

## A FAST METHOD OF ZONE MELTING AS AN AID IN ANALYTICAL CHEMISTRY

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Zone melting could be a powerful aid in analytical chemistry; it provides a means of preparing primary standards and of concentrating contaminants. Moreover, the (substance) distribution along a zone-melted column may give information concerning the components of the system dealt with. Zone melting operates without foreign chemicals or solvents, and it requires no unacceptable amounts of substance, no special skill and only a small amount of personal attendance.

In spite of these advantages zone melting has found only restricted application in analytical chemistry. There seems to be a tendency to prefer other methods to zone melting, unless other methods appear hopeless. This attitude is largely caused by the fact that zone melting of organic substances at zone travel rates down to 3 cm/h appeared to be almost completely ineffective. Even at somewhat lower zone travel rates, bad separations resulted and the relation between the actual and the theoretical distribution coefficient was severely obscured. As a consequence, effective zone melting of organic substances was an extremely time-consuming process, which was therefore already unattractive for analytical purposes. Moreover, many organic substances do not withstand very prolonged heating.

The causes of these drawbacks are relatively simple. During the liquid–solid transition some impurity must in most cases be expelled from the freezing part of the substance, and this amount will initially collect at the solid–liquid interface, before becoming dispersed throughout the bulk of the remaining liquid phase by means of diffusion and convection. If the speed of zoning is too high, the solid rejects

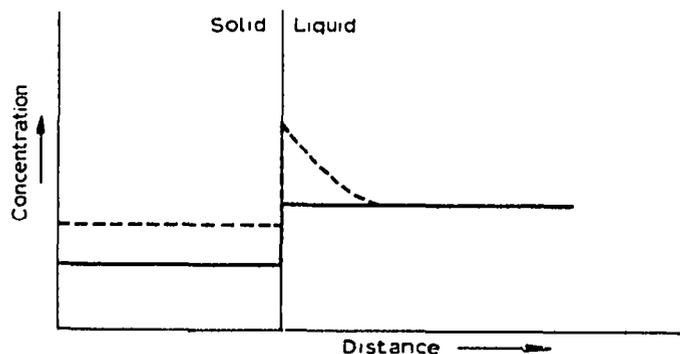


Fig. 1. Distribution of impurity near solid–liquid interface. (—) complete mixing; (--) restricted mixing.

impurities more rapidly than these can diffuse into the bulk of the liquid. Now the composition of the solid is determined by the composition of the liquid in the *boundary* layer. As soon as the concentration of the impurity in the boundary layer is higher than that in the bulk of the liquid, the amount of impurity contained in the solid to be formed will increase (see Fig. 1). As proven by experiments this increase may soon become so large that no purification is obtained at all. Thus the efficiency of a zone-melting operation depends on the effectiveness of mass transfer from the solid-liquid interface into the bulk of the zone.

The various mechanisms thus far devised for promoting this mass transfer appear to have had little effect on the stagnant boundary layer.

#### A FAST METHOD OF ZONE MELTING

In the Institute for Physical Chemistry TNO, an apparatus has been developed which is especially intended to reduce the effect of the stationary layer. The substance to be treated is contained in a tube and this tube is subjected to a high-speed rotation which is periodically reversed. In this way periodically shifting shearing forces are exerted at the boundary layer, resulting in an intensive mixing of the liquid by turbulence.

Another feature of this apparatus is the direction of zone travel. Zone-melting apparatus with vertical containers, usually operate with zones moving downwards. This direction of movement has several advantages; in the first place, zones are created at the open end of the container, so that the expansion of the melting substance does not lead to cracking of the tube. Secondly, the freezing occurs at the upper interface of the zone. At this upper interface the thickness of the stationary boundary layer is supposed to be somewhat reduced by thermal convection. Finally, recontamination of purified material due to seeping back of liquid is impossible when the zones move downwards. However, the downward movement of zones also includes a serious drawback. It is hardly possible to prevent the occurrence of voids or gas bubbles near the upper interface of the zone. When crystallization occurs at the upper interface, the voids or gas bubbles cause irregular crystallization which hampers the purification. Large voids or bubbles may even stop the purification by blocking the tube.

Because of the seriousness of this drawback, an attempt was made to design an apparatus with zones moving upwards. Zones moving from the bottom to the top guarantee a good contact of liquid and solid at the freezing interface. It was realized that the thermal convection at the freezing interface had to be sacrificed, but this loss could be more than compensated by the method of stirring applied. The good contact between solid and liquid combined with the fast flow of liquid along the interface satisfies the essential conditions for obtaining a smooth interface which favors the purification. Of course, the upward zone movement necessitates special precautions for preventing the breakage of containers during the formation of the zone; therefore, the lower side of the tube is closed by a PTFE stopper inserted into the tube. This stopper has a fixed position with respect to the apparatus. The expansion of the substance during the formation of a zone results in a temporary movement of the tube and its contents in an upward direction.

In the apparatus to be described no extremely careful control of factors such as ambient temperature, heater power and heater travel rate is necessary. Since the

zone travel rates are of the order of 60 cm/h a temporary increase in the crystallization speed, *e.g.* by 1 cm/h will not lead to entrapment of impurities. A special arrangement for preventing the breakage of containers due to a small increase in the amount of melted substance in a zone is described below.

In order to meet the different and somewhat contradictory demands of analytical chemists, it was deemed necessary to design 2 different apparatus: one to deal with 50–100 ml amounts of substance and another for quantities of about 4 ml. The 4-ml, or midget, apparatus is intended for the separation of multicomponent mixtures before analysis. Its dimensions were chosen so that the fractions obtained after the separation are large enough for further analysis, *e.g.* by means of the melting-curve method<sup>1</sup>.

The 100-ml apparatus is primarily intended for preparative purposes (*e.g.* the preparation of high-purity standard substances), and possibly for the preconcentration of minor amounts of impurities contained in a large sample. Further concentration may then be done in the midget apparatus. Both apparatus are intended for substances with melting points between 50 and 250°; it is possible to extend this temperature range, especially to lower temperatures. Whereas both apparatus operate on the same principle only the midget apparatus will be described.

## EXPERIMENTAL

### *Description of the apparatus*

A schematic diagram of the apparatus is shown in Fig. 2 and a photograph in Fig. 3. The container is a pyrex glass tube (4) placed vertically and closed at its lower end by a PTFE stopper (10) inserted to about 6 cm into the tube. This container is filled to a height of about 20 cm. The shaft (1) of a reversible electric motor protrudes into the lower end of the tube; the PTFE stopper rests on this shaft. The tube is connected to the shaft by a coupling device (2), permitting a simultaneous upward movement of the coupling device and the rotating tube. Thus the force on the stopper, due to expansion of the substance on melting, results in a small upward displacement of the tube. The maximum speed of rotation of the tube is 125 rev./sec and the direction of rotation is reversed twice per second. The time required for the reversal from 125 rev./sec in one direction to 125 rev./sec in the other direction is about 0.25 sec (see Fig. 4).

Five resistance heaters (5, 6, 7, 8 and 9) are placed around the tube at 4-cm intervals. Between the heaters the tube is cooled by compressed air streaming via a duct (3) through sets of small orifices, further indicated as coolers. Heaters and coolers gradually move 4 cm upwards and then fall rapidly, thus transferring each heater to the next zone; the lower heater starts forming a new zone. This reciprocating motion is repeated. The power of the 4 upper heaters (5, 6, 7 and 8) is somewhat less than that of the lower heater (9). Thus the amount of melted substance in a zone formed by the lower heater decreases when the zone is taken over by the next heater; this results in the formation of a void at the upper interface. This void does not hamper the separation but acts as a buffer capable of accounting for small changes in zone length due to changes in heat transfer or heater travel rate.

Each formation of a zone leads to a small upward displacement of the tube with respect to the stopper. As will be obvious this sets a limit to the total number

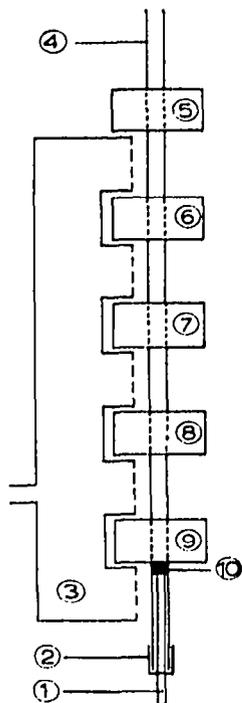


Fig. 2. F.C.I. zone-melting apparatus. Patents pending.

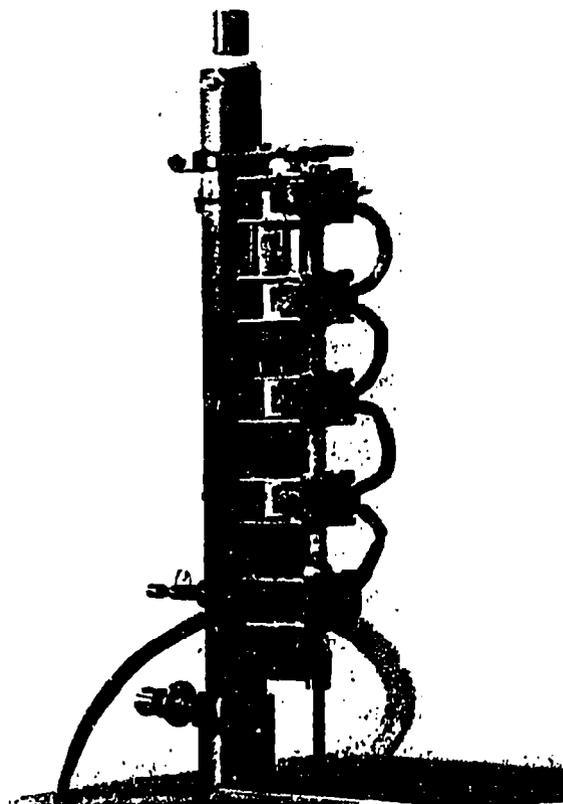


Fig. 3. Photograph of midget apparatus for zone melting (upper part).

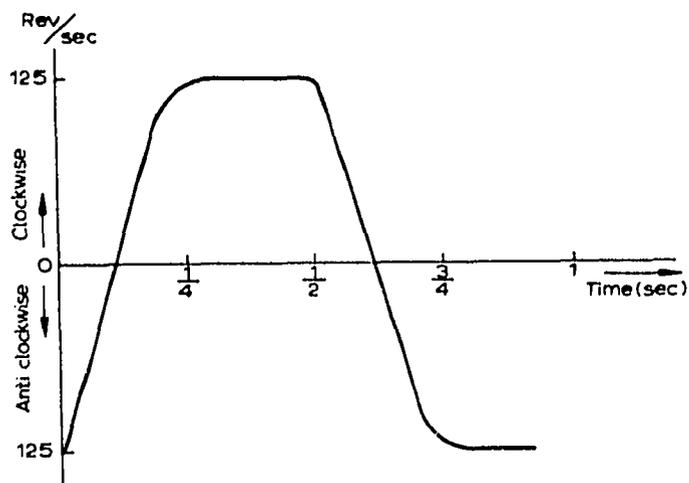


Fig. 4. Speed and direction of rotation of the container as a function of time.

of zones that can pass through the tube. The maximal number of zones is determined by the length of the tube under the stopper, the zone length and the percentage of volume increase on melting. As the zone length is about 1/10 of the length of the charge the maximal number of passes amounts to about 30 in most cases.

The efficiency of a zone refiner can be increased if the zone-melting operation is preceded by normal freezing. Therefore an automatic device enabling the contents of the zone-melting tube to freeze from the lower end is incorporated in the apparatus. The zone-melting operation starts immediately after normal freezing; the first zone follows 4 cm behind the freezing interface.

#### *Applications*

The following examples demonstrate the rapid and good operation of the apparatus.

(1) The system bismuth-antimony forms solid solutions. The theoretical distribution coefficient as determined from the phase diagram amounts to 2.1. A mixture of bismuth and antimony was submitted to normal freezing. The container was rotated as described above. The speed of crystallization was 80 cm/h. The effective distribution coefficient derived from the results appeared to be 1.9.

(2) The system naphthalene-sudan red is a simple eutectic system; 5 g of naphthalene containing 0.01 % of the dye was treated in the midget apparatus. The zone travel rate was 80 cm/h. It took 15 min to remove the dye completely from 80 % of the sample.

(3) The system biphenyl-phenanthrene forms solid solutions. The theoretical distribution coefficient is 0.27. Biphenyl containing 1 mol% phenanthrene was submitted to normal freezing followed by zone melting. The rate of zone travel was 60 cm/h. The distribution coefficient after the treatment was determined from melting curves. The effective distribution coefficient derived from these results appeared to be 0.30!

#### DISCUSSION AND CONCLUSIONS

On the strength of the results obtained with the system naphthalene-sudan red, it may be concluded that even at zone travel rates of 60-80 cm/h the entrapment of impurities is prevented and the effect of seeping back which is inherent in zones moving upward is compensated to such an extent that this effect becomes almost negligible.

The small differences between the effective and theoretical distribution coefficients found in the two examples of mixed crystals show clearly that the mass transfer in the boundary layer, which is essential for obtaining good separations, has been improved to a large and satisfactory extent. The time required for a normal freezing operation followed by the passage of 20 zones has been reduced from several days to about 1.5 h for a charge of 4 ml of *organic* substance and from weeks to about 6 h for a charge of 100 ml in the 100-ml apparatus.

Cracking of containers due to changes in heat transfer is completely overcome.

#### SUMMARY

A new zone-melting apparatus is described which allows relatively high zone

speeds up to 100 cm/h. The time required for effective separations is only a few hours so that the apparatus can be used for analytical purposes. The difference between the theoretical and actual distribution coefficients obtained is small; the distribution coefficients of unknown substances in mixtures can thus be derived from the result of zone melting, which offers a means of identification. The apparatus is fully automated and normal freezing is incorporated as a first step. A means of preventing the breakage of the glass tube containers is described. The principles of operation and possible applications are discussed.

#### REFERENCE

- 1 H. F. VAN WIJK, P. J. VAN DER MOST AND W. M. SMIT, *Anal. Chim. Acta*, 38 (1967) 285.  
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