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Column Crystallization with a Pulsating Spiral and Micro Column Crystallization*

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Summary

Column crystallization uses several theoretical plates through a countercurrent process of crystals and melt which are transported in a temperature gradient by a rotating spiral. An improved thermocouple-equipped 250-ml column type with rotating and oscillating spiral is described as are experiments to determine the HETP and the separation efficiency at different throughput rates (mixed crystals forming system, azobenzene/stilbene, and ϵ-caprolactam). A semitechnical pilot column of 10 cm diameter contains "counterwindings" at the lower end of the spiral as another method of improving the separation effect. Micro column crystallization with quickly rotating threaded pins instead of small spirals extends the method to the milligram range and reduces the separation time to ca. 1/100 of conventional column crystallization and 1/10,000 of zone melting.

The main problem in the purification of substances by crystallization from their own melt is the complete separation of crystals and mother liquor. Even high pressure is often not completely efficient in removing the liquid film which contaminates the crystal from the solid surface. However, it is possible to obtain materials of high purity by means of a countercurrent crystallization method which uses several theoretical plates. Column crystallization, which we have often described, employs such a countercurrent process (*1–6*).

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The column consists basically of two concentric tubes with a metal spiral rotating in the annular space between the tubes. Crystals are formed by removing heat from the top of the column. The crystals are transported down the column by the action of the spiral. Remelting of the crystals at the bottom of the column provides liquid for countercurrent contact with the descending crystals. The countercurrent part of the column is insulated to provide adiabatic conditions.

Many substances form agglomerates of crystals and cause blockage in the column. However, experiments reveal that these blockages can be avoided by an oscillatory motion of the rotating spiral (*7*). Thus, significant purification and separation are rapidly attained. In order to produce large amounts of high purity materials, the column crystallizer may be operated with continuous flow (Fig. 1).

Fundamental investigations have been made by using a column for the crystallization of high melting materials, as described in 1966 (*7*). Figure 2 shows an improved type with interchangeable glass tubes and thermocouples in the inner steel tube to indicate separation progress.

Various experiments showed the operating conditions necessary to attain and reproduce the best separation while maintaining the general working safety of the unit.

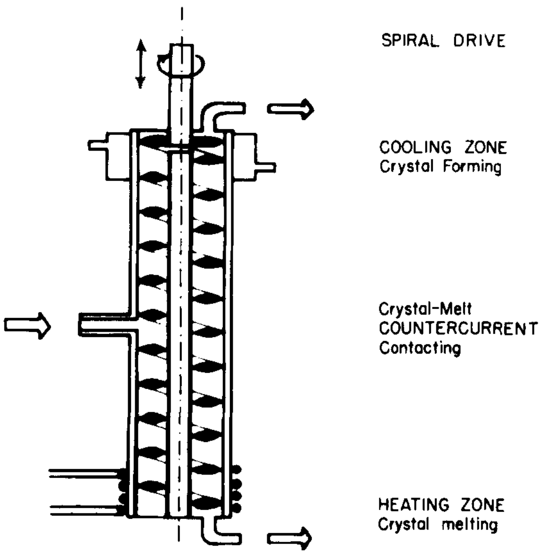

FIG. 1. Scheme of a continuous-flow column crystallizer with pulsation.

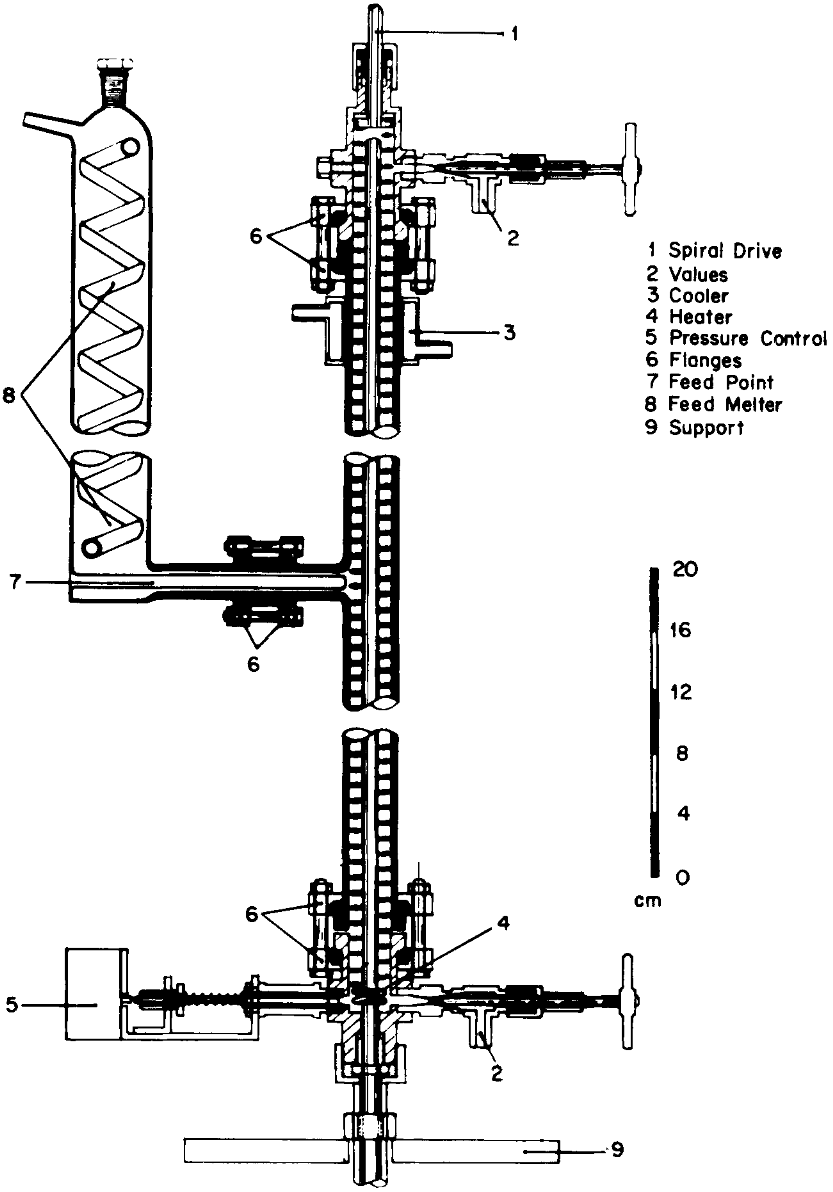

FIG. 2. Continuous-flow column crystallizer with pulsating and rotating spiral.

We observed good separation at relatively high rotational speeds of the spiral (i.e., 70 to 80 rpm) with medium amplitudes (such as 3 to 6 mm) and medium to high frequencies (i.e., 180 to 330 vibrations/min). A high density of the crystal melt mixture is desirable to force as much of the liquid from the crystals as possible; this effect is also promoted by pulsation of the spiral.

In our experiments we used a 1:1 mixture of azobenzene and stilbene, for these two substances form solid solutions in every range of concentration. In this case the concentration gradient could be detected visually, especially when the contents of the column were allowed to cool after column crystallization.

If samples are taken at various positions along the column and their compositions determined by measuring their uv absorptions or their melting points, quantitative information about the separatory effect achieved can be obtained.

The temperature-concentration diagram of the azobenzene–stilbene system was known to us; so we could construct a McCabe-Thiele diagram such as is used in the analysis of distillation processes. By using composition values determined at the top and the bottom of the column, we obtained the number of theoretical plates. Figure 3 illustrates both the number of theoretical plates and the concentration gradient in the column.

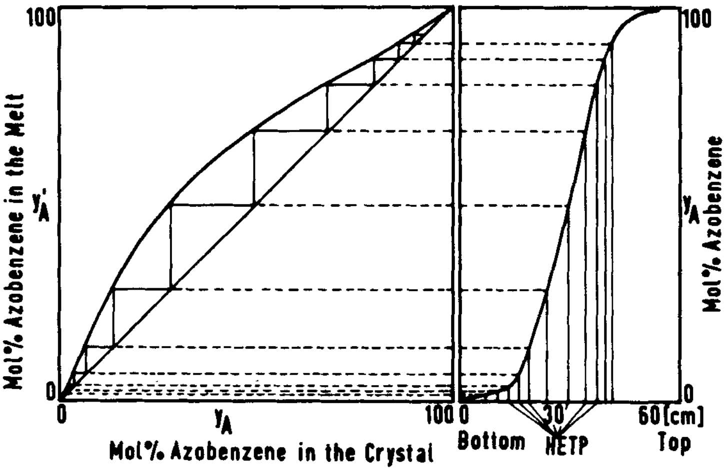

FIG. 3. Number of theoretical plates and concentration gradient in the crystallization column.

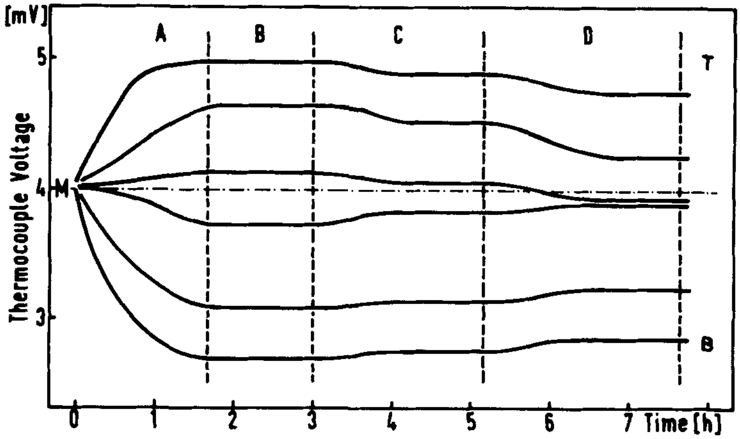

FIG. 4. Temperature in a column crystallizer at the start of the separation *process and with increasing throughput of substance.* B = *bottom* of column. T = top of column.

The S-form of the experimentally found concentration curve satisfies the requirement of the McCabe-Thiele diagram. It can also be seen that almost pure azobenzene is found at the top of the column and almost pure stilbene at the bottom. The number of theoretical plates is 15; at a column length of 70 cm there is a value of 4.7 cm for HETP (height equivalent to a theoretical plate).

The greatest advantage of column crystallization is that it can be used as a continuous process. It seemed interesting to observe the behavior of the column when increasing amounts of a 1:1 mixture of azobenzene–stilbene were separated in a continuous-flow process.

The theory of rectification demands a decrease of purity of the products when the throughput is increased. Figure 4 illustrates the course of the crystal melt temperature in the column, as detected by the inner thermocouples, at various rates of throughput. Section A shows how the temperatures spread along the column until at total reflux a steady state is reached in Section B. Sections C and D illustrate how the separation becomes poorer when larger amounts of substance are put through the column. Because of the larger amounts of other compound, the melting temperatures of the top and bottom fractions approach the temperature of the original mixture. The temperature curves O, I, II, and III in Fig. 5 correspond to concentration gradients in the column at various throughputs.

At increasing throughput the concentration gradient becomes flatter;

there exist uniform variations of temperature and concentration along the column. This fact is also shown in the McCabe-Thiele diagram, so we can describe column crystallization as analogous to distillation. Quantitative data are given in Table 1.

TABLE 1

Theoretical Stages of a Column at Various Throughputs of a Azobenzene/Stilbene Mixture (50/50); Heat of Fusion Considered

Throughput [g/h]	0	92	132	151
Reflux Ratio x = R/P	∞	21	15	13
Mol% Azobenzene	0.4 → 97.5	1.0 → 97.2	1.3 → 96.2	8.8 → 96.1
Theoretical Stages n	15	14	13.5	10

Comparison of the throughput and purity results in the table shows there is good separation up to a throughput of about 130 g/hr. For a column of 250 g capacity, 130 g of throughput means a good separation efficiency. We have determined the unit amount of reflux to be 5.4

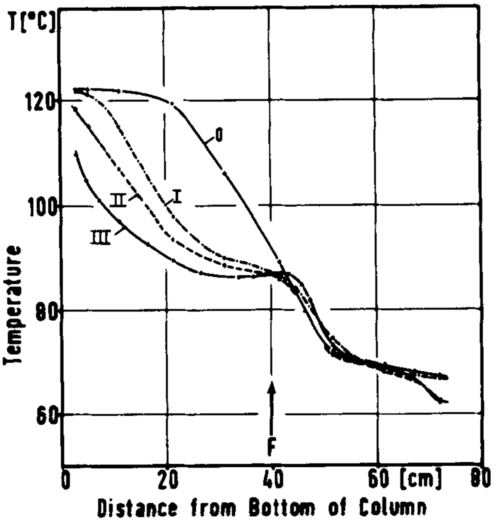

FIG. 5. Temperature gradients at various throughputs. F = feed point.

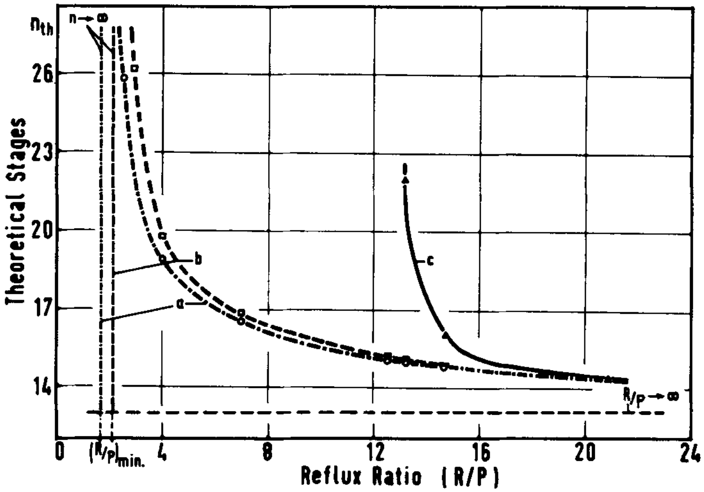

FIG. 6. Dependence of the number of theoretical plates on the reflux ratio for the separation of a 50/50 mixture of azobenzene and stilbene into fractions with 97.15% and 1.0% azobenzene.

moles/hr, i.e., about 1000 g; this value yields the ratio of reflux to product which is necessary to obtain the number of theoretical plates under conditions of continuous flow.

We can graphically determine the relationship between the ratio of reflux to product and the number of theoretical plates for a separation problem (Fig. 6).

Curves *a* and *b* illustrate the relationship which depends only on the material system, whereas Curve *c* shows the dependence which exists in practice in the column crystallizer described. That is, below a reflux ratio of about 15 or at a throughput rate of more than 130 g/hr, too many theoretical plates would be necessary to give the desired result. At this point the critical load of the column is reached. We have also found a value of 130 to 150 g/hr with other systems.

The investigations described served to determine both the behavior of the column during continuous flow and its load limit. It was then important to purify technical substances in good yield and high purity, and to prove their purity by appropriate methods.

To produce pure azobenzene for the testing mixture, we column crystallized azobenzene with a melting range of 65 to 68.8°C. At first we used a discontinuous method, but most azobenzene was purified in a continuous manner. The latter method is not only more convenient, but it also delivers materials of higher purity at the same throughput.

With nearly the same throughput and a fraction ratio of three parts of pure material to two parts of impurities, we obtain very pure azobenzene with a melting range of 68.6 to 68.9°C. Improvement of the yield at the same purity may be obtained by diminishing the throughput to 80 g/hr. However, by yielding a product with slightly more impurities, we can operate the column at high throughput and a feed ratio of 3:1.

By means of improved thermal analysis, we determined the total impurity of the best product to be 0.145%; another sample, which had been twice purified by zone melting with 25 zone passes, yielded a value of 0.134%. The fairly high impurity values probably result from self-decomposition of the azobenzene. But note that there is almost no difference in the purities obtained by column crystallization and zone melting. The economy of time is 100:1. The greatest advantage of column crystallization compared with zone melting is its use in continuous flow, which yields large amounts of pure compounds in short periods of time.

Caprolactam was also purified in a continuous process by column crystallization. The quality control for caprolactam is normally by the determination of its permanganate number. The permanganate number of our starting material was 2800. This value increased for the purest fraction collected at a throughput of 100 g/hr to the upper limit of 8000. Titration of the volatile bases and thermal analysis of the bottom fractions showed that the impurities had been decreased by a factor of ten. The purification factor was raised to 20 by reducing the rate to 60 g/hr, this product could not longer be improved even by zone melting.

In Fig. 7 the impurity content detected by gas chromatography before and after column crystallization are compared. All compounds in the starting material S have been enriched in the top fraction F_T and have disappeared from the bottom fraction F_B. The comprehension limit of the curve is below 10^{-4}, which means that the column-crystallized caprolactam is 99.99% pure, at least with respect to vaporizable compounds.

Consequently the pulsed column is to be preferred because it works without trouble. However, pulsing of the spiral in a larger scale is much more complicated and it seems better to pulse the crystal melt mixture by means of a vibrator or a pump outside the column. Nevertheless, we could enlarge the discussed type ten times by using "counter-windings" (semitechnical scale pilot column, Fig. 8).

The column consists of two concentric tubes of stainless steel and

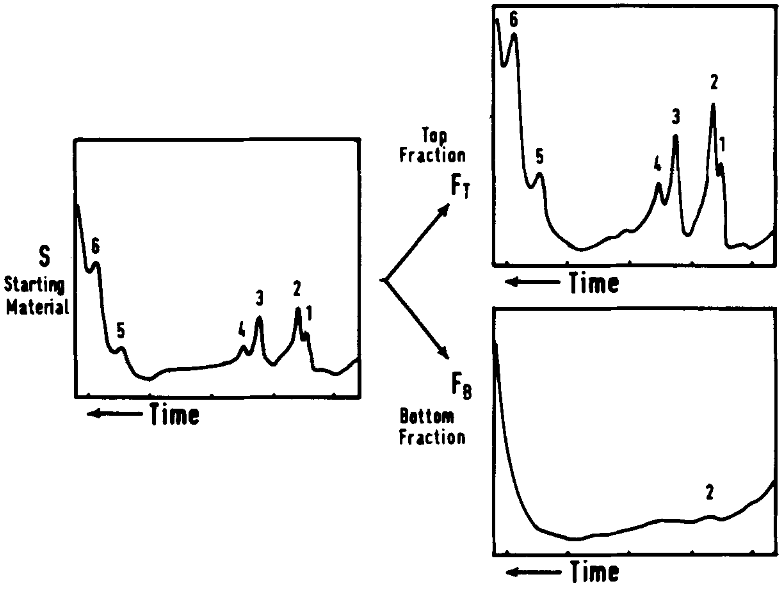

FIG. 7. Gas chromatograms of column crystallized caprolactam.

a spiral of 33 windings of the same material with lens-shaped profile. The feeding and the output of the lower melting top fraction and higher melting bottom fraction are controlled by needle valves which are connected with heatable tubings. The spiral is driven by a motor, which can be regulated between 25 and 125 rpm; with 30–60 rpm the preferred speed. In order to obtain good separation effects it is necessary to have a crystal melt mixture with a large amount of crystals, especially at the bottom of the column. On the other hand, this dense crystal melt mixture at the bottom presses the spiral upward and therefore the control of both the spiral position and the heat supply becomes difficult. The column of Fig. 8 overcomes these problems by means of "counterwindings." One or two windings in the counter-direction are welded at the end of the spiral. During operation of the column the crystals are normally transported down until they are stopped at the blind end. Below this point crystals are transported upward to the blind end. In this way a plug of crystals is formed which is melted slightly by the main heating. This device is fairly insensitive to irregularities in the column and places no pressure on the drive axis. It is important to take the bottom fraction at the blind end. An additional final outlet is situated below this point.

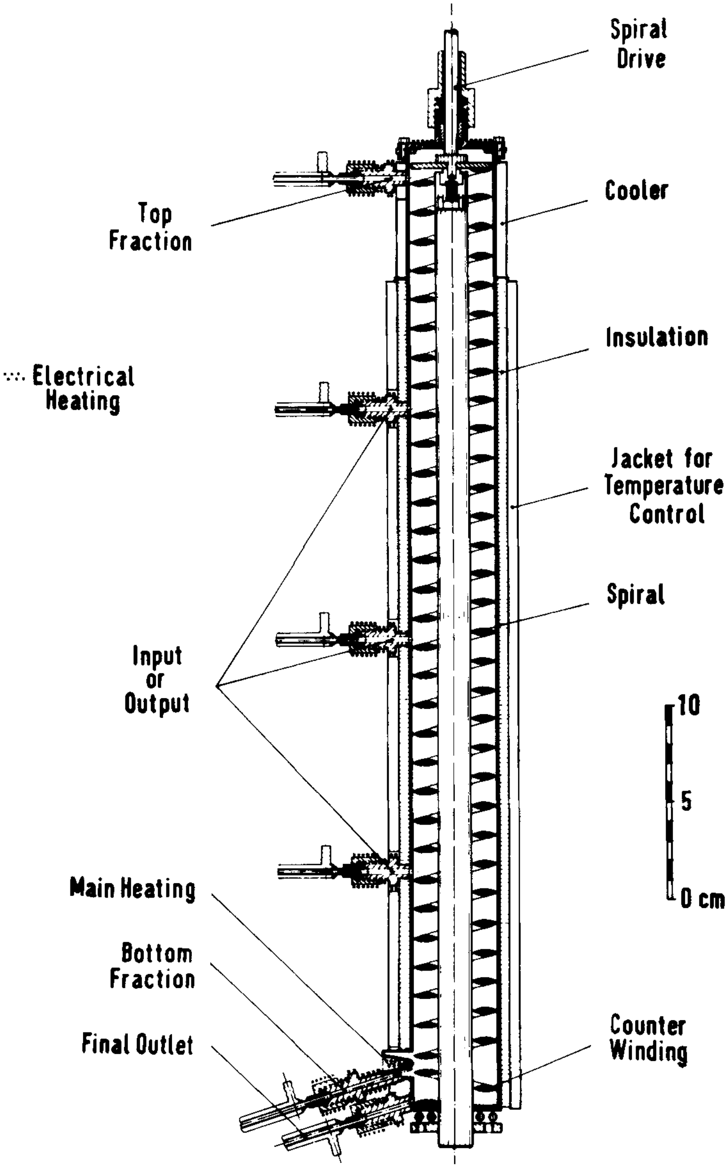

FIG. 8. Semitechnical scale column crystallizer.

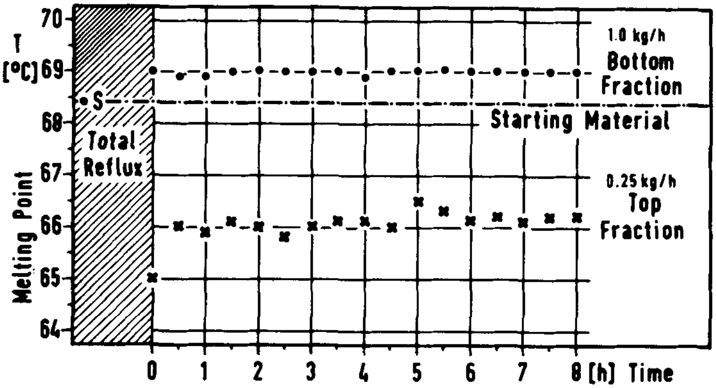

FIG. 9. Continuous column crystallization of ε-caprolactam; 60 rpm; melting points determined by Mettler FP1 apparatus.

According to the rule of thumb that the throughput through a good working column crystallizer with a spiral is nearly half its whole volume per hour, this column produces 1 to 1½ kg product per hour. We have tested the column in order to purify sea-water with a 3.5% NaCl solution. In a steady state this resulted in a drinkable water with 0.2% NaCl and a concentrate with 14% NaCl. We could produce 1 liter of water per hour with 0.5% NaCl for 10 hr and more. Due to the expansion of water upon freezing, a steel column instead of glass tubing is required.

Caprolactam with a melting point of 69°C is an excellent compound for column crystallization (cf. the gas chromatograms in Fig. 7, which demonstrate the purity of caprolactam taken from the pulsed column). Starting with a technical product, we could produce 1 kg/hr of pure white substance and 0.25 kg/hr of a brown impure concentrate with the semitechnical scale type. Figure 9, for example, gives the melting points of the top and bottom fractions from a continuous flow 8-hr experiment as determined by the automatic melting point apparatus, Mettler FP1.

In even larger dimensions this method could be interesting for industrial purposes. The next step is a column 2 m long with a diameter of 10 cm. This column with flanged glass and steel tubes, produces about 5 kg of substance per hour and allows studies of crystal transportation at greater dimensions.

Immediately after the first investigations in column crystallization, we tried to substitute micro zone melting by employing the 100-times faster column crystallization. An apparatus which operates down to a limit of 100 mg, and dated 1959, is shown in Fig. 10. It has the common arrangement: outer glass tube, spiral, and a steel wire as the inner tube. However, in these dimensions the spiral is very unstable and working with it is very complicated (*2*). A unit made from a spiral and steel wire to form a threaded pin is much more stable and only a small quantity of substance is required to fill the thread. From many experiments, it was known that screw conveyers are not good transportation elements in column crystallization, but surprisingly we obtained an excellent separation effect in micro dimensions.

The separation of colorless stilbene from the mixed crystals system azobenzene/stilbene was apparent 10 sec after the formation of the first crystals and was completed after 20 sec (*8*). The method works *100 times* faster than conventional column crystallization and *10,000 times* faster than conventional zone melting! This effect depends on a high speed of the threaded pin (between 500 and 2000 rpm), on a small depth of the thread (between 0.1 and 1 mm), and on a great difference between the melting point of the substance and temperature

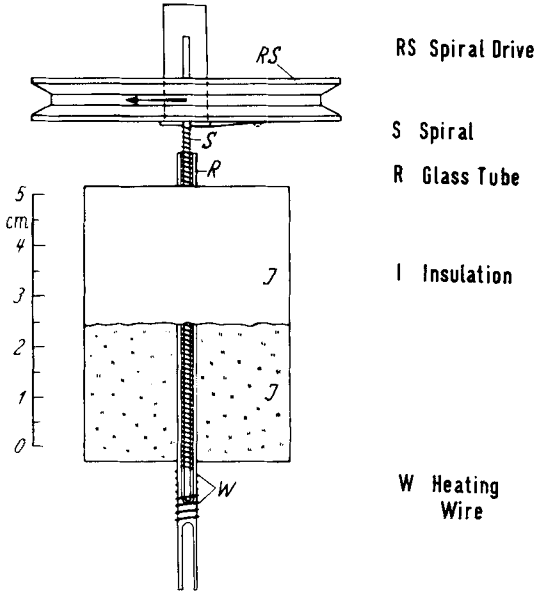

FIG. 10. Scheme of a micro column crystallizer with a spiral of thin steel wire (*2*).

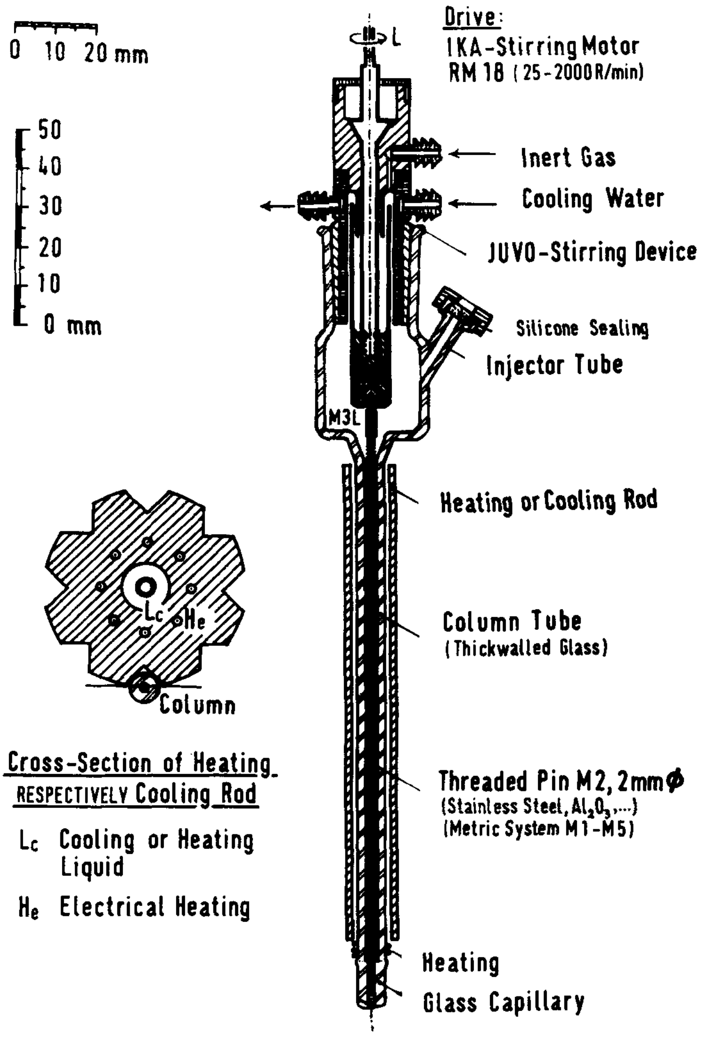

FIG. 11. Micro column crystallization with threaded pin under inert gas.

of the column wall. In our opinion, crystallization at the wall of the column, a large crystal-to-melt ratio, a very high pressure, and the sudden removal of the melt during crystallization by the high speed of the thread pin are the most important factors.

Micro column crystallization is not only a very quick but also a very simple method to purify small amounts of substances (between a few milligrams and several grams). Threaded pins with an outer diameter of 1 to 5 mm, thickwalled glass tubing (which is connected to a rod or to a glass capillary as an outlet for air during filling), a motor, and sometimes regulated electrical heating at the bottom of the column are needed (*8*). In contrast to conventional column crystallization, the temperature of the column wall can vary over a large range. Of course, cooling is necessary for liquids. It is possible to work with sensitive substances under inert gas with the apparatus shown in Fig. 11. After separation is achieved, the substance drains into the warmed capillary without being mixed. The cold capillary tube can be divided like a zone melting ingot.

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