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Correction of the sample weight in hermetically sealed DSC pans

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Abstract

The weight of a DSC sample is routinely determined as the difference between the weight of the pan containing the sample and the empty pan. If the sample is sensitive to atmospheric moisture, weighing is usually performed after sealing the pan. However, we have observed that sealing induced changes in the measured weight of the pan when aluminum DSC pans were hermetically sealed with a Perkin-Elmer Volatile Sealer Assembly. The difference between the weight of sealed and non-sealed DSC pans was about 10 μg and independent of the presence of a sample in the DSC pan. Correction for this difference is important in applications that require precise weights of DSC samples.

Keywords: DSC pans; DSC sample weight; Water content

1. Introduction

Precise determination of the weight of DSC samples is critical in applications dealing with quantitative measurements of the enthalpy or heat capacity changes accompanying a chemical reaction or phase transition (see, e.g. [1,2]) as well as in more specialized applications such as gravimetric determination of the water content in DSC samples [3–6]. Usually, the sample weight is determined as the difference between the weight of (pan + cover + sample) and (pan + cover). However, it is shown in this communication that determination of the sample weight may have a noticeable systematic uncertainty when weighing is performed after sealing the DSC pans. Weighing of the sample in a sealed pan is usually performed when the sample is sensitive to atmospheric moisture or oxygen and the time of sample exposure to the atmosphere should be minimized.

2. Results and discussion

In our DSC studies of lipid phase transitions (see [3], and the literature cited therein) the DSC scans were performed with Perkin-Elmer aluminum DSC pans and covers that were hermetically sealed with a Volatile Sealer Assembly [7]. After the DSC scans, pinholes were made in the covers of the pans and the pans were typically dried under vacuum at 70°C in order to perform gravimetric determination of water content [3–6]. The weight of the DSC pans was determined using a Cahn-31 micro-balance (250 mg

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Table 1
Weight (mg) of DSC pans with a sample to show difference between hermetically sealed pans and pans with a pinhole

Sample + pan + cover sealed	Sample + pan + cover with a pinhole	Difference in measured weight between sealed pan and pan with pinhole
27.045	27.055	0.010
26.678	26.688	0.010
27.400	27.409	0.009
26.940	26.951	0.011
27.038	27.044	0.006
26.989	26.999	0.010
26.218	26.225	0.007
26.256	26.267	0.011

range, 1 μg precision). In the majority of cases, the weight of the sealed pans was a few micrograms less than the same pan with a pinhole. Table 1 gives the results from one of the experiments as an example. To determine whether this difference was associated with the lipids in DSC pans, empty DSC pans were sealed and the weight of non-sealed, sealed, and sealed pans with a pinhole was determined (Table 2). The sealed pans weighed 9 ± 1 μg less than the non-sealed pan + cover whereas sealed pans with pinholes had the same weight as the non-sealed pan + cover.

To determine whether this difference depends on the presence of a sample in the DSC pan, several materials (pure water, a saturated solution of LiCl in water, and solid NaCl) were placed in DSC pans, sealed, and the weights of the sealed pans and pans

Table 2
Weight (mg) of empty DSC pans, to show difference between non-sealed pans, hermetically sealed pans, and pans with a pinhole

Pan + cover separately	Sealed pan + cover	Sealed pan + cover with pinhole
25.159	25.151	25.161
25.589	25.580	25.591
25.829	25.822	25.833
25.543	25.534	25.544
25.218	25.210	25.219
24.675	24.667	24.676
25.387	25.378	25.388
25.543	25.534	25.544
25.499	25.489	25.498

Table 3
Difference in measured weight, $\Delta W/g$, between sealed pan and sealed pan with a pinhole

Pan content	$\Delta W/g$ (μg)
Empty	11 ± 2 ($n = 5$)[a]
Water (15 μl)	8 ± 1 ($n = 4$)
Saturated LiCl solution (15 μl)	8 ± 2 ($n = 5$)
NaCl powder (15–21 mg)	9 ± 1 ($n = 3$)

[a] n is the number of replicates.

with pinholes were determined. For comparison, the same procedure was conducted with empty DSC pans. The results are given in Table 3. In all cases, the weights of the sealed pans were less than the weights of the pans with pinholes and were independent of the presence of different materials in the DSC pans.

To determine the reason for such a difference, let us consider the weight of the sealed pan and a pan with a broken seal (i.e., non-sealed pan + cover, or sealed pan with a pinhole). When the pan is sealed, it contains a volume of gas V with density ρ_i. When the seal is broken, it contains a volume of gas V with density ρ_o. Provided that the volume does not change when the seal is broken, the buoyancy force on the two is the same, so the difference between the weight W_s measured with the seal intact and the weight W_p measured with the seal broken is

$$\Delta W = W_p - W_s = V_2(\rho_o - \rho_i)g, \qquad (1)$$

where g is gravitational acceleration, ρ_i and ρ_o are the densities of air inside and outside the sealed pan, respectively, and W_s and W_p are measured weights with the seal intact and with the seal broken, respectively. By ‘‘measured weight’’, we mean the force measured by a balance.

If the density of the air inside (ρ_i) and outside (ρ_o) the sealed pan is the same, then W_p-$W_s = 0$, and $W_p = W_s$. However, we observed (Tables 1–3) that $W_s < W_p$. To explain this difference, we assume that $\rho_i < \rho_o$; in this case, $W_p > W_s$ as has been detected in the experiments. To account for the difference in the air density inside and outside sealed DSC pans, we suggest that during the sealing procedure part of the air is removed the from DSC pan. In this case, the difference of 10 μg can result from removing 7.7 μl of air (estimated assuming that 22.4 l of air has a weight of 29 g). The air can be removed from the pan if the sealing press reduces the volume of the (pan + cover) by about 8 μl at the moment of sealing. After the sealing pressure is released, the sealed pan is restored to its initial volume. It should be mentioned that it is possible that this effect might not be observed with other types of sealing presses (see [8] for a description of several types of sealing presses).

Let us illustrate the impact of this finding on gravimetric determinations of the water content of phospholipids performed in DSC pans [3–6]. The water content, X (wt.%), is determined as the loss of sample weight after drying under specified conditions (typically, by drying at 70°C under vacuum), and calculated as

$$X = 100 \cdot (W_i - W_d)/(W_i - W_e), \quad (2)$$

where W_i, W_d, and W_e are the weights of sealed DSC pan + sample before drying, after drying, and the weight of the empty DSC pan + cover, respectively.

Let us consider real weights from one of the our experiments as an example. The values are as follows: $W_d = 26.054$ mg, $W_e = 24.952$ mg, and $W_i = 26.109$ mg in the hermetically sealed DSC pan and $W_i = 26.119$ mg in the DSC pan with a pinhole. Calculating X with these values gives $X = 4.8$ wt.% if the weight of the hermetically sealed pan is used for W_i, and 5.6 wt.% if the weight of the pan with a pinhole is used. Failure to use the correction results in an underestimation of the water content by about 20% (i.e., 1 wt.%).

3. Conclusion

In conclusion, it has been shown that the actual weight of the material in a hermetically sealed aluminum DSC pan (using Perkin-Elmer Volatile Sealer Assembly) is approximately 10 μg more than the weight that is determined as the difference between weight of the (sealed pan + cover + sample) and the (open pan + cover). In the majority of practical applications, the correction is not large and may be ignored. However, in some applications, such as gravimetric determination of the water content in samples after DSC scans, this correction is critical.

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