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## An improved DSC glass sample container technique

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### Abstract

A simple method has been developed for the use of glass capillaries in DSC. The metal block holder used by previous workers was found to be unnecessary. It was found that different positions of the glass capillary in the cell or long term use of the same baseline do not affect the DSC curves for the same samples. The experimental results for  $\text{NH}_4\text{NO}_3$  and an organic dye show significant differences between a standard aluminum pan and the glass capillary due to the interference of volatilization from the aluminum pan.

**Keywords:** DSC; Glass capillaries;  $\text{NH}_4\text{NO}_3$ ; Volatile samples

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### 1. Introduction

The greatest number of applications of DSC (Differential Scanning Calorimetry) in recent years has been in the area of polymeric materials. The technique is routinely used to measure glass transition, melting point, degree of crystallinity, heat of fusion and/or crystallization, heats of decomposition and other parameters. In power-compensated DSC, the sample and reference cells are maintained at the same temperature by the use of individual heaters. When heat is evolved or absorbed in the sample the heater will keep the sample and reference cells isothermal to each other by proper application of

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electrical energy. The signal is a recording of heat flow,  $dH/dt$ , as a function of temperature or time.

Different kinds of sample containers are available for use with power-compensated DSC. The choice of sample containers depends on the nature of the samples and the desired application of the results. Below 600°C aluminum pans are mostly used, while above 600°C gold, copper, silver, platinum and quartz pans are available depending on the temperature range. For pressures up to 3 atmospheres, special aluminum pans crimped by a special tool can be used. If the pressure studied is as high as 150 atmospheres, stainless steel high-pressure capsules are available with three kinds of O-ring seals, copper, gold and titanium. At present, no commercial special liquid sample containers are available.

Some chemicals, especially small molecules or monomers, will be volatile before they decompose, or volatilize and decompose simultaneously. Sealed pans must be used for these kinds of samples. Although such pans are available, they are not without problems. Aluminum volatile-sample pans cannot be used for high temperature and for pressures higher than 3 atmospheres. Stainless steel high-pressure capsules can be used for the whole temperature range and can hold 150 atmospheres pressure, but might be corroded by residues at high temperature and pressure. Also, cleaning them is not easy for certain reactions and these pans are costly and not useful over 150 atmospheres. To overcome these problems, sealed glass capillaries have been introduced [1–3]. The work of Whiting et al. [3] describes in detail the features of such a system. They have the following advantages:

1. They can be used for the whole temperature range from  $-170^{\circ}\text{C}$  to  $725^{\circ}\text{C}$ ;
2. They can be used for liquid samples;
3. Most samples and residues will not react with glass;
4. Low cost glass capillaries make multiple experiments economical;
5. They can hold pressures as high as 250 atmospheres;
6. They can be disposed of or the residue can be rerun for further analysis;
7. Cells don't get dirty since no volatiles are released.

Recently, this technique was introduced to study the thermal hazards of explosives [4]. However, the technique as described still has some disadvantages, i.e.:

1. Aluminum blocks for sample and reference holders were used. This increases the heat capacity of the cell and leads to broadened transitions;
2. New baselines were required before each experiment as stated by Whiting et al. [3];
3. The sample block is not universal, but must be designed for each DSC apparatus.

This paper deals with the use of glass capillary techniques without a sample block and describes results obtained with several types of samples.

## 2. Experimental

The differential scanning calorimeter used in these experiments was a Perkin Elmer DSC 7, controlled by a DEC station PC equipped with the 7 Series/UNIX Thermal

Analysis System. All DSC runs were conducted at  $10^{\circ}\text{C min}^{-1}$  heating rate under nitrogen. The heating rate was chosen as a compromise between high sensitivity (higher heating rate) and high resolution (lower heating rate). Very high purity (greater than 99.9%) standard indium was supplied with the DSC 7. Ammonium nitrate (ACS Reagent, Aldrich Chem.) was used as received. *N*-(4 nitrophenyl)-L-prolinol (NPP) was prepared according to the method of Zyss et al. [5]. Kimax-51 capillary melting tubes ( $1.5\text{--}1.8 \times 90$  mm) were used for forming the sample containers.

The structure of the sealer tool for glass capillaries is shown in Fig. 1. A pin vise is used to hold the glass capillary. Samples were loaded in the bottom of the glass capillary. The other end of the pin vise was put into a vacuum flask full of liquid nitrogen. The pin vise acts as a heat sink as well as a holder. The glass capillary is sealed with a gas–oxygen micro torch, the liquid nitrogen cooling the sample through the pin vise preventing thermal decomposition of the sample. More details of this sealing technique are described in Ref. [3].

### 3. Results and discussion

By repeating runs periodically, it was determined that one baseline could be used for three months or more, only keeping the same empty glass reference capillary. Fig. 2 shows these results. It was thought that if the position of the glass capillary was changed in the sample holder without use of an aluminum sample block, the shape and position of the DSC curves may shift. The experimental results (Fig. 3) show no dependence of the DSC curves on changes in position. DSC curves of indium both in a standard aluminum pan and in a glass capillary are shown in Fig. 4. It was found that the DSC curve of indium for the aluminum pan and the glass capillary are not identical, but that the heats of fusion of indium measured by both techniques are the same within experimental error. Thus, the heat of fusion for indium is  $28.33\text{ J g}^{-1}$  in the aluminum pan and  $28.16\text{ J g}^{-1}$  in the glass capillary. The onset temperature for indium in the glass capillary is about  $1^{\circ}\text{C}$  higher than in the aluminum pan and the peak temperature is  $3.5^{\circ}\text{C}$  higher, presumably because the thermal conductivity of glass is less than that of aluminum.

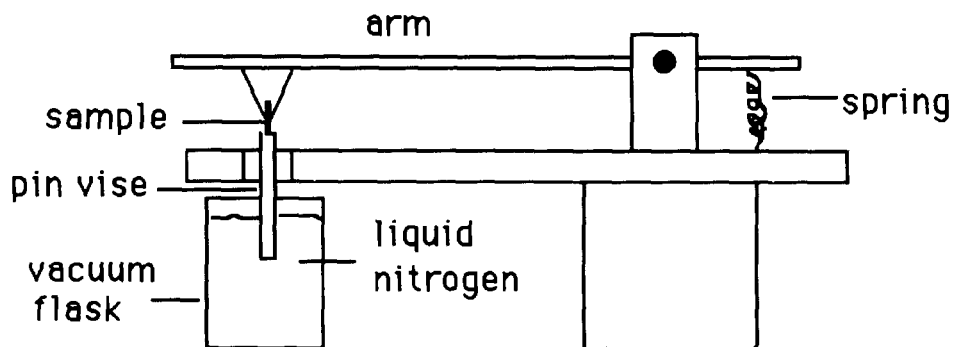


Fig. 1. Construction of the capillary sealer tool.

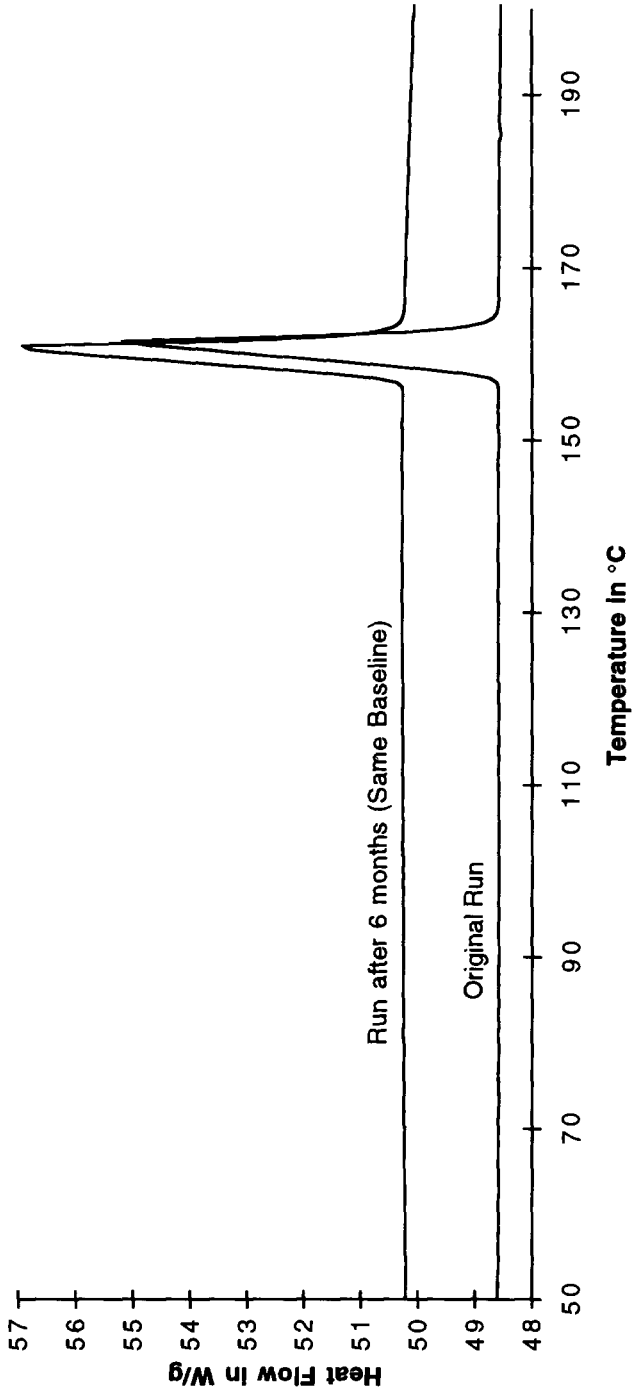


Fig. 2. DSC curves of indium after a six-month interval with the same baseline.

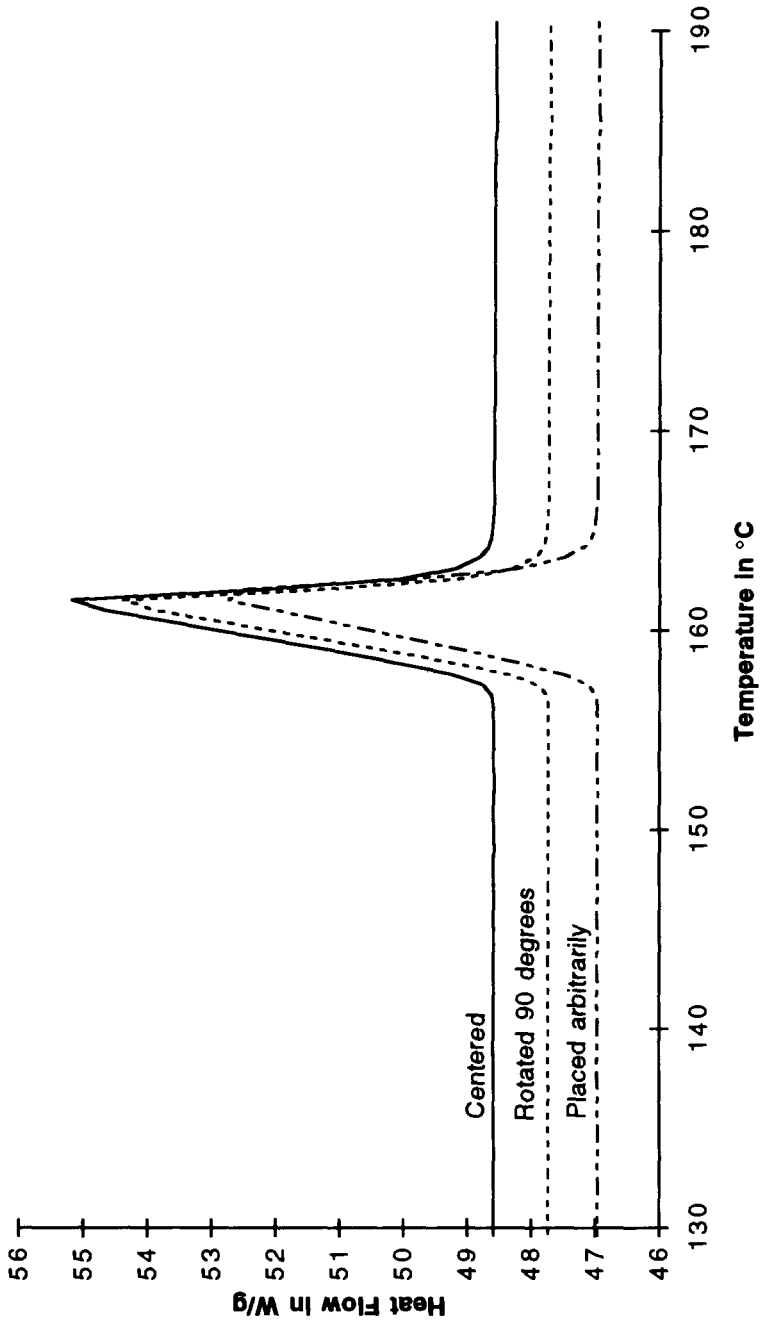


Fig. 3. DSC curves of glass capillaries containing indium in different positions in the DSC cell.

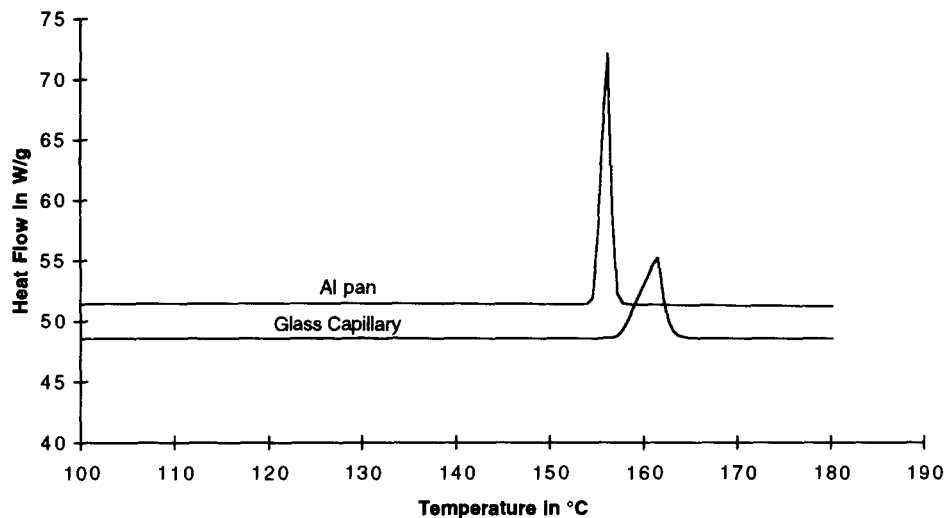


Fig. 4. DSC curves of indium in different containers.

In an attempt to estimate the effect of the glass capillary on heat transfer in the DSC cell and compare it to the heat transfer associated with the conventional aluminum sample pan, thermal resistance factors, or thermal lags, were calculated from the slope of the leading edge of the fusion endotherms for indium. The thermal lag was measured as  $0.517^{\circ}\text{C mW}^{-1}$  for our glass capillaries and  $0.085^{\circ}\text{C mW}^{-1}$  for the aluminum pan. Thus, the ratio of thermal lag for the capillary is approximately 6 times that of the aluminum pan. Whiting et al. [3] conducted similar measurements for aluminum pans and their glass capillary in an aluminum holder and obtained values of  $0.277^{\circ}\text{C mW}^{-1}$  and  $0.048^{\circ}\text{C mW}^{-1}$ , respectively for runs at a  $10^{\circ}\text{C min}^{-1}$  scan rate. Inasmuch as they were using a different DSC instrument, it is not surprising that their values were different from ours. However, their ratio of thermal lags for their glass capillary in an aluminum holder to the conventional aluminum pan is 5.8, virtually identical with ours without the holder.

Fig. 5 shows results for an organic compound that is of interest as a non-linear optical chromophore, NPP, contained in the aluminum pan and the glass capillary. The endothermic peak just above  $100^{\circ}\text{C}$  is due to the melting (fusion) of the material. The heat of fusion of this material is quite similar both in the aluminum pan and the glass capillary,  $111.6\text{ J g}^{-1}$  and  $110.9\text{ J g}^{-1}$ , respectively. It should be noted, however, that the exothermic heat of decomposition was found to be quite different for the two sample containers, i.e.,  $-769.1\text{ J g}^{-1}$  and  $-1435.3\text{ J g}^{-1}$ , respectively. This is because the thermal decomposition is accompanied by volatilization in the aluminum pan. A correct heat of thermal decomposition for volatile materials cannot be obtained with standard aluminum pans because of the interference of the endothermic heat of vaporization.

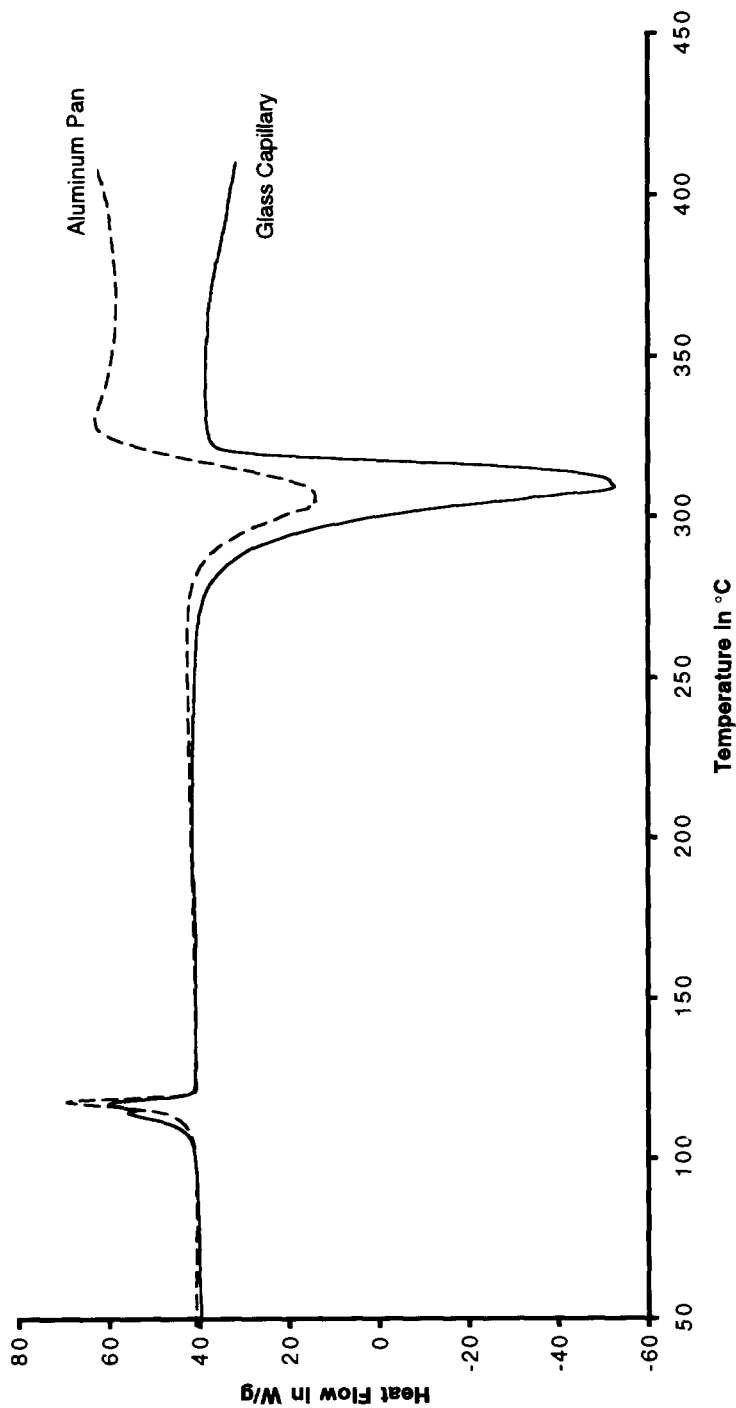


Fig. 5. DSC curves of NPP in different containers.

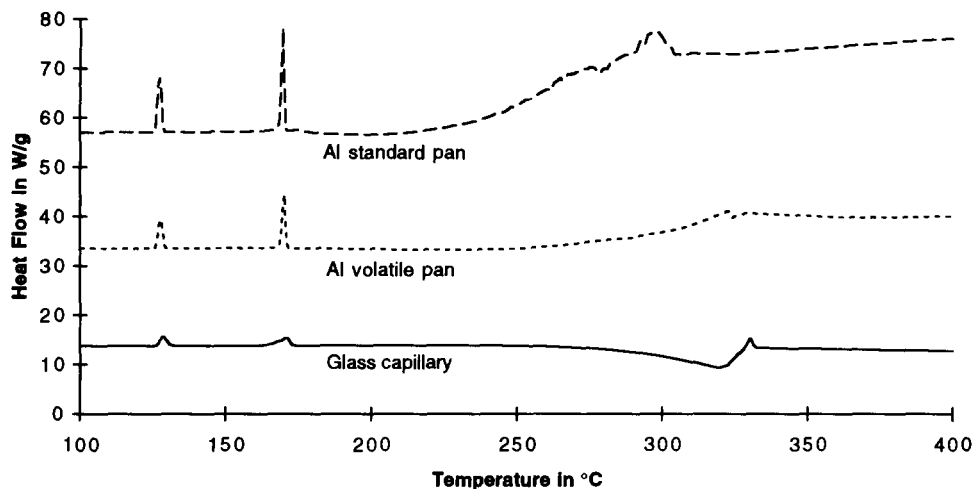


Fig. 6. DSC curves of ammonium nitrate in different containers.

Fig. 6 shows the thermal reaction of ammonium nitrate in standard aluminum sample pans, aluminum volatile sample pans and in the glass capillaries. The two also give very different results. An endothermic reaction takes place in the aluminum pan while an exothermic reaction is observed in the glass capillary. As is well known, ammonium nitrate is a thermally hazardous material and under certain conditions it can explode. Endothermic reactions are not typical for ammonium nitrate in any case. The apparent endotherm is once again the result of the endothermic heat of vaporization superimposed on the exothermic heat of reaction.

#### 4. Conclusions

It has been shown that the use of aluminum pans can be misleading for some materials where volatilization occurs, while with the use of glass capillaries one can obtain correct experimental results. The use of sealed glass capillaries in power-compensated DSC without any metal sample holder is possible and produces reliable results. Baselines do not need to be run daily except for a change of reference glass capillary. The use of glass capillaries avoids the confusing results sometimes obtained with standard aluminum pans for some materials (such as ammonium nitrate). More precise results can be obtained by using glass capillaries for volatile materials.

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