

Rapid R_F Measurement in Chromatography

THE device described here has proved very useful for the rapid measurement of R_F values on paper partition chromatograms¹. In the figure, AB is an aluminium strip 20 in. \times $\frac{1}{2}$ in. \times $\frac{1}{8}$ in., AC is a piece of white elastic 9 in. \times $\frac{1}{2}$ in. attached to the end A of the strip by sewing through a hole in the strip. The other end of the elastic C is attached to a small 'bulldog' clip. A scale (divided into 100 parts) is marked on the elastic. For use, the zero of the scale is placed at the origin line or spot and the 100 mark stretched out to coincide with the position



reached by the solvent front. The R_F values of the spots can then be read off directly on the scale. While α -amino-acids can be recognized simply from their relative positions on a chromatogram, the device allows a quick check on isolated or unknown spots or the spread of a spot. A smaller apparatus on the same expanding-scale principle can be used for measuring the R value² of substances on a column where the ratio, movement of band/movement of sample of liquid in unpacked part of the column above, is employed.

D. M. P. PHILLIPS

Courtauld Institute of Biochemistry,
Middlesex Hospital Medical School,
London, W.1.
March 12.

¹ Consden, R., Gordon, A. H., and Martin, A. J. P., *Biochem. J.*, **38**, 224 (1944).

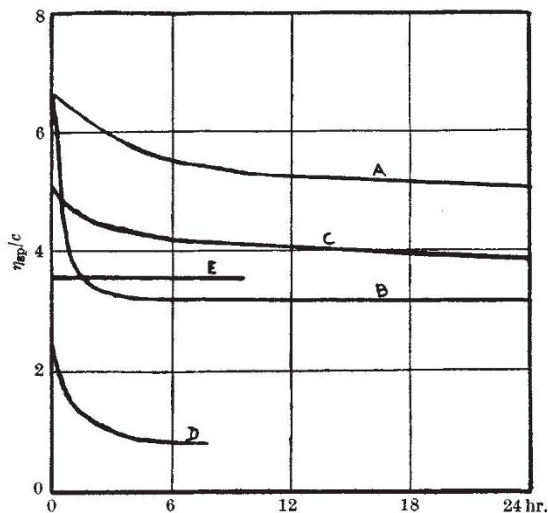
² Martin, A. J. P., and Synge, R. I. M., *Biochem. J.*, **35**, 1358 (1941).

Degradation of a Vinylidene Chloride Copolymer in Solution

SOME observations have recently been made on the changes in viscosity of solutions of a copolymer containing approximately 85 per cent vinylidene chloride, 13 per cent vinyl chloride and 2 per cent acrylonitrile (by weight). The polymer was soluble in hot, but not in cold, tetrahydrofuran: once it had been dissolved by heating in the solvent at 60–65° C. for 2–3 min., the solution could be cooled to room temperature without gelling or precipitation.

Copolymer solutions of different concentrations, made up in redistilled tetrahydrofuran by heating as above, were aged in sealed glass tubes in contact with air for varying times at 50° C. and 75° C. Typical curves showing the changes in η_{sp}/c (where η_{sp} is specific viscosity and c is concentration in moles per litre) of the solutions with time are reproduced here with (Curve A , 50° C., Curve B , 75° C.).

Investigation showed that the tetrahydrofuran used contained peroxides, and further work showed that: (a) a similar fall in η_{sp}/c was observed in cyclohexanone at 75° C., and in dioxane at 85° C., both in air (Curves C and D); (b) a slight reduction in η_{sp}/c took place in peroxide-free tetrahydrofuran at 75° C. in air; (c) little or no reduction in η_{sp}/c took place in peroxide-free tetrahydrofuran at 75° C. in nitrogen; (d) no reduction in η_{sp}/c took place in *o*-dichlorobenzene at 130° C. in air (Curve E).



AGEING OF VINYLIDENE CHLORIDE COPOLYMER SOLUTIONS

A.	In tetrahydrofuran at	50° C.
B.	" "	75° C.
C.	" cyclohexanone "	75° C.
D.	" dioxane "	85° C.
E.	" <i>o</i> -dichlorobenzene "	130° C.

These observations are consistent with the view that the viscosity decrease in these polymer solutions is due to a degradative attack on the long-chain molecules, not by oxygen directly, but by peroxides formed from the solvent and atmospheric oxygen. Tetrahydrofuran, cyclohexanone and dioxane are all known to peroxidize in the presence of oxygen (presumably with the formation of hydroperoxides at the carbon atoms adjacent to the ether oxygen or carbonyl group), while *o*-dichlorobenzene would not be subject to such an attack. Degradation of this type has previously been found to occur in the presence of oxygen^{3,4}, but the role of the solvent does not appear to have been appreciated.

That the changes in viscosity are most likely to be caused by polymer chain scission, rather than by any physical changes in the solution (breakdown of polymer aggregates, solvation⁵, etc.) is also indicated by the fact that copolymer from a solution in tetrahydrofuran aged at 75° C. for 5 hr. (isolated by precipitation, washing and drying) could readily be redissolved in tetrahydrofuran at 25° C. to give solutions of η_{sp}/c identical with that of the aged solutions. Further, calculations of the approximate overall activation energy of the process, based on rates of change in η_{sp}/c of a solution in tetrahydrofuran at 50° C. and 75° C., gave a value of about 24 kcal. Neither of these observations is conclusive in itself, but taken in conjunction with the results already quoted, they inevitably suggest that primary valency bonds are being broken.

Sufficient evidence is not yet available for a discussion of the mechanism of this degradation, but a study of the rate of change of peroxide content in tetrahydrofuran, in contact with air, both with and without dissolved copolymer, has given some indication that the initial attack on the polymer may be by a radical produced during solvent autoxidation reaction⁶, or by hydroperoxide fission.

The number of points in the copolymer molecule at which attack is possible may be limited, because copolymer isolated from solutions which have been aged to constant η_{sp}/c value at a particular temperature, when redissolved in fresh solvent containing