200 on the meter reading. The phototube probe was practically useless at low intensities, whereas the crystal cell gave adequate readings well below the minimum intensity needed for focussing.

In our opinion, the sensitivity of a large number of photometric devices can be improved by substituting crystal photocells in place of phototubes provided:

(a) the lower internal resistance of the crystal cell can be accommodated;

(b) the longer response and decay time is not objectionable;

(c) the comparatively high temperature coefficient can be compensated. The manufacturer's value of temperature drift for the CL-2 is 0.1% per 1°. This is negligible for the average laboratory in temperate climates.

Another significant advantage is the maximum operating voltage of 300 V DC as compared to 90 V for most phototubes. The extremely small size of the crystal photocell is a distinct advantage in probe design. Since these cells are so inexpensive we believe that they will find increasing application in photometry.

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Improved resolution on paper chromatograms

In paper chromatography the original solution is commonly allowed to spread over a small circular area. This results, after development, in the spots corresponding to the different substances being irregular circles. Two substances with close R_F values cannot easily be distinguished since overlapping spots appear only as a rather more irregular circle. On one-dimensional chromatograms this is sometimes overcome by applying the original solution as a long streak, but this introduces difficulties and cannot be used for two-dimensional chromatograms. The method described here is applicable to one- or two-dimensional chromatograms and enables substances with very close R_F values to be distinguished.

The solution for analysis (10 μ l) is applied to the paper and spreads as a small circular spot. This is dried and the operation repeated as many times as is needed to concentrate the material. The solvent (e.g. water if the original solution is aqueous) is applied in three 10 μ l portions to the centre of the dried spot, drying between applications. As the solvent spreads out it carries the solutes to the periphery of the original spot, forming a ring with an empty centre. On running the chromatogram as usual, each substance runs at its characteristic rate forming a discrete spot which maintains its ring shape, though there is some spread and the ring changes to a solid circle at R_F values greater than about 0.4. It is very much easier to detect overlapping rings than overlapping circles, particularly if the centres nearly coincide, and one can be

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Fig. 1. One-dimensional chromatogram of phenolic substances in four specimens of urine, showing effect of ring formation. Solvent: isopropanol-ammonia-water (8:1:1). Untreated urine $(30 \ \mu l)$ was applied on each cross. The solvent edge is marked.



Fig. 2. Two-dimensional chromatogram of amino-acid mixture. Alanine is overloaded, normally it shows clear ring formation. This is just visible in the β -amino-isobutyric acid spot. Solvents: *p*-cresol-ammonia from right to left followed by collidine-lutidine from top to bottom. The amino-acid mixture was applied at the cross visible in the right-hand top corner.

correspondingly more confident of the identity or non-identity of two substances (Figs. 1 and 2). The amount of material per unit area is much higher in the periphery of a ring than in a circle of the same area, increasing the sensitivity of the method as well as the resolving power. Although the method fails for substances with high R_F values, it is in the low R_F region that one most often wishes to separate substances of similar R_F value.

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