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APPLICATION OF THE DIFFERENTIAL SCANNING CALORIMETER TO PURITY MEASUREMENTS

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Introduction

This paper presents a new method for the calculation of the purity of organic, non-polymeric samples using the recorder trace from a Differential Scanning Calorimeter (DSC), Perkin–Elmer Corp. The entire DSC recorder trace is employed rather than only the initial portion of the curve. The previous trial and error choice of energy lost by the DSC trace has been replaced by a definite numerical value. Meaningful purity values have been obtained from a single DSC trace on samples of from 95 to 99.9% purity. This new method has been demonstrated to provide more accurate and less ambiguous results than the manufacturer's procedure.

Several hundred papers have been published which involve the use of the Differential Scanning Calorimeter (DSC). Over forty papers involving the DSC were given at a single meeting in 1968 [1]. Several of the authors at this meeting, G. T. Driscoll et al. and R. D. Ennulat, and scientists publishing elsewhere [2, 3] have utilized the DSC to determine sample purity by a method published by Perkin–Elmer, the DSC manufacturer [4—6] Norwalk Conn. USA. G. T. Driscoll et al. [1] have demonstrated that this method can give potentially misleading results. The purpose of this paper is to detail the ambiguities of the Perkin–Elmer method [4, 5] and to offer an alternative procedure for estimation of the purity of organic, non-polymeric samples by DSC.

Perkin–Elmer [4], in its purity method, recommends that measurements be made on the initial portion of the DSC recorder melting trace only, preferably in the range from 10 to 50% of the area enclosed by the trace and the baseline. Driscoll et al. [1] give an example of a purity determination by this method in which the mole per cent impurity calculated can be changed by more than a factor of ten by varying the lower and upper limits of this range. What is therefore needed is an improved method for purity calculation by DSC which employs the entire recorder melting trace and which does not involve an arbitrary choice of only a part of the forward section of the DSC trace. Such a procedure is outlined in this paper.

As stated by the manufacturer [5], except for samples of very high purity, a significant amount of melting occurs before the melting curve rises detectably above the baseline. In this purity method, Perkin–Elmer [4, 5] implies that this totally unrecorded energy is a value which can be adjusted until the plot of sample temperature *vs.* reciprocal of the mole fraction of sample melted fit along a straight line. However, with relatively pure samples, the addition of this unrecorded energy to the energy measured by the DSC trace results in heat of melting values which are too high. Although the estimation of how much of the actual sample transition heat has not been recorded by the DSC is a principle problem, the value of this lost heat can be quite definite. Consider the compound, naphthalene, whose heat of melting is well-established at 35.0 calories per gram [7] for a theoretically 100% pure, crystallizing compound. Mastrangelo et al. [7] have determined the heat of melting of naphthalene containing various mole fractions of thionaphthene by adiabatic calorimetry. Their data are presented in the first two columns of Table 1. As a simple mathematical model, the energy required to melt the sample can be attributed totally to the naphthalene present and the thionaphthene can be assumed to be dispersed in the naphthalene so as not to form crystals. At 0.9444 mole fraction naphthalene, this model can be shown to be applicable, since a ΔH of 35.0 calories per gram, as shown in column three of Table 1, for naphthalene, permits an accurate calculation of the transition heat. Thence from 0.9444 to 0.9958 mole fraction naphthalene, the sample heat of fusion in cal/g, ΔH, can be treated as the following linear function of the mole fraction naphthalene, N_a:

Table 1

Naphthalene — thionaphthene heats of melting

Mole fraction naphthalene	ΔH, cal/g of sample	ΔH, cal/g of naphthalene
0.9958[a]	34.92	35.0
0.9444	33.02	35.0
0.8095	29.00	36.1

a — purity of original sample of naphthalene.

$$\Delta H = 35.0\, N_a \tag{1}$$

In this laboratory, a Fisher triple point naphthalene sample was diluted with 0.05 mole fraction of 1,2 diphenyl ethane, with which it forms an ideal solution in the melt [8]. The resultant sample was melted at a heating rate of 2.5° per minute in the DSC, which gave a recorder trace corresponding to 21.0 calories per gram. From the mathematical model, 1.8 calories per gram would be the loss from the reduction in mole fraction of naphthalene, and 12.2 calories per gram, the energy unrecorded by the instrument. The unrecorded energy was 87% of the difference between the energy of the highly pure naphthalene and the energy of the impure sample, as determined by DSC. Similar results were obtained with Fisher triple point benzoic acid samples containing from 0.01 to 0.04 mole fraction naphthalene, when run on the DSC at a heating rate of 2.5° per minute. Their unrecorded energy varied from 85 to 89% of this difference when the sample heat was treated as a linear function of the mole fraction of benzoic acid present. A third system consisting of Fisher triple point naphthalene samples containing 0.01 to 0.04 mole fraction p-nitrotoluene, melted at a rate of 2.5°/min, had unrecorded energy of from 83 to 88% of this difference when the sample heat was treated as a linear function of the mole fraction of naphthalene present. In the purity method to follow, for samples melted at a heating rate of 2.5° per minute, 87% of the difference between the heat of melting of a highly pure sample and that of an impure sample, as determined by DSC, was estimated to be unrecorded heat. This estimate of per cent heat loss may eventually be shown to decrease a per cent or two as the sample size is increased from 3 to 6 mg.

The important property of a DSC trace, which is not known with reasonable certainty, is the location on the trace for the temperature where the sample can be considered to have just finished melting. A clue to its location comes from studies of melting point depression by impurity. Experiments have been made in this laboratory on systems of naphthalene diluted with 1,2 diphenyl ethane and cholesteryl myristate diluted with toluene. Tremendous broadening of the temperature range for the DSC melting peak trace is observed with increasing sample impurity. However, an excellent straight line relationship was achieved between the reciprocal of the melt temperature, when designated as occurring at the curve peak, and the log of the mole fraction of the major component. This means conformance with the Van't Hoff equation. This new procedure for the determination of sample purity by DSC is based on a trial and error method to estimate the location, near the curve peak, of where the sample has just finished melting

Function of the electrical loops in the DSC

Any valid method for determinations of sample purity requires an understanding of instrument operation. Transition temperatures and heats are determined from the DSC by measuring the differential power required to maintain the same temperature program on two nominally identical and symmetrically placed cups [9]. One cup holds the weighed sample in a sealed planchet; the second cup is the differential reference. Electrical power is supplied to the reference and sample holders through the operation of two essentially separate electrical control loops. An average temperature loop maintains the cups at a preset heating rate. The power for this loop is supplied equally to both cups and is *not* recorded. This loop operates by comparing the average temperature of the two cups to that demanded by the programmer, and the power required always is provided equally to both cups as needed. The temperature program is marked out on the abscissa of the DSC recorder.

A separate electrical loop is used to handle temperature differences between the cups. This second loop senses the temperature difference between the sample and reference cups, and supplies the differential power needed to compensate for the difference; this is the power input indicated on the DSC recorder ordinate. Before and after a sample transition (for conditions where the temperature of the sample cup does not change relative to the reference cup temperature), i.e. no transition or heat capacity difference, the differential power supplied to both cups is the same. During an endothermic transition, however, differential power is subtracted from the reference cup circuit and added to the sample circuit [9]. The DSC chart ordinate changes by an amount proportional to the temperature difference between sample and reference cups converted to units of power, dq/dt or $\dot{q}$, as the average temperature of the cups, T_p, is programmed on the abscissa at a rate dT_p/dt or $\dot{T}_p$. An exothermic transition merely reverses the electrical process. Importantly, each change in the differential temperature loop, as during the melting of the sample, causes the average temperature loop to add compensating power, divided equally between cups to maintain the preset heating rate. Note that the power supply for the average temperature loop is an order of magnitude larger than that of the differential temperature loop.

The functions of the electrical loops described above could provide a simple theoretical basis for a purity method. Unfortunately, there appears to be a threshold temperature difference, recognized to be several thousandths of a degree by the manufacturer [10], below which differential heat is not transferred and $\dot{q}$ is not recorded. There are at least two conclusions concerning the operation of the electrical loops which influence potential methods for sample purity. In melting a highly pure sample, for example the power put in at the start of the transition, to bring sample and reference cup temperatures together, is provided presumably by the average temperature loop. This energy addition and the energy required below the threshold response of the differential loop mentioned in the previous paragraph, are both made by the average temperature loop, and neither are recorded. The energy put in during the initial portion of a transition by the average temperature loop must eventually be transferred to the part of the recorded $\dot{q}$ curve that occurs after the sample has undergone the maximum melting rate, which is the region where the temperature of the sample cup must catch up to the temperature of the reference cup.

For relatively impure samples, a large fraction of the sample can be melted over a wide temperature range before the threshold temperature difference is reached and the differential temperature loop responds. The average temperature loop provides whatever extra power is required to maintain $\dot{T}_p$; this power is not recorded and little, if any, of it appears in the latter portion of the transition curve.

Immediately after the sample is completely melted, the average temperature loop returns to its operating level prior to the transition; however, the sample and reference cups are still at different temperatures. The differential temperature loop must continue to transfer energy until these temperatures are equalized. Thus, the recorded energy transferred by the differential temperature loop after melting is energy that had been added by the average temperature loop during melting.

Analysis of the DSC recorder trace

Fig. 1 presents a trace, exactly as it occurred on the recorder graph of a model DSC-1B, for the crystal-mesophase transition of cholesteryl propionate, sample obtained from Applied Science Laboratories, Inc., State College, Pa. The area between the curve and the baseline, AGC in Fig. 1, is a measure of the transition heat. The abscissa of Fig. 1 represents time and/or temperature. For example, at a $\dot{T}_p$ of 2.5°/minute, each mark on the abscissa means 1.0° or 0.4 minutes.

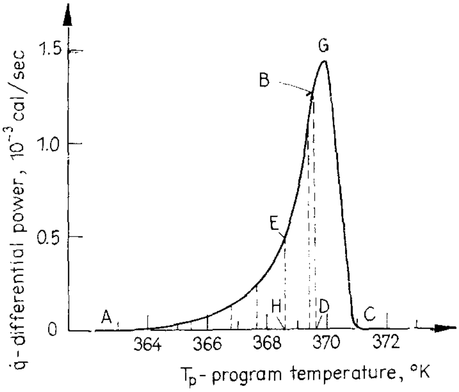

Fig. 1. Cholesteryl propionate, crystal-mesophase transition. $\dot{T}_p = 2.5°C/min$, scale = 4×, sample wt. = 5.306 mg

The level of impurity in a sample can be calculated from DSC data and the Van't Hoff equation which relates sample temperature, T_s, to sample mole fraction, F, melted at T_s:

$$T_s = T_0 - (RT_0^2N/\Delta H)(1/F) \tag{2}$$

where

ΔH = heat of fusion of the pure major component
R = gas constant
N = mole fraction of impurity
T_0 = melting point of the pure major component

A plot of T_s vs. $1/F$ will be a line of slope $-RT_0^2N/\Delta H$. A knowledge of ΔH obtained from the area under the DSC curve or from the literature permits a calculation of N, the mole fraction of impurity. The above equation was developed from Raoult's Law and in most cases, it can be expected to hold only for high purity samples, >95%. Also implicit in the equation is the assumption that the impurity must be insoluble in the solid yet completely soluble in the melt.

A sample temperature, T_s, can be derived from any point on the DSC trace AGC. Take point E as an example. Drop a line from E perpendicular to the abscissa intersecting the baseline at H. The line EH is proportional to the temperature difference between the reference, T_r, and the sample, T_s. The relationship between the programmed temperature T_p, T_s, and T_r is presented in the following equation:

$$T_s = T_p - 1/2(T_r - T_s) \tag{3}$$

The proportionality constant to determine the actual temperature represented by EH is derived from the shape of the DSC trace for an extremely high purity sample, e.g. 99.999% pure indium [4], at the same heating rate of 2.5°/min. If line EH is proportional to $T_r - T_s$, then:

$$R_0\dot{q} = T_r - T_s \tag{4}$$

where

R_0 = the proportionality constant in °C-sec./millical.
$\dot{q}$ = the actual value of EH in millical./sec.

During the melting of the extremely pure indium sample, T_s, the actual sample temperature does not change. From the differentiation of Eqs (3) and (4), R_0 can be evaluated for the indium sample since d^2q/dt^2 or $\ddot{q}$ is constant. R_0 is the valid proportionality constant for all distances between trace and baseline at a particular $\dot{T}_p$, or heating rate. Then from Eq. (4), the $T_r - T_s$ value of line EH can be determined and substituted in Eq. (3) to give T_s. All other points on trace AGC can be similarly converted to T_s values. Each of these T_s values then should be adjusted by reference to a temperature calibration correction curve similar to that presented by the manufacturer [4]. This calibration curve is a plot of correction to the dial reading versus dial reading, in degrees.

Generally samples change temperature throughout the tracing of the sample melting curve, AGC. Differentiation of Eq. (4) would give:

$$R_0\ddot{q} = \dot{T}_r - \dot{T}_s \tag{5}$$

At the curve peak, G, $\ddot{q}$ must equal zero and $\dot{T}_r$ equals $\dot{T}_s$. This fact suggests that the sample must have completed melting before the curve peak is reached. Essentially all compounds analyzed in this laboratory appeared to have their melting point near but before the peak of the DSC trace.

New purity method procedure

The method to be described for the calculation of $1/F$, the reciprocal of the mole fraction of sample melted, is entirely different from that of Perkin-Elmer [4, 5]. The following procedure is offered for estimating $1/F$ at each T_s:

Arbitrarily choose a likely locale for the final sample melting point which will be prior to—but near—the peak, G, on the DSC trace; for example, choose point B in Fig. 1. The choice of this point is not critical because the plot of T_s vs. $1/F$ must be a straight line with an intercept at $1/F$ equal 1.00 at the T_s corresponding to point B (see previous temperature correction method). This point where $1/F$ equals 1.00 corresponds to the melting of the last crystals, and, therefore, the theoretical melting point.

Divide the curve into two sections with a line from B perpendicular to the abscissa which intersects the baseline AC at D in Fig. 1. Area ABD of Fig. 1 can subsequently be divided into arbitrarily chosen segments, such as area AEH, which can be considered as proportional to an uncorrected F value. The sample temperature, T_s, at corresponding point E is determined as described previously. The uncorrected $1/F$ value for an area AEH is:

$$(1/F) \text{ uncorrected} = \frac{\text{Area AGC}}{\text{Area AEH}} \tag{6}$$

Area ABD represents energy added by the average power loop during the melting of sample, half to the sample holder and half to the reference holder. Therefore, energy of size 1/2 ABD is recorded by the differential temperature loop during the energy transfer represented by area BCD. Subtract 1/2 area ABD from area BCD to obtain an area P. This area P represents energy that was added by the average power loop before the differential power loop began to record and should be added to each chosen segment, such as area AEH. The value P implies that power transfer lags power input.

Calculate the trace area that a highly pure sample of equivalent weight would have, and from this value, subtract area AGC. Multiply the difference by 0.87. This is the area corresponding to the energy that was supplied by the average temperature loop, but not recorded by trace AGC. Call this value Q.

Area AEH should be further corrected by the addition of its share of the 1/2 ABD recorded by the differential temperature loop during the energy transfer represented by area BCD, or 1/2 AEH. Then the corrected $1/F$ value for an area AEH would be the following:

$$(1/F)\text{corrected} = \frac{(\text{Area AGC}) + Q}{3/2\ (\text{Area AEH}) + P + Q} \tag{7}$$

The calculation of a complete series of $1/F$ values would be handled similarly.

A plot of the T_s vs. $(1/F)$ correct values is shown in Fig. 2 for the curve presented in Fig. 1. If the points had not formed a straight line or did not intersect the $1/F$ equal 1.00 line at the corresponding T_s value for B, another locale for B close to the first would have been chosen and the calculations repeated. Experience indicates that the first trial is commonly successful or so nearly that only a second trial is required.

Discussion of results from the new purity method

Fig. 2 presents plots of T_s vs. $1/F$ for both uncorrected and corrected $1/F$ values. Note that the curvature is entirely removed with the corrected $1/F$ values and the line intersects the $1/F$ equal 1.00 line within 0.1 degree of its value at B from

Fig. 1. This permits a direct calculation of N, the sample impurity through the Van't Hoff relationship.

Estimates of the accuracy of the purity evaluations are presented in Tables 2 and 3. Known amounts of naphthalene were added to benzoic acid (Table 2) and p-nitrotoluene to naphthalene (Table 3), all Fisher triple point samples. The samples were melted, recrystallized from the melt and then remelted. The curves from the remelted samples were analyzed by this new method for purity. The data from both tables indicate that an accuracy within 15% of the actual impurity value can be anticipated in the 95 to 99.9% purity range.

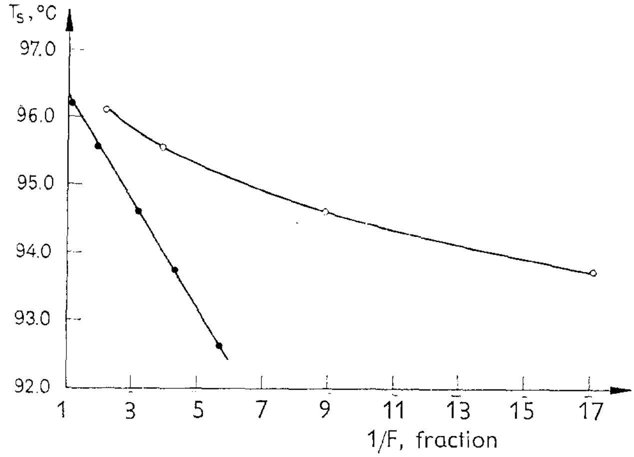

Fig. 2. Cholesteryl propionate purity determination. Slope = —0.80, ΔH = 5.98 kcal/mole, purity = 98.25%, intercept = T_m = 96.32°C. ○ $1/F$ uncorrected, ● $1/F$ after correction

Table 2

Summary of benzoic acid and naphthalene purity results
Major component — benzoic acid (Fisher triple point)
Impurity — naphthalene (Fisher triple point)

Mole % added impurity	Total impurity %	Experimental impurity %	Absolute error, %	Relative error, %
0	0.24[1]	0.24	—	—
0.77	1.01	1.12	+0.11	+10.9
1.07	1.31	1.24	—0.07	— 0.5
2.57	2.81	2.70	—0.11	— 3.9
3.91	4.15	3.85	—0.30	— 7.2

[1] Experimentally determined from the recrystallized melt.

This purity method is applicable to heating rates other than 2.5° per minute by replacement of the 0.87 factor in determining Q with the one proper for that

Table 3

Summary of naphthalene and p-nitrotoluene purity results
Major component — naphthalene (Fisher triple point)
Impurity — p-nitrotoluene (Fisher triple point)

Mole % added impurity	Total impurity %	Experimental impurity %	Absolute error, %	Relative error, %
0	0.38[1]	—	—	—
0.46	0.84	0.89	—0.05	— 6.0
1.10	1.48	1.67	+0.19	+12.8
2.66	3.04	3.17	+0.13	+ 4.3
4.32	4.60	4.89	+0.29	+ 6.3

[1] Experimentally determined from the recrystallized melt.

heating rate. For heating rates of 0.625 and 1.25° per minute the factor is larger, that is, the ratio of the unrecorded energy to the actual energy loss due to impurities is even greater. Generally, these low heating rates are reserved for samples of high purity where Q is approximately equal to zero. The actual trace of a triple

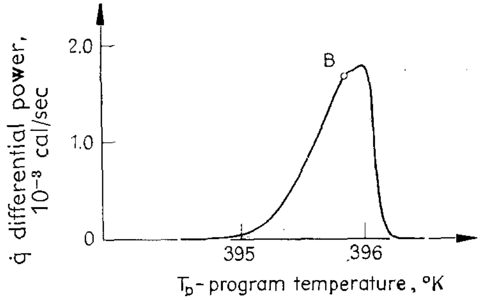

Fig. 3. Benzoic acid, melting curve, $T_p = 0.625$ °C/min, scale = 8×, sample wt. = 2.959 mg

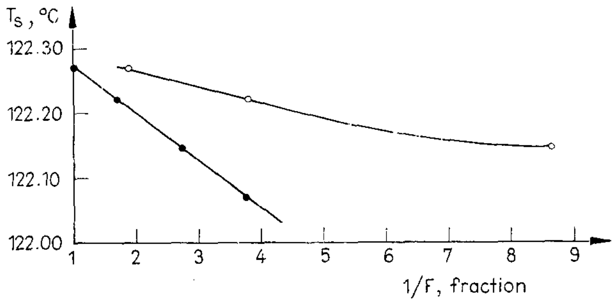

Fig. 4. Benzoic acid purity determination. Slope = —0.075, $\Delta H = 4.27$ kcal/mole, purity = 99.90%, intercept = $T_m = 112.27$ °C. ○ $1/F$ uncorrected, ● $1/F$ after correction

point benzoic acid sample from Fisher melted at a heating rate of 0.625° per minute is shown in Fig. 3. Its apparent melting point is marked by the letter "B". The plots of T_s vs. $1/F$ of both uncorrected and corrected $1/F$ values for this benzoic acid sample are presented in Fig. 4. Curvature in the plot of sample temperature, T_s, vs. $1/F$ is removed by the procedure described before and a melt temperature, T_m, is determined.

A change in sensitivity or ordinate scale factor does not seem to affect the 0.87 Q factor significantly. Sample heats of transition measured at different sensitivities give equivalent results, within experimental error. The threshold temperature difference does not seem to be dependent on sensitivity.

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Résumé — On décrit une nouvelle méthode à calculer la pureté des substances organiques non polymères à l'aide de la courbe enregistrée sur un "Differential-Scanning Calorimètre"Perkin–Elmer. Au lieu d'utiliser seulement la partie initiale du pic, on se sert du tracé complet. On attribue une valeur numérique définie à la perte d'énergie, précédemment déterminée par approximations successives. Un seul enregistrement sur le DSC permet d'obtenir des valeurs significatives de la pureté, avec des échantillons à 95-99.9%. On montre que cette nouvelle méthode fournit des résultats plus exacts et moins ambigus que celle des fabricants

Zusammenfassung — Es wird über eine neue Methode zur Ermittlung der Reinheit von organischen, nicht-polymeren Stoffen mit Hilfe einer durch ein Differential-Scanning Calorimeter Perkin–Elmer gezeichneten Kurve berichtet. Die Methode beruht auf der Verwendung der vollen Kurve und gibt für den Energieverlust definitive numerische Werte. Verläßliche Reinheitswerte von Proben von 95 bis zu 99.9% Reinheit können durch eine einzige Kurve erhalten werden. Die neue Methode gibt sicherere und eindeutigere Ergebnisse als die von den Geräterzeugern vorgeschlagene.

Резюме. — В работе описан новый метод расчёта чистоты органических неполимерных образцов с использованием сигнала прибора ДТЦ (Фирма Перкин—Элмер). При расчёте авторы использовали полную кривую ДТЦ, а не только её начальную часть. Получены значительные величины чистоты по одной кривой в случае образцов чистой от 95 до 99,9%. Новый метод расчёта обеспечивает более точные и достоверные результаты, чем получаемые в заводских условиях.