Design
Scientific

MiniZone

zone refiner

Ultra-Purification of Organic Chemicals
Concentration of Impurities

MANUAL

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Zone Refining Historical Note

For hundreds of years chemists have used the power of crystallization to enhance the purity of chemicals. Crystallization was the cornerstone technique of the work of Pasteur, Pierre and Marie Curie, and many of the early pioneers of organic chemistry.

In 1952, William G. Pfann at Bell Telephone Laboratories, looking for a method to obtain ultra-pure specimens of germanium, developed a powerful new technique that improved on fractional crystallization. He named the semi-automatic process zone refining or zone melting. With the new process, extraordinarily pure specimens of germanium and silicon could be obtained. Other workers successfully extended the process to the purification of organic chemicals. These early pioneers predicted that the technique would become a routine laboratory tool. These predictions were based on the fact that zone refining can be applied to a significant portion of organic chemicals and because the method is powerful, semiautomatic, simple and operates without consuming solvent.

In practice, however, the traditional method of zone refining is very slow, requiring days or even weeks to purify chemicals. Also, operators were often frustrated by the bursting of glass tubes used to contain the sample during purification due to the high thermal expansion of organic chemicals relative to glass.

Applications of Zone Refining

Zone refining can be used to purify virtually any solid that melts without decomposition. Thousands of examples are cited in the literature. Crystalline samples as low as 80% purity have been successfully zone refined; however, in order to obtain extremely high purity samples (>99.9% pure) it is necessary to start with samples having a purity of 98% or better. For an explanation of this refer to the zone refiner theory section below.

Among the applications to which Zone Refining can be applied include:

- Crystalline Polymorph Searches
- Purification of analytical standards
- Separation of stereo (chiral) and geometric isomers
- Concentration of sample impurities for further analysis or identification
- Purification of laser dyes
- Purification of organic semiconductors

A substantial amount of information is available on applications of melt zone refining. The following lists are taken from "Zone Melting of Organic Chemicals", E.F.G.Herrington, 1963, John Wiley & Sons, New York. This book is out of print. We are reproducing the lists as a service to our customers.

Compounds that have been purified using zone melting (details available) see below:

- Acetanilide
- l Amino 2 methylanthraquinone
- Anthracene
- Anthraquinone
- Benzene
- Benzoic acid
- Benzophenone
- p Bromoacetanilide
- p Bromotoluene
- Cetyl alcohol (C16H330H)
- p Chloroacetanilide
- 4 Chloro o cresol
- 4 Chloro 2 nitroaniline
- Chrysene
- m Cresol
- 3,4 Dimethylphenol
- 3,5 Dimethylphenol
- 2,6 Dimethylphenol
- 2,4 Dinitrotoluene
- Dioxane
- Diphenylsulphone
- Diphenyl sulphoxide
- Ethanol
- 3 Ethyl 5 methylphenol
- Fatty alcohols
- p Fluorobenzoic acid

- Hallowax
- Hexacosanol
- Hexacosyl hexacosanate
- Hippuric acid
- Indole
- p Iodobenzoic acid
- Lindane
- (Y 1,2,3,4,5,6 hexachlorocyclohexane)
- 3 Methoxybenzanthrone
- 9 Methylcarbazole
- 3 Methylindole (Skatole)
- 1 Methylnaphthalene
- 3 Methylpyridine
- Naphthalene
- b Naphthol
- Neopentane
- 2 Nitro 4 methylaniline
- Pentamethylpyridine
- Phenanthrene
- Phenazine
- Phenol
- Phenothiazine
- Pyrene
- Salicylic acid
- Sexiphenyl
- Stearic acid
- Stearyl alcohol
- Stilbene
- Succinic acid
- Sulphanilamide
- Terphenyl
- p Tolyl methylsulphone
- Di p tolylsulphone
- 1,4,5 Trichloroanthraquinone
- Vanillin
- Wax
- o Xylene
- m Xylene
- p Xylene

Compounds that have been purified using zone melting (no details are available):

- Acetamide [1,2,3]
- Aldrin [1]
- 1 Amino 2 cyanoanthraquinone [1]
- 4 Aminoquinoline [5]
- Aniline [1]
- p Anisidine [1]
- Anthranilic acid [1]
- Antipyrine [1]
- Azobenzene [1,2,3]
- Azuline [5]
- Benzamide [1]
- I,2 Benzanthracene [1]
- p t Butylphenol [1]
- 4 Chloro 1, 3 dinitrobenzene [2]
- 1 Chloro 2 methylanthraquinone [1]
- Cholesterol [3]
- Cholesteryl stearate [3]
- Cinnamic acid [2]
- 2 Cyanocyclopentylideneimine [1]
- d Cyanovaleramide [1]
- Cyclohexane [5]
- n Decane [5]
- Dibenzyl [1]
- Dichloromaleic anhydride [1]
- 1,5 Dihydroxyanthraquinone [1]
- 1,8 Dihydroxyanthraquinone [1]
- 2,3 Dimethylindole [1]
- N,N Dimethyl p nitrosoaniline [1]
- 2,5 Dimethylphenol [1]
- Dimethylterephthalate [1]
-
- Diphenyl [2,5]
- Diphenylacetic acid [1]
- Fluorenone [1]
- Hexamethylbenzene [5]
- 1 Hydroxyanthraquinone [1]
- I Indanone [4]
- Isoquinoline [5]
- Maleic anhydride [1]
- 1 Methylaminoanthraquinone [1]
- 2 Methyl 4 chlorophenol [1]
- 2 a Methyl cyclohexyl 4 methyl alcohol [1]
- 2 Methyl 4 nitroaniline [1]
- Naphthylamine [5]
- p Nitroaniline [1]
- 1,2,3,5,7 Pentamethylindole [1]
- Phenoxy acetic acid [1]
- Pyrazolone [1]
- Resorcinol [1]
- Sitosteryl acetate [3]
- Succinic acid [1]
- 1,3,5,7 Tetramethylindole [1]
- Tolane [2]
- 1 p Tolyl 3 methyl 5 pyrazolone [1]
- Urea [1]

The references for the above list are as follows:

[1] Beynon & Saunders (1960)

[2] Schildknecht (1961)

[3] Schildknecht & Vetter (1961)

[4] Chemistry Research (1957)

[5] Wolf (1957)

Acetanilide

Wynne (1961) reported that the melting point of a zone refined sample was 114.8 C, which may be compared with literature values of 113~114 C.

Amino 2 methylanthraquinone

Beynon & Saunders (1960) showed that after thirty three zone passes the concentration of amino dimethylanthraquinone at the top of the column was 0.5 per cent and that of diamino methylanthraquinone was 0.20 per cent. Initially the concentration of both impurities was 0.31 per cent.

Anthracene

Wolf (1957) reported that tetracene can be removed from anthracene by zone refining.

Joncich & Bailey (1960) found that Eastman White Label anthracene after zone refining showed a very sharp peak in the differential thermal analysis curve, indicating a considerable improvement in the specimen.

Light & Co (1959) produce zone refined batches of 1 to 5 lb weight which are used to grow single crystals for scintillators.

Wynne (1961) reported that the melting point of a zone refined sample was 219.10C (cf. literature values of 216~2l8 C) and that analysis of the refined material gave: C, 94.46; H, 5.78. Calc. for $C_{14}H_{10}$: C, 94.34; H, 5.1 6.

Hoesterey (1962) reported that single crystals were grown under helium by the Bridgman method from a zone refined specimen. The starting material was either Eastman Organic Chemical X 480 or hydrocarbon synthesized by the cyclization of o benzoyl benzoic acid followed by a two stage reduction.

I Anthraquinone

Wynne (1961) reported that the melting point of a zone refined sample was 288.90 C and compared this with literature values of 286~288 C.

Beynon & Saunders (1960) reported that anthraquinone can be purified satisfactorily by zone melting.

Benzene

Rock (1956) treated benzene in an apparatus. The purities of the original charge and of samples after treatment were determined by melting point measurements using a Beckmann thermometer. When technical benzene containing approximately 0.2 mole per cent impurity was refined, a fraction containing less then 0.0008 mole per cent impurity was obtained.

Sue, Pauly & Nouaille (1958) reported that a sample of benzene containing .002 fraction of acetic acid contained .001 fraction of the acid after ten zone passes. The concentration of thiophene in a sample of benzene was reduced from .001 to less than .0001 by fifteen zone passes.

Schildknecht & Mannl (1957) reported that the zone refining of a crude benzene produced a fraction at the end of the sample that was liquid when the rest of the specimen was solid. It was claimed that almost 90 per cent of the benzene was free from thiophene, but unfortunately the limits of the sensitivity of the test were not given. Removal of the portion enriched with thiophen during treatment assisted purification. The work of Hudson, Hillig & Strong (1959) illustrates the care that must be taken in the manipulation of samples of the highest purity. Phillips Research Grade Benzene, initially 99.93 per cent pure, was further purified by vacuum sublimation and zone refining. Purification of the sample was carried out in a vacuum system which included two cold traps to allow successive sublimation in a degassing process, a vertical zone refining tube and a manifold with capillaries for containing specimens. The zone melting tube was cooled by pumping alcohol at 0 C round a jacket. Four resistance heaters in series were used to produce molten zones. The purification apparatus was evacuated before use, flamed until the residual pressure was less than 0.01 micron and then filled with dry nitrogen. The benzene, introduced through a silica gel filter, was then frozen by means of liquid nitrogen. The opening through which the hydrocarbon had been admitted was sealed off and the system was pumped until the residual pressure was below 1 micron. Dissolved gases were removed by four sublimations between the two cold traps; the first two sublimations were made with the aid of liquid nitrogen and the other two by the use of a carbon dioxide acetone freezing mixture. After degassing the benzene was melted and condensed into the zone melting tube where it was again frozen. After each zone pass all residual vapor was frozen into one of the traps by means of liquid nitrogen and the condensed vapor was isolated from the rest of the system. The top inch of solid benzene was melted and a sample condensed into one of the capillaries. The specimen was frozen in liquid nitrogen and all the residual benzene was condensed into the other trap by use of the same coolant. The sample tube was then sealed off. In this manner, pyrolysis of benzene vapor during the sealing of the glass was avoided. Benzene samples with a triple point of 5.527 +/ 0.001C Were obtained after three or four zone passes; the degassed starting material had a triple point of 5.523 +/ 0.0020 C. Additional zone melting effected no further improvement.

Beynon & Saunders (1960) also reported successful zone refining of benzene.

Benzoic acid

Handley & Herington (1956) reported that the melting point of a specimen after treatment was 121 121.5 0C; before treatment it was 119.5 121.5 0C.

Joncich & Bailey (1960) studied the removal of carbon 14 labeled naphthalene from benzoic acid. An initial concentration slightly in excess of 0.1 mg of naphthalene per gram of benzoic acid was used, and it was found that after eighteen zone passes the concentration was reduced to below the detectable limit of 0.0001 mg of naphthalene per gram of benzoic acid.

Wynne (1961) reported a melting point of 124 C for the zone refined acid (literature values 122~123 C) and the analysis of that zone refined material gave: C, 68.82; H, 4.85. Calc. for $C_7H_60_2$: C, 68.84; H, 4.95.

Benzophenone

The zone refining of this material was studied by Schildknecht (1961) who presented a graph showing that after three zone passes at 3 mm/h through material with melting point 43.2~45 C, the maximum melting point of a portion of the specimen was 47.5 C. Eighteen zone passes through similar material gave colorless crystals with melting point 48.00 C and there was a large flat plateau in the curve of melting temperature plotted against distance along bar.

Schildknecht & Vetter (1961) reported the satisfactory purification of this compound on the micro scale.

p Bromoacetanilide

Wynn (1961) prepared a sample with a melting point of 167.3 C (cf. literature values 165~167 C) by zone refining.

p Bromotoluene

A specimen of this compound containing a fraction of .02 of o bromotoluene was shown by the use of 82Br labeled o bromotoluene to contain .0002 fraction of the ortho compound at the beginning of the sample after the passage of nine zones (Sue, Pauly & Nouaille, 1958).

Cetyl alcohol (C16H330H)

Hesse & Schildknecht (1956) prepared a sample with a freezing point of 50 C by zone melting a specimen with freezing point 48.50 C.

Beynon & Saunders (1960) also reported the successful purification of this compound.

p Chloroacetanilide

A sample with melting point 181.20 C (cf. literature values 178~180 C) was prepared by zone refining (Wynne, 1961).

4 Chloro o cresol

Sorenson (1959) found that a rather slow speed of zone movement and many zone passes were required to purify this compound. After eighteen passes (2 cm/h) a sample of technical 4 chloro o cresol (m.p. 40.90 C) remained rather impure, the first fraction having a melting point of only 46.20 C. In a further experiment, however, fifty zone passes gave a pure product with melting point 48.70 C in the first 25 per cent of the column.

4 Chloro 2 nitroaniline

Beynon & Saunders (1960) found that after two zone passes the following impurities were concentrated and were detectable, C6H3NH2Cl2, C~H3NO2Cl2, C6H4NH2Cl and C6H2NH2NO2Cl2. Further refinement was not attempted because concentration of explosive polynitrocompounds might have occurred.

Chrysene

Handley & Herington (1956) found that a sample with a melting point of 250~250.5 C could be produced by zone melting a commercial sample with melting point 248 249.5 C.

Wolf (1957) reports that an unidentified impurity was removed from this hydrocarbon by zone melting.

m Cresol

A zone melting apparatus erected in a refrigerator has been used for zone refining this compound (Chemistry Research, 1957).

3,4 Dimethylphenol

Schildknecht & Hopf (1961) studied the purification of a material that was pale red in color but was well crystallized and had a melting point of 62.30 C. A specimen 45 cm long was treated by twenty five passes of a zone 2 to 3 cm long, moving at the rate of 0.2 cm/h. Specimens taken at points 7.5 and 12.5 cm. from the beginning had the highest melting points, 62.60C. Specimens at points 25, 50, 150 and 25 cm from the beginning melted at 62.5 C, whilst at 27.5 cm the melting point was 62.3 0C and a specimen 31.0 cm from the beginning melted at 62.2 C.

3,5 Dimethylphenol

Colorless crystalline samples of this compound were obtained by zone refining a specimen in nitrogen (Report of the National Chemical Laboratory, 1958).

Schildknecht & Vetter (1961) have reported the successful purification of this phenol on the micro scale.

Schildknecht (1961) has studied the zone refining of a mixture containing 88 per cent of 3,5 dimethylphenol and 12 per cent of 3,4 dimethylphenol. A sample of the more abundant phenol was separated in a yield 97 per cent of that expected from the phase diagram, but the eutectic did not separate in a pure form.

2,6 Dimethylphenol

This material was successfully purified by zone refining a specimen in dry nitrogen (National Chemical Laboratory Report, 1958).

2,4 Dinitrotoluene

Schildknecht (1961) observed pale yellow transparent crystals 8 cm long at the beginning of a tube after fourteen zone passes. The end of the tube contained a brown mass of fine crystals. Infra red analysis showed that these contained o and p nitrotoluene and trinitrotoluene as impurities.

Dioxane

According to an unsigned report [Chem. Engr (1959), April 20, 66, 80] water and other impurities have been removed from this heterocyclic compound by zone refining to yield a solvent of spectroscopic purity [see also Chem. Engng (1959) March 9, p.74].

Diphenylsulphone

Mackle & O'Hare (1961 a) purified a sample of B.D.H. Laboratory Reagent Grade material by zone melting several times. Another sample was recrystallized eight times from pure ether. The melting point of both specimens was 124 C and the normal boiling point was 378 C, with appreciable decomposition. Analysis gave: C, 66.3; H, 4.66 compared with theoretical: C, 66.0; H, 4.62.

Diphenyl sulphoxide

Mackle & O'Hare (1961 b) prepared this compound by oxidizing Diphenyl sulphide in acetic acid with one equivalent of 30 per cent hydrogen peroxide added slowly under reflux. The reaction product was evaporated to dryness under vacuum and the solid was purified by zone melting.

Analysis of the purified compound (m.p. 70.20 C) gave: C, 71.1; H, 4.92, compared with theoretical C, 71.3; H, 4.98.

Ethanol

Izergin (1958) treated ethanol in a boat made of polytetrafluro ethylene. The alcohol was frozen by means of liquid air and the zone length was controlled by regulation of the power of the electrical heater. The alcohol initially contained 4 per cent of water, and after four zone treatments the water content was 1 per cent.

3 Ethyl 5 methylphenol

Purification of this compound in dry nitrogen was achieved by zone melting (National Chemical Laboratory Report, 1958).

Fatty alcohols

Hesse & Schildknecht (1956) separated the alcohols $C_{16}H_{33}OH$ and $C_{18}H_{37}OH$ in a micro zone refining apparatus having three heaters and interjacent coolers. See also Hexacosanol.

p Fluorobenzoic acid

Wynne (1961) prepared a sample with m.p. 187 C by zone melting.

Hallowax

McClelland, Jnr. (Pfann, 1958) showed that after fifteen zone passes through a hollow cylindrical charge of a capacitor impregnator known as Hallowax 1001, the material, a chlorinated naphthalene, exhibited variations in melting point, melting range and dielectric constant along the sample.

Hexacosanol

Schildknecht (1961) reported a study of a mixture of 80 per cent hexacosanol ($C_{26}H_{53}OH$) and 20 per cent eicosanol ($C_{20}H_{41}OH$). These compounds form mixed crystals; separation by zone melting was followed by melting point measurements. Segregation was found to be slow and difficult; but finally a specimen of hexacosanol with melting point 80.30 C was isolated.

Hexacosyl hexacosanate

Schildknecht (1961) reported the separation of a sample of hexacosyl hexacosanate by the zone refining of an insect wax. The specimen was identified by infrared spectroscopy.

Hippuric acid

This compound could not be purified by zone melting because the sample decomposed at a temperature only slightly higher than the melting point (Hubbard, Frow & Waddington, 1961).

Indole

A sample of this material was zone refined by the Bureau of Mines, Laramie, Wyo., U.S.A., to 99.9 per cent purity (Ball, Helm & Ferrin, 1958, 1959).

p Iodobenzoic acid

Wynne (1961) reported that a zone refined sample melted at 270.80 C.

Lindane (Y 1,2,3,4,5,6 hexachlorocyclohexane)

A very pure sample of this insecticide, free from musty odor and of melting point 112.84 C, was prepared by zone refining. This melting point should be compared with the most acceptable figure (112.86 C) hitherto published (Report of the National Chemical Laboratory, 1960).

3 Methoxybenzanthrone

The most abundant impurity (chloromethoxybenzanthrone) in a sample of this compound treated in a 24 in column by Beynon & Saunders (1960), had a partition coefficient greater than unity. The rate of movement of the impurity was therefore very slow. Experiments showed that it was helpful to use a much longer molten zone (e.g. 2 in) than usual so that the impurity, which could not move more than one zone length per pass, could move much further each time. The zone length was gradually reduced to a normal value of about 1 in. The original charge contained 2.0 per cent of chloro methoxybenzanthrone, 0.12 per cent of dimethoxybenzanthrone and 0.66 per cent of chlorobenzanthrone. After forty eight zone passes the material at the top of the column contained 3.4, 0.04 and 0.12 per cent of these impurities and the material at the bottom of the column contained 0.70, 0.17 and 0.78 per cent of the same compounds.

9 Methylcarbazole

This compound was zone refined to a purity of 99.9 per cent by workers at the Bureau of Mines, Laramie, Wyo., U.S.A. (Ball, Helm & Ferrin, 1958, 1959).

3 Methylindole (Skatole)

Beynon & Saunders (1960) reported that this compound, which is notorious for its overpowering odor of feces, completely lost all its objectionable smell when zone refined. Presumably the odor is due to a small amount of intensely odoriferous contaminant.

l Methylnaphthalene

This hydrocarbon, m.p. 30.80 C, was treated in a zone refining apparatus enclosed in a space cooled with solid carbon dioxide (Chemistry Research, 1957).

Wolf (1957) reported that anthracene can be removed from this compound by zone melting.

3 Methylpyridine

Workers at the Bureau of Mines, Laramie, Wyo., U.S.A., refined samples of this base to a purity of 99.9 per cent (Ball, Helm and Ferrin, 1958, 1959).

Naphthalene

Wolf and Deutsch (1954) showed that two zone passes at the rate of 1 cm/h through naphthalene containing 0.1 per cent of anthracene reduced the concentration of anthracene to less than one part per million. The fluorescence spectrum was used to measure the anthracene concentration. It was suggested that in any further attempt at purification the zone refining should be carried out in vacuum or under nitrogen.

Handley (1955) and Herington, Handley & Cook (1956) showed, by studying the fluorescence under ultra violet light, that seven zone passes reduced the anthracene concentration in a synthetic mixture of anthracene and naphthalene from 0.2 to 0.00002 per cent.

Beynon & Saunders (1960) demonstrated that it is possible to purify crude naphthalene. After nine zone passes through a sample with a melting point of 73.50 C, they obtained a specimen with melting point 80.20 C from the top portion of the sample.

Wynne (1961) reported obtaining by zone refining a specimen of naphthalene with melting point 82 C. Analysis of the purified material gave: C, 93.44; H, 6.23; Calc. for C10H8, C, 93.71;H, 6.29.

Schildknecht (1961) reported the successful purification of this hydrocarbon.

Fryer (1962) has published a photograph of a zone melting apparatus used in the laboratories of Hopkins and Williams Ltd, to prepare ultra pure naphthalene.

b Naphthol

Colourless crystalline samples of this compound were obtained by the zone refining of a specimen in nitrogen (Report of the National Chemical Laboratory, 1958).

Neopentane

This aliphatic hydrocarbon (melting point approximately 170 C) has been zone melted in an apparatus enclosed in a space cooled by solid carbon dioxide (Chemistry Research, 1957).

2 Nitro 4 methylaniline

The trace impurities C6H4NO2CH3 and C6H2(CH3)3NH2 were detected after two zone passes but further treatment was not carried out for fear of concentrating explosive poly nitro impurities (Beynon & Saunders, 1960).

Pentamethylpyridine

Brown & Buck (1961) zone refined a specimen of this compound before measuring the infra red absorption spectrum.

Phenanthrene

Joncich & Bailey (1960) reported that a sample of Eastman White Label phenanthrene purified by the method of Feldman, Pantages & Orchin (1951) showed an appreciable increase in purity after zone refining.

Beynon & Saunders (1960) also reported the successful purification of phenanthrene.

Phenazine

Aftergut & Brown (1961) studied the electrical resistance of a zone refined sample of this compound that had previously been purified by chromatography on alumina. As the zone refined material had a higher resistivity and a lower energy gap than material purified only by chromatography or by sublimation it was considered to be purer than other specimens.

Phenol

Sorenson (1959) made an extensive study of the conditions necessary for the removal of p nitrophenol from phenol by zone refining. With increasing impurity content it became relatively more difficult to purify the phenol.

Wolf (1957), Schildknecht (1961) and Schildknecht & Vetter (1961) have reported successful purification of this compound.

Phenothiazine

Brown & Aftergut (1962) measured the resistivity of crystals of phenothiazine that had been chromatographed, sublimed, zone refined and resublimed. Specimens that had been sublimed only did not show ohmic resistivity, and this behaviour was attributed to the presence of impurities. Zone refined material exhibited ohmic resistivity with an energy gap of l 6 eV and this was considered to be a good value.

Pyrene

Handley & Herington (1956) reported a melting point of 152 C for a zone refined specimen, a value which is to be compared with a melting range of 150 152 C for the starting material.

Wolf (1957), and also Beynon & Saunders (1960), reported purification of this aromatic hydrocarbon.

Salicylic acid

Wynne (1961) compared his observed value of 161.90 C for the melting point of a zone refined sample with literature values of 159 161 C.

Sexiphenyl

Nozaki, Tamura, Harada & Saito (1960) prepared a sample of sexiphenyl by a four stage synthesis from p terphenyl. The material obtained by sublimation from the crude product was yellow and contained copper and iodine. Neutron activation analysis of products obtained in a series of zone refining and vacuum sublimation operations showed that iodine containing compounds could be removed. It was considered that these compounds were probably decomposed during zone refining. However, too high a temperature decomposed sexiphenyl itself, especially when the purity was low. Temperatures between 440~ C and 450~ C were therefore used in the purification. After vacuum sublimation and recrystallization from tetralin, the carbon and hydrogen contents of the product were correct. Nevertheless the melting points rose with repeated alternate zone refining and vacuum sublimation until it reached a constant value after four repetitions of the cycle followed by a recrystallization from tetralin and a vacuum sublimation. The final sample contained less than 0.04 p.p.m. of iodine. The material was used as a scintillator and the photo multiplier pulse obtained was higher than that from anthracene.

Stearic acid

Wolf (1957) reported the removal of an unidentified impurity from this acid by zone refining.

Wynne (1961) reported a melting point of 70.1 0C for a zone refined specimen and compared it with values of 68~69.50 C from the literature.

Stearyl alcohol
Hesse & Schildknecht (1956) prepared a specimen with a melting point of 58.50 C from material with melting point 57.5 C.

Schildknecht (1957) treated 180 mg of a sample of stearyl alcohol and found that after twenty four zone passes the melting point of the material at the front of the specimen was 60.30 C and at the back was 55.90 C. The pure alcohol was in the middle portion and melted at 58.40 C.

Stilbene
Light & Co (1959) treat batches of 1 to 5 lb of this hydrocarbon by zone refining as a step in the manufacture of single crystals for scintillators.

Schildknecht & Hopf (1961) zone melted a 39 g sample of stilbene with a melting point of 119 1240C in a tube 2 cm in diameter and 46 cm long. After a 2 cm long zone had been passed twelve times at the rate of 0.3 cm/h a specimen 1 cm from the beginning of the tube had a melting point of 125.4 0C. Samples between the third and eighteenth centimeters had a melting point of 125 C and a specimen near the far end had a melting point of 80 C.

Schildknecht (1961) and Schildknecht & Vetter (1961) also reported successful purification of stilbene by zone treatment.

Succinic acid
Wynne (1961) reported a melting point of 187.8 C for a zone refined specimen (literature values 185~187 C). Analysis of the refined material gave: C, 40.98; H, 5.07. Calc. for C4H604: C, 40.68; H, 5.2.

Suiphanilamide
Wynne (1961) reported a melting point of 165.2 C for a treated specimen literature values cited 164 165 C).

Terphenyl
Light & Co (1959) zone refined this compound as a step in the preparation of single crystals.

p Tolyl methylsulphone
Crude p tolyl methylsulphone was zone melted by Mackle & O'Hare (1961 a) to give a product with a melting point of 83.6~84.10 C (literature values 83~87.50 C), and a normal boiling point of 316 + 10 C. Analysis gave: C, 56.5; H, 5.90 compared with theoretical: C, 56.4; H, 5.92.

Di p tolylsulphone
Mackle & O'Hare (1961 a) reported that a sample from Eastman Kodak Ltd was zone refined four times and another specimen recrystallized eight times from diethyl ether was fused several times. Both batches had a melting point of 158~159 C (lit. 158 C); the normal boiling point was 403+ 10C and analysis gave: C, 68.4; H, 5.71 compared with theoretical C, 68.3; H, 5.73.

1,4,5 Trichloroanthraquinone
Thirty zone passes were found by Beynon & Saunders (1960) to produce segregation of impurities, one of which, namely 1,4,5,8 tetrachloroanthraquinone, moved in the opposite direction to the zone. The color of the molten zone was found to give a sensitive indication of the presence of impurities.

Vanillin
A melting point of 84.0 C for a zone refined specimen was reported by Wynne (1961); literature values cited were 82 83.50C. Analysis of the sample gave C, 63.16; H, 5.20.

Theoretical: C, 63.15; H, 5.30.

Wax
Various types of wax have been treated; it is reported [Chem. Engr (1959), April 20, 66, 80] that on the industrial scale low melting waxes are improved by alternatively heating and cooling closely spaced pipes so as to cause a number of zones to pass through a bed of material over the pipes.

Hesse & Schildknecht (1956) used a micro zone~melting apparatus to treat a wax obtained from the larva of the butterfly Attacus edwardsii and found that three zone passes were more effective than recrystallization from solvents.

Schildknecht (1961) zone refined the wax of the insect Etiopeltisfestucae and hence showed the presence of hexacosyl hexacosanate.

o Xylene
This hydrocarbon, the approximate melting point of which is 29 C, was treated in a zone refining apparatus enclosed within a space cooled with solid carbon dioxide (Chemistry Research, 1957).

m Xylene
This hydrocarbon was treated in zone melting equipment cooled by solid carbon dioxide (Chemistry Research, 1957).

p Xylene
A sample of p xylene containing 10 per cent of o xylene was treated by nine zone passes. Sije, Pauly & Nouaille (1958) then found by measurements of the freezing point depression that a portion of the sample contained .005 fraction of the o isomer.

Zone Refiner Operation
In zone refining, a short molten zone or zones travel slowly through an elongated sample of a crystalline material. A molten zone traversing a solid sample has two liquid solid interfaces; a melting interface and a freezing interface. At the melting interface the sample is merely melted and mixed with the contents of the molten zone. At the freezing interface, the just-frozen solid is generally higher in purity than the molten zone. Extraordinarily high purification of chemicals can be obtained by repeatedly passing the molten zone or zones through the sample. The impurities are concentrated at the end of the sample, generally in the direction of the movement of the molten zone.

A conventional zone refiner is operated by sealing a sample into a glass tube which is then suspended by a cable/hook and inserted into stationary heating modules (3). As the glass tube containing the sample is moved slowly upward by the mechanism, the heaters melt a zone of sample immediately inside the heater loops. As the sample tube travels a distance equal to the spacing of one heating module the mechanism is reversed and the tube is moved rapidly downward exactly the spacing of one heater module. The primary reason for conventional zone refining being so slow is that the transfer of heat into and out of the sample is very slow. The thermal conductivity of both glass and organic chemicals is relatively low. This limits the speed with which the zone can be moved through the specimen to rates of .1 to 1 cm per hour. Another complicating factor that requires special experimental techniques is that the coefficient of thermal expansion of organic chemicals is about 50 times higher than glass. If the heating is too vigorous or too fast, the glass tube will burst.

Zone Refiner Theory

Pfann discusses the theory of zone refining quite extensively in his book (1). We have developed a short computer program that allows the rapid calculation of zone refiner operation. In the example displayed, a zone rate of 10 cm/hour is selected and the purification profile of an impurity having a distribution coefficient of 0.5 at the 1% level is simulated. Twenty curves are displayed indicating four hours of operation or the passage of 20 molten zones. Each line represents one passage of a molten zone through the sample; the migration of the impurities to one end of the sample is readily apparent. This Zone Refiner Simulator Program helps greatly in understanding the power and limitations of the zone refining technique. This program gives results that are identical to the theory described in Pfanns book. The Zone Refiner Simulator Program runs on Windows operating systems.

The Zone Refiner Simulator Program divides the 10 cm sample length into 1000 increments. As each increment freezes at the face of the moving frozen zone the impurity will invariably have a lower concentration in the crystalline phase than in the liquid phase. This ratio is known as the distribution coefficient. The program adds the amount of impurity frozen out of the solid increment to the total concentration of the impurity in the entire molten zone (the molten zone is 100 increments or 1 cm long). This assumes that stirring in the molten zone is fast relative to the zone movement. As each molten zone passes through the sample the cumulative effect of the melting/freezing process can be easily studied. When the molten zone moves to the end of the sample container, the computer program adds the impurity concentration to the smaller molten zone. This causes the concentration of the impurity to appear to have a discontinuity at a distance of 1 cm from the edge.

Examination of the concentration curves shows why starting with reasonably pure starting material is important if extremely high purity materials is desired. As the impurities accumulate at one end of the sample they tend to limit the purification level possible for at least the last half of the sample.

Bibliography

1. Pfann, William G., Zone Melting, 1958, New York, John Wiley
2. Herington, E.F.G. Zone Melting of Organic Compounds, 1963, London, John Wiley
3. Pahler, L.F. et. al. Zone Refining organic compounds: apparatus modification and procedure, Am Lab 1981, 13(6) 46-8, 50-1
4. Design Scientific Web Site address: http\::www.designscientific.com

Preparing to Operate the MiniZone

Unpacking the Unit

Each complete unit should include:

- Purifier 10 MiniZone Refiner Instrument
- One (1) power cord.
- Purifier 10 Instruction Manual
- Package of assorted Teflon sample tubes
- Please report any missing items.

Retain all packing materials until the instrument is connected and functioning properly. Any unit return, regardless of the reason, must have prior approval by Design Scientific, Inc. All returns should be shipped to the address listed below. To ensure the safe arrival of the unit, we suggest shipping the unit in its original box and packaging or a replacement box and packaging provided by Design Scientific, Inc.

Design Scientific, Inc.

90 Jay-Bob Lane,

Afton Wyoming 83110

Phone: 770/536-6195

E-mail – dsi@silverstar.com

Web Site:

Setting Up the Unit

Choose a location for the unit on a stable bench or table with convenient access to required AC power. Insert the power cord into the receptacle at the rear of the unit and plug into a convenient power outlet. Check for proper operation by turning on the power to the unit using the switch on the back of the unit

Operating the MiniZone Refiner

Verify that the unit is operating properly by dialing in a temperature of 60 C for the melt temperature and 40 C for the freeze temperature. When the unit is operating properly, the small lamps located above the Melt Temperature control and the Freeze Temperature Control will flicker when the operating temperature is reached. If the temperature of the sample block is lower than the temperature set on the control the light will light continuously, indicating that the block is heating up to the operating temperature. If the light is off continuously the temperature of the block is above the set temperature. Also, if the set temperature of the freezing block is more than about five degrees lower than the actual block temperature, a cooling fan will turn on to cool the freeze temperature block.

The tube transport mechanism is moved by a stepping motor. Each pulse or step of the motor moves the transport mechanism (and Teflon Tubing if the sample is inserted) 0.0254 mm (0.001 inch). Verify that the tube transport is operating properly by dialing in 10 cm/hr on the Zone Rate control. You can feel the pulses on the top of the mechanism. At the rate of 10 cm/hr the pulse rate should be a little faster than one per second (1.09 pulse per second)

NOTE: The spring clips that hold the PEEK sample plugs are intended to be loose. DO NOT TIGHTEN THE SCREWS HOLDING THESE CLIPS. If these screws are tightened and the spring clips are not allowed to "float" the tube movement mechanism may bind and improper operation will result.

Tubing Selection

The tubing for the MiniZone is available in the two diameters listed below.

MZLARGE: 4.72 mm ID X 100 mm Long; internal volume = 174.9 microliters per 10 millimeters.

MZMEDIUM: 3.38 mm ID X 100 mm Long; internal volume = 89.7 microliters per 10 millimeters.

Although the tubes are approximately 100 mm long, the maximum active fill length is approximately 82.5 mm.

The amount of sample being purified will determine which tubing size is selected and the number of tubes to be used. A maximum of about 2.89 ml of sample can be refined at one time by completely filling and loading two of the large tubes at one time. A minimum of about 0.179 ml of sample can be purified by filling the smallest tubing about half full (2 cm long fill length).

We do not recommend mixing tube sizes. Purifying more than one kind of a sample at a time is only recommended if the melting points are within 2 or 3 degrees of one another.

Preparing and Loading the Sample

The first step in preparing a sample is to plug the end of the sample tube with one of the PEEK tubing plugs supplied with the unit. (NOTE: PEEK is an inert, high temperature polymer that will not contaminate your sample.) The powdered sample is then poured into the open end of the tube until it is full. Most powders will contract 30% to 50% when the sample is melted. In order to completely fill the sample tube the sample must be melted to remove the air. This can be conveniently done by heating the sample tube with a heat gun or by inserting into the heated blocks of the MiniZone Zone Refiner.

After the sample is melted and the air is removed, allow the sample tube to cool until it is again crystalline. Additional powdered sample can be added to the tube and the melting process repeated until the sample tube is filled with the solid sample.

When the proper amount of sample is loaded into the tubing push another PEEK Tubing plug into the upper end of the sample tube.

Placing the loaded tube in the MiniZone Refiner.

When the sample is loaded and fully crystallized in the sample tube, push the bottom end of the PEEK tube plug into the lower spring clip then push the upper PEEK tube plug into the upper spring clip.

NOTE: The spring clips that hold the PEEK sample plugs are intended to be loose. DO NOT TIGHTEN THE SCREWS HOLDING THESE CLIPS. If these screws are tightened and the spring clips are not allowed to “float” the tube movement mechanism may bind and improper operation will result.

Instrument Settings; Purification of the sample

Next, the instrument settings are adjusted for the sample being purified. The Melt Temperature should be set between 10 and 20 degrees above the melting point of the substance being purified and the Freeze Temperature should be set between 10 and 20 degrees below the melting point of the substance.

The Zone Rate should be initially adjusted to 2-3 cm/hr

The molten and crystalline zones should form as shown in the photograph to the right. The hot zones are formed by the block on the left and the cold zones are formed by the block on the right. The tube will move down at the rate set on the Zone Rate control. After moving about 2 centimeters the mechanism will reverse and the tubes will be moved rapidly up two centimeters.

This operation will make the crystalline zones move up with respect to the tubing. Bubbles of gas will sometimes form as the zone refining proceeds. This is because dissolved gases are also an impurity in a crystal and as the crystallization proceeds, the dissolved gases will be forced out of the crystal lattice. These gases can be removed by gently striking the ends of the tubing with a pencil or similar object to dislodge the gases upward in the molten zone. Eventually the gas bubbles will collect at the top of the tubing.

When the zones have formed as shown in the photograph, the MiniZone can be left to operate unattended. The number of recrystallizations (zone passes) desired is a matter of personal judgment and will depend on the sample being purified. The number of crystallizations per hour for each part of the sample for various zone rates are listed below:

Zone Rate (cm/hr)	Crystallizations per hour
1	.5
2	1
5	2
10	4
20	8

Thus at 2 cm/hour in 18 hours each part of the sample will be recrystallized 18 times. This number of recrystallizations will give a level of purification that is adequate for most purposes.

Removing the sample from the tubing

While the sample is being refined the lower and upper limit of the molten zones should be marked on the outside of the tubing. This can be done using tape or by slightly cutting the tube at the limits of the molten zones.

Turn the unit off or turn the temperature controls down until the sample fully crystallizes in the MiniZone. The two ends of the sample tube are easily confused once the tubes are removed. You may want to permanently mark the tube in some way to avoid confusion.

After the sample is cooled, remove the tube by pulling up on the PEEK end plugs. Remove these plugs and save them for future use.

The sample can be recovered from the tubing by cutting sections of the tubing with a sharp knife, scalpel or scissors. The sample may be removed from each section by dissolving in a suitable solvent, melting the sample or by physically pushing the solid sample from the tubing. The purest sample will be adjacent to the lower molten zone limit mark. The sample purity will be slightly less pure as the samples are cut from the tubing until the final cut just before the upper mark. This zone will contain most of the impurities.

Troubleshooting

For assistance in troubleshooting your Purifier 10 Zone Refiner, consult the troubleshooting guide below. However, if you are unable to resolve the problem, call Design Scientific for assistance.

Troubleshooting Guide

- Problem
- Possible Cause
- Solution

Purifier 10 does not have power.

- Power switch located on back of unit is turned off, fuse is blown or power cable is loose
- Turn unit on, check fuse or push power cable into socket

The entire sample remains molten.

- Freeze and/or Melt Temperature setting is too high.
- Decrease the Freeze or Melt Temperature until sample begins to crystallize

The entire sample remains crystallized

- Freeze and or Melt Temperature setting is too low
- Increase the freeze or melt temperature until the sample begins to melt

Sample remains molten and the freeze temperature is below the melting point.

- Seed crystals are not contacting the lower part of the sample.
- Insert seed crystals in the lower part of the sample tubing below the heated zones.

Sample forms bubbles that block the crystallization

- Out gassing of the sample when crystallization occurs
- Vibrate the sample tube to dislodge the bubbles to the upper part of the tube

Sample darkens during the zone refining process

- Decomposition of the sample is occurring
- Sample is not stable at the melting point–not suitable for zone refining.

Purifier 10 Limited Warranty

In addition to other manufacturers' warranties, Design Scientific Inc. ("the Company") warrants all products delivered to and retained by their original purchasers to be free from defect in material and workmanship for one year from the date of the Company's invoice to the purchaser. For a period of one year from the date of such invoice, the Company will correct, either by repair or replacement at the Company's sole election, any defect in material or workmanship without charge for parts and labor. This does not include defects due to misuse, abuse, abnormal conditions or operation, accidents, or to service or modification to the unit without prior authorization of the Company. The determination of whether any product has been subject to misuse or abuse will be made solely by the Company.

The Company shall not be liable for any special, incidental, or consequential damages, or any damage to plant, personnel, equipment or products, directly or indirectly resulting from the use or misuse of any product sold by the Company except as set forth in and limited by the foregoing warranties. Representations and warranties made by any person, including dealers and representatives of the Company, which are inconsistent, in conflict with, or in excess of the terms of this warranty shall not be binding upon the Company unless placed in writing and approved by an officer of the Company.

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