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APPLICATION OF DSC FOR THE DETERMINATION OF PURITY OF ORGANIC SEMICONDUCTORS

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DSC method was developed for the analysis of organic and inorganic substances. Beside the "common" method "short" method is applied. Comparison of these two methods for the determination of purity on standard samples like indium, benzil, caffeine showed good similarity of the results so it allowed to use a "short" method for the determination of the amount of impurity in semiconductors such as bis(ethylenedithio)tetrathiofulvalen and tetrathiotetracene. These compounds are unstable and begin to decompose some times during melting.

The development of the differential scanning microcalorimetry (DSC) [1–3] allowed to obtain a fast, sensitive and enough accurate variant of the crysoscopic method to determine the purity of organic and inorganic substances, working under dynamic heating conditions. In contrast to classic cryscopic methods DSC allows to determine the enthalpy and temperature of melting and the amount of impurity from one experiment in a short time (~ 30 min), heating at a rate less than 10 deg min^{-1}, using a small sample (1–10 mg).

The change of melting temperature indicating the presence of an impurity in the material, is expressed in the Van't-Hoff equation:

$$T_f = T_o - \frac{xRT_o^2}{\Delta H_f} \frac{1}{F}$$

x – mole fraction of impurity in the original sample,
T_o – melting temperature of the pure main component, in K,
ΔH_f – heat of fusion of the pure main component in $J \cdot mol^{-1}$,
F – fraction of sample melted at T_f,
R – gas constant, 8.314 J mol^{-1} deg.

The graph of the dependence of T_f on $1/F$ gives a straight line with a point of intersection of ordinate T_o and a slope $-xRT_o^2/\Delta H_f$. Linearization of experimental data was made with Sondack's method [4]. Figure 1 shows a typical DSC curve obtained at determining the purity of benzil. Value F is determined as the ratio of partial area from the beginning of the curve to the total area under the whole curve.

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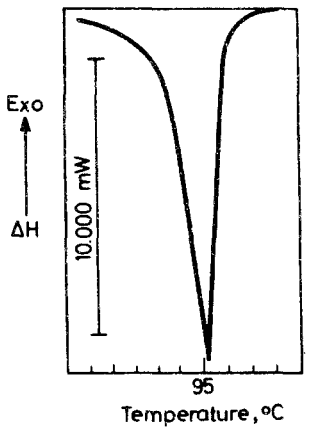

Fig. 1 DSC curve obtained at determining the purity of benzil (99.77 mol %) by the "common" method

The technique was developed by means of a DSC apparatus (Mettler TA–2000B–TA–3000) for various classes of compounds (see Table 1). Beside "common" we applied (according to the instruction) a "short" method for the determination of purity of organic semiconductors such as bis(ethylenedithio)tetrathiofulvalene (BEDTTF) and tetrathiotetracene (TTT). These compounds are unstable and begin to decompose some time after the melting starts. The following Equations (2) (3) are used to calculate the amount of impurity

$$X = \frac{M}{RT_0^2 m} \cdot \frac{T_3 - T_1}{\dfrac{1}{\Delta H_1 + K} \quad \dfrac{1}{\Delta H_3 + K}} \tag{2}$$

$$K = \frac{\Delta H_3 \dfrac{T_3 - T_2}{T_2 - T_1} - \Delta H_1 \dfrac{\Delta H_3 - \Delta H_2}{\Delta H_2 - \Delta H_1}}{\dfrac{\Delta H_3 - \Delta H_2}{\Delta H_2 - \Delta H_1} - \dfrac{T_3 - T_2}{T_2 - T_1}} \tag{3}$$

M – molecular mass of the main component,
m – sample mass in mg,
$\Delta H_{1,2,3}$ – partial heats of fusion at T_1, T_2, T_3 in $J \cdot mol^{-1}$,
K – correction for linearization in mJ.

Table 1 DSC purity analysis of various compound by the "common" and "short" method

Compound	Heating rate, deg·min^{-1}	ΔH_f, kJ·mol^{-1}	Purity, mol %	T_f, °C
Indium mol.v.114,82 "common" method	2	3.35 ±0.08(5)	99.99 ±0.01(5)	156.8±0.3(5)
Indium mol.v.114,82 "short" method	2		99.99 ±0.01(5)	156.6±0.1(5)
Benzil mol.v.210,22 "common" method	2	23.13 ±0.27(7)	99.77 ±0.11(7)	95.4±0.1(7)
Benzil mol.v.210,22 "short" method	2		99.75 ±0.05(5)	95.5 ±0.1(5)
Caffeine mol.v.194,15 "common" method	2	21.39 ±1.02(6)	99.98 ±0.01(6)	236.1±0.1(6)
Caffeine mol.v.194,15 "short" method	2		99.96 ±0.06(5)	236.1±0.1(5)
BEDTTF mol.v.384,59 "short" method	5		99.74 ±0.14(5)	244.6±0.5(5)
TTT mol.v.352,42 "short" method	5		99.98 ±0.01(6)	348.4±0.1(6)

It is clear from equation (2), (3) that it is not nesessary to know ΔH of total melting to determine the amount of impurity, i.e. it is possible to calculate the purity of a compound using the part of a curve from the beginning to the peak. The comparison of the two methods "common" and "short" for the determination of purity on standard samples like indium, benzil, caffeine coincided (see the table), so it allowed to use the "short" method and technique for the determination of the amount of impurity of semiconductors (Table, Fig. 2) [5–7].

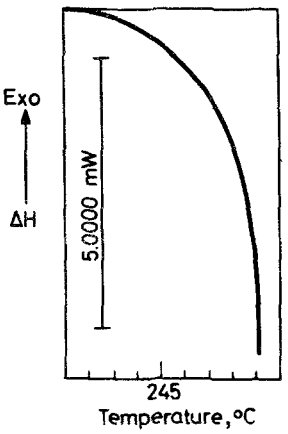

Fig. 2 DSC curve obtained at determining the purity of benzile (99.75 mole%) by the "short" method.

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Zusammenfassung – Für die Analyse von organischen und anorganischen Substanzen wurde ein DSC-Verfahren entwickelt. Neben dem "herkömmlichen" wurde auch ein "Kurzverfahren" angewendet. Der Vergleich der Ergebnisse der zwei Verfahren bei der Reinheitsbestimmung von Standardproben, wie z.B. Indium, Biphenyl und Koffein zeigte eine gute Übereinstimmung. Das Kurzverfahren kann somit gut zur Bestimmung des Verunreinigungsgrades von Halbleitern wie z.B. Bis-(äthylendithio)-tetrathiofulvalen und Tetrathiotetrazen genutzt werden. Diese Verbindungen zeigen nämlich während des Schmelzens mitunter Zersetzungserscheinungen.

РЕЗЮМЕ — Метод ДСК был разработан для анализа органических и неорганических веществ. Кроме "общего метода", был использован и "короткий" метод. Сопоставление этих двух методов для определения чистоты таких стандартных образцов, как индий, бифенил и коффеин, показал хорошее совпадение результатов, что позволило использовать "короткий" метод для количественного определения примесей в таких органических полупроводниках, как бис/этилендитио/тетратиофульвален и тетратиотетрацен. Эти соединения неустойчивы и в некоторой степени начинают разлагаться при плавлении.