USE OF DIFFERENTIAL CALORIMETER
FOR ESTABLISHING TEMPERATURE STANDARDS

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A differential calorimeter was used to set up and critically evaluate a series of organic substances as temperature standards over the range 50—330°. The conditions for acceptance of a standard substance were a sufficient degree of purity, thermal stability, absence of polymorphism, a suitable cryoscopic constant, low volatility and ready availability.

Zone refining was mentioned as a method of purification to obtain the minimum degree of required purity at 99.9 mole per cent.

In practice it is impossible, even if all the variables of the equipment and the technique are known and may be controlled, to obtain a perfect relationship between the true temperature of a given transition proceeding in a real system and that measured with any temperature measuring device. With conventional thermometers the main source of error is due to the fact that the mercury column is subjected to indetermined heat exchanges outside the region in which the temperature must be measured. With other devices the main error is caused by the frequent lack of linearity of the response of the thermosensitive element. This source of error has also been found in the Perkin–Elmer DSC-1B differential scanning calorimeter, used for accurate temperature measurements. In fact the true temperature does not correspond closely to that recorded by the instrument. Thus the temperature readings obtained with any of these devices must be corrected using calibration curves constructed from temperature reference points conveniently and usually provided by the solid–liquid equilibria (or other transition point) of selected compounds of high purity and thermal stability.

Apart from the internationally agreed fixed points taken as primary reference temperatures for calibration purposes, several series of temperature standards, intended for practical use in a more restricted temperature range and based on the melting points of selected compounds, have been proposed by Timmermann and Burriel [1], Kofler [2] and Oehrner et al. [3]. Each of these is open to criticism: the Kofler and the WHO series because of the choice of unsuitable substances, and all of them because they do not give temperatures of a thermodynamically true melting point, i.e. a melting point whose temperature reading is independent of the method and technique used for its determination.

To improve this situation, triple point measurements were carried out recently [4]. Despite this improvement a considerable error is caused by the fact that the solid–liquid equilibrium temperature depends on the degree of purity of the substance and can be accepted as valid only if a certain level of purity is attained. The availability of a series of temperature standards of substances with the required purity (with reference points spread evenly over the temperature range from 50 to 350°) for which the reference temperature can be exactly defined as that of the thermodynamically true melting, solidification, or triple point, is a prerequisite common to the differential calorimeter and to all other instruments for thermal analysis.

We have tried therefore to assemble a series of substances suitable as primary standards for the calibration of the differential calorimeter and of other similar instruments. Also, in view of the special characteristics of the Perkin–Elmer calorimeter, a number of substances were chosen to provide some more points between 50 and 100°, where the calibration graph of the DSC instrument has a marked slope, and to provide intermediate reference points between the melting temperatures of the primary standards.

Required properties of reference substances

Substances were selected for use in the calibration scale according to the general specifications of the desired series, and also according to the following requirements, which we believe necessary for the purpose:

1. Molar purity not less than 99.9%*
2. Thermal stability
3. Absence of polymorphism
4. Suitable cryoscopic constant
5. Low vapor pressure of the solid phase
6. Ready availability

1. The required purity is of the utmost importance since a thermometric standard must have the minimum possible depression of the melting point due to the cryoscopic effect of impurities and therefore a minimum melting temperature interval, so that the temperature of the transition may be defined and read with the least uncertainty.

The purity requirement is extended to the moisture content and therefore the substance chosen must be perfectly dry and not hygroscopic.

2. The thermal stability means that each substance of the series must undergo several solid–liquid transitions without decomposition. This is also very important during preparation: the required purity of 99.9% can be obtained in most cases only by zone refining, which requires repeated heating of the sample above the melting temperature without decomposition. Some substances previously used

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* For an uncertainty in the melting point of less than $\pm 0.1°$.

as temperature standards [e.g. adipic acid (m.p. 151.4°), mannitol (m.p. 166.55°), salophen (m.p. 192°) and phenolphthalein (m.p. 262°)] proved to be unreliable because of insufficient thermal stability.

3. Absence of polymorphism has not been considered previously because of lack of adequate instrumentation for its identification. The presence of polymorphism can give rise to errors in measurements of the melting point, particularly when the polymorphic transition temperatures are close to the melting point. The differential calorimeter gives a diagram in which all changes requiring or liberating
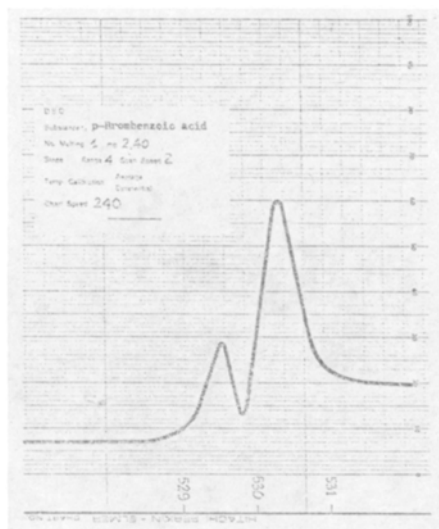

Fig. 1. DSC curve of p-bromobenzoic acid

heat are resolved. Thus different crystalline forms may be identified. In some cases, when a substance is melted and then rapidly solidified, monotropic polymorphism causes the formation of different crystalline forms with very close melting points: in such cases repeated melting of the sample will show an apparent raising of the melting point. Examples of substances showing such false melting points and which are therefore unsuitable as temperature standards are: p-acetotoluidine (m.p. 153°), p-bromobenzoic acid (m.p. 256 − 257°) and chloranil (m.p. 290 − 293°). Fig. 1 shows the curve obtained by DSC of p-bromobenzoic acid.

4. The cryoscopic constant is a very reliable physical constant for evaluating the influence of the impurities on the depression of the melting point of the pure substance. The calculation of the cryoscopic constant (given in Table 2) has been carried out using the equation $K_f = RT_0^2/\Delta H_f$, where R is the constant of the ideal gas law, T_0 the absolute temperature of fusion of the pure substance and ΔH_f its molar heat of fusion.

Obviously a good temperature standard should have a low K_f value. Substances with high K_f values must be very highly purified. The minimum level of purity of 99.9 mole per cent was fixed especially for substances having high K_f values.

5. A low vapor pressure in the solid phase is required so that the sample does not sublime before melting. This is needed not only when using open pans, but also when other instruments are used. Substances otherwise suitable and sometimes used as temperature standards, but which are too volatile, are phthalimide (m.p. 233°) and caffeine (m.p. 236°).

6. The criterion of ready availability is dictated by practical considerations. This condition, along with numbers 1, 2 and 3, accounts for the adoption of structurally simple substances with the exclusion of more complex ones.

Choice of temperature standards

Substances chosen for use as temperature standards fulfilling the six requirements discussed are listed in Table 1. The upper part of the column shows ten

Table 1

Proposed temperature standards and their melting points

Substances	Temperature °C		Ref.	Source of standards
p-Nitrotoluene	TP	51.537	4	Carlo Erba
Naphthalene	TP	80.270	12	Carlo Erba
Phenanthrene	MP_1	99.943		Carlo Erba
Benzoic acid	TP	122.362	5	Carlo Erba
Diphenylacetic acid	MP_1	147.094		B.D.H.
Anisic acid	TP	182.986	4	Carlo Erba
2-Chloroanthraquinone	TP	209.034	4	Fischer Scientific Company
Carbazole	TP	245.337	4	Carlo Erba
Anthraquinone	TP	284.592	4	Carlo Erba
Hexabromobenzene	MP_2	328.90		E.G.A.
2-Chloronaphthalene	MP_2	57.80		Schuchard Munchen
p-Diethoxybenzene	TP	70.44	11	Schuchard Munchen
Imidazole	MP_2	89.50		Schuchard Munchen
Acetanilide	MP_3	114.30	13	Carlo Erba
Phthalic anhydride	MP_3	131.22	13	Carlo Erba
Dimethylterephthalate	MP_3	140.683	6	Carlo Erba
Benzanilide	MP_3	163.20	13	Schuchard Munchen
Triphenylene	MP_2	198.40		E.G.A.
Hexachlorobenzene	MP_2	227.80		Carlo Erba
p-Iodobenzoic acid	MP_2	271.60		B.D.H.

TP   = Triple point;
MP_1 = Melting point measured as described in section "measurement";
MP_2 = Melting point measured with the DSC;
MP_3 = Melting point from the literature.

proposed primary temperature standards, which provide fixed reference points suitable for the calibration of any temperature-measuring apparatus. The lower part of the column shows an additional list of ten substances, also useful as temperature standards, but particularly so for use with the differential calorimeter; these are called secondary temperature standards. For the majority of primary standards and for some of the secondary, the melting or the triple points are available (see Table 1). The melting point is usually a few hundredths of a degree higher than the triple point [5]. As a reference temperature for three of the primary standards could not be found, the precise solid–liquid transition temperatures for phenanthrene and diphenylacetic acid were determined by a special method and apparatus [6]. Phenanthrene proved to have a melting temperature closer to 100° than any other substance examined.

With hexabromobenzene, the amount of sample available was too small for a determination of the melting point by the above method [6]; however, it was

Table 2

Physical constants of temperature standards

Substances	Melting point		Molec-ular weight	ΔH_f cal/mole	K_f**	$T_0 - T_m$ (°C)*** for molar purity 99.8 −99.9 %	
	(°C)	(°K)					
p-Nitrotoluene	51.54	(324.70)	137.12	3670[15]	57.08	0.114	0.057
2-Chloronaphthalene	57.80	(330.96)	162.61	3150*	68.85	0.138	0.069
p-Diethoxybenzene	70.44	(343.60)	166.21	7160*	32.64	0.066	0.033
Naphthalene	80.28	(353.44)	128.16	4560[16]	54.24	0.108	0.054
Imidazole	89.50	(362.66)	68.08	2860*	91.05	0.182	0.091
Phenanthrene	99.94	(373.10)	178.22	4330[16]	63.87	0.128	0.064
Acetanilide	114.30	(387.46)	135.16	4850*	61.50	0.123	0.061
Benzoic acid	122.37	(395.53)	122.12	4140[16]	75.08	0.150	0.075
Phthalic anhydride	131.22	(404.38)	148.11	5380*	60.39	0.120	0.060
Dimethyl terephthalate	140.68	(413.84)	194.19	7100*	47.92	0.096	0.048
Diphenylacetic acid	147.09	(420.25)	212.24	6820*	51.45	0.103	0.051
Benzanilide	163.20	(436.36)	197.23	6900*	54.83	0.110	0,055
Anisic acid	182.98	(456.14)	152.14	7560*	54.68	0.110	0.055
Triphenylene	198.40	(471.56)	228.28	5470*	80.77	0.162	0.081
2-Chloroanthraquinone	209.04	(482.20)	242.66	7850[15]	58.85	0.118	0.059
Hexachlorobenzene	227.80	(500.96)	284.80	6190*	80.55	0.161	0.081
Carbazole	245.34	(518.50)	167.20	6100*	87.57	0.175	0.088
p-Iodobenzoic acid	271.60	(544.76)	248.03	7240*	81.44	0.163	0.081
Anthraquinone	284.60	(557.76)	208.20	7810*	79.14	0.158	0.079
Hexabromobenzene	328.90	(602.06)	551.58	7800*	92.33	0.184	0.092

* Obtained with DSC method

** From measured ΔH_f according to the equation: $K_f = \dfrac{RT_0^2}{\Delta H_f}$

*** Calculated using the van't Hoff equation: $T_0 - T_m = \dfrac{RT_0^2}{\Delta H_f} - x_2$

possible to measure it accurately by the DSC technique. The missing data for some of the secondary standards (2-chloronaphthalene, imidazole, triphenylene, hexachlorobenzene and p-iodobenzoic acid) were determined with the same technique. Since it has been shown [7] that the accuracy of the measurements with the DSC is of the order of ±0.1°, the values for the above compounds are therefore accurate to ±0.1°.

It was difficult to find an appropriate secondary standard that would melt between 260 and 270°; the only substance available and not subject to decomposition was p-iodobenzoic acid.

Table 2 shows the physical constants important for the characterization of all the substances selected as temperature standards. The table also shows the theoretical lowering of the melting point for purity levels at 99.80 and 99.90 mole per cent, respectively. It is clear from these data that 99.90 mole per cent purity is needed to reduce the error of the melting point to less than 0.1°. Substances with a purity of 99.90 mole per cent give a very sharp melting peak, i.e. they melt at a practically constant temperature within the limits of readability of the DSC.

Zone refining was applied throughout for purification; the degree of purity obtained for each substance is shown in Table 3.

Adipic acid, the triple point of which has been determined [4], was rejected because of its insufficient thermal stability; this substance melts without alteration,

Table 3

Purification of standards by zone refining

| Substance	Purity (mole %) of starting material	Purity (mole %) of purified material
p-Nitrotoluene	99.9	99.980
2-Chloronaphthalene	99.4	99.988
p-Diethoxybenzene	99.5	99.924
Naphthalene	99.7	99.991
Imidazole	99.6	99.988
Phenanthrene	99.8	99.996
Acetanilide	99.6	99.980
Benzoic acid	99.7	99.943
Phthalic anhydride	99.8	99.992
Dimethylterephthalate	99.8	99.993
Diphenylacetic acid	99.8	99.982
Benzanilide	99.7	99.975
Anisic acid	99.7	99.986
Triphenylene	99.3	99.988
2-Chloroanthraquinone	98.7	99.981
Hexachlorobenzene	99.6	99.994
Carbazole	99.0	99.974
p-Iodobenzoic acid	98.8	99.950
Anthraquinone	99.4	99.977
Hexabromobenzene	—	99.986

but undergoes decomposition a few minutes after prolonged melting; it also shows an appreciable loss of purity after two zone refining runs. This behaviour is not surprising, since it is typical of polycarboxylic acids [8].

Only in the case of high-melting substances, such as p-iodobenzoic acid and hexabromobenzene, did we notice a tendency to sublimation. The degree of volatility of compounds usually regarded as highly volatile, such as hexachlorobenzene, anthraquinone and carbazole, decreased with increasing purity. The proposed set of temperature standards is not intended to exclude other substances with suitable characteristics. Some further substances suitable as thermometric standards, except for the unsuitable location of their melting point, are: benzophenone (48.1°), diphenyl (68.7°), azobenzene (68.8°), vanillin (81.5°), p-dibromobenzene (87.5°), benzyl (94.8°), phenacetin (134.7°), p-bromoacetanilide (167.5°), benzimidazole (172.2°), hippuric acid (191.5°), anthracene (216.8°) and nicotinic acid (236.0°). The melting points were obtained by the DSC technique.

Zone refining

Zone refining was carried out with a "Zone Refiner" apparatus made by Fischer Scientific Co. Starting materials had a purity of not less than 99%.

Purification was carried out automatically and stopped when the substance was 99.9 mole per cent pure. If the purity check [9] showed an insufficient purity, another sample of the same substance was purified until the desired purity was obtained. The column was cut into suitable sections and emptied by drilling using
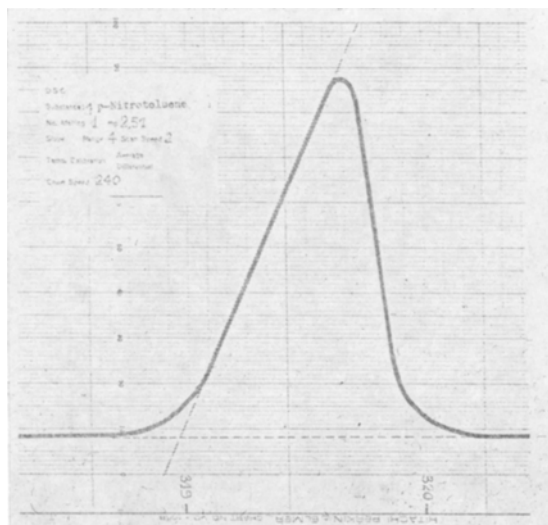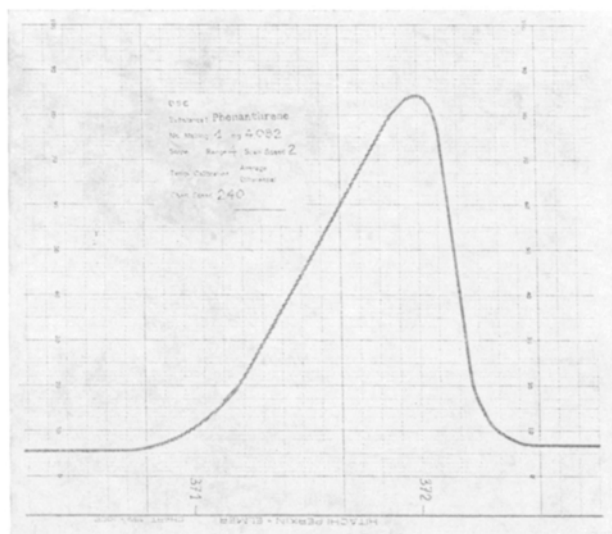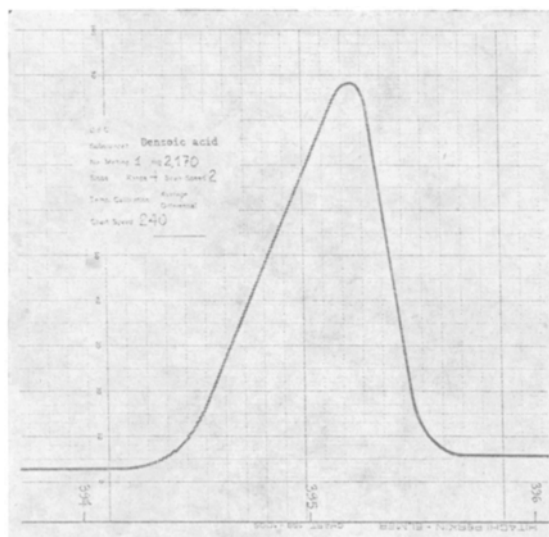

N. 1

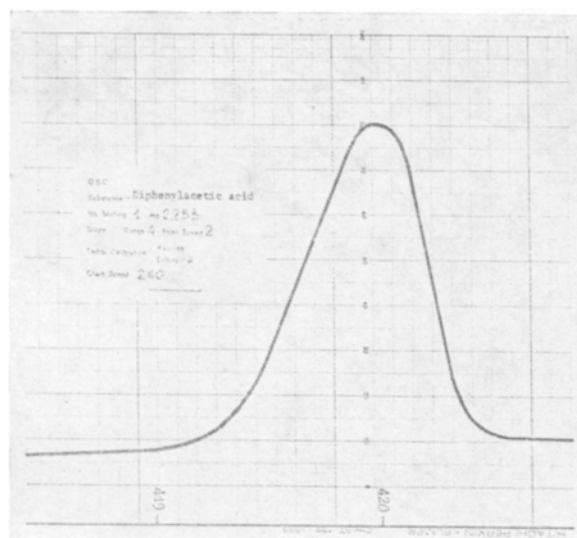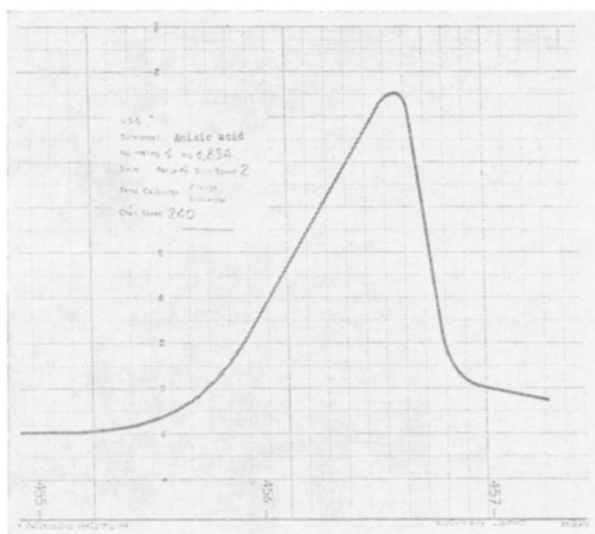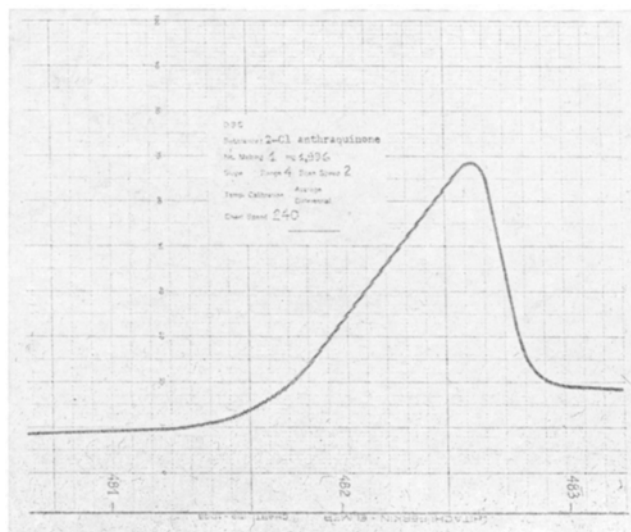Fig. 2. Melting curves of the primary standards (N. 1 — N 10)
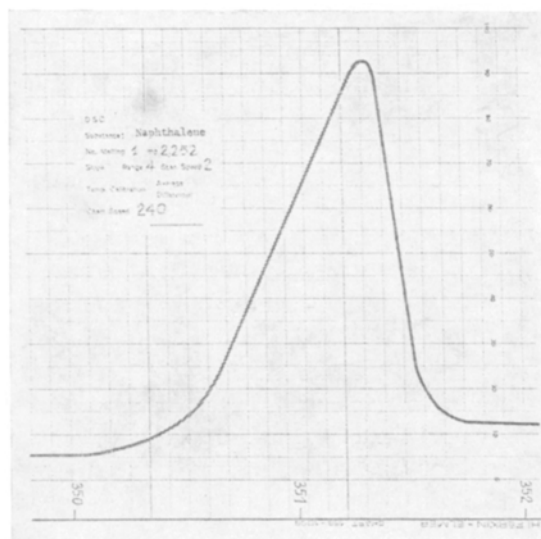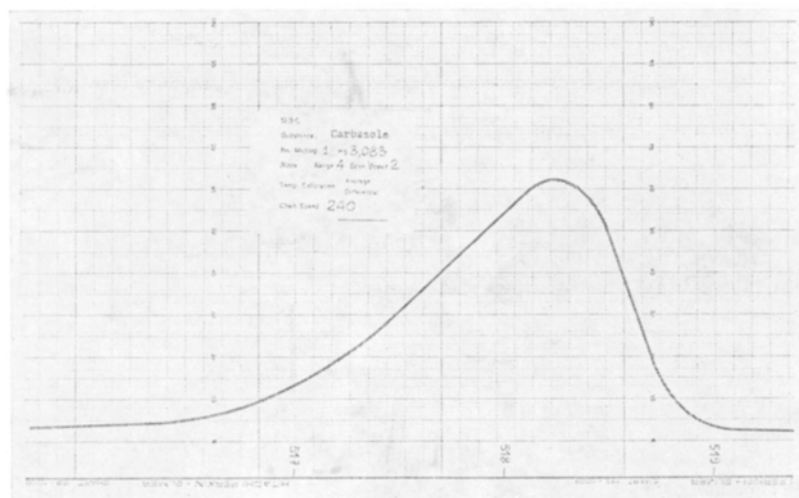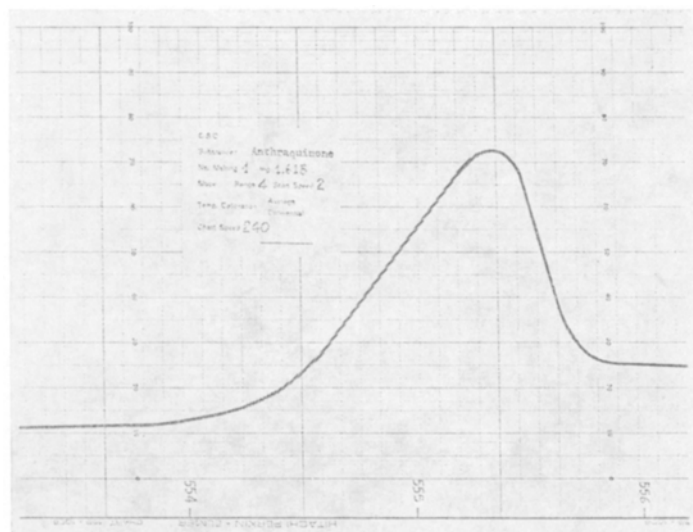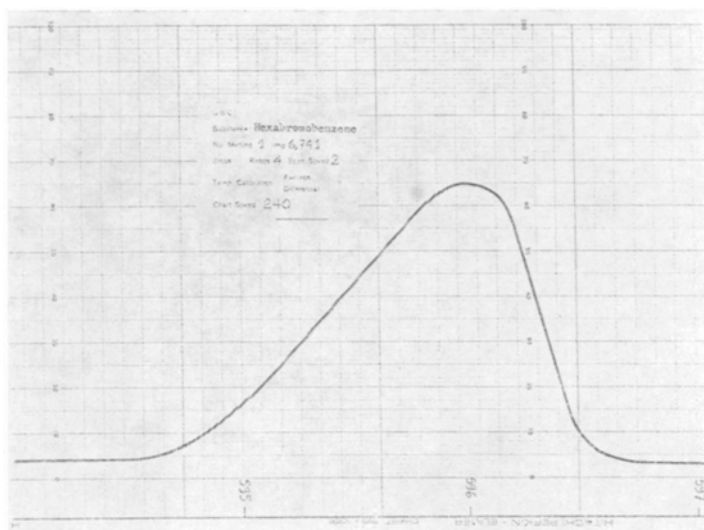
N. 2

N. 3

N. 4

N. 5

N. 6

N. 7

N. 8

N. 9

N. 10

a 2 mm stainless steel bit. This obviated the need for remelting and pulverised the sample. The column of product consisted of three layers; an upper layer, usually of the highest purity (except in the case of p-nitrotoluene, phenanthrene and p-diethoxybenzene), an intermediate layer and a bottom layer, which was discarded. The purity of the two layers was then checked, thus obtaining the value of x_2, i.e. the molar fraction of impurities, and hence the "absolute" purity, which was needed for the evaluation of a "standard". In the case of substances of high purity, accurate results are only possible with this method if precautions are taken in the calculation [10]. These precautions are even more necessary for substances of extreme purity such as those purified by zone refining. The evaluation of purity was possible even in the case of ultrapure substances. The method will be described in a future communication.

Figure 2 shows the melting curves of the primary standards. The substances most difficult to purify were 2-chloroanthraquinone and carbazole. The former required 80 passes; with the latter, after the first passes, a considerable carbonization of impurities occurred, but after further passes the upper portion became white and a satisfactory degree of purity was achieved.

Calorimetric measurements

Several values of molar heat of fusion, not available in the literature, were obtained using the DSC technique. Experimental conditions were: sample size 2−4 mg; scanning speed 2°/min; chart speed 240 mm/min.

Sealed pans were used. The calorimetric curve was integrated with a planimeter and the area was calibrated in mcal/cm² using pure indium as calorimetric standard (6.80 mcal/g). For each standard several measurements of ΔH_f were conducted; the mean values are shown in Table 2.

The precision of calorimetric measurements was reduced by factors such as: a) insufficient purity of the sample [10], b) loss of sample through evaporation, c) baseline shift before and after melting, and d) irregularities in the melting peak. Factor a) was not important in this work, b) and c) were eliminated by the use of sealed pans, and d) must be eliminated by placing one or two aluminium discs inside the pan and repeating the test several times until a regular curve is obtained.

The molar heat of fusion of carbazole was recalculated as the value reported in the literature [16] was apparently wrong.

Temperature measurements

The melting temperatures of all the proposed standards were measured using the Perkin–Elmer DSC-1B differential calorimeter. The source of the standard materials is shown in Table 1. The experimental conditions and measuring technique were those described in the paper [7]. The temperature corrections (i.e. the difference between the theoretical temperatures, T_0, and those read) were plotted against the temperature; this provided the calibration curve shown in Figure 3. For a substance whose exact melting temperature was unknown, the proper correction was derived from the calibration curve and applied to the measured melting point, thereby obtaining the true melting point shown in Table 1.
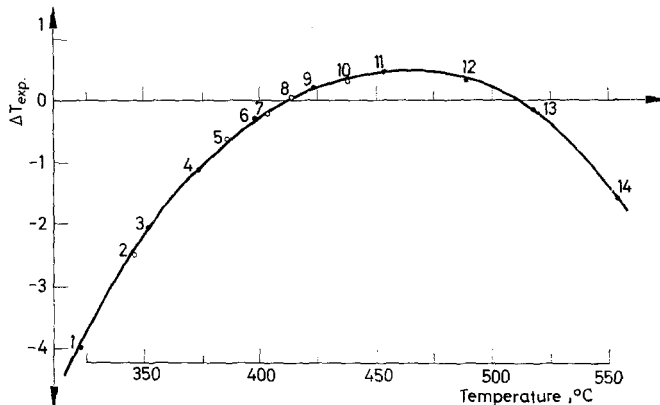

Fig. 3. Temperature corrections in the function of temperature. 1. p-Nitrotoluene; 2. p-Diethoxybenzene; 3. Naphthalene; 4. Phenanthrene; 5. Acetanilide; 6. Benzoic acid; 7. Phthalic anhydride; 8. Dimethyl terephthalate; 9. Diphenylacetic acid; 10. Benzanilide; 11. Anisic acid; 12. 2-Chloroanthraquinone; 13. Carbazole; 14. Anthraquinone

For phenanthrene and diphenylacetic acid the temperature determination was carried out according to a method described recently [6]. The melting temperature (T_m) of about 60 g of sample purified by zone refining was determined to 0.001° using a high-precision cryoscope; the degree of purity of the sample was then assessed by the DSC method [6]. From this degree of purity, the theoretical lowering $(T_0 - T_m)$ was calculated. Then T_m and the difference $(T_0 - T_m)$ were summed to give T_0, i.e. the melting point of the 100% pure compound. The data are shown in Table 4.

Table 4

Melting temperature determination on phenanthrene and diphenylacetic acid

Substances	Purity (mole %)	T_m (°C)	$T_0 - T_m$	T_0 (°C)
Phenanthrene	99.988	99.936	0.007	99.943
Diphenylacetic acid	99.913	147.049	0.045	147.094

Conclusions

On the basis of the theoretical relationship between melting temperature and molar fraction of impurities, a rational selection of substances to be used as temperature standards depends on the possibility of obtaining a very high degree of purity and measuring the degree of purity obtained.

The differential calorimetry, which does effectively scan and resolve the specific solid–liquid transition on which the function of the standard is based, is the best method for evaluating substances considered as suitable for temperature standards and also provides a rapid indication of their degree of purity.

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Résumé — Emploi d'un calorimètre différentiel pour sélectionner plusieurs substances organiques comme étalons thermométriques dans le domaine de température de 50 à 330°. Les conditions requises pour retenir une substance comme étalon ont été les suivantes: degré suffisant de pureté, stabilité thermique, absence de polymorphisme, constante cryoscopique convenable, faible volatilité et disponibilité rapide. Mention de la méthode de la zone fondue comme procédé de purification pour obtenir le degré minimal de pureté nécessaire (99.9 moles pour cent).

Zusammenfassung — Man benützte ein Differentialkalorimeter zur Einstellung und kritischen Auswertung einer Serie von organischen Substanzen, geeignet als thermometrische Standardstoffe im Temperaturbereich von 50 bis 330°. Die Bedingungen der Annahme als solche waren ein genügender Grad von Reinheit und thermischer Stabilität, Abwesenheit von Polymorphie, geeignete kryoskopische Konstanten, niedrige Flüchtigkeit und leichte Verfügbarkeit. Die Zonenreinigung erwies sich als geeignetes Verfahren, um den minimalen Grad der erforderlichen Reinheit von 99.9 Molprozenten zu erhalten.

Резюме — С целью подбора и критической оценки ряда органических веществ в качестве температурных стандартов в области температур 50—330° использован калориметр дифференцирующего типа. Требованиями к стандартным веществам являются их достаточная степень чистоты, термостабильность, отсутствие полиморфизма, пригодная криоскопическая константа, низкая летучесть и легкая доступность. Указано на рафинирование зоны как на метод очищения, с помощью которого можно получить самую низкую степень требуемой чистоты 99,9 мол%.