# Note

## RELATION OF THE REPORT BY G. WILLMAN TO ICTA'S STANDARDIZATION PROCEDURES

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(Received February 6, 1976)

The inference by Willman [1] that ICTA's Committee on Standardization had proposed [2] a procedure for *determining* the temperature of a DTA effect is erroneous. Instead, the Committee proposed that certain batches of selected materials be used to relate results from one laboratory to another. These materials were *known by coordinated experiments* to provide clear and reproducible solid-solid or solid-liquid transitions [3]. Use of the same source of material is important because some transitions are quite sensitive to impurities, hence the use of the same compound from different batches could lead to mistaken conclusions regarding agreement or disagreement in temperature of thermal events observed in different laboratories. See, for example, the example given by Deshpande et al. [4] of the behavior of potassium nitrate from another source and the further explanations of the behavior of the SRM potassium nitrate by Garn et al. [3] and the ascription of some of the anomalous behavior to the slowness of the III → II reversion under certain circumstances [6]. The procedure recommended by the Committee on Standardization avoids the effects of the slow reversion by first heating through the transition before making the calibrating run.

The Committee had agreed very early in its work that there were inherent errors in the measurement of the temperature of a thermal effect and these error were related to the type of furnace assembly and, to a lesser degree, upon the heating rate. In its work preliminary to the certification of a group of Standard Reference Materials it had ascertained that the variation due to heating rate was much less than that due to variation in instrument types. Willman's data show that the variation of $T_{on}$ for lead is about 5 °C over a ten-fold change in heating rate. This is less than the average standard deviation for the ten materials certified.

For its Second International Test Program which led to this certification, a range of heating rates (4−10°/min) within ordinary practice was specified to the participants [3]. The extrapolated onset temperature and the peak temperature were chosen as the values to be reported. The initial temperature, corresponding to the departure temperature, $T_{ab}$, reported by Willman to be the correct measurement, was dropped from consideration because the previous testing had shown that reported values were less reproducible than the measurement points adopted.

This author recently ascribed the variation in the reported values to the differing position the temperature measuring point with respect to the specimen from one apparatur to another [7]. In some instruments the temperature is measured within the specimen, in some at the edge of the specimen, and in others at a less well defined position.

In 1951, Smyth [9] analyzed the DTA peak with some simplifying assumptions and showed that if the temperature is measured at the center, the peak temperature is the best measure of the temperature of the event, whereas if the temperature is measured at the edge (corresponding more closely to Willman's measurement), the initial or departure temperature is best. Neither position can be treated as a general truth for DTA. The variation in furnace types used by the participants indicate need for a common measuring technique. The extrapolated onset has been used for many years (See, for example, Smothers and Chiang [9]) and, in the experience of the Committee, is a reproducible point on the DTA curve. It is less justifiable in theory but more easily used than the initial temperature. The apparent agreement of the extrapolated onset temperature with the equilibrium values results from a skewing of statistics – the preponderance of measuring points outside the sample [7], not to any intrinsic merit other than good reproducibility.

To summarize, the report by Willman [1] has no valid relationship to the work of the Committee on Standardization. The Committee had taken into account the measuring technique and the temperature dependence cited. Willman's data, interpretation and conclusion should be considered solely on their own merits – without comparison to the standardization program of the International Confederation for Thermal Analysis.

## References

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