Rapid Screening Test for Carbaryl

In a rapid, qualitative screening method for carbaryl in carrots, oranges, and cabbage, the carbaryl is extracted with isooctane–methylene chloride in the presence of calcium stearate and sodium sulfate. A liquid-liquid partition cycle from isooctane–methylene chloride into *N,N*-dimethylformamide (DMF) and back into methylene chloride provides sufficient cleanup for the qualitative detection of carbaryl with *p*-nitrobenzenediazonium fluoborate after hydrolysis to 1-naphthol. Cabbage requires no cleanup; the test works in the presence of the light-colored extract. The procedure requires about 1 hour if the DMF cleanup step is required.

Screening methods for carbaryl using thin-layer chromatography (TLC) report a range of 1 to 20 p.p.m. for carbaryl in foodstuff extracts without preliminary cleanup (Chiba and Morley, 1964; Engst and Kubel, 1965).

Carrots and oranges can be sufficiently cleaned up by a liquid-liquid partition cycle to permit a qualitative test for carbaryl at the 10-p.p.m. level without any TLC. With foodstuffs which give light-colored extracts, such as cabbage, no cleanup is necessary. Calcium stearate is used in the extraction step to prevent emulsion formation and reduce the amount of interferences extracted from the foodstuffs. The use of calcium stearate has been reported for chlorinated hydrocarbon pesticides (Onley and Bertuzzi, 1966).

EXPERIMENTAL

Apparatus. A Waring Blendor and a 500-ml. glass container (Eberbach Catalog No. 8470) were used for contact of the foodstuff with the extraction solvent mixture. The screw cap on the container was lined with polyethylene sheet to prevent contamination from the lid liner or possible loss of pesticide to the liner. Blank runs showed no interference from the polyethylene sheet in the detection step. Separatory funnels fitted with Teflon stopcocks were used in the liquid-liquid partition steps.

Reagents. Stir 200 grams of calcium stearate (Fisher Scientific Co., technical grade) with 800 ml. of diethyl ether for 3 minutes, centrifuge down the calcium stearate, and discard the liquid layer. Allow the calcium stearate to air-dry at room temperature before using it.

Other chemicals were generally reagent grade; 2,2,4-trimethylpentane, isooctane (Phillips Petroleum Co.), was pure grade, 99 mole %, and other solvents were certified grade (Fisher Scientific Co.) or equivalent.

Prepare a 0.5% mixture of *p*-nitrobenzenediazonium fluoborate in powdered sodium chloride for use as the chromogenic reagent. About 100 mg. of this mixture is required for a determination; it is easily dispensed from a bottle fitted with a DispensAR cap (Mallinckrodt Chemical Works).

Procedure. Weigh 25 grams of foodstuff into the blender cup. Add 1.5 grams of calcium stearate, 6 grams of sodium sulfate, and 100 ml. of isooctane–methylene chloride (9 to 1). Extract the sample for 4 minutes, transfer the mixture to centrifuge tubes, and centrifuge it for 2 minutes to separate the liquid from the residue. Transfer the liquid from the centrifuge tubes to a 100-ml. glass-stoppered cylinder or volumetric flask and dilute the solution to volume with methylene chloride.

Place a 10-ml. aliquot of the foodstuff extract in an Erlenmeyer flask containing 5 grams of sodium sulfate, and shake the flask to dry the solution. Decant the solution into a 60-ml. separatory funnel. Add 5 ml. of N,N-dimethylformamide (DMF) saturated with isooctane to the separatory funnel and shake for 1 minute. Draw off DMF layer and wash it twice with 10-ml. portions of isooctane saturated with DMF. Add 30 ml. of 0.5*N* hydrochloric acid–1% sodium chloride to the DMF layer in a separatory funnel, shake the funnel to mix the solution, and allow the contents to cool to room temperature. Add 10 ml. of methylene chloride to the separatory funnel. Shake the separatory funnel for 1 minute, venting excess pressure as required.

Draw off the lower layer in the separatory funnel into a 50-ml. beaker or place a 10-ml. aliquot of the original extract from cabbage in the beaker. Evaporate the solution in the beaker nearly to dryness; do not heat the beaker during the evaporation. Add 10 drops of potassium hydroxide (1*N*, in 95% ethanol) to the beaker, mix the contents of the beaker, and allow the beaker to stand for 3 minutes. Add 100 mg. of 0.5% *p*-nitrobenzenediazonium fluoborate reagent to the beaker. If carbaryl was present in the foodstuff sample, a green-to-blue color will result; if no carbaryl was present, a light yellow color will result.

RESULTS AND DISCUSSION

This procedure has been checked for carrots and oranges using the DMF cleanup cycle and for cabbage, without any cleanup. While some coloring matter equivalent to about 1 p.p.m. of carbaryl comes through this procedure, it does not give the green-to-blue color of the 1-naphthol under the conditions of this test. The lower limit of detection was not determined.

The test may be run in about an hour, if DMF cleanup is required, or in about 30 minutes without DMF cleanup. Any 1-naphthol present in the cabbage extract would interfere in this screening test.

LITERATURE CITED

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