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CERTIFIED REFERENCE MATERIALS FOR THERMAL ANALYSIS

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Eight inorganic substances recommended by ICTA as temperature standard reference materials for DTA and DSC were studied: KNO_3, $KClO_4$, Ag_2SO_4, K_2CrO_4, quartz, K_2SO_4, $BaCO_3$ and $SrCO_3$. The content of pure component in each of these substances was determined by classical chemical analysis. The temperatures and the heats of polymorphic transformations of these substances were measured with a Perkin-Elmer DSC–2 differential scanning calorimeter, and DTA studies were performed on a MOM 1500 D Q-derivatograph. The plot heat of transformation by DSC *vs.* DTA peak area is advanced as a calibration line for the approximate estimation of quantitative DTA effects. The substances studied will be certified as temperature standard reference materials for use in DTA and DSC.

The thermal methods of analysis are today commonplace in studies of material properties, being applicable to virtually every substance, provided the apparatus used is of a suitable design and the conditions of the experiment are properly chosen. The great diversity of instrumentation and experimental procedures employed strongly affects the results, thereby creating the need for a common basis for relating independently obtained data and for comparing and calibrating all available instruments.

A comprehensive effort relating to the standardization of the methods of thermal analysis has been launched by the International Confederation for Thermal Analysis (ICTA). Several ICTA-sponsored international research programs resulted in the certification of six sets of reference materials which are now available from the National Bureau of Standards (NBS). These were designed for calibration of the temperature axis in DTA, DSC and TG. The ICTA-NBS standards for temperature calibration in DTA and DSC encompass the range from $-83°$ to $925°$. The reference materials at present recommended for calibrating the heat of transformation in DSC are two metals of high purity (tin and zinc) certified by the NBS and a set of six materials, comprising indium and five organic substances, supplied by the National Physical Laboratory, G. Britain (NPL). The range of reproduced heats of fusion is from 28 to 147 J/g.

Irrespective of the certified reference materials mentioned above, some literature studies are known to deal with the possible use of other com-

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pounds that feature well-defined and highly-reproducible temperature points or values of the heats of certain phase transitions [1–4]. Among these substances are metals of high purity, which are recommended for this purpose by the ASTM standards [5–10]. Table 1 lists the substances certified as reference materials, as well as those whose properties make their use as such possible.

Table 1 The standard reference materials used in DTA and DSC

Substance	RM recommended by	RM available from	Substance	RM recommended by	RM available from
Polystyrene		1	Bismuth	5	
1,2-Dichloroethane	6	1	Cadmium	5	
Cyclohexane	6	1	Antimony	5	
Phenyl Ether	6	1	Aluminium	5	
o-Terphenyl	6	1	Silver	5	
Potassium Nitrate	6, 11	1	Gold	5	
Indium	4, 5, 6, 7, 8, 10, 11	1, 2	Copper	5	
			Nickel	5	
Tin	5, 6, 7, 8, 10, 11	1	Cobalt	5	
			Palladium	5	
Potassium Perchlorate	6, 11	1	Platinum	5	
Silver Sulphate	6, 11	1	Rhodium	5	
Quartz	6, 11	1, 3	Iridium	5	
Potassium Sulphate	6, 11	1	Adipic Acid	7, 9	
Potassium Chromate	6, 11	1	Naphthalene		2
Barium Carbonate	6, 11	1	Benzil		2
Strontium Carbonate	6, 11	1	Acetanilide		2
Benzoic Acid	5, 7, 8, 10, 11,	2	Diphenyloacetic Acid		2
Zinc	4, 5, 7, 8, 10, 11	1	Sapphire	4	
			Phenoxybenzene	5	
			Lead	4, 5, 7, 8, 9, 10, 11	
			Mercury	5	
			Water	5	

1/NBS, 2/NPL, 2/WZORMAT;
ASTM Standards: 4/E 968–83, 5/E 967–83, 6/E 474–80, 7/E 794–81, 8/E 928–85, 9/E 793–85, 10/D 3417–83, 11/D 3418–82.

One noteworthy fact is that there are differences in the methods of studying and certifying reference materials. Specifically, the temperature reference materials for DTA and DSC uses are certified by the multi-laboratory tests method (ICTA-NBS standards [11]); the usefulness of certain substances as reference materials for the same use is checked with the aid of one DTA instrument [1]; or the usefulness of some substances as reference materials for the heat of transition is verified by means of two DSC instruments [2]. Some authors [3] describe the quantitative calibration of a DTA apparatus by means of organic compounds previously examined by DSC. The measurements involved in the certification of selected organic substances as reference materials for the heat of transition in DSC, carried out by the NPL, were made with an adiabatic calorimeter [12]. A study conducted at the NBS laboratories with some organic compounds involved the use of a differential scanning calorimeter calibrated in conformity with the ASTM procedure using indium and sapphire [13].

The aim of the work performed in our laboratory was to study the properties of the inorganic salts recommended by ICTA as temperature reference materials for use in DTA and DSC and available on the domestic market, with the purpose of their possible certification as standards. The salts examined included KNO_3, $KClO_4$, Ag_2SO_4, K_2SO_4, K_2CrO_4 and $BaCO_3$ (cz.d.a. quality, i.e. analytical reagent grade; from the domestic suppliers). $SrCO_3$ (pure quality; imported from the USSR), and natural quartz from deposits in Poland. The contents of the pure components in these compounds were determined by classical chemical analysis. For the analytical reagent grade salts, the contents were found to conform with the Polish Standards requirements. Results of chemical analyses of the substance (pure component contents) are listed in Table 2.

Table 2 Purity of the substances selected for the standard reference materials

Substance	Assay,%
Potassium Nitrate	99.65
Potassium Perchlorate	99.92
Silver Sulphate	99.95
Quartz	99.2
Potassium Sulphate	99.3
Potassium Chromate	99.87
Barium Carbonate	99.0
Strontium Carbonate	95.8

The temperatures of polymorphic transformations of six of the compounds studied (all except $BaCO_3$ and $SrCO_3$) and the heats of these transformations were measured with a Perkin-Elmer DSC–2 differential scanning calorimeter. Subsequently, routine runs were carried out with these substances on a 1500 D Q-derivatograph (MOM) under the following conditions: heating rate 5 deg/min, a porcelain crucible with a lid, weighed portions of 150 to 550 mg depending on the specific weight of the substance, DTA sensitivity 250 μV, and a stationary air atmosphere. The results of these studies are listed in Tables 3 and 4. The equilibrium values

Table 3 Certification of temperature standards for DTA and DSC on the basis of temperature measurements by DSC and comparative DTA study performed on a Q-Derivatograph model 1500 D using NBS certified reference materials

Substance	Transition temperature data, °C				
	Equilibrium value		DSC value of our material	DTA value (onset) of our material	DTA value for NBS CRM (onset)
KNO_3	127.7	[1]	130	125	123
$KClO_4$	299.5	[1]	298	299	297
Ag_2SO_4	430	[2]	426	423	420
Quartz	573	[1]	574	576	577
K_2SO_4	583	[1]	585	586	587
K_2CrO_4	665	[1]	674	674	672
$BaCO_3$	810	[1]	–	821	816
$SrCO_3$	925	[1]	–	937	932

[1] Nat. Bur. Stand. (US), Circ. 500 (1952).
[2] J. A. Hedvall, R. Lindner, and N. Hartler, Acta Chem. Scand., 4 (1950) 1099.

Table 4 Attempt at quantitative calibration of Q-Derivatograph model 1500 D for the measurements of the heats of transition

Substance	Heat of transition, J/g			
	Literature value		Value obtained from DSC	Value obtained from DTA
KNO_3	25.1	[1]	45.2	50.0
$KClO_4$	100.5	[2]	93.8	91.5
Ag_2SO_4	25.1	[3]	41.9	42.8
Quartz	8.4	[2]	8.0	9.3
K_2SO_4	46.1	[2]	28.5	29.0
K_2CrO_4	54.4	[2]	33.9	27.0

[1] A. P. Gray, Communication to ICTA Committee on Standardization. Rep. No. ICTA. 73–02, Appendix 4 (1973).
[2] Nat. Bur. Stand. (US), Circ. 500 (1952).
[3] J. A. Hedvall, R. Lindner, and N. Hartler, Acta Chem. Scand., 4 (1950) 1099.

of temperatures and heats of transition obtained from the literature have been included for the sake of comparison. Table 3 also gives the results of the measurements of the NBS certified temperature standards made on the 1500 D Q-derivatograph.

Certain materials that had successfully been used to develop reference temperature points for DTA and DSC were also tested for application as standards of the heats of transition for DTA under the ICTA project [11]. This idea, however, was soon abandoned, in view of the lack of reproducibility of the results. Nevertheless, analogous studies on the heats of polymorphic transformation of eight temperature reference substances have been resumed by Mackenzie and Ritchie [14]. The graphical relationship between the peak areas in deg s/mg and the ΔH values in cal/mg, taken from the literature, was found by these authors to be a practically straight line.

In the study performed in our laboratory, an attempt was also made to correlate the peak surface area and the heat of transition. The values ΔH employed were determined in this study with a Perkin-Elmer DSC–2 instrument. The resulting straight line is shown in Fig. 1, which includes the calibration plot obtained by Mackenzie and Ritchie.

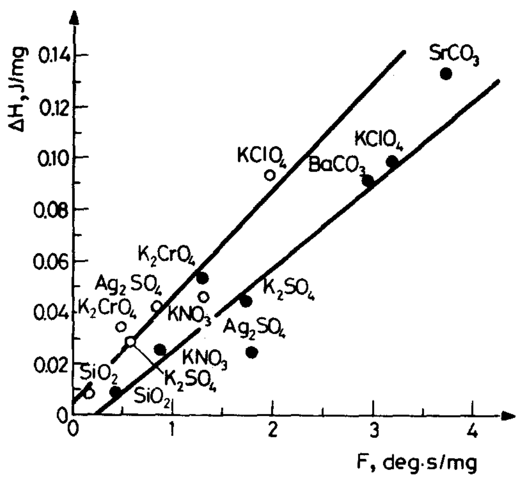

Fig. 1 Comparison of the calibration plots
–●–●–●– Literature data of transition heats H *vs.* DTA peak area (Mackenzie and Ritchie [14]) standard deviation $s = 0.0155$ J mg^{-1}
–○–○–○– Transition heat by DSC *vs.* DTA peak area, both obtained in this work standard deviation $s = 0.00837$ J mg^{-1}

It should be pointed out that the plot cannot be treated as a universal means for calibration of the heat of transition in the DTA method. Its limitation stems primarily from the fact that it holds true merely for certain specific experimental conditions, especially for the weighed portion on which the measurements were made. Nevertheless, because of the lack of other measures that would result in the more precise use of DTA instruments for quantitative measurements, the plot may be regarded as a useful approximation.

The aim of the research reported in this paper is the certification by 1989 of the above-mentioned eight substances as temperature standard reference materials for use in DTA and DSC.

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Zusammenfassung – Acht von der ICTA als Temperaturstandard-Referenzmaterialien für DTA und DSC empfohlene und im Lande verfügbare Substanzen wurden untersucht: KNO_3, $KClO_4$, Ag_2SO_4, $K_2Cr_2O_4$, Quarz, K_2SO_4, $BaCO_3$ und $SrCO_3$. Der Gehalt der Substanzen an diesen Verbindungen wurde klassisch chemisch-analytisch bestimmt. Temperaturen und Enthalpien der polymorphen Umwandlungen wurden mit dem Gerät DSC 2 (Perkin-Elmer) bestimmt, DTA-Untersuchungen erfolgten mittels Derivatograph Q 1500 D (MOM). Eine Darstellung (Umwandlungsenthalpie aus DSC-Messung) über der DTA-peak-Fläche wird als Eichgerade für die näherungsweise quantitative Bewertung der DTA-Effekte vorgeschlagen. Die genannten Substanzen sollen als Temperaturstandards für DTA und DSC geprüft werden.

РЕЗЮМЕ — Изучены восемь неорганических соединений (нитрат-, перхлорат-, сульфат, и хромат калия, сульфат серебра, карбонаты бария и стронция, и кварц), рекомендуемых ICTA в качестве стандартных веществ для калибровки температуры в приборах для ДТА и ДСК. Содержание чистой компоненты в каждом из этих веществ определялось классическим химическим анализом. Температуры и теплоты полиморфных превращений этих веществ измерялись дифференциальным сканирующим калориметром ДСК—2 фирмы Перкин-Эльмер, а ДТА измерения были проведены на Q-дериватографе 1500 Д фирмы МОМ. Графическая зависимость в координатах теплота превращения (метод ДСК) — площадь ДТА пика была предложена в качестве калибровочной кривой для приближенной оценки количественных эффектов ДТА. К каждому веществу был приложен сертификат и все вещества рекомендованы в качестве стандартных реперных материалов для использования в ДТА и ДСК.