A Fully Automatic Apparatus for Solid-liquid Phase Counter-current Distribution

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In recent years much attention has been attracted to the use of discontinuous counter-current extraction between a pair of immiscible liquid phases as a method of purification. Craig and his associates (for references see Craig & Craig, 1950) have suggested two forms of apparatus suitable for this purpose. Craig, Hausmann, Ahrens & Harfenist (1951) have described an all-glass unit in which the processes of equilibration, settling of the two phases and transfer of the upper phase to the next unit can all be carried out automatically. The complete apparatus has 220 of these units. Fresh solvent was fed into the first tube and fractions collected automatically from the last tube, so that the whole operation was analogous to chromatography.

Discontinuous counter-current distribution between liquid and solid phases has attracted less attention, although Craig, Golumbic, Mighton & Titus (1946) described the separation of chrysene and anthracene by solid-liquid phase counter-current distribution between alumina and *cyclohexane*. The separation was carried out manually in glass tubes, the *cyclohexane* phase being transferred by decantation to the next tube after each equilibration.

The present paper describes a fully automatic apparatus for carrying out the stages of equilibration, filtration and transfer of the filtrate to the next unit. The advantages of automatic operation, stressed by Craig & Craig (1950) for liquid-liquid systems are even more marked for solid-liquid systems where both equilibration and filtration stages may be slow.

Solid-liquid phase counter-current distribution is very similar to adsorption chromatography and at first sight may appear to offer little advantage over the latter. However, when equilibrium of a solute between solid and liquid phases is slow and it is desired to operate in exactly defined non-equilibrium conditions, the method offers certain advantages. Results obtained with batch experiments, especially when the adsorption isotherm shows marked curvature, can be readily transferred to cascade operation.

APPARATUS AND METHOD

The apparatus consists essentially of two parts, the glass units and the electrical and mechanical equipment necessary for the operation cycle.

Fig. 1. Glass units for solid-liquid phase counter-current distribution. (a) Main units; (b) special metering unit.

The standard glass unit is shown in Fig. 1 (a). The dimensions shown are suitable for liquid-phase volumes of 5 ml. but the units can of course be scaled up or down. Part A of each unit is joined to part B of the next unit by a sleeve of plastic tubing. This sleeve also holds in position a disk of filter paper (preferably Whatman no. 54), placed between the two units. Equilibration takes place in tube A by oscillation through an angle of about 15° on either side of the horizontal position. At the end of the equilibration period, the unit is rotated through 90° in a clockwise direction. The liquid phase in A then filters through B into C, D is an air

vent. Rotation of the unit through 90° in an anticlockwise direction then transfers the liquid in *C* into the *A* portion of the next unit. Any desired number of units can be assembled into the train. Fig. 1 (*b*) shows the special first unit which delivers a constant volume of fresh liquid phase into tube *O* of the train. Fresh liquid phase enters continuously from a reservoir via tube *E* and fills the bulb *F* (5 ml. capacity). Excess liquid flows over into the drain tube *G*. Maintenance of a constant level is facilitated by the oscillating movement of the whole unit. During the filtration stage when the unit has been rotated through 90° in a clockwise direction, the contents of *F* are transferred to *I*, tube *H* acting as an air vent. During this stage, liquid phase entering through *E* passes directly out through *G* and does not enter the bulb *F*.

Fig. 2. Actuating mechanism for automatic operation. *A*, main shaft; *B*, notched supporting bar for glass units; *C*₁, *C*₂, *C*₃, *C*₄, actuating cams for switches; *D*, upper clamping bar; *E*, locating bolts and wingnuts; *F*, main driving wheel; *G*, driving pin on *F*; *H*, slotted driving bar; *I*, slot in *H*; *J*, driving crank; *K*, cam follower; *L*, cam; *M*₁, *M*₂, motors; *N*, timing shaft; *P*, main support; *S*₁, *S*₂, *S*₃, *S*₄, switches.

On return to the equilibration position the liquid in *I* is transferred to the equilibration tube *A* of the next unit. The liquid phases leaving the last tube of the train are collected in tubes held in a turntable-type fraction collector, an empty tube being brought into position once per cycle.

The mechanical design of the support for the units and the actuating mechanism is shown in Fig. 2. The support for the glass units is a duralumin bar *B*, 2 in. wide, 0.5 in. thick, of a length adequate to accommodate the required number of glass units. The bar is provided with equidistant machined notches to locate the units. The latter are fastened in place by the upper duralumin bar *D* and the bolts and wingnuts *E* spaced every five notches. The whole unit is carried on 0.5 in. shafts, *A*, at each end. These shafts run in self-aligning ballraces mounted on the main supports *P*. Shaft *A* carries the metal bar *K* and the wheel *F*. Bar *K* is kept in contact with cam *L* by a counter weight on *A*. *L* is driven by motor *M*₁. Operation of *M*₁ thus results in an angular oscillation of *A*, the magnitude of which is controlled by the size of *L* and the distance between the spindle of *M*₁ and *A*. An angular oscillation of about 30° has been used in the present apparatus. Shaft *A* also carries the wheel *F* with the pin *G* engaging in the slotted bar *H*. During oscillation of *A* by *M*₁ the pin *G* rides freely in the slot *I*. Rotation of crank *J* through 360° by motor *M*₂ causes rotation of shaft *A* through about 90° and back to the original position. This provides the

filtration and transfer position for the glass units. The angular rotation of *A* can be varied by altering the throw of crank *J*. The spindle of motor *M*₂ carries, in addition to crank *J*, the three cams *C*₁, *C*₂, *C*₃, operating the three mercury switches *S*₁, *S*₂, *S*₃, which together with the timing clock, control the operating cycle.

The electrical circuit shown in Fig. 3 comprises essentially the two operating motors *M*₁, *M*₂, three mercury switches (230 v, 1 A rating) *S*₁, *S*₂, *S*₃ and the timing clock *T*. The latter is a Flexopulse signal timer (Eagle Signal Corporation, Moline, Ill., U.S.A.). It consists of a single-pole two-way switch, the duration of contact in each position being continuously and independently variable from 3 min. to 5 hr. Motor *M*₁ is provided with a rheostat, *R*₁, so that the

Fig. 3. Circuit arrangement of electrical components. *M*₁, *M*₂, motors; M.B., magnetic brake; *R*₁, *R*₂, rheostats; *S*₁, *S*₂, *S*₃, mercury in glass switches; *T*, Eagle signal timer.

speed of shaking can be varied. Motor *M*₂ has a magnetic brake in parallel with it to prevent overrunning of the cams *C*₁, *C*₂, *C*₃ when *M*₂ is switched off, and a rheostat, *R*₂.

The cycle of operating is as follows.

(1) The timer switch is in the *x* position, *S*₃ is closed so that motor *M*₁ is in operation for the equilibration period. *S*₁ is closed, *S*₂ is open, motor *M*₂ is thus switched off.

(2) At the end of the equilibration period determined by the timer *x* setting, the timer contact moves over to the *y* position. Motor *M*₁ is thus switched off. Since *S*₁ is closed, *M*₂ begins to rotate, opening *S*₃. Shaft *A* is rotated via *F*, *H* and *J* through approximately 90° , when the filtration position of the glass units is reached. At this position, cam *C*₁ opens *S*₁ switching off *M*₂. Simultaneously cam *C*₂ closes *S*₂.

(3) At the end of the filtration period determined by the timer *y* setting, the timer contact moves over to the *x* position. Since *S*₂ is now closed, motor *M*₂ begins to rotate and completes the remainder of its 360° rotation. *S*₂ is opened by *C*₂ at the end, thus switching off *M*₂. Shaft *A* is rotated through 90° in an opposite direction to its initial movement, thus completing the transfer stage of the glass units. When *A* is in its initial position, *S*₁ and *S*₃ are closed by *C*₁ and *C*₃. Motor *M*₁ is thus switched on, equilibration shaking begins and the cycle is completed.

Shaft *N* also carried a cam, *C*₄, operating a switch, *S*₄, which is closed momentarily once per cycle. This actuates the fraction collector, moving it on one tube. The fraction collector also serves as a counter for the number of cycles completed.

The mechanical and electrical mechanism can also be readily adapted for automatic operation of a liquid-liquid counter-current distribution apparatus. This only involves rotation of C_1 on N so that it opens S_1 rather earlier in the cycle, for example after A has rotated through about 30° . M_2 is then switched off and the glass units stay in the settling position, i.e. until the two liquid phases have separated, for the period determined by the timer y position. When the timer switches over to the x position, M_2 completes its 360° rotation as described above, A completes its clockwise 90° movement to the first transfer position and its anticlockwise return to the initial position. The upper phase in the Craig units is thus decanted into the upper tube and then passed on to the next unit.

SUMMARY

1. A glass counter-current apparatus suitable for working with solid-liquid systems is described. Provision is made for equilibrating a solute between the two phases, separation of the phases by filtration and transfer of the liquid phase to the next unit.

2. An electrically operated mechanism is described suitable for carrying out the operation cycle automatically.

3. Adaptation of the mechanism to operation of a liquid-liquid counter-current apparatus is also described.

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The Oxidation of Corticosteroids with Sodium Bismuthate

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Lead tetraacetate and periodic acid are the reagents commonly chosen for the selective fission of 1:2-glycols under mild conditions (cf. Jackson, 1944; Criegee, 1948; Johnson, 1951). Both reagents are also capable of cleaving 1:2-ketols, though for substances of this type their effectiveness can vary greatly with the molecular environment of the ketol grouping. The two oxidants differ in their action on α -hydroxy acids, which are cleaved by lead tetraacetate but remain unaffected by periodate. In general, when the effect of either reagent is expected to be the same, lead tetraacetate is taken for reactions in organic solvents, while periodate is preferred for oxidations in aqueous media and for analytical purposes.

Periodate oxidation has proved of great value in elucidating the structures of corticosteroids (cf. Reichstein & Shoppee, 1943), and forms the basis of the analytical determination of 'formaldehydogenic' steroids (Lowenstein, Corcoran & Page, 1946; Daughaday, Jaffe & Williams, 1948; Corcoran, Page & Dustan, 1950), 'acetaldehydogenic' steroids (Butler & Marrian, 1937, 1938; Cox, 1952) and corticosteroids which are converted by periodate to 17-ketosteroids (Talbot & Eitington, 1944; Fieser, Fields & Lieberman, 1944). The application of lead tetraacetate in this field was less

successful: Reichstein (1937) succeeded in converting $11\beta:17\alpha:21$ -trihydroypregn-4-ene-3:20-dione (V) to 11β -hydroxyandrost-4-ene-3:17-dione (XII) with this reagent, but observed that the reaction was sluggish and the yield poor.

A consideration of the mechanism of glycol fission with lead tetraacetate and with periodic acid led Heidt, Gladding & Purves (1945) to postulate certain physical properties required of any oxidant capable of cleaving glycols by the same mechanism. Two oxidants found to have such properties were tervalent silver and sodium bismuthate. The latter reagent, in particular, was shown to effect smooth cleavage of ethylene glycol: quantitative yields of formaldehyde were obtained by shaking a dilute aqueous solution of glycol (at $\text{pH} \leq 4.7$) with a large excess of sodium bismuthate. The reaction was complete within 30 min. at room temperature. Rigby (1949, 1950) has independently investigated the action of sodium bismuthate on various simple 1:2-glycols, 1:2-ketols and α -hydroxy acids. The oxidations were performed, in general, with the theoretical amounts of reagent, the medium being either glacial acetic acid or an aqueous solution containing a slight excess of phosphoric acid. The author concluded that* in its effect, selectivity and rate of reaction sodium bismuthate closely