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TEMPERATURE STANDARD REFERENCE MATERIALS FOR THERMAL ANALYSIS

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The feasibility of the use of potassium nitrate and potassium perchlorate as temperature standards in Differential scanning calorimetry has been studied. The solid-state phase transition temperatures of KNO_3 and $KClO_4$ were determined by means of DSC. The metrological properties of these salts as calibration materials were examined. The reliability of KNO_3 and $KClO_4$ calibrations was investigated by twofold determination of the bismuth melting temperature after the apparatus had been calibrated with indium and lead, and with KNO_3 and $KClO_4$. Conclusions were drawn concerning the suitability of these salts for use as DSC temperature calibrants.

Keywords: DSC temperature calibrants, potassium nitrate, potassium perchlorate

Introduction

Temperature standard reference materials for thermal analysis constitute a research subject which the authors have been pursuing since 1985. Temperature standards for differential thermal analysis (DTA) were discussed in a paper [1] presented at the Fourth European Symposium on Thermal Analysis and Calorimetry in Jena in 1987, whereas temperature standards suitable for use in thermogravimetry and in evaluation of quasi-isothermal operation quality were presented at the Fourth Symposium on Temperature and Thermal Measurement in Industry and Science in Helsinki in 1990 [2].

A list of thermoanalytical certified materials available from the Polish Committee for Standardization, Measures and Quality Control is given in Table 1. The metrological significance of the temperature difference (t_2–t_1) reproduced by standards in the quasi-isothermal mode of thermogravimetric operation is explained in Fig. 1.

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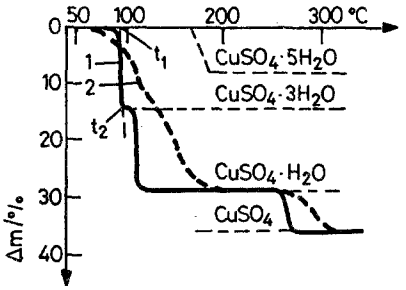

Fig. 1 TG curves for $CuSO_4 \cdot 5H_2O$. 1 – quasi-isothermal conditions, 2 – dynamic heating

Study on feasibility of use of potassium nitrate and potassium perchlorate as temperature standards in differential scanning calorimetry (DSC)

The direct motivation for our investigations of potassium nitrate and potassium perchlorate was provided by the frequently encountered statement [3–5] to the effect that the best results in DSC are obtained when like substances are used for the calibration.

The calorimetric measurements were carried out on a Perkin-Elmer DSC 7 differential scanning calorimeter. The substances examined were potassium nitrate and potassium perchlorate of analytical reagent grade quality manufactured in Poland.

The experimental method employed throughout this work was the GEFTA recommended procedure [5] based on the linearity of the relationship between transition temperature values obtained at various heating rates and the respective heating rates maintained with a high degree of accuracy.

From a mathematical viewpoint, the GEFTA procedure regards the transition temperature under consideration as the intercept T_o of the linear function

$$T = T_o + a \cdot q$$

where q denotes heating rate, the physical meaning of T_o being the transition temperature value at zero heating rate.

The first part of the study had the aim of the precise determination of the solid-state phase transition temperatures of potassium nitrate and potassium perchlorate using DSC. Prior to the measurements, the instrument was calibrated over two temperature ranges including the temperatures of the examined transitions. Two pairs of calibration standards were used: benzoic acid and indium, and tin and lead. According to the GEFTA recommendation. the two-specimen duplicate measurements were carried out at six heating rates (10, 5, 2.5, 1, 0.5 and 0.2 deg/min) for both pairs of calibration materials, and the melting

temperature values found by extrapolation to zero heating rate were subsequently utilized for the calibrations. The same method was followed in the determination of the solid-state phase transition temperatures of potassium nitrate and potassium perchlorate, the duplicate experimental runs being performed on each of five specimens at the heating rates specified above. The values obtained and the standard errors of evaluation are listed in Table 1.

In the second part of the study, the analysis was performed to answer the question of whether the relation established for indium melting [6] between the peak width and the sample mass and heating rate holds for the salts under examination. An affirmative answer would provide evidence of the universal metrological properties of the studied salts.

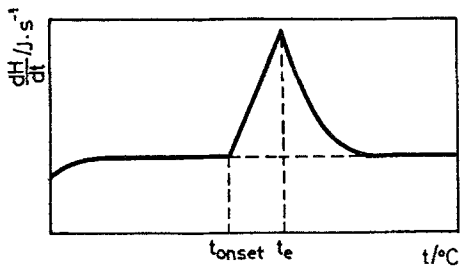

Fig. 2 Curve of a first-order phase transition (melting or solid-state phase transition)

The mathematical equation derived by Miltenburg and Cuevas-Diarte [6] relating the temperature difference ($t_e - t_{onset}$) (Fig. 2) characteristic of the peak shape to the heating rate (q), sample mass (m), enthalpy of fusion (dH) and heat transfer coefficient (K) is as follows:

$$t_e - t_{onset} = \left(\frac{2 \cdot q \cdot m \cdot dH}{K} \right)^{\frac{1}{2}}$$

Figures 3 and 4 illustrate the juxtaposition of the ($t_e - t_{onset}$) values measured at various heating rates and calculated from the above equation for potassium nitrate and potassium perchlorate, respectively. Figure 5 presents the same relations in the case of the fusion of indium. The measurement results corroborate the model developed by Miltenburg and Cuevas-Diarte. A similar functional relationship was found to be valid for the solid-state phase transition which both potassium nitrate and potassium perchlorate undergo. The differences between the measured and calculated ($t_e - t_{onset}$) values for both examined salts are comparable with those obtained for indium.

The third part of the study consisted of an examination as to whether the calibrations performed with the metals could be regarded as metrologically interchangeable with those made with the salts under study. The reliability of the calibrations involving potassium nitrate and potassium perchlorate was ex-

Table 1 Certified temperature standards for thermal analysis available from the Polish Committee for Standardization, Measures and Quality Control

Temperature standards for DTA			Temperature standards for TG quasi-isothermal mode of operation				
Substance	Certified temperature / °C	Standard error, σ / °C	Substance	t_1 / °C	Standard error, σ (t_1) / °C	$t_2 - t_1$ / °C	Standard error, σ ($t_1 - t_2$) / °C
KNO_3*	129.22	±0.02	$CaC_2O_4 \cdot H_2O$	221	±2	12	±2
$KClO_4$*	300.41	±0.06	$CaCO_3$	924	±4	11	±4
Ag_2SO_4*	426.20	±0.11	$CuSO_4 \cdot 5H_2O$	99	±2	0	±1
Quartz	571	±7	$CuSO_4 \cdot 5H_2O$	111	±2	3.5	±1
K_2SO_4	582	±5					
K_2CrO_4	665	±7					

* Value found by DSC.

Temperature values for unstarred substances were found by replicate measurements on the 1500 D Q-derivatograph (values of scale intervals of the measuring rule used for temperature evaluation from the experimental records were 1 deg, 2 deg and 10 deg for the temperature ranges 125°, 250° and 1000°C, respectively)

amined by twofold determination of the bismuth melting temperature, which has been reported to be 271°–442°C [7].

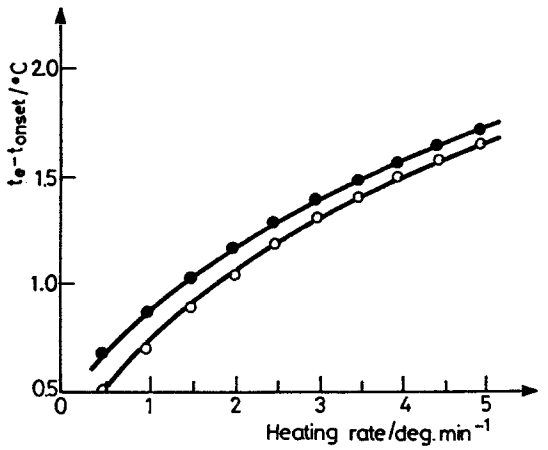

Fig. 3 (t_e–t_{onset}) values *vs.* heating rate for potassium nitrate.
o values calculated according to [6]. • values measured, $K = 13.95 \cdot 10^{-3}$ W/deg, sample mass $m = 4.47$ mg

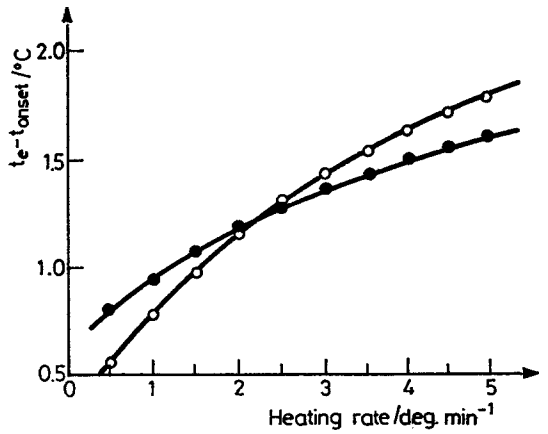

Fig. 4 (t_e–t_{onset}) values *vs.* heating rate for potassium perchlorate, o values calculated according to [6].
• values measured, $K = 13.95 \cdot 10^{-3}$ W/deg, sample mass $m = 2.47$ mg

The procedure employed was as follows. First, the instrument was calibrated by means of indium and lead, and the bismuth melting temperature was determined. Subsequently, the determination was repeated after the apparatus had been calibrated with potassium nitrate and potassium perchlorate. In the latter

case, the transition temperatures of potassium nitrate and potassium perchlorate measured in the first part of this work were utilized as the reference values.

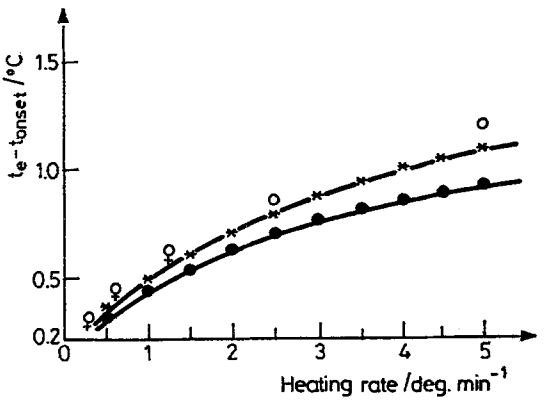

Fig. 5 (t_e–t_{onset}) values *vs.* heating rate for indium, * values calculated according to [6]. • values measured, K = 13.9510^{-3} W/deg, sample mass m = 3.46 mg, o values calculated [6], + values measured [6], K = 16·10^{-3} W/deg, sample mass m = 4.81 mg [6]

The metrological performances of indium, lead, potassium nitrate and potassium perchlorate as calibration materials were expressed in terms of precision measures of the regression lines of the $t_{onset} = f(q)$ (onset temperature *vs.* heating rate) function used for extrapolation according to the employed GEFTA procedure. The regression lines were characterized by the standard error of the function σ_y, the standard error of the intercept σ_A (i.e. the standard error of the extrapolated temperature t_{onset} value) and the correlation coefficient.

Table 2 Precision measures of the regression lines of the $t_{onset} = f(q)$ function (onset temperature *vs.* heating rate)

Substance calibrant	Correletion coefficient / r	Standard error of function σ_y / °C	Standard error of intercept σ_A / °C
Indium	0.997	±0.05	±0.01
Lead	0.973	±0.15	±0.04
Potassium nitrate	0.993	±0.10	±0.03
Potassium perchlorate	0.975	±0.26	±0.07

The numerical values of these parameters are given in Table 2. From Table 2, the conclusion can be drawn that the metrological parameters of potassium nitrate and potassium perchlorate as DSC temperature reference materials are comparable to those of indium and lead in the analogous capacity, the two latter substances long having been recommended as DSC temperature standards.

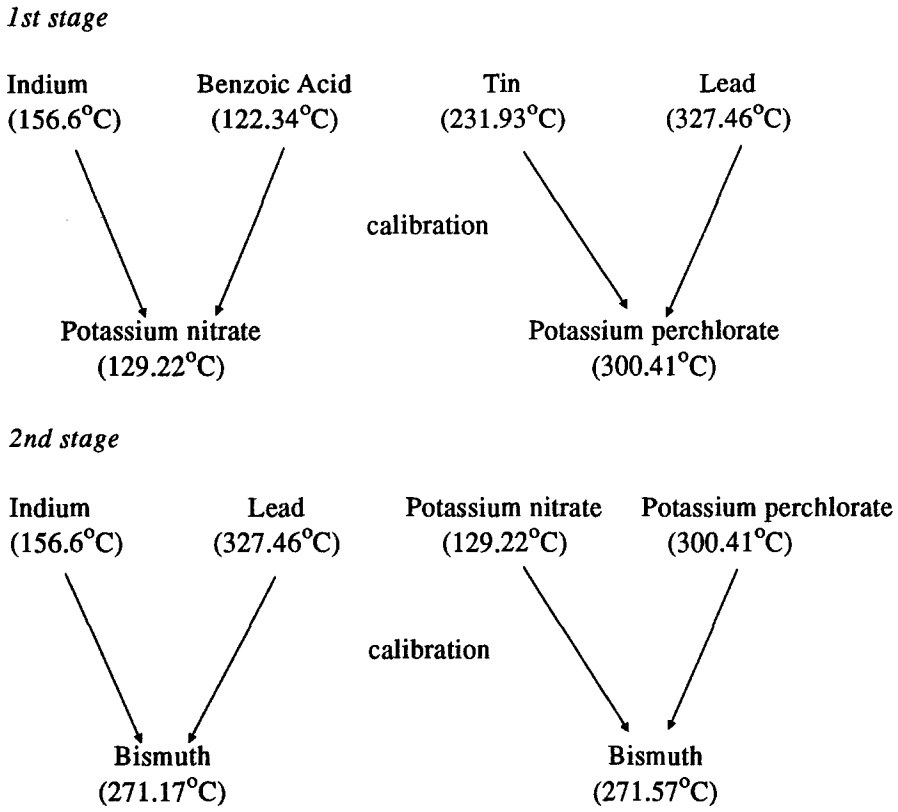

Fig. 6 Schematic depiction of the measurements relating to the reliability of the use of potassium nitrate and potassium perchlorate for calibration

The logical scheme followed to establish the validity of the use of potassium nitrate and potassium perchlorate for calibrations is shown below.

The difference between the bismuth melting temperature values obtained in the two measurement series described above amounts to 0.4 deg, which can be stated to be a satisfactory result in view of the reported [7] boundary accuracy of DSC temperature calibration.

Conclusion

The measurement results show the possibility of utilizing potassium nitrate and potassium perchlorate as secondary temperature standards in differential

scanning calorimetry when an increased demand for accuracy requires that substances with similar structures be used for the calibrations.

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Zusammenfassung — Es wurde die Möglichkeit der Verwendung von Kaliumnitrat und Kaliumperchlorat als Temperaturstandard für DSC untersucht. Die Bestimmung der Temperaturen für Feststoff-Phasenumwandlungen von Kaliumnitrat und Kaliumperchlorat wurde mittels DSC erreicht. Weiterhin wurden die meßtechnischen Eigenschaften der untersuchten Salze (KNO_3 und $KClO_4$) als Bezugssubstanzen geprüft. Die Zuverlässigkeit der Kalibrierung mittels KNO_3 und $KClO_4$ wurde durch eine zweifache Bestimmung der Schmelztemperatur von Wismut überprüft: einmal nach der Kalibrierung des Gerätes mit Indium und Blei und andererseits nach der Kalibrierung mit Kaliumnitrat und Kaliumperchlorat. Angesichts der Resultate kann man feststellen, daß die untersuchten Salze zur Temperaturkalibrierung in der DSC geeignet sind.