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The reliable measurement of DSC onset points by internal referencing.
Part 1 [1]

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Abstract

Frequent calibration checks are desirable, yet troublesome and tedious. Where applicable, powdered pure metals added to samples serve as internal references, thus avoiding many errors. One of these, the often-cited difference in thermal conductivity between calibrating metal and sample, is shown to be small. The method is tested on the tetraphenyl derivatives of the Group 4 elements.

INTRODUCTION

Calibration of a DSC apparatus, either for temperature [1–5] or for heat of fusion [1, 3, 4, 6], seems trivial, especially as manufacturers furnish convenient, though approximate [4], computational programs. Low-temperature calibration [5] is often ignored. Commonly, pure indium and tin are used, with the perhaps unstated assumption that linear interpolation and extrapolation are appropriate. However, for temperature the literature reveals substantial instrumental variability. A roughly parabolic (quadratic) correction is sometimes observed [7–9], and the German Society for Thermal Analysis (GEFTA) specifies that "at least three calibration substances should be selected which cover the temperature range in question" [1, 2]. Even this may not suffice for crucial measurements on purified materials, for comparisons between instruments or between heating rates, or over time, especially when the DSC apparatus is heavily used and may suffer indignities such as messy thermal decompositions. The amount of recalibration and/or rechecking that would be required becomes impractical, and as a rule is neglected.

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An alternative that may often be applicable is “internal referencing”, by addition of high-purity (5N means 99.999%) metal fragments or powder directly to the test sample. Despite considerable searching of the DSC literature, no valid precedent for this has been found. Metals are mutually immiscible with virtually all other substances; therefore, unless reaction occurs, their thermal behaviors are expected to be independent [10]. Reactivity is an obvious concern, but can be detected by DSC and/or predicted. Internal referencing cannot compensate for non-linearity of calibration, but will facilitate recognition of sudden or gradual instrumental changes. With appropriate weighing, the method should be applicable to heats as well as temperatures of transition. The present work is intended as a first examination of “internal referencing”.

EXPERIMENTAL

Except for the first trial on a Du Pont 910/2100 DSC at 10°C $\min^{-1}$, all measurements were made on a Seiko DSC-220c at 3.16°C $\min^{-1}$ heating rate. Metal powders were sprinkled onto or gently stirred into the test samples in the DSC pan, the latter being either 6 mm “open” (covered) or hermetic. For substances found to be volatile at or somewhat above their onset points, a Du Pont hermetic sealer was used, and the lids were placed concave upwards on the pans, better to define the sample shape. Despite compression of the 6.8 mm o.d. pans to a final diameter of 7.9 mm, vapor leakage often occurred at the highest temperatures with the tetraphenyl compounds, making heats of fusion from repeat runs too low but causing no detectable shift of the onset point.

The 5N metal powders, approx. 50–100 mesh, were obtained from Aldrich (In, Bi, Pb) and Alfa (Sn, Cd); the cadmium powder (200 mesh) was old and gave low heats of fusion indicative of approx. 30% oxide. An old, impure sample of tetraphenylmethane (Aldrich, mp 270–280°C) was twice vacuum-sublimed (gradient-temperature deposition), then acetone-washed, recrystallized from acetic anhydride and, after treatment with acidic silica gel and basic alumina, was recrystallized from toluene and vacuum-sublimed once again. The tetraphenylsilane (Petrarch), tetraphenylstannane (Alfa), tetraphenylgermane and tetraphenylplumbane (both Aldrich) were each similarly sublimed once. The 12% crosslinked polystyrene powder (Biobeads S-X12) came from Bio-Rad Inc., and the 4,4′-dihydroxytetraphenylmethane was a laboratory sample and had a melting point of 284–287°C.

Metal-calibrated [10] capillary melting-point ranges for the Group 4 tetraphenyls are listed here for comparison with the internally-referenced onset points: Ph_4C 284–284.7°C; Ph_4Si 236.5–237.3°C; Ph_4Ge 234–234.7°C; Ph_4Sn 227–229°C; and Ph_4Pb 229.2–229.7°C.

TABLE 1

The effect of a non-melting matrix on measured onset points of metals

Metal powder[a]	Wt. (mg)	Matrix powder	Wt. (mg)	Initial onset point (°C)	Repeat onset point (°C)	Repeat onset point (°C)
Tin	0.82	–	–	231.87[d]	231.13[d]	231.00[d]
Tin	0.81	$Ph_4C(OH)_2$[b]	4.14	231.82[d]	230.97[d]	230.86[d]
Cadmium	1.38	–	–	320.7[e]	320.6[e]	320.5[e]
Cadmium	0.59	CuPc[c]	7.32	320.7[e]	320.6[e]	–

[a] ITS-90 melting points are: tin, 231.93°C; cadmium, 321.07°C. [b] 4,4′-Dihydroxytetraphenylmethane. [c] Copper phthalocyanine. [d] Du Pont DSC, 10°C min^{-1}. [e] Seiko DSC, 3.16°C min^{-1}.

The Seiko DSC-220c was used in the "manual" mode for measurement of onset points; however, slope-fitting was done automatically, rather than by the optional "manual" choice. Although peaks were expanded by narrowing the span of the plots to a few degrees, little or no difference in

TABLE 2

The effects of matrix on metal onset points and on heats of fusion

Metal[a]	Wt. (mg)	Matrix powder	Wt. (mg)	Onset point (°C) and $\Delta_{fus}H$ (J g^{-1})				
				Melt #1	Melt #2	Melt #3	Melt #4	Melt #5
Indium	1.53	–	–	156.8	156.8	156.7		
powder				29	28	29		
Indium	19.92	–	–	156.8	156.7	156.7	156.8	
(piece)				30	30	30	30	
Indium	0.45	CuPc[c]	6.05	156.8	156.8	156.8		
powder				27	27	27		
Indium	0.42	XL-PS[d]	2.62	156.8	156.8	156.8		
powder				29	29	29		
Indium	0.17	XL-PS[d]	11.39	156.7	156.8			
powder				34	34			
Indium	0.825[b]	–	–	156.7	156.6	156.7	156.7	156.6
(piece)				28.9	28.6	28.8	28.8	28.9
Tin	0.737	–	–	231.8	231.2	230.3	229.4	228.9
(piece)				61.5	61.0	61.1	61.9	62.9
Bismuth	0.797	–	–	271.2	271.1	271.1	271.1	271.1
(piece)				53.5	53.5	53.2	53.0	53.9
Lead	0.916	–	–	327.1	326.8	326.8	327.0	326.8
(piece)				22.5	22.7	22.4	22.7	22.5

[a] ITS-90 melting points (°C): In 156.60, Sn 231.93, Bi 271.40, Pb 327.46. [b] In "hermetic" sealed pans. [c] Copper phthalocyanine. [b] 12% Crosslinked polystyrene.

onset point values was found, even when plot spans of 30–50° were used. Peaks were typically narrow and similar in shape, both for metals and for compounds.

A current software limitation of the Seiko DSC-220c is that it provides only the first decimal place for temperatures above 100°C, thus preventing finer discrimination; such non-Gaussian rounding-off errors are ±0.1°C in the temperature differences in each run between onset points of sample and reference, and cannot reliably be reduced by averaging of repeat measurements. This error, or some fraction thereof, must be appended to all Gaussian errors computed using data from Tables 1–4.

TABLE 3

Onset points (°C) for Group 4 tetraphenyls and internal references

Compound and internal reference	Wt. (mg)	Onset points (°C)				
		Melt #1	Melt #2	Melt #3	Melt #4	Melt #5
Tetraphenylmethane	2.762	282.2	282.0	281.9	282.1	282.2
Bismuth (piece)	0.121	271.4	271.0	270.8	270.7	270.7
ΔT		+10.8	+11.0	+11.1	+11.4	+11.5
Tetraphenylmethane	2.05	282.2	282.1	282.4	282.6	
Bismuth (powder)	0.45	271.2	271.0	270.9	271.1	
ΔT		+11.0	+11.1	+11.5	+11.5	
Tetraphenylmethane	4.07	282.6	281.8	281.9	282.0	282.1
Bismuth (powder)	0.68	271.3	271.2	271.1	271.2	271.1
ΔT		+11.3	+10.6	+10.8	+10.8	+11.0
Tetraphenylsilane	3.069	236.4	236.2	236.2	236.2	
Tin (piece)	0.511	231.9	231.8	231.8	231.8	
ΔT		+4.5	+4.4	+4.4	+4.4	
Tetraphenylsilane	4.58[a]	236.5	236.4	236.4	236.4	236.4
Tin (powder)	0.60	231.8	231.8	231.8	231.8	231.7
ΔT		+4.7	+4.6	+4.6	+4.6	+4.7
Tetraphenylgermane	1.964	233.2	233.3	233.2	233.1	233.2
Tin (piece)	0.145	231.7	231.7	231.7	231.7	231.7
ΔT		+1.5	+1.6	+1.5	+1.4	+1.5
Tetraphenylgermane	4.95[a]	233.3	233.3			
Tin (powder)	1.56	231.8	231.7			
ΔT		+1.5	+1.6			
Tetraphenylstannane	3.293	227.2	227.1	227.3	227.4	227.3
Tin (piece)	0.273	231.8	231.8	231.9	231.8	231.9
ΔT		−4.6	−4.7	−4.6	−4.4	−4.6
Tetraphenylplumbane	2.386	228.8	223.0			
(no internal reference)	4.168	228.8	226.7			
	6.11[a]	228.7	228.6	227.1		

[a] In "open" (covered) pans.

TABLE 4

Heats of fusion for Group 4 tetraphenyls and as estimated from internal references

Compound and internal reference	No. of runs	"Best" $\Delta_{\text{fus}}H$ (J g^{-1})	Estimated from internal reference $\Delta_{\text{fus}}H$			
			Wt. (mg)	$\Delta_{\text{fus}}H$ (J g^{-1})	Wt. (mg)	$\Delta_{\text{fus}}H$ (J g^{-1})
Tetraphenylmethane	6	152	2.05	152	2.762	171, 167
Bismuth			0.45		0.121	
Tetraphenylmethane	(6)	(152)	6.30[a]	159[a]	4.07	147, 142
Bismuth			2.92		0.68	
Tetraphenylsilane	6	133	4.58[a]	159[a]	3.069	152, 144,
Tin			0.60	(155[a])	0.511	144, 142
Tetraphenylgermane	2	116	4.95[a]	119[a]	1.964	214
Tin			1.56		0.145	
Tetraphenylstannane	6	98	3.85[a]	113[a]	3.293	117, 125,
Tin			0.27		0.273	132, 125, 129
Tetraphenylplumbane	3[b]	95[b]	(No internal reference)			

[a] In "open" (covered) pans; repeat runs showed rapidly falling $\Delta_{\text{fus}}H$ values, owing to vaporization losses. [b] Values in these columns are obtained by conventional technique.

DISCUSSION

Tests of the internal referencing concept were made by comparison of onset points of powdered metals in non-melting matrices (of lower thermal conductivity) with those for the undiluted powder (and particulate) metals. The first results (Table 1) showed no significant differences, either initially or on remelting of the metal. Next (Table 2) the melting of indium was observed over two powers of ten in weight and in the presence of large amounts of non-melting diluent. Again the onset points did not differ significantly.

The thermal behavior of several metals upon remelting was also checked. Good reproducibility of onset points was shown by all except tin, for which the falling melting point suggests accumulation of impurities. It is noteworthy that such behavior was not observed when tin was used as an internal reference (Table 3), a fact which is unexplained at this time.

The non-melting and insulating powder matrices which prevent contact of the metal with the pan would be expected to cause maximal shift (to higher temperatures) of the observed onset points for the metal powders. Molten substances that allow the metal to settle and contact the pan should cause little or no error. Because the former showed no detectable shift, the internal referencing technique may be presumed appropriate in the latter case as well; a practical test was therefore undertaken.

Melting points of the tetraphenyl derivatives of the Group 4 elements have been variously reported, but are difficult to compare due to differences among investigators as well as uncertainties in temperature calibration. Because these compounds were commercially available, they were chosen to exemplify the internal referencing technique. The results, shown in Tables 3 and 4, provide evidence of the utility of the method.

The "best" value for the onset point for tetraphenylmethane relative to pure bismuth is +11.10°C (±0.08°C standard deviation of this average value) from the data of Table 3. This is converted to 282.50 ± 0.08°C, and is taken to be the melting point of tetraphenylmethane; however the visual (capillary) melting range is 284.0–284.7°C. This is the poorest agreement observed between the two methods and may indicate incomplete purification of the initially quite impure compound.

By similar calculations, the best onset points/melting points for the other Group 4 tetraphenyls are: Ph_4Si 236.47 ± 0.05°C; Ph_4Ge 233.44 ± 0.02°C; Ph_4Sn 227.35 ± 0.04 ± 0.04°C; and Ph_4Pb 228.92 ± 0.03°C. For tetraphenylplumbane the internal referencing technique was inapplicable, owing to closely overlapping onset points and, perhaps, to reactivity; the compound is thermally unstable above its melting point, as is evident from the falling onset points upon repeated melting. Its initial onset point is referenced by tin in the other samples, run before and after it. For each of the tetraphenyl compounds the uncertainties should be regarded as slightly larger than the above standard deviations (as a result of the previously noted rounding-off errors) by amounts perhaps as much as ±0.1°C.

Internal referencing may also be used for estimation of heats of fusion. In Table 4, the "best" values for the tetraphenyls are listed; these were obtained using the instrument's calibration, and errors probably do not exceed ±3%. Contrasted with these are single-run values calculated from the internal reference heat of fusion observed in that run. Not surprisingly the latter are much less reliable, especially when the peaks overlap badly, as with tetraphenylgermane and tetraphenylstannane, and less so with tetraphenylsilane. Errors of less than 10% can be expected when there is no overlap (as with tetraphenylmethane) and when there is ample reference metal to minimize weighing and rounding-off errors.

CONCLUSION

Internal referencing is shown to be viable and useful in validating DSC data. The following potential errors in temperature measurement [1, 2, 4, 7–9] are minimized or eliminated: poor thermal contact between sample pan and sensor; unequal thermal conductivity of sample and calibrating metal; inaccurate or incomplete calibration; differing pan designs; calibration shifts owing to choice of heating rate; long-term and/or run-to-run instrumental variability.

Many of these errors are of particular concern when the DSC apparatus is in heavy use by several workers, such that little time is available for maintenance or standard calibration checks. Changes in the "normal" onset point observed for an internal reference may signal a developing instrumental problem.

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