Evaluation of Commercial Photographic Developers Which Intensify Silver Halide Spots on Paper Chromatograms

SIR: Many organic compounds containing halogens can be detected on paper chromatograms by converting the halogen to silver halide and decomposing this to give a dark spot. Lederer (*1*) used sulfides to visualize the silver spots. Mitchell and Patterson (*5*) decomposed the silver halides by exposure to sunlight, and later, Mitchell (*2*) used pyrogallol to obtain greater intensity in the spots. More recently, Mitchell (*3*, *4*) used strong ultraviolet light to define insecticide spots which were sprayed with a mixture of silver nitrate and 2-phenoxyethanol.

When used to follow the separation of derivatives of a chlorine-containing epoxy resin on paper chromatograms, these methods lacked sensitivity and had other undesirable qualities. Spraying with sulfide produced papers with an odor and on which the spots were a yellowish brown color of poor visibility. Developing with sunlight or artificial light produced erratic results. Ultraviolet light used according to Mitchell's method (*4*) does not liberate the halogens from some compounds and did not liberate sufficient chlorine from the epoxy resin used in these studies to permit detection at a concentration containing 10 μg. of chlorine. However, under the same conditions, citrate buffers which contain no halogens produced strong spots. Pyrogallol solutions are quite unstable and, unless made up fresh for each use and thoroughly washed from the paper after development, cause discolorations of the paper. Several commercial photographic developers and a photographic toner were evaluated for their ability to intensify the spots.

EXPERIMENTAL

Epoxy resin containing about 10% chlorine was dissolved in ethyl acetate and diluted to prepare solutions containing 0.1, 0.2, 0.3, 0.5, 0.75, 1.0, 2.5, 5.0 μg. of chlorine per μl. One microliter of each concentration was spotted in ascending order on a paper strip. One strip was treated by the method of Mitchell and Patterson (*5*). Four similar strips were treated by a modification of their method, spraying first with 1*N* KOH and drying in a convection oven at 130° C. for 30 minutes. They were then sprayed on both sides with 0.05*N* silver nitrate in ethanol and

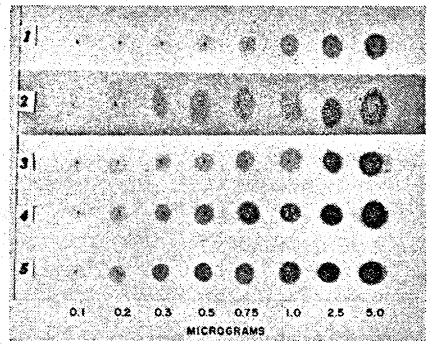

Figure 1. Comparison of methods for detecting halogens on paper chromatograms

allowed to stand for 10 minutes. The strips were then dipped in a mixture of one part concentrated nitric acid and one part 30% hydrogen peroxide. After the color had been completely removed, the strips were washed thoroughly in water to remove the excess silver nitrate and air dried. One strip was sprayed with a 0.2*N* solution of sodium sulfide and air dried. A second strip was exposed to strong sunlight for 1 hour. The other two strips were exposed to fluorescent light (two 15-watt bulbs, 2 inches away) for 10 minutes on each side and then developed with undiluted Dektol (*4*) developer solution for 1 minute. The developer was neutralized by soaking the strips in 3% acetic acid for 1 minute. The strips were then thoroughly washed in running water and dried. One of these strips was then treated with a gold chloride toner and dried again.

DISCUSSION

The results of these experiments are shown in Figure 1. Strips 1 and 2 were developed in sunshine. Strip 1 was prepared by the method described; strip 2 was prepared by Mitchell's method and shows the dark background due to the residual silver salts not removed from the paper. The 0.1 and 0.2 spots are more pronounced in the photograph than on the original paper strips.

Strip 3 was sprayed with sodium sulfide. The low concentration spots were barely visible on the original because of their yellow color.

Strips 4 and 5 were developed with the photographic developer. Strip 5 was also treated with gold chloride toner solution. Since all silver salts were removed from these two strips, the backgrounds should remain white. The 0.2 spot of strip 4 corresponds in intensity with the 0.3 spot of strip 2 and the 0.1 spot of strip 5 on the original chromatograms. Therefore, the photographic developer method is twice as sensitive as the Mitchell method and can be made three to four times as sensitive when combined with a photographic toner to deepen the intensity of the spots. With this combination, 0.1 μg. of organic chlorine could be detected on a paper chromatogram.

Several other commercial developers made by Eastman Kodak Co. (DK-50, DK-11, and high contrast "photostat" developer) were tried, but they did not produce as deep a black as the Dektol developer. The method described here can be used with all of the common paper and column chromatographic solvents except the halogenated ones. It will detect organic halides of most aliphatic organic compounds and some activated aromatic compounds such as the resorcinols or quinones, but some of the simple aromatics such as orthochlorobenzoic acid require a more drastic treatment to liberate the halogens.

For compounds which can be dehalogenated by alkali at 130° C., photographic development of the silver halide is superior to development by either sunlight or sulfides.

Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

LITERATURE CITED

(1) Lederer, M., *Science* **110**, 115 (1949).
(2) Mitchell, L. C., *J. Assoc. Offic. Agr. Chemists* **38**, 832 (1955).
(3) Mitchell, L. C., *ibid.*, **39**, 891 (1956).
(4) Mitchell, L. C., *ibid.*, **44**, 644 (1961).
(5) Mitchell, L. C., Patterson, W. I., *Ibid.*, **36**, 553 (1953).

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