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THERMOMETRIC STANDARD FOR CONTINUOUS SCALE VERIFICATION IN THERMAL ANALYSIS

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Ionic temperature detectors are described and discussed as possible internal temperature standards for thermal analysis and calorimetry. The available scale from 200 °C to 900 °C is shown, together with the miniature dimensions.

The metrological quality of the thermometric instruments (thermocouples and resistance thermometers) used in thermal analysis is usually not questioned, simply because their stability is not expected to be really endangered. Generally, such as expectation is sound, but it should be taken into account that real working conditions, such as thermal cycling, the influence of the ambient atmosphere, or the faulty design of the supporting structure, could introduce some errors into the e.m.f. readings as a function of the thermodynamic temperature.

In the case of the Pt-Pt/Rh (10%) thermocouple, the main danger comes from the possibility of the rhodium oxide gas transport in the range 500°–900° in the presence of oxygen. Rhodium created in such way inside the platinum branch (oxide decays at 1200°unpredictably changes the accuracy). The depletion of the original alloy enhances the effect. The influence of the ambient atmosphere could be important in the case when the thermocouple is not sheathed and the studied samples emit reactive vapours.

Similar problems could occur if chromel-alumel thermocouples are used. The platinum resistance thermometer, if used up to approx. 600°, shows very stable and correct values. However, long thermocycling could mechanically damage the thin platinum wire, because of the thermal expansion differences between the ceramic support and platinum.

Therefore, an improvement in the certainty of the correct correlation between the thermometric instrument used and the thermodynamic temperature scale (e.g. IPTS), preferably continuously and in situ, would be welcomed. The introduction of ionic thermometric detectors (ITD) could provide a possible answer for the DTA and calorimetric technique.

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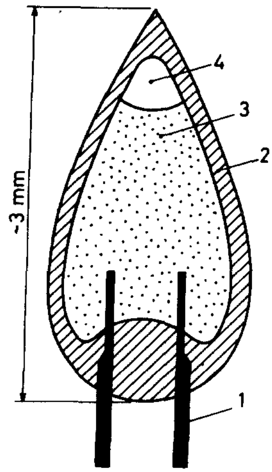

Fig. 1 Ionic temperature detector
1. Platinum contact
2. Glass bulb
3. Ionic salt
4. Vacuum

Experimental

The ITD, or incorrectly ionic thermometers, are miniaturized temperature-point standards (Fig. 1). The temperature point is defined by the phase transformation or melting of assorted and well-selected ionic compounds (Table 1). The defined point is measured as a steep jump of the electrical conductivity [1–4].The Table shows the temperature points so far available inside borosilicate glass or quartz containers. The long-term stability (up to 2 years) is ± 0.1 deg, while with higher sensitivity a certainty of ± 0.05 deg could be reached. This represents the stability in comparison with the thermodynamic temperature, and the limits within which the user could be sure of the thermodynamic certainty of his own measurements. The detector dimensions are 2 mm dia, 3–4 mm length, and overall average weight 0.1 g, which make its introduction into the DTA or calorimetric feasible. The ITD are widely used in the nuclear energy industry for temperature measurement unification, in the form of a samll portable temperature-point unit (furnace) controlled by ITD. This instrument makes it possible to check the thermometers directly in situ, inside the industrial plant [5]. It has even been proved that these elements are usable as internal standards inside the core of the nuclear reactor, though of course with higher error [4]. The ITD could be placed inside the measuring block of the DTA or DSC without losses on the thermal balance side. The signal of the ITD is taken as a resistance measurement, using the industrial frequency (50 s^{-1}). The resistance jump (Fig. 2) is to a high degree characteristic of all ITD, so the temperature-point value could easily be recognised and compared with the value of a thermometer employed in a simple electronic circuit.

Table 1 Temperature points applied in ITD practice

Compound	Type of transformation	Temperature, °C
HgI_2	melting	256.0
$NaNO_3$	melting	306.5
CdI_2	melting	386.6
KIO_3	probably s-s transition	460.7
$CdBr_2$	melting	568.3
Na_2WO_4	s-s transition	593.0
RbI	melting	642.5
Bi_2O_3	s-s transition	707.0
$BaCl_2$	s-s transition	906.0

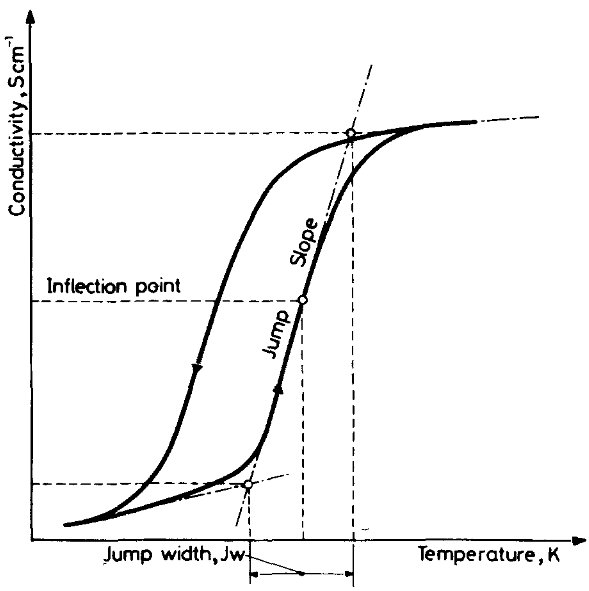

Fig. 2 Idealised curve of electrical conductivity behaviour at melting and solidification of employed salts. Real curves are less symmetric, steeper at solidification (arrows are showing the temperature change). The temperature is read usually at the inflection point, or at 65% of the jump.

Conclusion

The introduction of ionic thermometric detectors is recommended for all measurements in DTA and calorimetry experiments, where continuous checking of the agreement of a measured temperature with a thermodynamic temperature scale is required, i.e. in cases where phase tranformation effects, melting, pyrolysis, or other phenomena with critical temperature points are studied. The temperature scale covered by ITD so far is shown in Table 1.

References

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Zusammenfassung – Ein neuer Typ von Temperaturstandards ("Ionische Temperaturdetektoren") wird beschrieben und ihre Verwendung in der thermischen Analyse und Kalorimetrie diskutiert. Hervorzuheben sind ihre geringen Abmessungen. Ein Meßbereich von 200 bis 900 °C kann abgedeckt werden.

РЕЗЮМЕ — Описаны и обсуждены ионные температурные датчики как возможные внутренние температурные стандарты для термического анализа и калориметрии. Наряду с их очень малыми размерами, доступной для них является широкий интервал температур 200—900°.