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Improvement of Zone Melting Apparatus. I. Zone Melting Apparatus with a Device to Prevent Breakage of a Sample Tube

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A glass sample tube is widely used in zone melting of organic substances since it is transparent, inert to most substances and easily prepared in the laboratory. The glass tube, however, is frequently broken owing to the volume increase of the sample. A new device was worked out to prevent breakage of the sample tube, to purify the sample efficiently and to make replacement of the atmosphere inside the sample tube possible. The apparatus requires much less space than for one ever reported and consists of a sample tube with a set of stainless steel spring and Teflon plug and a new mechanism for carrying it. It was successfully used for biphenyl and *p*-dichlorobenzene.

Zone melting with a sample container is sometimes useful in preparing very pure materials which have high vapor pressure and low surface tension. A glass tube is usually used as a sample container because of its transparency, inertness to most substances and applicability up to 500 °C. However, it undergoes frequent breakage due to volume increase of the sample during zone melting. This paper deals with a new zone melting apparatus which prevents breakage and operates safely and reliably.

The following two methods have been reported to prevent breakage of the sample tube. (a) A glass plug is inserted into the open end of a Teflon sample tube, or a Teflon stick is used as a plug of a glass sample tube for absorbing the volume change of the sample.[1,2] (b) A spring and a tapered glass are put at the bottom of the sample tube for the same purpose.[3]

In order to obtain ultra-pure organic compounds by the zone melting method, gases which react with molten organic compounds and produce some impurities must be removed. Thus for the preparation of the ultra-pure sample for phosphorescence and fluorescence

1) M. J. Joncich and D. R. Bailey, *Anal. Chem.*, **32**, 1578 (1960).
2) N. J. G. Bollen, M. J. van Essen, and W. M. Smit, *Anal. Chim. Acta*, **38**, 279 (1967).
3) F. Ordway, *Anal. Chem.*, **37**, 1178 (1965).

measurement, the atmosphere of the sample tube should be kept under vacuum or replaced by an inert gas. When compounds such as alkali halides, which decompose at melting in the air are to be purified, the atmosphere should be replaced by gases such as halogens.

Thus attention should be focused on replacement of atmosphere as well as protection from breakage of the sample tube. Method (a) is insufficient for replacing atmosphere because of lack in air-tightness.

In our method we used a sealed glass sample tube containing a Teflon plug and a stainless steel spring as a buffer for volume change of sample as shown in Fig. 1 (a), (b). A Teflon plug is more easily made than a glass bar. It is inert to organic compounds and has low thermal conductivity, but is not suitable for use at temperature above 250 °C. When this sample tube is used, each molten zone should be formed first at a point adjacent to the Teflon plug with the heater H 1 in order that the volume increase caused by melting is absorbed by the spring.

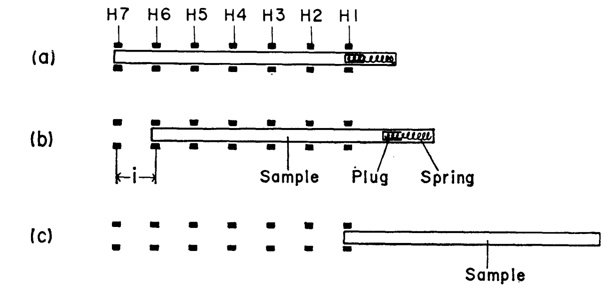

Fig. 1. Reciprocal motion in zone melting. In our mechanism a sample tube reciprocates the distance *i* between the position (a) and (b). With Sloans' mechanism, at first a sample tube starts from the position (c).

Sloan and McGowan[4] reported a method preventing breakage of the sample tube without the use of a spring and a plug. All the heaters are kept on during the operation in their case. At first a sample tube is located out of the row of the heaters as shown in Fig. 1(c). It slowly moves through the row of the heaters till the left end of the sample tube comes across the left end heater. Then the sample tube reciprocates the distance between the two neighbouring heaters.

We have devised a new mechanism of carriage which requires half the space used by Sloan and McGowan for movement of the sample tube. It operates automatically from beginning to end. First the tube is located at position (a) in Fig. 1. While the heater H 1 is on, it travels one interval *i* slowly to position (b). The volume increase of molten zone pushes the plug in order to be absorbed by the spring. The tube then returns to the initial position (a) in a few seconds. The zone molten by H 1 is now located at the position H 2. At this moment the heater H 2 is switched on and the sample tube moves from position (a) to (b) again slowly. The heater H 1 makes a new molten zone again. The volume increase of a newly molten zone is also absorbed by the spring. Thus at each return the heaters are switched on one by one, H 1, H 2, H 3, ······ starting from the bottom of the sample tube. After all the heaters are switched on, they are maintained until the end of the zone melting operation.

Even if any buffer is placed at one end of the sample tube, it cannot absorb the volume increase in the middle of the tube when all the heaters are switched on at once. Thus when many heaters are used to improve the efficiency of zone melting, mere insertion of a plug and a spring is unsatisfactory for preventing breakage perfectly. Our new mechanism of carrying the sample tube and switching on the heaters makes the spring absorb every volume increase of a molten zone, thus preventing breakge of the sample tube perfectly, purifying the sample efficiently and requiring much less space than that previously reported. In addition the replacement of atmosphere is accomplished.

4) G. J. Sloan and N. H. McGowan, *Rev. Sci. Instr.*, **34**, 60 (1963).

Description of Apparatus

A diagram of the sample tube is given in Fig. 1 (a), (b). Tubes with 10 or 25 mm in outer diameter and 1200 mm in length were used. The apparatus is shown in Fig. 2. The sample tube driven by a motor M 1 travels horizontally one interval *i* (50 mm) for 2/3, 1, 2 or 4 hours and returns rapidly by another motor M 2 through the row of sixteen heaters H and seventeen coolers C. The rate of the tube is changeable by the combination of the gears G 1,2. Water flows through the coolers. The heaters are made of nichrome wire. Switching on the heaters and movement of the tube are controlled by a microswitch Ms. The tube supported by a roller R rotates by a motor M 3 (44 r.p.m.) to make the concentration of liquid zone uniform.

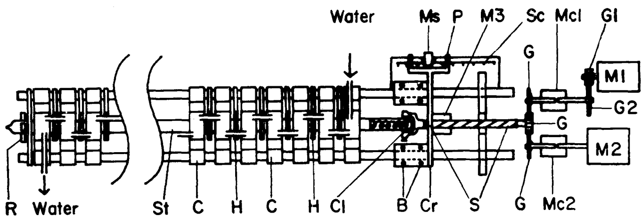

Fig. 2. The figure of zone meting apparatus.
B: Ball-bearing, C: Cooler, Cl: Clamp to connect St and M3, Cr: Carriage of M3, Cl and P, G, Gl, 2: Gear, H: Heater, Ml, 2: Synchronous motor to move Cr, M3: Motor to rotate St, Mc: Magnetic clutch, Ms: Microswitch, P: Piece to push microswitch Ms, R: Roller to support St, S: Male and female screw, Sc: Scale, St: Sample tube.

Results and Discussion

Most organic compounds expand when they melt. The apparatus was tested with biphenyl (volume change 12%, mp 71 °C) and *p*-dichlorobenzene (22%, 53 °C) in nitrogen atmosphere. In the case of biphenyl the sample near the plug was colorless and transparent crystals with cracks. Far from the plug yellowish crystals rich in impurities were observed. When biphenyl was zone refined using a 25 mm O. D. sample tube, the movement of the plug was observed. The result was as follows: The number of zone passes 3- the distance of the movement 7 mm, 8—18 mm, 13—26 mm, 24—41 mm, 27—50 mm. A similar result was obtained for *p*-dichlorobenzene. The apparatus will be useful for other organic compounds which expand on melting.

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