

AN APPARATUS FOR DETERMINING THE PURITY OF ORGANIC COMPOUNDS

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An apparatus is described for determining with an accuracy of 10 per cent the total amount of impurities in small (0.05 cm^3) samples of organic compounds, containing more than 98 mole per cent of the main component. A simple method for calculating the degree of purity, applicable to Skau's method, is proposed. A correction for the heat of melting of eutectic mixtures formed by the main component with impurities is introduced.

The purpose of the present work was to construct an apparatus suitable for rapid, reliable and quantitative determination of the purity of organic compounds. In addition to the chemical nature and percentage of each individual impurity, the overall content, i.e. the degree of purity, plays a significant role in the evaluation of errors involved in measuring the physico-chemical properties of organic compounds and mixtures thereof. Only thermal methods, e.g. ebulliometry and cryometry, are suitable for measurement of the degree of purity [1].

Cryometry involves measuring the solid-liquid equilibrium temperature as a function of the fraction melted, F . The short measuring time, small-size sample, and easy automatability speak in favour of the method developed by Skau [2] and widely used by other workers [3–8], which was chosen for further investi-

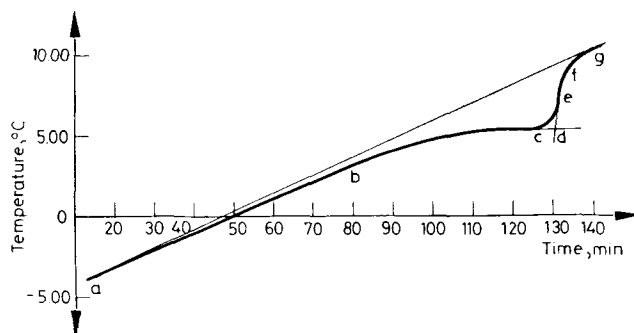


Fig. 1. A sample temperature–time plot recorded in the integral system for naphthalene-contaminated benzene

gations. This method is based on the fact that, under the conditions of a linear temperature-time relationship for the cryometric vessel, the measurement of sample temperature as a function of time is sufficient to determine the amount of heat exchanged in the system. A typical measurement is presented in Fig. 1. The area enclosed by the curve $a-b-c-d-e-f-g$ and the straight line $a-g$ is a linear function of the heat of fusion and thereby of the fraction melted. The apparatus described enables simultaneous determination by differential (Fig. 4) and integral (Fig. 1) methods.

Barrall and Diller [11] cite several guidelines for the differential method, involving the determination of at least six experimental points, small sample size, slow heating rate, encapsulation of sample with good thermal contact, precise determination of temperature, adjustment of heating rate and sample size, and accurate determination of thermal lag. All these conditions apply to the integral method as well, and are fulfilled in the apparatus.

Experimental

Apparatus

A block diagram of the proposed dynamic cryometer and cryometric vessel are presented in Figs 2 and 3, respectively. The vessel accommodates three nickel test-tubes, two of which contain the sample investigated, while the third contains a thermally passive substance (dummy) added in such an amount that, as regards heat capacity, this test-tube equals the two test-tubes holding the substance investigated. The temperature is measured with two 60% Au, 40% Pd-Pt thermocouples. One measures the temperature difference between the sample and the dummy

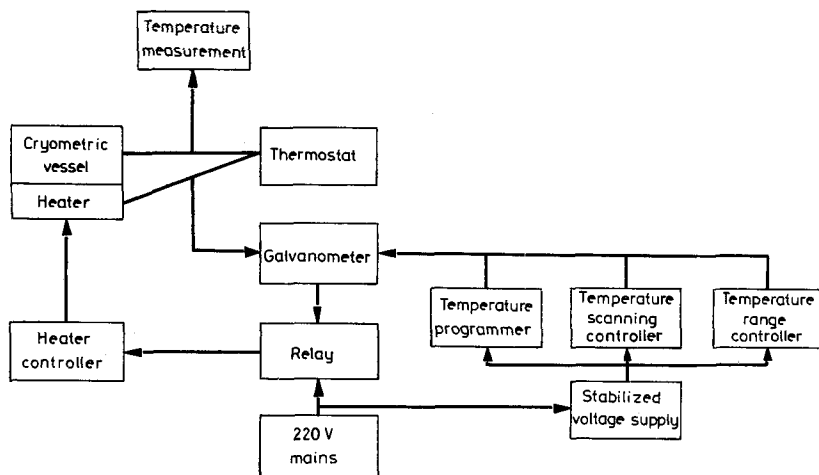


Fig. 2. A block diagram of the cryometer

(the differential system), and the other the temperature difference between the sample and a reference (e.g. water triple-point) kept outside the cryometer (the integral system). Measurements can be carried out simultaneously in the differential (Fig. 4) and in the integral system (Fig. 1). With a single sample test-tube only, errors would arise on account of thermal conduction through the thermocouple leads, which could be significant in view of the small weight of the sample, 0.05 g.

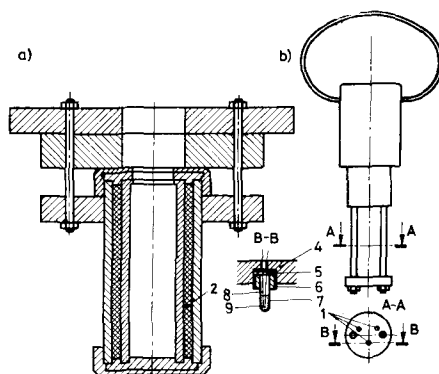


Fig. 3. The cryometer: (a) vessel, (b) test-tubes holder: 1. test-tubes, 2. heater with controlling thermocouple. B—B. The test-tube holder: 4. stainless steel plate, 5. polytetrafluoroethylene-neoprene membrane, e.g. Sovirel code 4—708, 6. stainless steel screw, 7. nickel test-tube, 8. thermocouple wires, 9. sample

The cryometric vessel is placed in a Dewar-type cold bath. According to the temperature range involved, liquid nitrogen, solid carbon dioxide, or ice is used as coolant. For substances melting above 60°C , no cooling agent is required. The apparatus is operable within the range 120 to 500°K .

The quantity of heat added to, and taken from, the system is controlled so as to ensure equal periods of heating and cooling. The measuring time is at most 2 hours; the available temperature scanning rates are: 0.1 , 0.2 and $0.4^{\circ}/\text{min}$. The measuring ranges are 12 , 24 and 48° , respectively.

A copper-constantan thermocouple, placed close to the heater to respond sensitively to thermal impulses, controls the temperature in the cryometric vessel. Its potential is compensated by a standard voltage from a built-in unit. A galvanometer and two photoresistors fixed on its scale follow the equilibrium. When the light spot due to the thermal e.m.f. falls on the photoresistor, a relay switches the heater on and when the spot disappears, the heater is switched off. The relay used is a logical type, which, with the use of two photoresistors, senses the direction of the spot's movement and eliminates errors due to overshooting of the photoresistors by the spot, or due to sticking to the galvanometer's buffer. The schematic diagram of the relay is presented in Fig. 5.

The standard voltage, and thus also the temperature of the cryometric vessel, is adjusted to within 2°C by means of a set of potentiometers. With an additional

slide potentiometer switched in, the compensating voltage and the cryometer temperature vary linearly. Deviations from linearity are below 0.1 microvolt, or 0.003°C .

Procedure

The substance investigated is fused and placed in test-tubes. The thermocouples are centered in the test-tubes and the samples are cooled till complete solidification; the test-tubes are then placed in the cryometric vessel. The standard voltage is adjusted so that it corresponds to a temperature somewhat lower than where the melting and the liquid-liquid equilibration proceeds entirely within the range

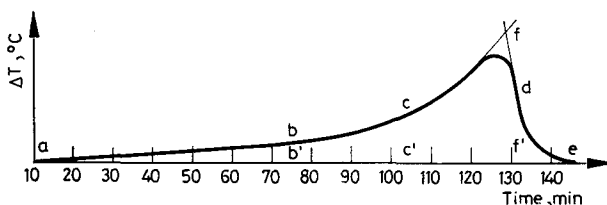


Fig. 4. A sample temperature-time plot recorded in the differential system for naphthalene-contaminated benzene

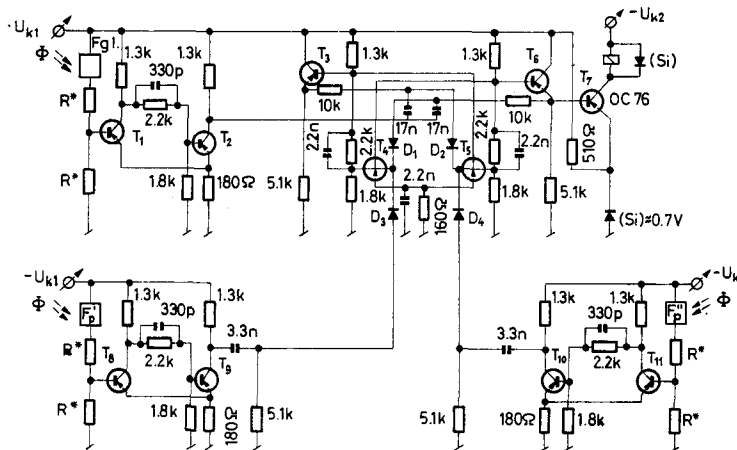


Fig. 5. Schematic picture of the electronic relay

of linearity of the temperature scanning. Once thermal equilibrium has set in, the scanning potentiometer is switched on and the thermocouple e.m.f. is measured as a function of time. For this purpose a five-decade voltage compensator is used. The data recorded are presented in Figs 1 and 4. The portion *a-b* represents

an almost linear increase in temperature during heating of the completely solidified sample. At point *b* fusion begins and the sample temperature rises slowly compared with the dummy temperature, which continues to increase linearly. When the sample becomes completely fused (Fig. 4, beneath point *f*), its temperature rises rapidly (Fig. 4, line *d-e*) owing to the equalization of the temperatures between the cryometric vessel and the fused sample until a linear increase is reestablished.

Since the liquid–solid transformation proceeds within a small temperature range (Fig. 1), it may be assumed that the total heat corresponding to the area *b-c-f-f'-c'-b'* (Fig. 4) has been adsorbed by the sample during this transformation, and that the total heat corresponding to the area *f-d-e-f'* has been used up for equalization of the temperatures of the cryometric vessel and the sample. Under the conditions of linear variation of the cryometric vessel temperature, the fraction melted may be expressed as:

$$F = \frac{bb'c'c}{bcff'c'b'} = \frac{\sum_{i=1}^k a_i}{\sum_{i=1}^n a_i} ; \tag{1}$$

for any *k* if $1 \leq k \leq n$

where: *a_i* are strips of graphical integration, the total area consisting of *n* strips.

The mole fraction of impurities (*x*) is a function of the melting point depression:

$$x = \frac{\Delta H_0}{RT_0^2} (T_0 - T_m) ; \tag{2}$$

- where: ΔH is the molar heat of fusion of the solvent,
- R* is the universal gas constant,
- T₀* is the m.p. of the pure solvent,
- T_m* is the solid–liquid equilibrium temperature.

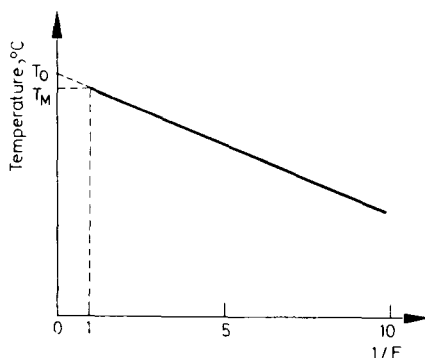


Fig. 6. Reciprocal of the fraction melted vs. temperature

To find the melting point depression ($T_0 - T_m$) it is sufficient to plot the phase equilibrium temperature against the reciprocal of the fraction melted. An illustrative plot is presented in Fig. 6. According to Eq. (2), this is a straight line with a slope equal to the m.p. depression. Deviations from linearity are usually explained in terms of solid solution formation [1]. However, the following reasons of non-linearity are also important. One minor reason arises from the nature of the heat transfer between the sample and the cryometric vessel, i.e. it is due to non-allowance for heating of the test-tube and its contents and also to thermal losses through the thermocouple leads. A suitable correction straightens the upper part of the T vs. $1/F$ plot significantly.

Mention must be made of a correction in Eq. (1) for the Z -area corresponding to the small area missed in integration at low temperatures, viz.:

$$F = \frac{Z + \sum_{i=1}^k a_i}{Z + \sum_{i=1}^n a_i}; \quad (3)$$

The Z -correction may be evaluated either graphically by the trial-and-error procedure or analytically by minimizing the value of Eq. (4), as the non-linear function of the reciprocal of the fraction melted, with a subsequent non-linear least-squares procedure.

$$T_0 - (T_0 - T_m) \frac{1}{F} = 0; \quad (4)$$

The use of the correction permits the use of this method with samples much more contaminated than those suitable for the constant-heat-exchange method, e.g. that of Rossini [9], in which no correction can be allowed for.

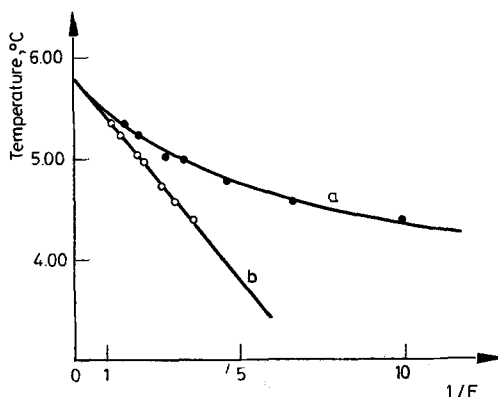


Fig. 7. Reciprocal of the fraction melted vs. temperature for naphthalene-contaminated benzene: (a) uncorrected, (b) corrected for the heat of fusion of the eutectic

The method is illustrated (Fig. 7) by the determination of benzene purity. A 99.98 mole per cent pure benzene was first analyzed by Świątosławski's dilatometric method [10] and then 0.67 mole per cent of naphthalene was added to it. The benzene was reanalyzed by the present method, and 0.61 mole per cent of naphthalene was found, which means that the relative error of the method is 10 per cent. Similar errors were obtained with other hydrocarbons.

The apparatus enables accurate measurements of the activity coefficients in dilute solutions. The pure solvent and the solution are placed in the test-tubes, and the temperature differences between the samples and the dummy are recorded simultaneously. The freezing point depression is calculated from the difference between the times corresponding to the peaks. In a similar way comparative determinations of purity [1] can be made.

Summing up, it is evident from the above data that the present method yields accurate values, and requires short measuring times, and small samples.

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RÉSUMÉ — On décrit un appareil pour déterminer le taux total d'impuretés, avec une précision de 10 *p. cent*, dans de petits échantillons (0.05 cm³) de composés organiques contenant plus de 98 moles *p. cent* du constituant principal. On propose une méthode simple pour calculer le degré de pureté en appliquant la méthode de Skau. On introduit une correction pour la chaleur de fusion des mélanges eutectiques formés par le constituant majeur avec les impuretés.

ZUSAMMENFASSUNG — Eine Vorrichtung zur Bestimmung von Verunreinigungen mit einer Genauigkeit von 10%, bezogen auf die Gesamtmenge kleiner Proben (0.05 cm³) organischer Verbindungen, welche mehr als 98 Mol % der Hauptkomponente enthalten, wird beschrieben. Eine einfache Methode der Berechnung des Reinheitsgrades, welche bei der Skau-Methode anzuwenden ist, wird beschrieben. Eine Korrektur für die Schmelzwärme der von der Hauptkomponente mit den Verunreinigungen gebildeten eutektischen Mischungen wird eingeführt.

Резюме — Описан прибор для определения общего количества примесей в небольших (0,05 см³) образцах органических соединений, содержащих более чем 98 мол.% главного компонента, с точностью 10%. Предложен простой метод расчета степени чистоты. Введена поправка для теплоты плавления эвтектических смесей, образованных главным компонентом и примесями.