

height of the p-terphenyl peak was about 0.13 scale units in every case.

5) Evidence has been produced that shows that certain pairs of phosphors in some solvents at certain concentrations emit more fluorescent energy in mixed solutions than they do when each phosphor is alone in the solvent (at the same concentration as was used in the mixture).

6) A purely spectrographic method has been devised for the study of the fate of the energy that is involved in the fluorescence of liquid scintillation phosphors. This avoids the complexities introduced by energy transfer from radioactive emanations to the solutions and by the variable response of photomultiplier tubes.

Studies of these and other primary phosphors and "bandshifters" in a variety of solvents and plastics are being continued. The use of filters to allow only portions of the mercury spectrum to enter the solutions is proving most fruitful. Detailed reports of the various facets of these investigations are in preparation.

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1 June 1954.

Continuous-Flow Operation of Electroconvection Cells

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Electroconvective separation and purification of proteins is becoming more useful as a result of the availability of practical and efficient apparatus for this purpose. Recently two papers have appeared (1, 2) describing continuous-flow electroconvection for the fractionation of protein solutions. (Continuous-flow has also been practiced industrially for many years, chiefly for the purification of rubber latex (3-6).) Contrary to expectation, continuous-flow electroconvection is theoretically much slower and much less efficient than batch operation; this has also been confirmed experimentally.

Consider the batch operation in which V (ml) of solution containing C_A (g/ml) of A (at its isoelectric point) and C_B of B is placed in each reservoir. After a period t (hr) of electroconvection the upper

reservoir still contains the original concentration of the isoelectric A , but the concentration of B has been reduced to yC_B in the upper reservoir and increased to $(2-y)C_B$ in the lower reservoir, where y is a fraction determined from the equation

$$t = 1.9\theta \int_0^{1-y} [(1-y)^{-3/5} - (1+y)^{-3/5}]^{5/4} dy; \quad (1)$$

θ is the experimental transport constant as defined by Brown *et al.* (7). If y is taken as 0.001, $t = 5\theta$, so that for a batch operation the average rate of purification VC_A/t is $0.2VC_A/\theta$.

If now we begin to force buffer up through the bottom reservoir and channel at such a rate that the upward transport of B owing to buffer flow is just equal to the downward transport of B owing to electroconvection, the conditions at the top of the channel remain essentially constant insofar as B is concerned; A , however, is carried upward by the buffer stream and out the top of the cell, carrying with it the steady-state concentration yC_B of the B -component. For a buffer flow rate F (ml/hr), the upward buffer-flow transport of B is $2C_B F$ (g/hr) when y is a small fraction. This must not exceed the downward electroconvective transport $VC_B dy/dt$. The derivative dy/dt from Eq. 1 reduces to $0.53y^{3/4}/\theta$ when y is a small fraction; hence, the maximum F is given by

$$F = 0.26Vy^{3/4}/\theta. \quad (2)$$

For a typical system, if $y = 0.001$, the theoretical rate of purification in continuous-flow operation approximates $0.005 VC_A/\theta$. The average batch rate is 40 times this rate.

For an amount A_t of the immobile component recovered in the effluent, conservation of mass gives

$$A_t = A_0(1 - e^{-Ft/V}), \quad (3)$$

where A_0 is the amount initially present in the bottom reservoir and Ft is the total volume of buffer passed through the cell.

The foregoing equations are derived on the assumptions of the Kirkwood theory (8), specifically that of complete mixing in the reservoirs. In practice, mixing is far from complete; how far may be seen by comparing the foregoing equations with the experimental results obtained by Timasheff *et al.* (2). In their report 94 percent of BGG was recovered from a volume of 50 ml by passing 930 ml of buffer. The theoretical volume required is 140 ml; thus the mixing of the buffer stream with the reservoir contents was only 15 percent efficient.

The analysis of mixing in the bottom reservoir is further complicated by the fact that, although the concentration of the immobile component A remains uniform throughout the reservoir, the mobile component B concentrates as a result of electroconvection in a layer on the bottom of the reservoir, whereas the buffer stream, since it is less dense than the reservoir contents, tends to form a layer at the top of the reservoir. If the degree of mixing between these two layers is very small, as would be expected, the buffer entering the channel will not carry $2C_B F$ (g/hr) of the mobile component but a small fraction k of this amount. The

buffer flow rate F can then be increased without exceeding the desired carry-over of B .

Nonmixing greatly increases the over-all efficiency of the continuous-flow operation; it is nevertheless much slower and much less efficient than batch fractionation. For example, separating BGG and BSA by a three-stage batch electroconvection gave 94-percent recovery of 100-percent pure BGG in 200 ml of solution and 100-percent recovery of 97-percent pure BSA in 40 ml of solution; total time, 72 hr, as compared with 155 hr for the continuous-flow operation.

A more complete treatment, including an extension of the foregoing theory to other systems, is given elsewhere (9).

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10 May 1954.

Retention of Chromium by Glass Following Treatment with Cleaning Solution

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Over a period of years we have heard the remark that traces of chromium are retained on glassware that has been treated with the common laboratory cleaning solution of alkali metal dichromate and sulfuric acid. These comments frequently included cautions against possible interferences of the retained dichromate ions in precision measurements of surface tension and in some biological enzyme reactions. A literature search has revealed only one direct assay of the magnitude of this effect. In 1934, Laug made a colorimetric estimation of the retention of dichromate ion on several pieces of Pyrex brand and of lime glasses (1). He reported a few micrograms as $K_2Cr_2O_7$ in the wash waters following treatment by cleaning solution for 6 to 30 days. In view of the semiquantitative nature of this study and a limit of sensitivity of about 0.2 μg $K_2Cr_2O_7$, it was thought desirable to reconsider this problem in the light of modern radiochemical techniques.

Low-level counting techniques (2) and in particular the use of a stable sodium iodide scintillation spectrometer (3) for counting a gamma emitter such as Cr^{51} make possible detection sensitivities of orders of magnitude greater than the conventional colorimetric methods. High specific activity chromium chloride

from the Atomic Energy Commission was converted to dichromate cleaning solution and used for a study of the retention of chromium on quartz, Pyrex brand, and commercial plate glass. The limit of detection by direct measurement of the glass surfaces was 10^{-4} μg as $K_2Cr_2O_7$, despite the fact that only 8 to 10 percent of the disintegrations of Cr^{51} are accompanied by gamma emission. The observed retentions exceeded this limit. It was, therefore, possible to count these samples by both the scintillation spectrometer and a Geiger counter.

The Cr^{51} was precipitated as the hydroxide and freed from chloride ion. The chromic ion was converted to dichromate by oxidation with excess hydrogen peroxide in basic solution. The excess peroxide was destroyed, and water and sulfuric acid were adjusted to approximate the usual cleaning solution (4). Some fused quartz disks $1\frac{1}{2}$ in. in diameter and $\frac{1}{4}$ in. thick were on hand. Disks of the same dimensions were cut from Pyrex brand and commercial soda-lime plate glass.

In the initial experiment an area of approximately 7 cm^2 on one side only of these glasses was soaked at room temperature for 24 hr in radioactive cleaning solution. Each piece of glass was rinsed for about a minute in running water, dried, and counted. Tests showed that continued washing or strenuous rubbing with Kleenex did not alter the retention. The observed net counts per minute by the scintillation spectrometer (5) and by the Geiger counter are shown in Table 1. Although considerable variation is shown in Table 1, significantly more Cr^{51} was retained by the Pyrex brand glass.

Table 1. Retentions of Cr^{51} on glasses following treatment with cleaning solution (net counts per minute by Geiger counter and by scintillation spectrometer).

Instrument	Set	Fused quartz	Pyrex	Plate
Geiger counter	I	5	9	3
	II	5	12	7
Scint. spect. (Photo-peak)	I	60	229	33
	II	106	178	93

Two additional experiments were made to obtain information on the form of this retention. Samples of all three glasses were treated with a solution of chromium chloride in sulfuric acid containing the same specific activity of chromium as used in the dichromate cleaning solution. Also a sample of Pyrex brand glass was coated with grease from the face and hands and treated with the radioactive dichromate solution. These retentions are shown in Table 2.

The similarity between the data of Table 1 and set III of Table 2 suggests that the primary retention is adsorption of chromic ion rather than dichromate ion. Furthermore, the high retention on the greasy sample suggests either that adsorption of both ions occurs