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EVALUATION OF A CAPILLARY TUBE SAMPLE CONTAINER FOR DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

A specially designed capillary tube and tube holder have been developed for thermal hazard evaluation using differential scanning calorimetry. This capillary tube container has several important advantages compared to other common sample encapsulation approaches. The glass container is inert to most materials and is capable of withstanding pressures in excess of 21 MPa (3000 psi) and temperatures up to 500 ° C. The vaporization effect, often present in scanning calorimetry of fluids to high temperatures, will be negligible in most analyses because high sample volume to total volume ratios are possible. The device gives a stable baseline and provides better temperature resolution than do previous glass ampoule devices. The onset temperature and the enthalpy of fusion of indium have been measured with 95% confidence intervals of 2.1° C and 1.1%, respectively. The calorimetric response of the device is linear for indium fusion between 0.6 and 14 mg of sample. The heat of thermal decomposion of a solution of AIBN in methylene chloride was determined to be 277 ± 7 J g^{-1} with a peak temperature of 124.2 ± 0.8 ° C at the 95% confidence level.

INTRODUCTION

The evaluation of thermal reaction hazards in the chemical industry is an important aspect of safety and loss prevention. One of the most common analytical techniques utilized in assessing thermal reaction hazards is differential thermal analysis (DTA). More recently, however, techniques based on differential scanning calorimetry (DSC) have been developed [1–4]. Differential scanning calorimetry is, in principle, preferred over DTA because DSC typically is more sensitive, quantitative, and affords better temperature resolution. Unfortunately, the common sample encapsulation devices available for DSC have very limited pressure capabilities. The alternative to sealed container encapsulation is the pressurized detector approach which elevates the boiling point of the sample. However, a pressurized sample atmosphere is not representative of most processes in the chemical industry. In addition, conventional sample containers are chemically reactive towards the materials being analyzed, e.g. chlorinated organics

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and mineral acid solutions react with stainless steel or aluminum sample pans.

A few sample containers for DSC have been reported which provide moderate pressure capabilities along with general chemical inertness [5–8]. These devices typically exhibit poor temperature resolution and calorimetric sensitivity or limited pressure capabilities. In addition, sample movement in some of the sample containers may lead to erroneous results due to changes in heat and mass transfer effects during the experiment. Wendlandt has recently reviewed sealed sample containers for DTA and DSC [9].

A modification of the glass ampoule micro-reactor used by Chiu [8] was reported by Tou and Whiting [3] which improved both the sensitivity and temperature resolution of the measurement. The glass ampoule device of Tou and Whiting [3] has been utilized continuously in this laboratory for the past several years for thermal hazard evaluation and has proven to be a valuable tool. However, we have noted a few areas for improvement of the glass ampoule device. First, although the glass ampoule utilized in our work typically will withstand pressures exceeding 7 MPa (1000 psi), many samples exceed this pressure capability due to either decomposition to gaseous products or due to the vapor pressure of the sample. As a result of overpressuring the glass container, the ampoule will rupture and often cause damage to the DSC detector. One can attempt to minimize the number of ampoule ruptures by reducing the amount of sample in the container so that the pressure limit is seldom exceeded. This reduction in sample size leads to the second problem encountered in using glass ampoules. When analyzing volatile liquids by DSC the liquid will come close to achieving vapor/liquid equilibrium during the experiment. If using small sample sizes in a glass ampoule, a major portion of the liquid may vaporize during the experiment. Under these conditions one may actually be measuring the thermal stability of the vapor phase sample and not the liquid phase. If the kinetics of the reaction in the vapor phase are slower than in the liquid phase, one would necessarily underestimate the rate of reaction at lower temperatures. A more insidious problem can occur where a material reacts rapidly and exothermically in the liquid phase but essentially does not react in the gas phase. If the material is allowed to volatilize in the DSC sample container prior to reaction, one might erroneously conclude that the material did not decompose in a hazardous manner. An example of this sort of problem will be presented later in this report.

In order to overcome the above problems inherent in the use of glass ampoules, or other large-volume sample containers, a glass capillary tube sample container for DSC analysis has been developed and its characterization is the subject of this report. The advantages of the glass capillary tube over the ampoule are high pressure capability exceeding 21 MPa (3000 psi) and high sample volume to container volume ratio. It should be mentioned that a thick-walled ampoule was initially considered in solving the pressure and vaporization problems. This approach was not pursued for two reasons. First, more glass from the thick wall construction would result in additional loss of temperature resolution and sensitivity. Second, the larger the sample the more energy that must be dissipated when an ampoule ruptures which leads to more damage to the DSC detector.

EXPERIMENTAL

The instrumentation used in this study consisted of a Dupont 910 DSC cell, Omnitherm cell base module, and an Omnitherm Atvantage data acquisition and controller system.

Standard, non-hermetic, aluminum sample pans were obtained from Dupont Instruments. Glass ampoules and glass capillary tubing were obtained from Wilmad Glass Co. The glass ampoules were 4.0 mm O.D. sample containers for NMR, part No. 529A. The capillary tubing, the same tubing used in the manufacture of the glass ampoules, was purchased in 25-cm lengths, cut to 2-cm lengths and sealed on one end. The dimensions of the aluminium glass ampoule holder and its use have been described previously [3]. A simple drawing of the sealed glass capillary tube and its holder are shown in Fig. 1. The length of the capillary tube should not

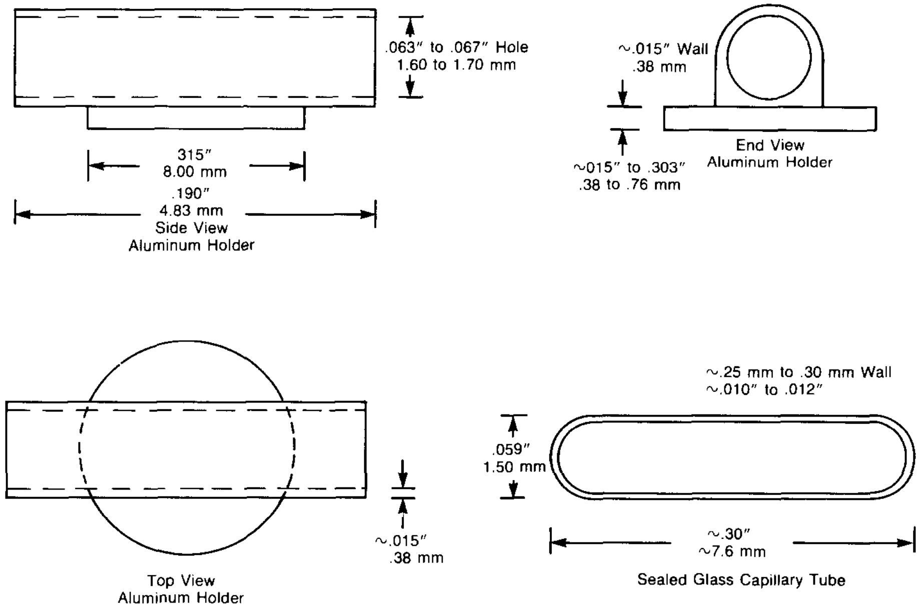

Fig. 1. Diagram of aluminum capillary tube holder and glass capilllary sample container. The sealed capillary is made from Pyrex glass tubing normally used for making PN 529A glass ampoules (Wilmad Glass Co., Inc., Route 40 and Oak Road, Buena, NJ 08310, U.S.A.).

extend beyond the ends of the aluminum holder because this may lead to poor calorimetric response. A sealed capillary tube, as shown in Fig. 1, will have an internal volume of approximately 4.0 μl.

Sample preparation for the ampoules and the capillary tubes was similar and consisted of weighing a clean and dry container, securing the container in the top of a copper cold finger, which had the other end immersed in liquid nitrogen, purging the container with high purity nitrogen, introducing about 1 μl of the sample via a microliter syringe or a solids injector, purging the sample once more with nitrogen, sealing the glass tube with a microtorch so as to minimize the tube length but without decomposing any material, and finally weighing the two remaining pieces of glass to determine by difference the actual sample weight in the sealed container. It is recommended that initially one inspects each tube seal microscopically to determine that the seal is uniform in thickness and that there are no pin holes in the center. To facilitate loading of liquid samples, a short piece of Teflon capillary tubing was placed on the syringe needle to serve as a centering device in the glass capillary tube. This centering device helps prevent the contamination of the inner walls of the glass tube. Any contamination of the tube wall may cause difficulty in the sealing operation and can result in erroneous sample weights. Liquified propane gas (LPG) and compressed oxygen were used to provide a very fine flame from a 0.89 mm O.D. (20 gauge) hypodermic needle which was adequate for rapidly sealing the glass tubing. Solids are more difficult to load than liquids due to the narrow restrictions of the glass tubing. However, they can be loaded by pressing about 1 mg of material into the end of a 0.56 mm O.D. (24 gauge) hypodermic blunt-tip needle, cleaning the outside of the needle, inserting the needle to the bottom of the capillary tube, and pushing the solid out of the needle with an appropriately sized plunger. After completion of a DSC experiment, the sample container is always reweighed to ensure that no material was lost during analysis.

There is always the possibility that a sealed container will leak due to either a poor seal or simple overpressuring from gas buildup or high vapor pressure. Due to the non-ductile nature of glass, ampoules and capillary tubes rupture catastrophically when overpressured. When either a glass ampoule or capillary tube ruptures, the entire silver lid must be raised approximately 0.5 cm to the top of the furnace cylinder for the pressure to be relieved in a Dupont 910 DSC cell. Unless the relatively heavy silver lid is modified, the detector volume is easily overpressured which can result in deformation of the detector disk. In order to minimize damage to the DSC detector, the silver lid to the cell was cut into three sections as shown in Fig. 2. The modified silver lid allows for the pressure to be relieved rapidly via the small side pieces which need only move or rotate a small amount to expose a relatively large vent area. In order to achieve flat, reproducible baselines and reliable sample runs, the modified silver disk must be ex-

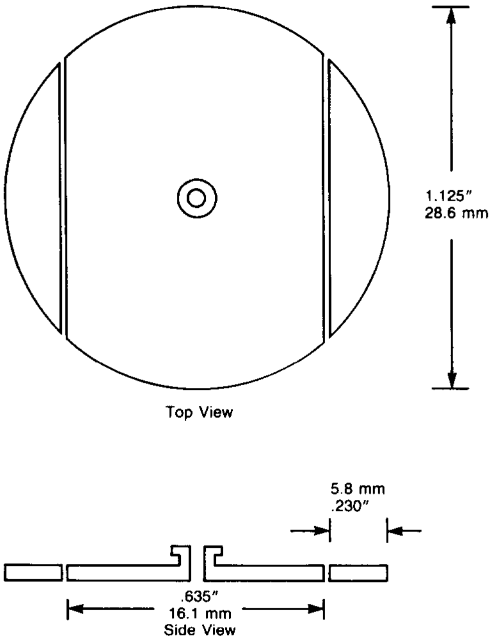

Fig. 2. Design of split silver lid for Dupont DSC cell using modified Dupont silver lid.

amined frequently to be sure that all pieces are flat and make good thermal contact with the furnace. In addition, there must not be any space between the three silver pieces. This requires precise machining of the pieces.

RESULTS AND DISCUSSION

Acetone cyanohydrin experiment

One of the main considerations in the development of the new sample holder was the minimization of vaporization of the sample. A comparison between the DSC results on acetone cyanohydrin using the capillary tube holder and the glass ampoule will serve to illustrate the sample vaporization problem. Acetone cyanohydrin is a material which can thermally decompose to acetone and hydrogen cyanide. One can observe this endothermic process between 150 °C and 250 °C in the DSC curves for both the glass ampoule and capillary tube sample containers as shown in Fig. 3. As the material decomposes in the glass ampoule container, the products volatilize into the ampoule volume and no further detectable reaction takes place. There is also an indication that some vaporization of the undecomposed sample was occurring in the ampoule prior to the decomposition. If the acetone cyanohydrin is evaluated using the capillary tube DSC holder where one can achieve much higher sample volume to container volume ratios, a very different result is obtained as also illustrated in Fig. 3. One does not observe

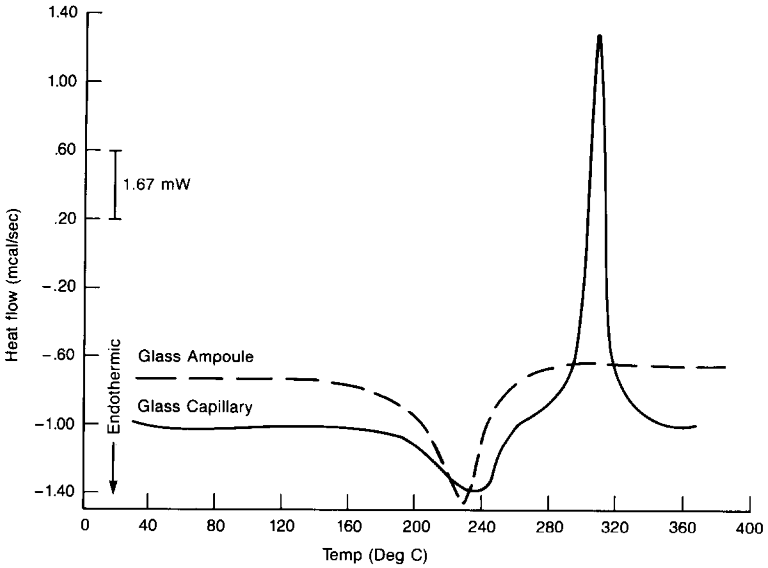

Fig. 3. DSC curve of acetone cyanohydrin (10 °C $\min^{-1}$), nitrogen, sealed glass ampoule in aluminum cradle and sealed glass capillary tube in aluminum holder, sample size approximately 1 mg.

the lower temperature sample vaporization as seen in the ampoule but does detect the endothermic decomposition peak at approximately the same temperature as in the glass ampoule. However, following this decomposition, there is a rather rapid exothermic reaction detected in the capillary tube but not seen in the glass ampoule. It is believed that this exotherm is due to the polymerization of the hydrogen cyanide formed during the decomposition of the acetone cyanohydrin. The polymerization of the hydrogen cyanide occurs in the capillary tube because most of it is in the liquid phase in the capillary tube due to the high sample volume to container volume. The polymerization is not detected in the glass ampoule as the hydrogen cyanide can vaporize into the relatively large volume of the ampoule. It is expected that the kinetics of polymerization are much slower in the gas phase relative to the liquid phase.

It should be obvious that, in this case, the potential hazard of exothermic polymerization of the decomposition product of acetone cyanohydrin can only be observed if one utilizes a high pressure, high sample volume to container volume device. Conventional sample containers such as hermetic aluminum pans, or O-ring seal high-pressure stainless steel pans from Perkin-Elmer would not be adequate.

High-pressure capability of capillary tubes

In order to demonstrate the high-pressure capabilities of the capillary tube DSC sample holder, eight tubes, each of approximately 4 μl total volume, were sealed containing deionized water of sample weights ranging from 0.55 to 0.96 mg. No special precautions were taken in sealing these tubes, hence the following results are expected to be typical and not the best case. All containers with less than 0.9 mg water survived a temperature program up to 400 ° C without rupture. The pressure in the glass capillary tubes at 400 ° C is significantly in excess of 22.7 MPa (3300 psi) because that is the critical pressure of water at 374 ° C and since the sample loadings were close to critical density. The tube containing 0.96 mg water ruptured at 350 ° C and may have been caused either by a poorly formed seal or by reaching a hydraulically full condition in the tube at this high loading because the liquid volume of water at this temperature has increased nearly four times relative to room temperature volume. It should be noted that the tube that ruptured in this set of experiments did not cause any damage to the DSC detector. The capillary tube sample container described in this report has been in use in this laboratory for more than one year and has been used to examine several hundred samples. We have experienced approximately twenty tube ruptures, none of which caused significant detector damage. Detector damage is determined by examining the baseline linearity and change in temperature and enthalpy calibration constants following tube rupture. Baseline runs and instrument calibrations are carried out after tube ruptures.

Baseline stability

Quantitative calorimetric measurements require a stable, repeatable, and preferably linear baseline in DSC analyses. Each day, prior to any sample runs, an instrument baseline is acquired with empty, sealed capillary tubes in their aluminum tube holders for both sample and reference. To demonstrate the linearity and stability of the capillary tube baseline, DSC baseline curves are illustrated in Fig. 4. If the baseline is not sufficiently linear and smooth, appropriate remedial action is taken such as heating the detector and sample containers/holders to 500 ° C in air and "baking out" any oxidizable residues following the instrument manufacturer's instructions. Occasionally, the aluminum tube holders become contaminated with inorganic residues from ruptured sample tubes and must be replaced.

Thermal response / resolution

It is important to have the highest temperature resolution possible in differential scanning calorimetry in order to precisely measure reactions which may occur over a relatively short period of time due to the dynamic nature of the instrument. Several experiments have been carried out on indium to compare the thermal response of the new glass capillary tube sample holder to that of glass ampoules and of conventional aluminum

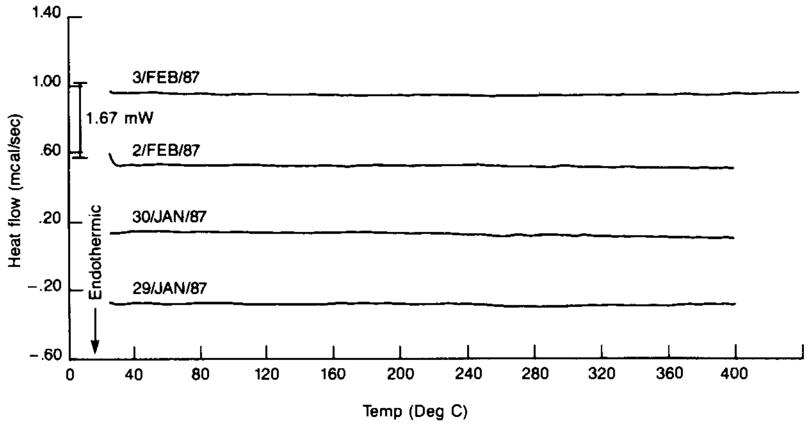

Fig. 4. DSC daily baselines, empty capillary tubes, 10 °C min^{-1}.

pans. Indium samples of approximately 5.0 mg were analyzed at 5, 10, and 20 °C min^{-1} in each of the three types of sample containers following temperature and enthalpy calibration at 10 °C min^{-1}. The DSC curves were analyzed for extrapolated onset temperature, peak temperature, thermal resistance factor, thermal time constant, and enthalpy of fusion. The results are presented in Table 1. The thermal resistance factor, or thermal lag, is calculated from the slope of the leading edge of the fusion endotherm and has units of °C mW^{-1}. The thermal time constant is a first-order decay constant calculated from the trailing edge of the fusion peak and has units of seconds. The thermal resistance factor is an indication of how easily heat

TABLE 1

The thermal response of various sample containers

Container	Scan rate (°C min^{-1})	Onset temp. (°C)	Peak temp. (°C)	Thermal resistance factor (°C mW^{-1})	Thermal time constant (s)	Heat of fusion (J g^{-1})
Aluminum pan	5	156.03	156.9	0.052	6.18	28.9
	10	156.40	157.5	0.048	5.80	28.5
	20	156.90	158.7	0.064	5.52	28.7
Glass ampoule	5	155.60	157.9	0.406	9.70	28.8
	10	156.88	160.3	0.598	9.09	28.6
	20	158.00	163.0	0.681	9.50	29.0
Glass capillary	5	155.40	156.7	0.202	11.08	28.6
	10	156.20	158.3	0.277	11.08	28.6
	20	157.51	160.7	0.368	10.97	28.9

is transferred into the sample. The smaller the resistance the more easily heat is transferred. The thermal time constant is a measure of how rapidly the system responds to an instantaneous heat event. The smaller the time constant, the faster the detector responds to the change. It also follows that the smaller the time constant, the higher the temperature resolution of the detection system. A more detailed review of heat transfer in a DSC is presented in Wendlandt [10]. The data in Table 1 illustrate several findings. First, all sample-container types give the same enthalpy of fusion within experimental error for all three scanning rates. Second, the thermal resistance of the glass capillary holder is half that of the glass ampoule but four times that of the aluminum pan. Third, the thermal time constant for the capillary tube holder is only 50% larger than the aluminum pan and a little better than the glass ampoule. Fourth, the effect of scanning rate on the observed onset temperature is most severe for the glass ampoule, least for the aluminum pan, and intermediate for the capillary tube, as would be expected from the values of the thermal resistance factors. A visual idea of the relative thermal behavior of the sample containers can be obtained by examining an overlay plot of indium runs carried out under similar experimental conditions (Fig. 5). Overall, the glass capillary tube sample holder exhibits better thermal-response characteristics than does the glass ampoule holder, but is still inferior to an aluminum pan.

One other area to address in the characterization of the thermal response of the capillary tube device is the enthalpy calibration factor. The enthalpy

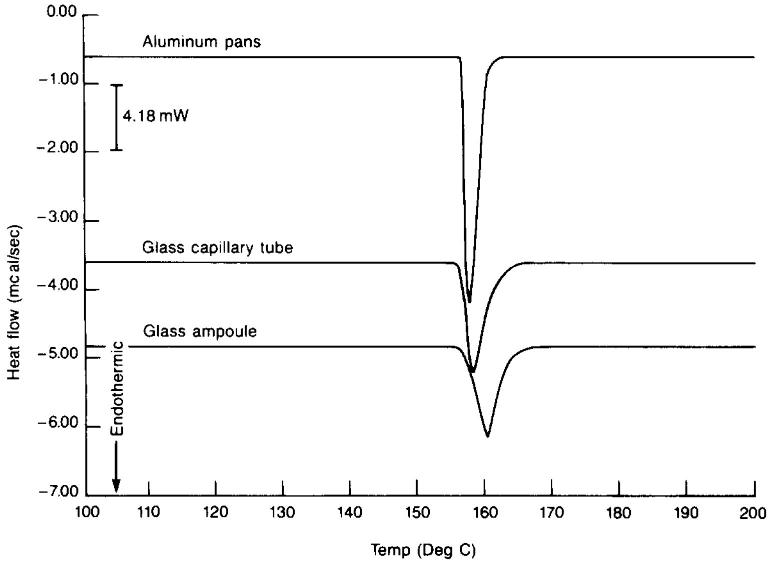

Fig. 5. Comparison of DSC curves of indium for different sample containers after separate temperature and enthalpy calibrations (10 °C min^{-1}), approximately 5 mg sample size.

of a transition is measured by first calibrating the detector response using the enthalpy of fusion of a standard material such as indium. When using the Dupont DSC detector, enthalpy measurements are made by integrating the temperature difference, in voltage units, between the sample and reference over the time period of the transition of interest. A calibration factor is then applied to convert the voltage–time area to enthalpy. This calibration factor is a measure of the amount of heat that flows through the detector thermocouple pads versus that which flows via all other pathways. In order to compare the enthalpy response of the capillary tube device to other sample containers, heats of fusion of indium at 10 °C min^{-1} were measured in all three types of containers and the calibration factor for standard non-volatile aluminum pans was defined as 1.00. Relative to the aluminum pan, the calibration factor for the glass capillary tube container is 1.11, while that of the glass ampoule is 1.16. These values indicated that in the glass capillary tube device approximately 11% less heat transfers to the sample through the detector than for the aluminum pan. This does not appear to be a gross change in instrument behavior. The corresponding relative calibration factor for the glass ampoule indicates that the ampoule transfers approximately 16% less heat through the detector compared to the aluminum pans.

Higher temperature performance

Two other standards were examined using the capillary tube sample holder, lead and tin. The DSC was calibrated in enthalpy by using the heat of fusion of indium at its melting point for a fixed point and using the heat capacity of sapphire from room temperature to 500 °C to determine the temperature dependence of the enthalpy calibration factor. This method of instrument calibration has been described previously [10]. The results on tin and lead are shown in Table 2. It can be seen that the observed onset temperatures for the fusion of lead and tin are biased by −2.5 °C and −1.6 °C, respectively. A two-point calibration of the temperature scale can be used to improve the temperature accuracy of the measurement. Using indium and lead melting points as calibrations of the temperature scale, the observed onset temperature for the fusion of tin is biased by only −0.6 °C, assuming a linear interpolation of the indium and lead results. All calibrations were carried out at 10 °C min^{-1}. The observed enthalpy of fusion values for lead and tin shown in Table 2 are biased by −2.5% and −1.2%, respectively. This appears to be related to the nonlinear response of the instrument during the sapphire heat capacity calibration. If a two-point calibration of the enthalpy is used versus temperature with the heats of fusion of indium and lead, then the enthalpy of fusion of tin would be biased by less than 0.5% assuming a linear response curve.

TABLE 2

Evaluation of thermal response of glass capillary at various temperatures

Sample	Sample size (mg)	Scanning rate (°C min^{-1})	Onset temp. (°C)	Peak temp. (°C)	Measured heat of fusion (J g^{-1})	Literature heat of fusion (J g^{-1})	Literature melting point (°C)
Lead	5.007	5	324.8	325.9	22.5	23.0	327.47
		10	325.0	327.3	22.4		
		20	326.9	329.9	22.3		
Tin	5.054	5	229.4	231.7	59.6	60.5	231.88
		10	230.3	233.3	59.7		
		20	232.3	236.6	59.9		

Sample-size effects

The linearity of thermal response of the capillary tube sample holder as a function of sample size was determined using indium samples varying in weight from 0.624 mg to 14.231 mg. The measured heats range from about 20 to 400 mJ. The results are illustrated in Table 3. The response is very linear and yields enthalpy of fusion values that do not appear to have any dependence on sample size. The mean enthalpy of fusion of indium showed a bias of $+0.17$ mJ mg^{-1}, $+0.6\%$ relative, with a confidence interval of 1.1% at the 95% confidence level. The measurement of the onset temperature was biased by -0.2°C and gave a confidence interval of 2.1°C at the 95% confidence level.

TABLE 3

Indium sample size study

Sample size (mg)	Melting onset temperture (°C)	Melting peak temperature (°C)	Heat of fusion (J g^{-1})
0.624	155.9	157.4	28.4
1.691	156.1	157.7	28.6
2.820	156.1	158.6	28.7
3.794	156.3	158.2	28.5
5.010	156.0	158.7	28.5
7.704	156.2	158.7	28.5
9.105	156.2	158.5	28.5
14.231	156.3	158.7	28.7
Mean	156.44		28.6
Standard deviation	0.92		0.13
Confidence interval (95%)	2.1		0.31

TABLE 4

Repeatability study: 5.01 mg indium in glass capillary, 10 °C min^{-1}

Run	Melting onset temperature (°C)	Melting peak temperature (°C)	Heat of fusion (J g^{-1})
Run 1	156.0	158.7	28.5
Run 2	156.3	158.6	29.0
Run 3	156.3	158.6	29.0
Run 4	156.3	158.6	28.9
Run 5	156.4	158.5	28.9
Run 6	156.3	158.6	29.1
Run 7	156.2	158.7	28.8
Run 8	155.9	158.6	28.8
Run 9	156.0	158.7	28.4
Run 10	156.1	158.6	28.9
Mean	156.2		28.8
Standard deviation	0.2		0.25
Confidence interval (95%)	0.4		0.50

Repeatibility on a single sample

A series of runs on the same 5.01-mg sample of indium in a sealed glass capillary tube was carried out at 10 °C min^{-1} to examine the effect of sample-tube introduction on the results. In each experiment, the sample was removed from the aluminum holder and then replaced and positioned normally in the detector. The results are shown in Table 4. The onset temperature had a bias of −0.5 °C with a confidence interval of 0.4 °C at the 95% confidence level. The enthalpy of fusion exhibited a bias of +0.42 J g^{-1}, +1.5% relative, with a confidence interval of 1.8% at the 95% confidence level. These results indicate that the precision of the measurement of the onset temperature is significantly better for repetitive runs on one single sample than for multiple samples of varying weight. This suggests that heat transfer, thermal resistance, between the sample and the detector may be critical in temperature measurements and that reproducible sample placement is important for high-precision measurements. The results also indicate that the precision of the enthalpy measurement is independent of sample placement. The significant biases in the enthalpy of fusion and onset temperature data suggest that to improve the accuracy of the measured values one should carry out several calibration runs and use the average of the calibrations. For the purpose of thermal hazard evaluations, confidence intervals of 5% relative on the enthalpy measurement are usually more than adequate.

Sample-position effects

Previous characterization of the glass ampoule sample holder had shown that the precise position of the sample in the ampoule could greatly affect

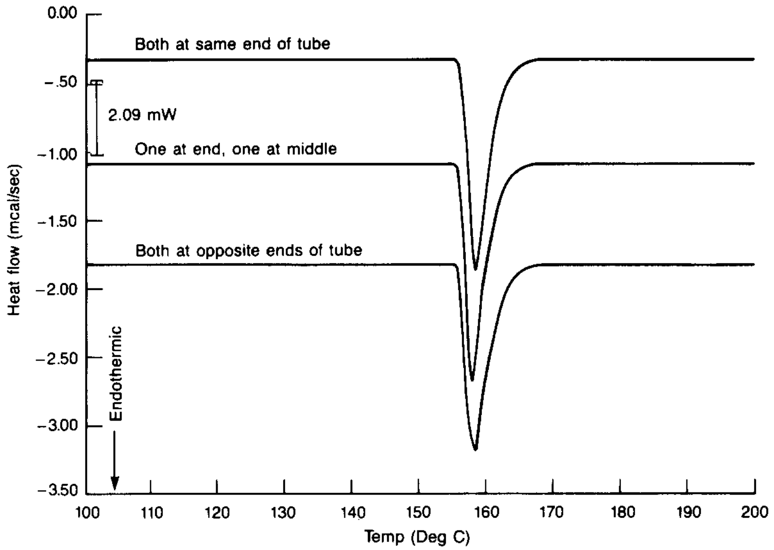

Fig. 6. DSC curves illustrating sample-position effects in the glass capillary tube container: two pieces of indium at varying locations in a capillary tube, 10 °C min^{-1}.

the DSC results [3]. This potential problem was also addressed in this study. Two pieces of indium of approximately equal size and of combined weight of 4.95 mg were placed in a glass capillary tube which was sealed at one end and open at the other. The actual position of the indium pieces in the tube was varied in a series of three runs, both together at the sealed end of the tube, one at the sealed end and the other at the middle of the tube, and one at the sealed end and at the open end of the tube. The three corresponding DSC curves are presented in Fig. 6. The curves have been offset in the vertical direction to allow for direct comparison. The peak shapes are virtually identical in all three curves. The observed onset temperatures are the same within experimental error based on the previous reproducibility study. The enthalpy of fusion value for the sample with the two pieces at opposite ends of the tube appears to be biased by -0.63 J g^{-1} or -2.2% relative. The other two samples are consistent with the expected enthalpy of fusion of indium within experimental error. These results indicate that the glass capillary tube is much less sensitive to sample position than the glass ampoule device. This is believed to be due to surrounding the glass sample container almost completely with aluminum, a material of very high thermal diffusivity. In this configuration heat losses or gains are minimized via heat paths other than through the detector.

AIBN decomposition

In an effort to demonstrate the repeatability of the results from the capillary tube sample tube device on a material other than pure metal

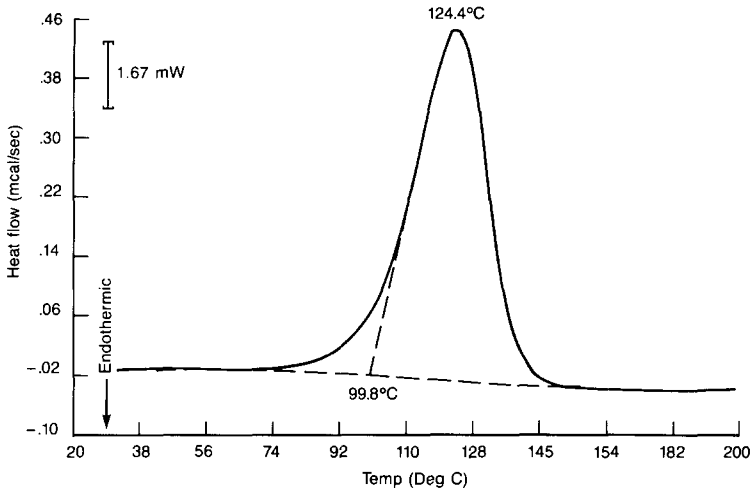

Fig. 7. DSC curve of 20% AIBN in methylene chloride in a capillary tube at 10 °C $\min^{-1}$, in a nitrogen atmosphere.

standards, a series of six runs were carried out on a 20% solution of 2,2′-azobis(2-methylpropionitrile) (AIBN) in methylene chloride under typical experimental conditions of 10 °C $\min^{-1}$ and a sample size ranging from 0.93 to 1.15 mg. The AIBN (Eastman Organic Chemicals) used in this study was not analyzed, but is believed to be greater than 90% pure. A representative DSC curve for the exothermic decomposition of the AIBN is shown in Fig. 7. The DSC curves were analyzed for peak temperature and enthalpy of reaction. Table 5 illustrates the results. The mean heat of reaction was −277 J g^{-1} of solution with a confidence interval of 7 J g^{-1}, 2.4% relative, at the 95% confidence level. The mean peak temperature was 124.2 °C with a confidence interval of 0.8 °C at the 95% confidence level. These results show that the capillary tube device yields superior data to the glass ampoule

TABLE 5

Decomposition of AIBN in methylene chloride

Run	Size (mg)	Onset temp. (°C)	Peak temp. (°C)	Heat of reaction (J g^{-1})
Run 1	0.905	99.60	123.9	−274.8
Run 2	1.148	100.10	123.9	−275.3
Run 3	0.964	99.90	124.4	−275.1
Run 4	0.904	100.00	124.6	−279.2
Run 5	0.961	100.20	124.4	−281.4
Run 6	0.932	100.50	123.9	−275.2
Mean			124.2	−277.0
Standard deviation			0.3	2.9
Confidence interval (95%)			0.8	6.7

sample container and approaches the precision and accuracy or conventional aluminum pan containers for non-volatile samples [11].

CONCLUSIONS

The capillary tube DSC sample holder has been shown to provide higher pressure capabilities, improved temperature resolution and calorimetric sensitivity , higher precision enthalpy measurements, less sensitivity to sample placement or movement, and less detector damage on container rupture than the glass ampoule device.

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