Improvement of Zone-melting Apparatus: A New Apparatus with a High-precision Heater-temperature-controlling Mechanism

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A new zone-melting apparatus with a high-precision heater-temperature-controlling mechanism has been designed and constructed. The apparatus can control the width of several melting zones at an equal temperature and thus can obtain smooth concentration profiles after zone refining. The effect of zone refining with this apparatus was examined with fair success, using phenanthrene and naphthalene as samples.

The zone-melting technique has been recognized as a useful method for purifying organic compounds, and many apparatuses for this purpose have been manufactured. Most of the automatic zone-melting apparatus have several heaters to refine the samples efficiently.[1] However, when the heater temperatures are not precisely controlled, the difference between them causes differences in the widths of the molten zones[2] and, consequently, a difference in the impurity transfer, which results in an inefficient refining. Thus, impurity concentration profiles after zone-refining experiments have bumps and are not smooth. To avoid this disadvantage, the heater temperatures must be controlled so as to have equal values in all operating zones. On the other hand, other causes of differences in the widths of molten zones over a long period of experiment, such as changes in the electric power added to the heaters, the ambient temperature, *etc.*, must also be borne in mind.

In this paper, the design and construction of a new zone-melting apparatus which has precisely controlled heaters, as well as a few results obtained by using it, will be reported.

Experimental

Heaters and their temperature controls: A unit of the heater consists of nichrome wire and the other elements shown in Fig. 1. The nichrome wire (NTK No. 3, 0.23ϕ, 110 cm length, Ishikawa Co., Tokyo) is wound around two Turner rings (22 mm o.d., 12 mm i.d. and 2 mm in thickness), and a sheet of mica is put between these two Turner rings as an electric shield. This part of heater is wound around with a glass wool ribbon and set inside two Turner lids. A chromel alumel thermocouple is inserted through a groove of the Turner lids into the inside so as to touch the glass wool ribbon. The temperature of the heaters thus constructed rise to *ca.* 440 °C if an electric voltage of 50 V is supplied.

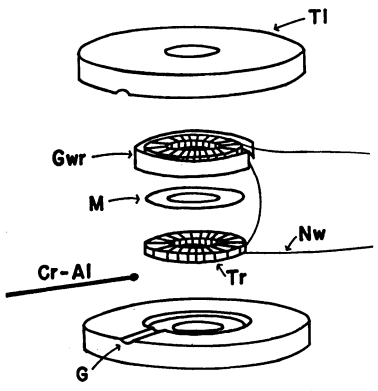

Fig. 1. Composition of a heater.
Tl: Turner lid. Gwr: Glass wool ribbon. Tr: Turner ring. M: Mica sheet. Nw: Nichrome wire. Cr-Al: Cr-Al thermocouple. G: Groove for a thermocouple.

Eighteen heaters are used in this zone-melting apparatus and are connected parallel. They are precisely controlled using eighteen thermocouples and three sets of an automatic temperature controller Model E-500 (Chino Works, Ltd., Tokyo) and a multicontroller Model P-885-6 (Chino Works, Ltd., Tokyo). The temperature of the automatic temperature controller is set 1—2 °C higher than the melting point of the sample. The heater temperature is measured for 12 s every 72 s; the electric voltage applied to the heaters is maintained until the next measurement time by means of a relay circuit memory system included in the multicontroller. When the heater temperature is lower than the setting temperature, the setting voltage which is preliminarily chosen is applied to the heater. On the other hand, when it is higher than the setting temperature, 80% of the setting voltage is applied. With this mechanism, the heater temperature is maintained constant and does decrease rapidly to temperature lower than the setting temperature, particularly for the samples with high melting points. By this mechanism the heater temperature is maintained within 100 ± 3 °C when it is set at 100 °C. This precision is mainly a result of the precision of the automatic temperature controller, Model E-500.

Apparatus: An apparatus with a device to prevent the breakage of the sample tube was previously constructed by the present author and his coworkers.[3] The new apparatus reported here is improved in several points: 1) No buffer is used to prevent the breakage of the sample tube. Instead, a vacant space which is considerably large in the sample tube and which is filled with an inert gas, is regarded as a buffer for the expansion of the sample at melting. 2) The sample tube moves twice the distance of two neighboring heaters to smooth out the difference in the performances of the two neighboring heaters which is caused by a slight difference in the structures of the heaters. 3) The sample tube rotates and the direction of rotation reverses periodically in order to stir the liquid zones vigorously.[4] 4) The sample tube moves in a slant-wise manner so as to prevent the formation of voids in the sample during the purification.[5]

A diagram of the apparatus is shown in Fig. 2. A Pyrex tube (10 mm o.d., 110 cm length) is used as a sample tube (St). 10—50 g of a sample is compactly packed into the tube, and then the tube is sealed with 1/2 atm of an inert gas. The sample tube is set so that the end filled with the sample is supported by a clamp (Cl) and the other end, filled with the inert gas, is supported by a support (S). Eighteen precisely controlled heaters (H1, H2,···, H18) and nineteen coolers (C) are alternately arranged; the distance between neighboring heaters is 5 cm. The part shown by a heavy line in

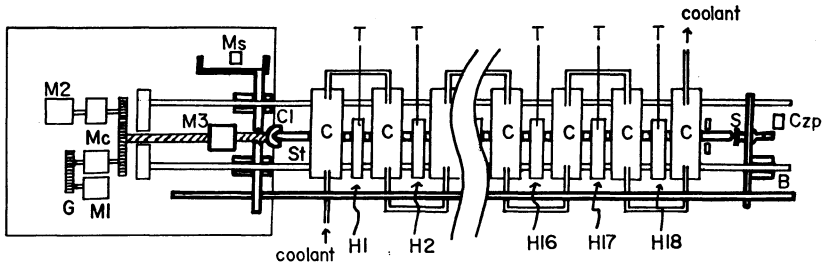

Fig. 2. Diagram of zone melting apparatus.
St: Sample tube. H: Heater. C: Cooler. T: Thermocouple. Cl: Clamp. S: Support. B: Ball bearing. Mc: Magnetic clutch. M1, M2: Motor. M3: Reversible motor. G: Gear. Ms: Microswitch. Czp: Counter for zone passes.

the figure is moved slowly 10 cm to the left by a motor (M1) and then rapidly returned to the initial position by another motor (M2). This alternating movement of the sample tube is controlled automatically by means of a microswitch (MS) and a pusher mechanism. The velocity of moving the tube to the left, which determines the solidifying velocity of the sample, can be selected by changing gears (G) at 150, 75, 50, 37.5, 30, or 18.8 mm/h. The time required for returning to the initial position is several seconds. Starting from H1 and H2, two heaters are switched on in the order of the number of heater every time the reciprocating movement stops. After all heaters are switched on, the sample tube continues the reciprocating movements for the needed time. Then two heaters are turned off in the order of the heater number every time the reciprocating movement stops until all the heaters are turned off. This mechanism of turning off the heaters makes the number of zone passes equal at every point of a refined sample. To stir the melted part of a sample, the sample tube is rotated around the axis of the tube by means of a reversible motor (M3, 100 r.p.m.), and the direction of the rotation is periodically reversed every 1, 1/2, or 1/3 s.

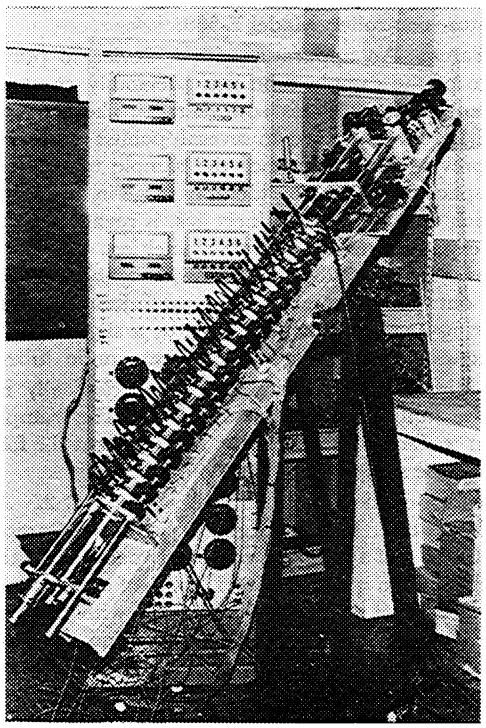

Fig. 3. Zone melting apparatus.

Figure 3 shows the temperature-controlled zone-refining apparatus in the front part and the controlling part in the rear part. The apparatus operates in a slant posture so as to make the vacant space of the sample tube higher than the sample. The slanting angle is continuously changed.

Results and Discussion

The zone-refining performance of the new apparatus was examined with two samples, naphthalene and phenanthrene. In both experiments the solidifying

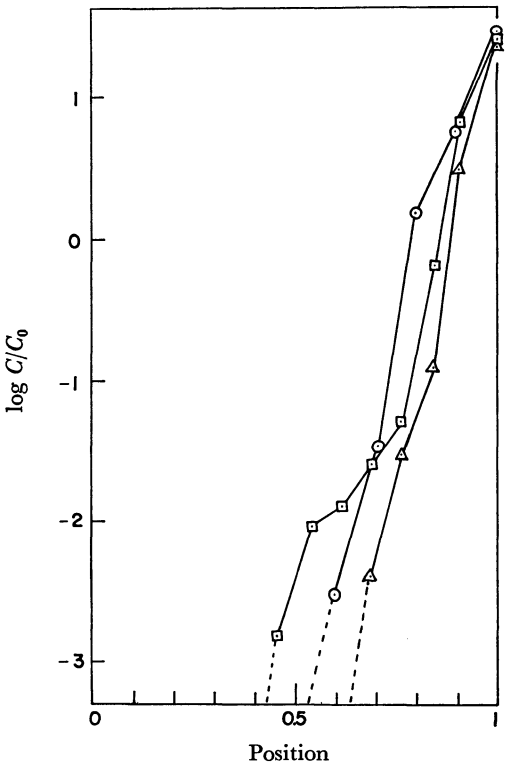

Fig. 4. Concentration (C) of 2-methylnaphthalene in the naphthalene sample after the zone refining. As for the abscissa the total sample length was regarded as 1.0 and each sample position was measured from the vacant space side. Initial concentration (C_0) was 1%. Detectable limit was 5 ppm.
—○—: 9 zone passes with the apparatus reported here.
—△—: 20 zone passes with the apparatus reported here.
—□—: 60 zone passes (33 mm/h solidifying speed) with the apparatus reported previously.[3)]

velocity was kept at 50 mm/h, the slanting angle to a vertical line, at 50°, and the reversing cycle of the rotation, at 2 cycle/s.

2-Methylnaphthalene was doped in naphthalene (Kokusan Chemical Works Ltd., Tokyo) as an impurity so that the concentration of the impurity was 1%. The quantity of 2-methylnaphthalene in the refined sample was examined by means of a gas chromatograph equipped with F.I.D. A sample solution for the gas chromatograph was prepared using 200 mg of the refined samples taken every 5 cm starting from the vacant space side. As is shown in Fig. 4, the 2-methylnaphthalene in the naphthalene sample moves in the same direction as the movement of the melting zone. After only 9 zone passes, the concentration of the impurity decreases to less than 5 ppm in the first 40% of the naphthalene sample, starting from the vacant space in the sample tube, and then increases smoothly for the next 60% of the sample. Figure 4 also shows that naphthalene is more effectively refined with the new apparatus than with the apparatus previously reported.[3]

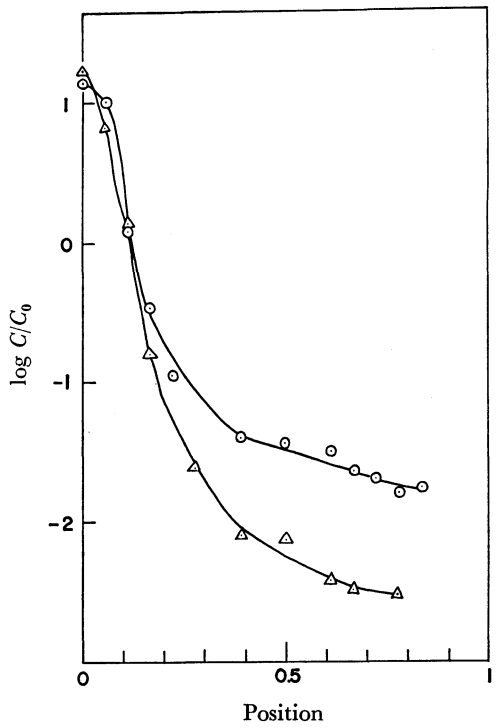

Fig. 5. Concentration (C) of anthracene in the phenanthrene sample after the zone refining. The abscissa is the same as explained in Fig. 4. Initial concentration (C_0) was 1%.
—○—: 304 zone passes, —△—: 774 zone passes.

The phenanthrene sample (Tokyo Kasei Kogyo Co., Ltd., Tokyo) includes 1% anthracene as a major impurity. The concentration of anthracene in the zone-refined sample is examined by means of the absorptivity of a 379 nm band of anthracene in a benzene solution. In this case, 100—250 mg of the refined sample, cut in the same way as the naphthalene sample, is used to make the benzene solution. Figure 5 shows the results after 304 and 774 zone passes. In this case, the impurity moves in the direction opposite to the movement of the melting zone. Both results show that phenanthrene samples are effectively refined and that anthracene as the impurity is smoothly distributed. In the 0.8—1 range in the figure, the phenanthrene samples are colored by other impurities.

The equal widths of the melting zones resulting from the equal temperatures realized by the high-precision controlling mechanism of the heater temperatures and the reverse rotation of a sample tube make the efficient refining possible. With this new apparatus, organic materials with high melting points can be refined effectively without the breakage of the sample tube.

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