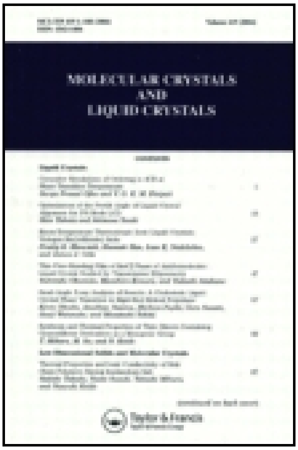

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N. Karl [a] & K.-H. Probst [a]
[a] Kristallabor and II. Phys. Inst. der Universität, Stuttgart, Germany

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Studies on the Efficiency of Purification by Various Zone Refining Devices Using the System Anthracene-Phenazine. Suggestion of a Critical Standard Test.

N. KARL and K.-H. PROBST

Kristallabor and II. Phys. Inst. der Universität Stuttgart
Germany

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Abstract—In this paper a critical standard method is suggested for the testing of zone refining equipment used in purifying low melting volatile organic compounds. The removal of phenazine doped into anthracene was used for this purpose by applying four zone passes and determining the resulting phenazine distribution profile by gas-chromatographic analysis down to 10^{-6}. A quality test number is derived which for several zone refiners of various design showed great differences. The possible causes of these differences are discussed.

Introduction

In the last ten years investigations on the properties of organic molecular crystals have been of expanding interest. Single crystals of extreme purity (impurity content less than 1 ppm) are needed for many studies such as fluorescence, ESR, NMR, photoconductivity etc. However, in nearly all publications on molecular crystals no detailed information on purity and quality of the crystals is given. Specifications such as " purified by 100 zones " are of little value in this respect because the efficiency of purification by various zone melting devices may vary greatly.

Therefore, it would be of great value to have some knowledge of the efficiency of zone melting equipment used. A test system and an analytical procedure are needed for standardization. As there exists no single technique which allows identification of *all* impurities down to the ppm-range† it is important to determine the efficiency of a particular zone melting device in order to estimate the purity obtainable. Furthermore, this knowledge enables one to compare purified materials produced by different devices. (Difficulties arising from the theoretical impossibility of efficient separation of impurities with a distribution coefficient close to unity are not considered here.)

General Considerations on Zone Refining Efficiency

Zone refining depends on the fact that the content of impurities in a crystalizing material differs from that in an adjacent melt. A molten zone is passed through a solid ingot of the material to be purified (see Fig. 1).

A distribution coefficient describing the ratio of the impurity concentration in the resolidified material (C_s) to that in the melt (C_l) can be defined for each impurity. It is a direct measure of the efficiency of the purification by one zone passage.

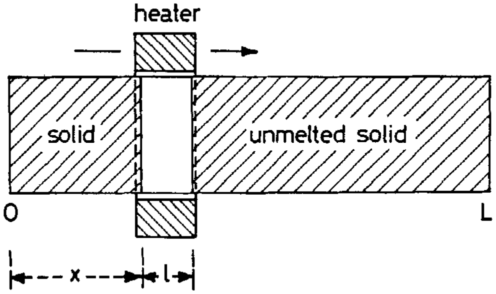

Figure 1. For purification a molten zone is passed through an ingot.

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† There is little hope that *all* impurities can be observed by measuring optical absorption, low temperature fluorescence, charge carrier lifetimes, or the effective mobility of charge carriers—in spite of the fact that these methods may be very sensitive for special impurities.(1) A sensitive detection of impurities by gas-chromatography is only possible if there is a good separation from the main peak, thus that impurity peaks are not eclipsed by the tailing of the peak of the matrix substance. (If this happens, sometimes choice of another type of stationary phase can help.) The determination of total impurity level by melting point depression (cryoscopy)(2) and melting interval does not extend down to the ppm-range. For the systems of interest here, detection of *all* trace impurities in the ppm-range by mass spectrometry has not yet been experimentally studied.

$$C_s = k \cdot C_l$$

For small concentrations and with the assumption that interactions between different impurities can be neglected, k is independent of concentration.

If k is smaller than unity, the impurity concentrates in the molten zone and is transported to the end of the ingot. After one zone passage (zone length l) the concentration distribution in an ingot of constant diameter, length L, and initial concentration C_0 can be described by Pfann's$^{(3)}$ equations

$$\frac{C}{C_0}(x) = 1 - (1 - k)\exp\left[-\frac{kx}{1}\right] \qquad 0 < x < (L - l)$$

$$\frac{C}{C_0}(x) = k\left(1 - \frac{x - (L - l)}{l}\right)^{k-1} \qquad (L - l) < x < L$$

the latter being the equation for the normal freezing process. The various multipass distributions can be approximated using recursion relationships.$^{(4-6)}$

For impurity concentrations less than about $C_0 = 10^{-2}$, k can be assumed to be independent of concentration.$^{(3)}$ For thermodynamic equilibrium, k is determined solely by the nature of the impurity and the matrix, and is called the equilibrium distribution coefficient k_0.

The practical efficiency of purification is always less than that calculated using the value k_0 because of the following effects:

(1) For $k < 1$, a layer of relatively high impurity concentration builds up in the liquid next to the crystallization interface. The magnitude of this concentration effect is determined by the ratio of the crystallization velocity to the impurity diffusion velocity in the melt$^{(3,7)}$ and is diminished by convectional and mechanical stirring,† see reference 8.

(2) Constitutional supercooling,$^{(8)}$ fluctuations in the transport velocity, inconstancy of zone length caused by unstabilized power supply for the zone heating elements, and nonconstant cooling temperature may cause variations in the crystallization velocity.

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† The effective distribution coefficient determined under practical conditions is called k_{eff}. k_0 itself can be obtained by extrapolation from measurements at low crystallization velocities at conditions near equilibrium (under the assumption that back diffusion can be neglected).

(3) The zone transport volume (zone length) and the area of the crystallization front may be decreased by gas bubbles which eventually form in the melt.
(4) For $k < 1$, concentration enrichment in the melt lowers the freezing temperature and thus increases the zone transport volume.
(5) Impurity diffusion through the polycrystalline solid material is not included in the Pfann equations. Even though diffusion in undisturbed single crystals is a very slow process—the self-diffusion constant of anthracene is 10^{-11} cm^2 sec^{-1} at the melting point(9)—diffusion along dislocations can be very much more rapid. (An increase of the diffusion constant by 10^6 and even more along grain boundaries has been reported for anthracene.(10)) The diffusion constants of impurities in matrix substances are expected to have values in this order of magnitude.

Choice of a Suitable Model System and Analytical Procedure

A model system with known properties is needed for a standard test of different zone melting apparatus. A suitable test system should meet the following criteria:
(1) In order that k be more or less independent of concentration even at the initial concentration impurity doping should not be higher than 10^{-2}.
(2) To get sufficient experience on purification efficiency of a certain equipment it is reasonable to apply not only one but a few zone passes and to select a special test system with a distribution coefficient k of a value, that provides that after the desired number of zone passes the impurity content at the purest point is still just measurable by the analytical procedure used, but is as low as possible. It is necessary to extend measurements to low concentrations as separation properties may become worse in this concentration range (e.g. by back diffusion).

The system *anthracene* doped with *phenazine* was regarded to be a suitable test system as we found a k of 0.11,† which after four zone passes theoretically leads to a concentration of 10^{-6} (3) at the purest point (using a starting concentration of about $5 \cdot 10^{-3}$). Further, we

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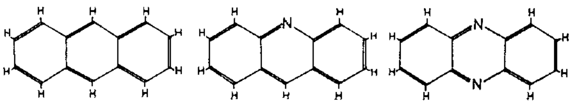
† By normal freezing and single pass zone refining.



	ANTHRACENE	ACRIDINE	PHENAZINE
MELTING POINT	218 °C	110-111 °C	171°C
MOLECULAR WEIGHT	178.2	179.2	180.2
CRYSTAL	MONOCLINE	RHOMBIC	MONOCLINE
SPACE GROUP	$P\,2_1/a$	$P\,2_1/n$	$P2_1/a$

Figure 2. The structure of anthracene, acridine, and phenazine.

succeeded in extending the limit of gas-chromatographic determination of phenazine in anthracene down to this concentration.

Pure anthracene and pure phenazine can be melted undecomposed in vacuum or inert atmosphere. Both crystallize in the space group $P2_1/a$, their molecules being plane and of nearly equal size. It can, therefore, be expected that phenazine should be readily accepted by the anthracene lattice without substantial distortion and form mixed crystals with anthracene even at a high initial impurity concentration.

Acridine in anthracene was considered as well and showed properties similar to phenazine with a measured distribution coefficient of $k = 0.14$. Unfortunately, the gas-chromatographic detection limit was on the order of 10^{-4} because the acridine peak overlaps with the tailing of the anthracene main peak.

Gas-chromatographic Analysis

Provided that a good separation from the principal component can be obtained, analytical gas-chromatography allows the detection of compounds in the ppm-range. However, *separation* of compounds of very similar structure and molecular weight—characteristics of many impurities in molecular crystal research—has not been extensively studied for ppm-impurities in a host. We investigated several columns, stationary phases and techniques, and after extended studies finally succeeded in the separation and detection of 1 ppm phenazine in anthracene.

In our experiments we used a VARIAN type 1527 B gas-chromatograph with N_2 (99.999%) as carrier gas and a flame ionization detector fed with pure H_2 and synthetic air containing 20% O_2. Packed columns, stationary phases, and support materials tested are compiled in Table 1.

For experiments with capillary columns, a column (50m × 0.01″) coated with poly-*m*-phenyl-ether, 5-ring, was available. Even at the maximum working temperature of 192 °C the column had the very long retention time for anthracene of 300 min. Furthermore, thin film capillary columns are not convenient because of the limited capacity and resulting limited detection sensitivity. Support coated open tubular capillary columns were not available.

The best results were obtained with packed columns (lengths 1m and 1.5m) of 4% XE 60 on Chromosorb G, AW-DMCS (Perkin-Elmer). For the system anthracene-phenazine the efficiency of separation calculated from

$$\bar{n} = 8 \cdot \ln 2 \left[\frac{t_{tr}}{b_{1/2}}\right]^2 \cdot \frac{1}{L} \qquad \text{(see reference 11)}$$

with t_{tr} total retention time; L length of column; $b_{1/2}$ half width of peak, is about $\bar{n} = 1100$ at working temperatures of about 180–200 °C. Quantitative detection limit of phenazine in anthracene is 1 ppm imposed by the detection limit of the flame ionization detector and the maximum capacity of the columns (about 100 μg) before overload. The efficiency of separation was constant and the measurements were reproducible throughout 2000 analyses.

The identification of acridine in anthracene failed below the concentration $3 \cdot 10^{-3}$ in a 1m column and $1 \cdot 10^{-4}$ in a 1.5m column because the acridine peak follows the tailing of the main anthracene peak too closely [t_{tr} (acr)/t_{tr} (anthr) = 1.2]. Quantitative detection of carbazole in anthracene succeeded down to about 10^{-5} [t_{tr} (carb)/t_{tr} (anthr) = 2.4].

All analyses were carried out by injection of solid samples (about 20–200 μg) enclosed in small thin walled glass tubes of 1–2 mm diameter and 15–20 mm length, made by extension of Pyrex-test tubes.† A special injector for solid samples was constructed (Fig. 5) tightened by Viton o-ring seals. Liquid injection was not used because of the

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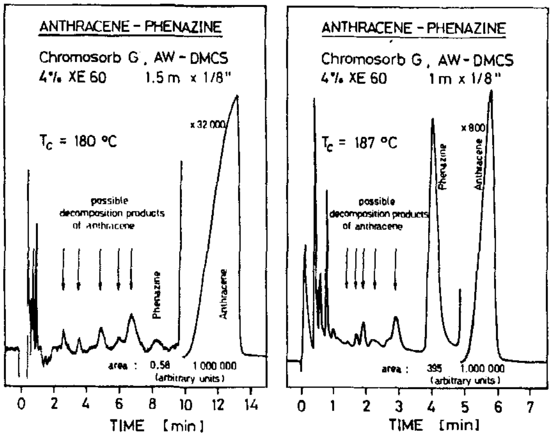
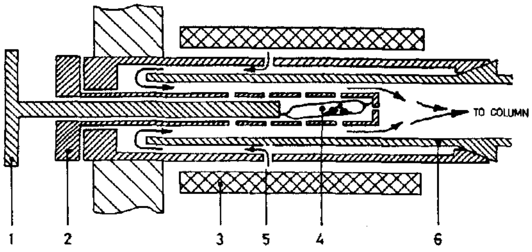
† The point where the small glass tubes are sealed must be extremely clean to avoid peaks in the chromatograms resulting from decomposition.

Table 1 Columns, Stationary Phases, and Support Materials Tested

%	Stationary phase	Support material	Treated with	ϕ	L	$T_{\max}$ °C	Separation properties
20	Apiezon L	Firebrick 45/60 mesh	AW	1/8″	5′	300	separation to 10^{-1} for phenazine in anthracene
5	SE 30	Chromos. W 70/80 mesh	AW	1/8″	5′	280	separation to 10^{-3} for phenazine in anthracene
5	SE 30	Chromos. W 70/80 mesh	AW	1/8″	10m	280	sep. to 10^{-3} for phen. in anthr., ret. time too long
10	XE 60	Chromos. W 80/100 mesh	AW-DMCS	1/8″	5′	230	separation to 10^{-4} for phenazine in anthracene
2.5	SE 52	Chromos. G 80/100 mesh	AW-DMCS	1/8″	2m	280	separation to 10^{-3} for phenazine in anthracene
20	LiCl	Chromos. P 100/120 mesh	NAW	1/4″	5′		anthracene decomposes
4	XE 60	Chromos. G 80/100 mesh	AW-DMCS	1/8″	1m	230	separation to 10^{-6} for phenazine in anthracene, separation to $3 \cdot 10^{-3}$ for acridine in anthracene
4	XE 60	Chromos. G 80/100 mesh	AW-DMCS	1/8″	1.5m	230	separation to 10^{-6} for phenazine in anthracene, separation to 10^{-4} for acridine in anthracene
4	XE 60	Chromos. G 80/100 mesh	AW-DMCS	1/8″	10m	230	separation better than above, ret. time too long



Figures 3, 4. Chromatograms: System anthracene-phenazine.



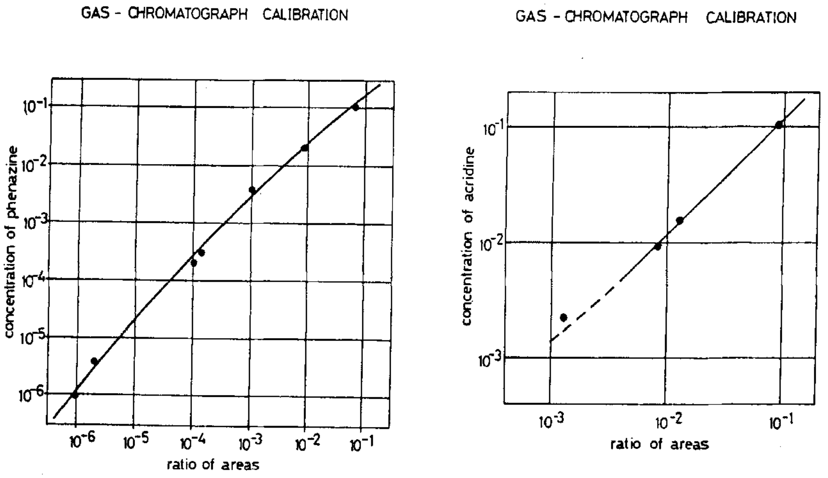
1 RAM
2 DELIVERY TUBE (WITH HOLES FOR EXHAUST OF THE EVAPORATED SAMPLE)
3 INJECTOR HEATER
4 SAMPLE
5 CARRIER GAS (N_2, 99.999%)
6 INLET INSERT

Figure 5. Injector for solid samples (schematic diagram).

small solubility of anthracene in any suitable solvent and because large amounts of solvent affect the detection limit and the performance of separation adversely.

Calibration curves (Figs. 6, 7) were measured from samples of known concentration. Concentrations of unknown samples were determined using these calibration curves from the ratio of measured peak areas. Samples of known concentrations were prepared by mixing weighed amounts of components; the molten samples were chilled by immersion into liquid nitrogen in order to obtain a homogeneously mixed solid.

Possible problems arising from detector nonlinearity or sample decomposition are accounted for by the calibration method. No dependence of the calibration curves on the quantity injected (range 20–200 μg) could be observed.



Figures 6, 7. Calibration curves for the systems anthracene-phenazine and anthracene-acridine.

Zone Melting Devices and Results

For comparison of various zone melting devices we selected four characteristic types of different design. A concentration profile of phenazine in anthracene after four zone passes obtained by the method described above is given in Fig. 8 for each zone refiner.

As expected, there are differences in the distribution profiles produced by the different designs as well as deviations from the theoretically expected shape. Characteristics of the four zone refining devices are discussed in the following paragraphs.† Only the

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† For every zone refiner there should exist an optimum zone velocity for the highest efficiency of purification.(8) We selected those speeds that usually had been applied in our laboratory and that after a large number of previous experiments seemed to yield the best results. However, we did not use the anthracene-phenazine test for further proof.

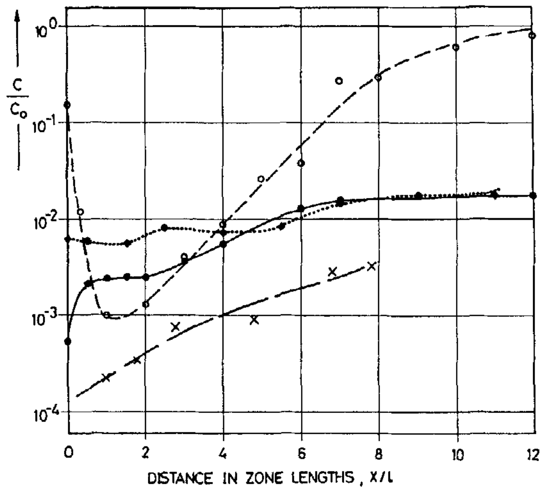

Figure 8. Concentration profiles of phenazine in anthracene after four zone passes.

-x- X zone melting device A; ◆-◆-◆ zone melting device B;
-o-o- o zone melting device C; ●-●-● zone melting device D.

results for the range $0 < x < (L - 4l)$ are considered. The range $(L - 4l) < x < L$ resulting from normal freezing (the molten zone becomes smaller as the zone leaves the ingot) is of minor interest for the discussion of the purification efficiency.

Zone melting device A

This apparatus developed by Fischer(12) operates with the zone melting tube fixed horizontally. The construction of heating coils and cooling elements provides nearly complete independence of the zone length on changes in room temperature and yields high temperature gradients in the charge. The device is installed in a tight glass tube and may be filled with inert gas of high heat conductance (He) to improve heat transfer to the sample tube. The zone length (10 mm) is further stabilized by a constant voltage power supply, by temperature control of the coolant, and by intermittent rotation of the glass zone melting tube (stirring effect by inertia and friction). Zones enter the charge at the closed end of the ampoule preventing formation of gas bubbles in the melt. The set of heaters and cooling elements is moved at 5 mm/h in an " intermittent technique ".†

Because of the high constancy of zone length and good crystallization conditions, the rise of the concentration curve (A) is in good agreement with the theoretically expected curve. The reduced concentration $C/C_0 = 1.7 \cdot 10^{-4}$ at the purified end of the charge suggests a distribution coefficient even smaller than the measured average value of $k = 0.11$.

Zone melting device B(14)

Two heating coils—thermally isolated by glass rings—and two cooling elements are mounted vertically (Fig. 9). The coolant

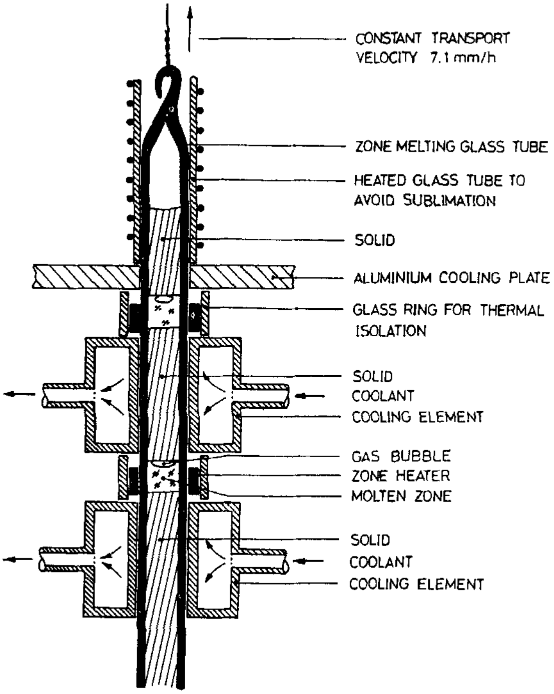

Figure 9. Zone melting device B.

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† With this technique, the zone melting tube is moved relative to the heaters for a distance equal to the separation of two heaters and then quickly returns to its initial position so that the subsequent heater takes over the molten zone.

temperature of 90 °C was maintained by a thermostat but the power supply was unstabilized. A cylindrical oven was installed to avoid vapor condensation, and an aluminium cooling plate guaranteed freezing of the melt. The zone melting tube was moved up at a constant speed of 7.1 mm/h and the zone length was 10 mm.

Sublimation as well as formation of gas bubbles could not be avoided completely even though the zone melting tube was filled with 400 Torr N_2. The sublimation oven produced a variation of the zone length of the upper zone. These initial effects cause the high initial phenazine concentration and the slow rise in the curve (*B*).

Zone melting device C(13)

16 heating coils and 16 cooling elements are installed vertically; power supply and cooling temperature are stabilized (Fig. 10). The main difference between apparatus *B* and *C* is that *C* has no oven for preventing the accumulation of sublimed material.

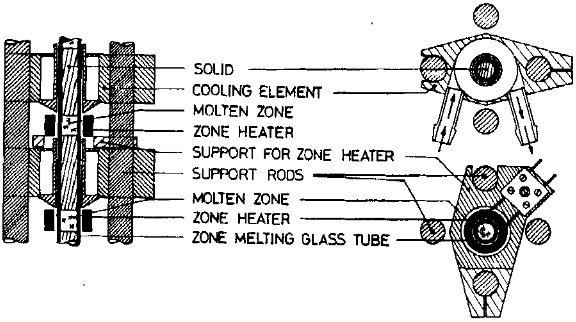

Figure 10. Zone melting device *C*.

A rate of 30 mm/h seemed to be an optimal compromise between sublimation and purification efficiency. The strong sublimation and gas bubble formation typical for this apparatus cause the very high phenazine concentration at the starting end of the ingot (*C*). As can be seen, the concentration curve might be extrapolated to an initial concentration $C/C_0 = 3 \cdot 10^{-4}$, if the sublimation effect could be avoided. The high slope in the range 2–8 zone lengths is probably due to the formation of gas bubbles which reduce the zone transport volume continuously until they eventually prevent the contact of melt and crystallization interface.

Zone melting device D

The apparatus is a simple glass tube supplied with 18 heating coils with a separation of 50 mm. Installed at the top is a sublimation oven fixed relative to the zone melting tube. The heaters are moved downwards by the intermittent technique at a rate of 13.2 mm/h (Fig. 11). Sublimation transfer is avoided completely. Gas bubbles form, however, as is typical for zone melting with this technique. Furthermore, the zone length of the upper zone slowly decreases as the distance to the sublimation oven increases. The initial high slope of the concentration curve (*D*) may be caused by this change in zone length.

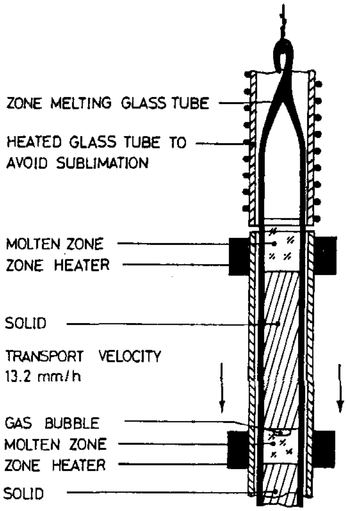

Figure 11. Zone melting device *D*.

Critical Test

Zone melting equipment very often should meet one of the following requirements:

(*a*) Extremely pure material is required. The amount of extremely pure material and the time needed for purification are of minor importance.

(*b*) As much material as possible of medium purity should be delivered by the zone melting process in a reasonable time.

(*c*) Material of high purity or a large quantity of material showing a certain purity desired should be available in a time as short as possible.

High efficiency of purification of zone melting equipment therefore is a very general requirement, the time factor however needs a compromise and mostly is determined by economy considerations.

The following test is suggested:

Mix anthracene and phenazine at an initial mean concentration of phenazine $C_0 = 10^{-3} - 10^{-2}$. Both components should be zone refined to assure that the distribution coefficient is not affected by impurities. Using the apparatus to be tested, cause four zones to travel the length of the charge. Apply gas-chromatography to determine the resulting phenazine concentration profile, use solid sample injection and columns packed with 4% XE 60 on Chromosorb G, AW-DMCS, length 1–1.5 m, at a working temperature of about 190 °C.

Plot the logarithm of the reduced concentration C/C_0 versus number of zone lengths and consider the range $0 < x < (L - 4l)$.

A simple estimate of purification efficiency may be made by calculation of the area of the triangle formed by the ordinate, the line $C = C_0$, and the concentration curve approximated by a straight line in the range $0 < x < 8l$ (if the total ingot length L is $> 12l$). The area would be a measure for the purification efficiency. It is evident, however, that this method would involve serious errors, if strong deviations of the concentration profile from a straight line are found.

The following alternative procedure is suggested for more accurate evaluation of the purification efficiency:

Consider the portion of the charge which is of maximum interest in respect to further utilization, for example the range $0 < x < 8l$ (eight zone length from the beginning). In the logarithmic diagram (Fig. 12) calculate graphically the value A of the area $C = C_0$ and the real concentration curve in this region:

$$A_8 \text{ (four zone passes)} = -\int_0^8 \log \frac{C(x)}{C_0} \cdot dx$$

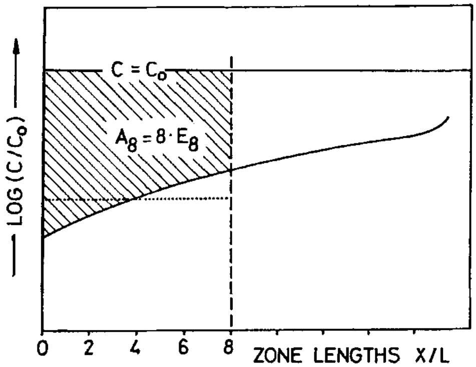

Figure 12. Determination of the area between the concentration curve and $C = C_0$ as a measure for the purification efficiency.

Divide this value by the number n of zone lengths considered (eight). The value thus obtained is a reasonable measure for the efficiency of purification that was intended to be characterized.

$$E_8 \text{ (four zone passes)} = \frac{A_8 \text{ (four zone passes)}}{8}$$

Using the concentration profiles measured (compare Fig. 8), the efficiency E of the four zone melting devices has been calculated to be

TABLE 2

	E_8 (four zone passes) [decades]
Device A	3.1
Device B	2.1
Device C	1.9
Device D	2.3

Consider that a difference of 1 in these E-values means a decade in purity. High numbers characterize high purification efficiency.

If the time needed for purification is an important consideration, it is useful to account for this by multiplying E by the travel velocity and the cross-section of the bar:

$$\bar{E}_8 \text{ (four zone passes)} = \frac{A_8 \text{ (four zone passes)}}{8} \cdot v \cdot q$$

To find out optimal conditions measurements at different travel velocities are necessary.

Summary

In this paper a critical standard method is suggested for testing zone refining equipment used in purifying low melting volatile organic compounds. Evaluations of zone refining equipment by means of this method will allow more meaningful reporting of the purity attained in zone refining. At present, the common description of purification involves simple reporting of the number of zones passed through the original charge. Our work demonstrates that such statements are not very meaningful for comparison of crystal quality from laboratory to laboratory.

The system anthracene doped with phenazine was found to show a suitable distribution coefficient and to allow an analytical treatment by gas-chromatography down to the 10^{-6} (ppm-)range. In addition, phenazine is readily built into anthracene even at concentrations of 10^{-2} which is a good starting value for a test.

We have tested four different types of zone refiners built in our laboratory and we found substantial differences. The " horizontal method " which is characterized by the fact that zones are introduced to the ingot from the closed end is much more effective than other methods which cannot completely avoid the formation of gas bubbles and sublimation.

We imagine that comparisons by this test may help where different results on crystals of different provenance obtained by different investigators are confusing.

On the other hand, the gas-chromatographic trace analysis described using solid sample injection and a flame ionization detector has been shown to provide a means for a direct search for impurities in the ppm-range which are not removed by zone refining or for the determination of the true concentration of doping materials voluntarily added before crystal growth.

Acknowledgement

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