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Apparatus for Laboratory Batch Distillation

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In the course of work on liquid furan compounds, mixtures, in volumes of 2—200 ml, containing 2—5 components were regularly obtained. These mixtures were separated by distillation into their components in a reasonably pure state (97—99 %) by using one of the four setups described in this article. Two of the setups are for simple distillation, of small and of large charges respectively, and two are for fractional distillation. Since it may be inferred from observations by Rossini, Mair and Streif [1] that most organic compounds decompose too rapidly above 200° C to make prolonged fractionation possible, the setups for fractional distillation are only intended for distillation temperatures up to 200° C.

A. SETUPS FOR SIMPLE DISTILLATION

Mixtures of components boiling more than 100° C apart were separated by using one of the Claisen-type setups shown in Figs. 1 and 2. In both stills the tube leading from the still pot to the condenser has a rather large inner diameter so that the stills can be used for distillations at pressures down to 0.1 mm. During the past five years more than one thousand distillations have been carried out by us in one or the other of these setups, including all simple distillations reported in earlier publications on furan compounds [2] from this laboratory.

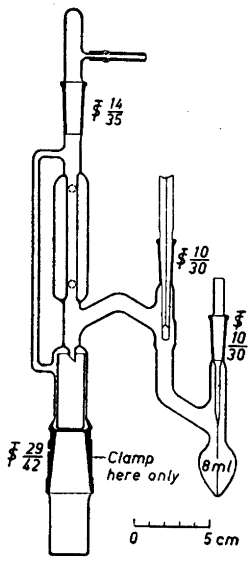

Fig. 1. Setup for simple distillation of 0.5—6.0 ml.

B. SETUP INCLUDING A 5 CM COLUMN

Components boiling 30—100° C apart were separated by fractional distillation using the setup shown in Fig. 3, consisting of a Widmer-type column and a fraction collector for four flasks holding 8, 8, 32 and 125 ml, respectively. The column is packed with 1/16-in. Dixon gauze rings [3] or with 1/8-in. glass helices. The efficiency of the column may be roughly regulated, partly by regulation of the boilup rate, and partly by

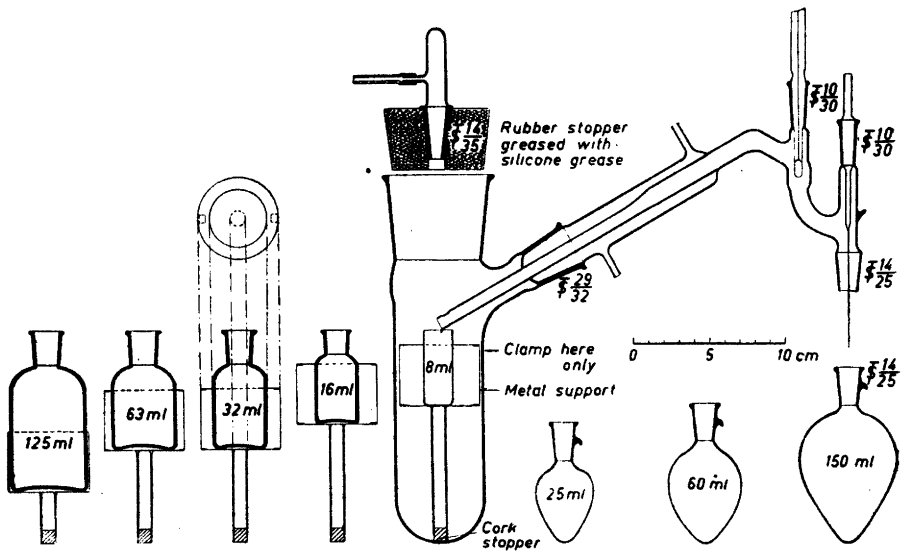

Fig. 2. Setup for simple distillation of 5—120 ml.

regulation of the reflux ratio by cooling (with a stream of air) or insulating (with a cloth) the vertical air condenser at the top of the column.

With this setup, which also has been in regular use for five years, all previously published distillations [2], where the use of a 5 cm column was reported, were carried out.

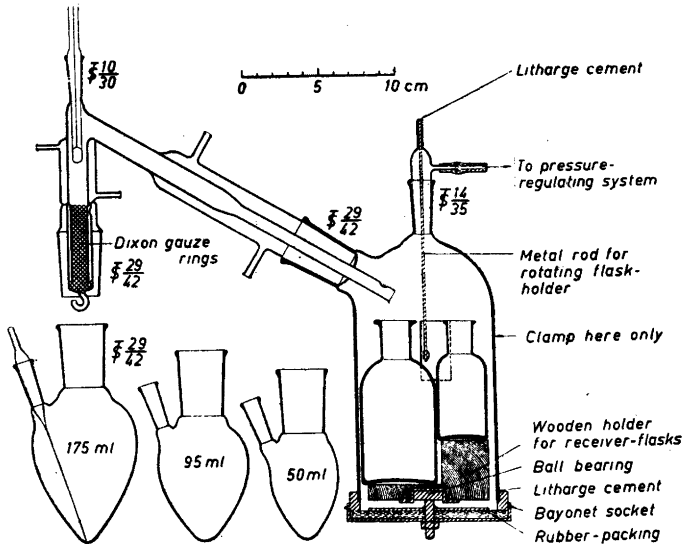

Fig. 3. Setup including a 5 cm Widmer-type column.

C. SETUP INCLUDING LARGER COLUMNS

Mixtures of components boiling 3—30° C apart were separated by using a new type of particularly well insulated stills. The distilland in the still pot is heated by an internal heater, and the efficient insulation makes it possible to carry out an entire distillation without changing the heat input. The stills are connected with a pressure-regulating system and an automatic fraction collector, so that the whole setup becomes automatic and needs no attendance by the operator.

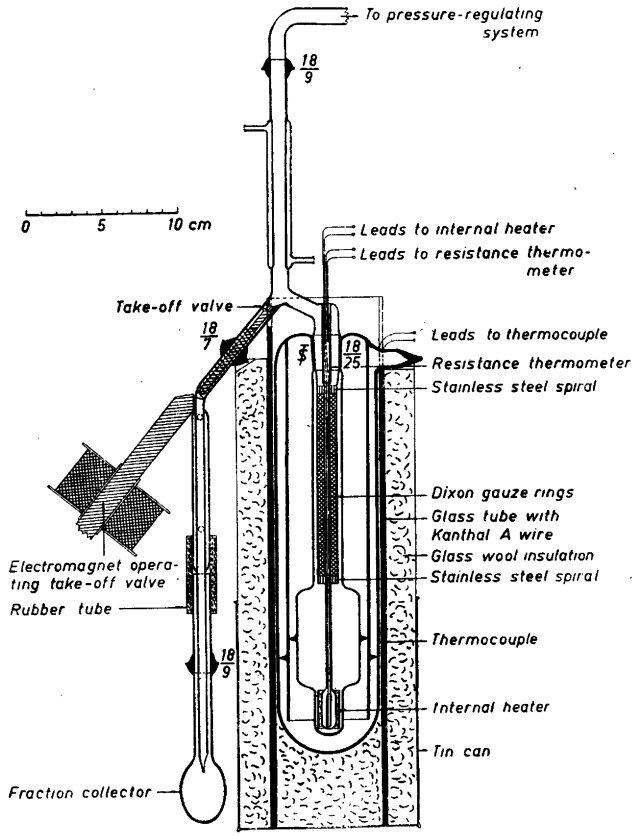

Fig. 4. Still including a 12 cm column.

The stills

Three stills of similar design but of different sizes were found sufficient to meet all our requirements. The dimensions of the stills are summarized below.

Still No.	Rectifying section		Volume of cylindrical part of still pot ml	Maximum charge of still pot ml
	Area cm²	Length cm		
I	0.97	12	70	60
II	0.97	25	140	120
III	0.97	50	280	240

A detailed drawing of the smallest still (I) is shown in Fig. 4. In the following the construction and use of the different parts are described.

The still pot, the wall of which is a vacuum jacket with four silvered surfaces, is constructed of the thinnest possible pyrex glass. The pot, which with its long neck also insulates the rectifying section of the still, thus has a small heat capacity but is at the same time efficiently insulated. It will be seen that all parts of the still pot inside of the outer wall of the vacuum jacket are sealed to the outer wall only at their upper end, *so that stills of any length may be constructed without risk of breakage due to expansion.*

The silvering and sealing of the vacuum jacket were carried out after the directions of Barr and Anhorn [4]. Prior to sealing, the jacket was evacuated with a mercury vapor pump (single stage jet pump T/Sl/626 from *The Thermal Syndicate Ltd.*, Wallsend, Northumberland, England) to 1.0×10^{-6} mm and baked, by wrapping with electrical glass-cloth heating tape, at about 400° C under this pressure for 24 hours.

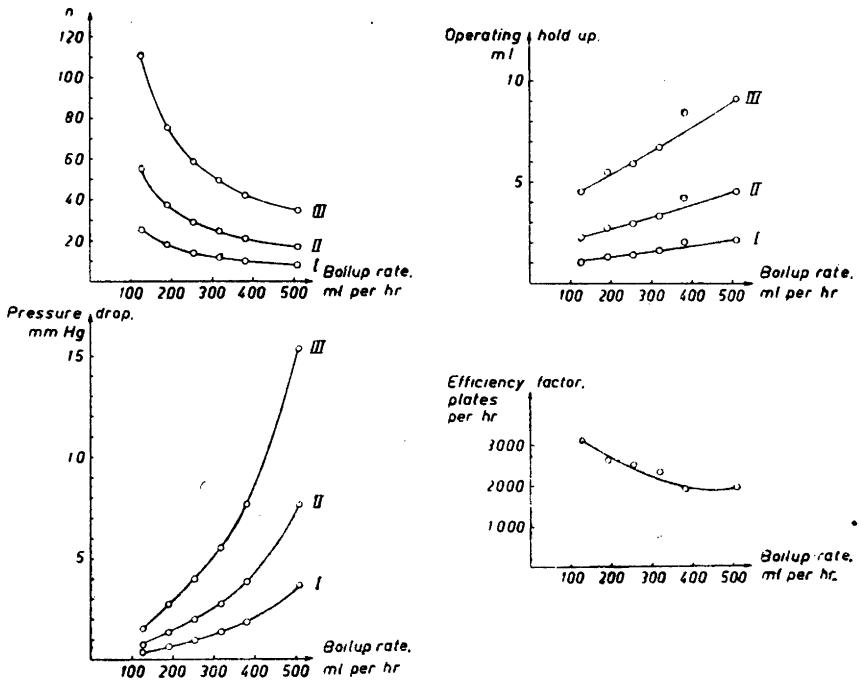

Fig. 5. Performance data for columns I—III.

The rectifying section (the column) consists of a 12 mm (ID) tube packed with 1/16-in. Dixon gauze rings. A 4.5 mm (OD) tube supporting the internal heater runs concentrically through the column. Two spirals of stainless steel keep the packing in place. It is a simple matter to change the packing as well as the spirals, if they should become corroded.

Taking into account all important factors characterizing a column packing, *viz.* the efficiency factor, the H.E.T.P., the pressure drop and the ease of manipulation, Dixon's packing is in our opinion the best reported. Dixon tested his packing with a mixture of 20 parts by volume of *n*-heptane and 80 parts of methyl*cyclo*hexane under atmospheric pressure (2,2,4-trimethylpentane was used in the holdup experiments). Performance data for our columns, calculated from Dixon's data [5], are shown in Fig. 5.

The internal heater is filled with a silicone oil (DC 550 from *Dow Corning Corporation*, Midland, Michigan, U.S.A.) in which a small heating coil of kanthal A wire (0.15 mm, 70 ohm, maximum load 70 watt) wound on a porcelain tube is placed. The two leads to the coil, one of which is insulated by a thin-walled capillary glass tube, are of silver wire (0.7 mm). The coil is fed from a *variable transformer* connected with the network through a *constant voltage device*. The heat input may vary from 2—8 watt, for distillations under 10—20 mm, to 12—50 watt for distillations under atmospheric pressure.

The internal heater is surrounded by a slightly larger glass tube which is pressed over a layer of loosely packed glass wool. This arrangement efficiently prevents bumping under all distillation conditions. The glass wool is usually renewed after each distillation. If the heat input is large, say above 10—25 watt, the glass wool layer is no longer necessary and should be omitted to avoid thermal destruction of the distilland.

The tube supporting the internal heater widens out immediately above the column packing to make place for the small *resistance thermometer (cf.* Willingham and Rossini [6]) (100 ohm, 3 × 30 mm from *Degussa Hanau*, Hanau, Germany), which registers the distillation temperature continuously by means of a *recorder*. Changes of 0.1° C can be read on the chart. The leads to the thermometer are insulated by capillary glass tubes.

The distillate is taken off intermittently from the still head into the take-off line through a 2—3 mm hole. The *take-off valve* consists of a spring, a 4-in. nail shortened to about 7 cm and a 5/32-in. steel ball, which fits into the spherically ground outer opening of the take-off hole. At the upper end of the tube leading from the still head to the fraction collector a spherical ground joint is interspaced, enabling the metallic parts of the take-off valve to be put in place. No special care was taken to protect these metallic parts against corrosion, since they all are cheap and easily replaceable, but they may well be coated with teflon. The valve is opened intermittently for about one second at a time, which is sufficient to allow the small volume of liquid (about 0.1 ml) accumulated above the steel ball to run off.

The strong *electromagnet* operating the valve is activated by an *electrical timer*, which was chosen in preference to a clockwork because of the ease with which the time interval between two activations can be adjusted. With a take-off of 0.1 ml per activation, time intervals of 10 seconds (minimum interval) and of 30 minutes (maximum interval) correspond to product rates of 36 and 0.2 ml per hour, respectively. When a pure compound is distilled at constant boilup rate and a fixed setting of the timer, the product rate remains constant within 3 %.

The electrical heating mantle insulating the still pot consists of a glass tube wound with kanthal A wire (0.40 mm, 500 ohm) and insulated by 20 mm thick tubing of glass wool, the lower end of which is fitted snugly into a tin can, so that the still can stand on a platform without support. The glass tube extends at the upper end about 35 mm above the glass wool insulation and is slotted here to receive the take-off line and the seal-off tube of the vacuum jacket of the still pot (*cf.* Todd [7]). The extension is used to support a 25 mm broad electrical glass cloth *heating tape* (250 ohm, length 40 cm) not shown in Fig. 4, which is wound loosely around the lower part of the still head and the outer surface of the glass tube. The upper end of the glass tube is then covered by an asbestos plate. The heating tape and the asbestos plate serve to insulate the lower part of the still head, so that the distillate reaches the take-off hole even at minimum boilup rate (about 20 ml/hour). The heating tape and the heating mantle surrounding the still pot are connected in series, both being fed from a *variable transformer*. At a distillation temperature of 150° C, the effect of the tape is about 13 watt and of the mantle about 26 watt.

The temperature between the still pot and the inner surface of the glass tube is measured by means of a *thermocouple*. If the temperature is adjusted to the boiling point of the distillate at the beginning of a distillation, there will be practically no heat exchange between the still pot and its surroundings. If, at the end of the distillation, the distillation temperature has risen 30° C, a certain amount of heat will be lost from the still pot. Judging from crude measurements of heat losses at larger temperature differences, we believe that this loss does not exceed 0.4 watt. Since the lowest boilup rate used in these stills corresponds to a heat input of 2.0 watt, the maximum decrease in boilup rate during a distillation is 20 %. This is an extreme case, and in general the decrease is only 1—10 %. It follows that the insulation of the still is such that, provided the compounds to be separated have approximately the same heat of evaporation, no increase of the heat input of either the outer heating or of the internal heater is necessary to keep the boilup rate almost constant during an entire distillation. This is also true of the two larger stills, which, while having a larger heated surface, at the same time have a smaller rise in distillation temperature during a distillation (maximally about 15° C and 7° C, respectively).

The pressure-regulating system

At the top of the reflux condenser the stills are connected by means of a spherical ground joint with a 10 mm (ID) glass tube leading through a cooling trap to the pressure-regulating system. Two branches of the tube carry vacuum rubber tube connections to the fraction collector and to a manometer showing the distillation pressure. The pressure-regulating system, which is situated in an air thermostat (accuracy ± 1° C), consists of a 10 l flask, serving as surge tank, and a sintered glass disk manostate of new design (Fig. 6). The manostate is tilted about 45° during evacuation and reverted into vertical position when the desired pressure has been reached. The low pressure side of the manostate is connected with an oil pump, which is stopped automatically at 1—2 mm. During a distillation under 10—20 mm the pump operates less than one per cent of the time (*cf.* Cox [8]).

In order to evacuate the system rapidly it is convenient to by-pass the manostate by a tube leading directly from the oil pump to the surge tank. To make sure that the by-pass tube can be efficiently interrupted, an ordinary stopcock as well as a three-way stopcock is inserted, so that the tubing between the stopcocks can be opened to the atmosphere. At the same time the three-way stopcock serves to let air into the system after a distillation.

The vacuum rubber tubing used for the by-pass tube has an inner diameter of 5 mm. All other rubber tube connections are made of thinner tubing (2 mm ID, 6 mm OD), fitting 4 mm (OD) glass tubes.

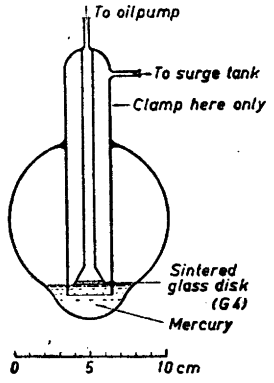

Fig. 6. Sintered glass disk manostate.

The above pressure-regulating system keeps the pressure constant within 0.3% (or better) at any pressure between 10 mm and atmospheric pressure. In particular there is no drifting of the pressure over long periods of time.

The fraction collector

The fraction collector is automatic and can collect 48 fractions during a single distillation, so that distillation curves based on other properties than the boiling point may be drawn. The collector is shown in Fig. 7. The distillate, coming from the tube leading to the take-off valve, drops directly into the small receiver tubes, in which it later is to be stored. At intervals the three solenoids (1—3) are energized in rapid succession by a system of relays accentuated by an electrical clockwork, allowing a new fraction to be collected.

The clockwork, which was chosen in preference to other timing devices because of its ability to accurately reproduce long time intervals, is adjustable to intervals from 5 minutes to 24 hours.

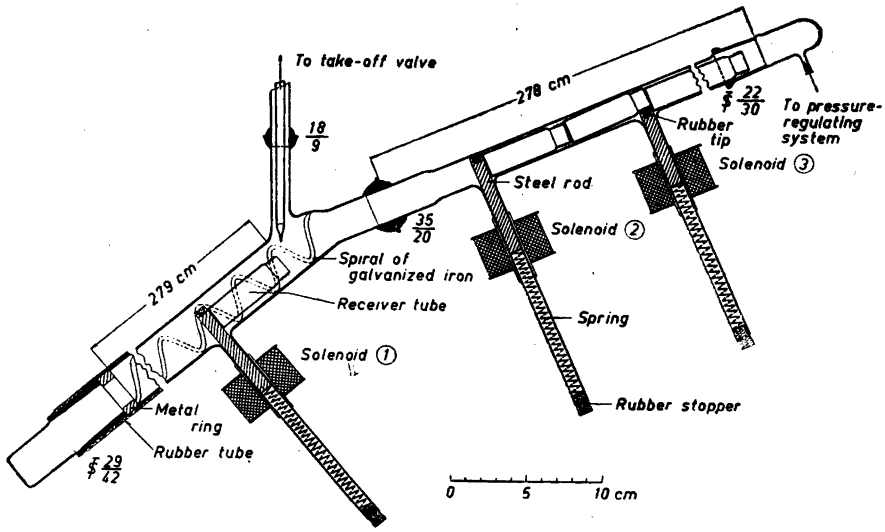

Fig. 7. Automatic fraction collector.

The spiral of galvanized iron wire (3.0 mm) in the lower end of the collector makes the filled receiver tubes fall smoothly. The tubes hold 8—9 ml when filled to the neck, but should only contain a maximum of 5—6 ml in order to prevent the distillate from splashing over during the fall. The filled tubes stand on top of each other, thus minimizing distillation from one tube to another.

An electrical fan is placed directly in front of the take-off tube in order to prevent warmth from the still from heating the middle section of the collector.

The volume of the collector is about 2 liter. Since the volume of the surge tank of the pressure-regulating system is 10 liter, sudden fluctuations in room temperature of ± 5° C will only cause the distillation pressure to change ± 0.3 %, corresponding to a change in boiling point of ± 0.1° C.

Assembly and operation

Assembling the setup presents no special problems. All rubber to glass connections are greased with Dow Corning Silicone Stopcock Grease as are the conical ground joints at both ends of the fraction collector and the large spherical joint in the middle. The conical joint connecting the still head and the column with the still pot is greased with Dow Corning Silicone High Vacuum Grease. The two spherical joints on the take-off line and the one at the top of the still head are greased with Cello-Grease No. 14—637 (*Fisher Scientific Company*, New York, U.S.A.).

When the fraction collector is charged with receiver tubes, all openings should be closed, so that the falling tubes are checked by the air.

Starting a distillation is rapid and simple. After charging, the system is evacuated to the distillation pressure and the outer heating adjusted roughly to the distillation temperature. The column is flooded and the input to the internal heater then reduced to give the desired boilup rate. The boilup rate may be calculated accurately from the heat of evaporation of the distilland, but it will usually be sufficient to reckon 1 watt equivalent to 10 ml per hour.

After equilibrium is reached, the take-off begins. If there is a small fore-run, the take-off may usually be started shortly after the flooding, in particular when the smallest

still is used. We have often started charging the small still for a distillation under 10—20 mm just before closing time and left it distilling without attention overnight.

Using maximum still pot charges the yield of distillate is 97—98 % of the distilland. After a distillation the setup should be taken apart and cleaned immediately. We have never experienced sticking of the conical joint of the still pot. A tar-like residue in the still pot may easily be removed with chromic acid. Examples of the use of the setup are given in another article [9] in this journal. Further examples will possibly appear in later articles.

SUMMARY

The construction and use of four new setups for laboratory batch distillations under reduced or atmospheric pressure are described. The setups, which we mainly have used for the separation of mixtures of furan compounds, are easy to operate and are intended for general use.

Technical assistance. The glass blowing was carried out by Erik Christensen of *Dansk Glasapparatur*, Kongens Tværvej 5, Copenhagen F. The vacuum jackets were silvered by Zdeněk Tyle. The drawings were in part made by Niels Grue-Sørensen.

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