY PERFORMED TRIAL OF JUDGING THE DTA-PROCEDURE

No. of measuring series	*No. of measuring values, n*	*Standard deviation, s*
1	12	10.9
2	6	3.0
3	12	4.2
4	6	4.6
5	12	4.0
6	12	34.1
7	6	1.8
8	6	8.2
9	8	3.3
10	12	2.5
11	12	4.6
12	12	2.7

sponding standard deviations. On application of the Bartlett-test, it becomes clear that the standard deviations of the measuring series 2, 9 and 11 are significantly greater than the others. With these measuring series there are obviously errors which could be expected to be eliminated on a second check of the evaluation procedure. The remaining laboratories produced data which may be considered to belong to one and the same basic set. The standard deviation of the procedure of differential thermal analysis in the temperature interval from 25 to 1000°C may thus be considered the best estimated value for the common standard deviation. The numerical value of same amounts to 3.6 K in the compass of the Bartlett-test.

We come to the conclusion that the results obtained are suitable to serve as a basis for standardization operations and to supply essential hints for the work of the committee.

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