Gas Chromatographic Determination of Captan Residues

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A rapid procedure for the determination of captan [*N* - (trichloromethylthio) - 4 - cyclohexene - 1,2-dicarboximide] residues on apricots, peaches, tomatoes, and cottonseed is presented. The residues are extracted with benzene or acetonitrile and analyzed by electron-capture gas chromatography. Residues as low as 0.01 p.p.m. can be detected. The over-all average recovery of captan residues obtained from fortified control samples was 92%.

Captan, *N*-(trichloromethylthio) - 4 - cyclohexene - 1,2-dicarboximide, is used for the control of various fungus diseases on a variety of fruits, vegetables, and ornamentals. Existing methods for the determination of captan residues on these commodities are based upon the reaction of captan with resorcinol (Kittleson, 1952; Wagner *et al.*, 1956) or pyridine (Burchfield and Schectman, 1958) to form a yellow product. Sensitivities of these procedures, however, have been restricted mainly to a minimum detectable quantity of 5 to 10 μg. of captan. Also, extraction and cleanup procedures frequently vary from specimen to specimen.

The present paper describes a rapid but sensitive procedure for the extraction and gas chromatographic determination of captan residues on apricots, peaches, tomatoes, and cottonseed. The main advantage of this procedure over the existing colorimetric technique is the ease with which the samples can be analyzed. Also, a much smaller quantity of crop is required for the analysis, even though a higher degree of sensitivity can be obtained. In this new procedure, as little as 0.5 nanogram can be detected with considerable reliability.

MATERIALS AND EQUIPMENT

Gas Chromatograph and Recorder. An Aerograph Model 204 gas chromatograph (Varian Aerograph, Walnut Creek, Calif.) equipped with an electron-capture detector was used for the analyses. The electrometer was operated at an output sensitivity setting of 3×10^{-11} afs. The detector signal was supplied to a 1-mv. Westronics dual pen recorder operated at a chart speed of 20 inches per hour.

Column and Operating Conditions. The chromatograph was equipped with a 6-foot × 1/8-inch O.D. spiral borosilicate glass column packed with 10% DC-200 (w./w.) on 110- to 120-mesh Anachrom ABS. The column temperature was held constant at 185° C. and the glass-lined injection port was maintained at 210° C. Nanogram amounts of captan were injected onto the column until a constant response was obtained. All solutions were injected onto the column with a 10-μl. Hamilton syringe (No. 701). The nitrogen carrier gas, which was filtered through a molecular sieve (Varian Aerograph), was regulated to provide a flow rate of 50 cc. per minute through the column.

Planimeter. A Lietz polar planimeter (Model 236) was used to convert strip-chart analog data to digital data.

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Reagents. Double distilled reagent grade acetone, acetonitrile, and benzene, captan standard (Chevron Chemical Co., Ortho Division, Richmond, Calif.), Florisil, 60- to 100-mesh (activated for 2 hours at 650° C. followed by 2 hours at 130° C.) (Floridin Co., Tallahassee, Fla.) resorcinol, analytical grade, and glacial acetic acid were used.

PROCEDURE

Preparation of Standard Curve. Prepare a standard solution containing 1 mg. of captan per ml. of benzene. Prepare working solutions containing 0.5 μg. per ml. (0.5 nanogram per μl.) and 0.1 μg. per ml. (100 picograms per μl.) from the standard stock solution. Inject aliquots of these solutions, ranging from 1 to 10 μl. onto the column. Construct a standard curve by plotting the average area of three injections for each aliquot against the amount injected.

Extraction Method. A representative sample of the crop is prepared for analysis as described by Cheng and Kilgore (1966). The procedure, as used in this study, is as follows: Macerate 500 grams of fresh frozen crop in a suitable food chopper. Deposit 100 grams of the macerated material in a 1-gallon can equipped with a metal baffle for mixing. Add 400 ml. of benzene to the macerate, then seal the can tightly with a lid. When extracting samples (such as cottonseed) containing large amounts of oils, use acetonitrile rather than benzene. Roll the tightly sealed can on a mechanical roller (35 r.p.m.) for 30 minutes. At the end of this time, set the can aside for 10 minutes. Cautiously open the can, and filter the solvent layer through 100 grams of anhydrous sodium sulfate into a storage bottle. Seal the bottle with a Poly-Seal closure cap and store the eluate until analyzed. For recovery studies, fortify the sample with a known amount of captan before adding the appropriate solvent.

Removal of Interfering Materials. Fruit and vegetable extracts can be analyzed directly, whereas cottonseed extracts must be subjected to a cleanup procedure before analysis. For cleanup of the cottonseed extracts, prepare a Florisil chromatographic column as follows: Tamp a plug of glass wool into a 1.5 × 30 cm. borosilicate glass chromatographic tube having a 100-ml. reservoir attached to the top. Pour into the tube a 1-inch layer of granular anhydrous sodium sulfate. Add a 2.5-inch layer of dry activated Florisil and top with a 1-inch layer of granular anhydrous sodium sulfate. Tap the column to obtain good packing. Wash the column with 25 ml. of benzene and discard the wash.

Evaporate a 100-ml. aliquot of cottonseed extract, representing 25 grams of crop, just to dryness with a rotary-vacuum evaporator (CaLab, Berkeley, Calif.). Displace the last traces of acetonitrile vapor from the flask with a stream of dry air. Wash down the interior of the flask with 20 ml. of ethyl ether and again evaporate just to dryness. Remove any remaining solvent vapor in the flask with a stream of dry air. Transfer the residue remaining in the flask to the chromatographic column with three 5-ml. portions of benzene. Discard the benzene eluate. Then elute and collect the captan from the column with 25 ml. of 1% acetone in benzene. However, because of variations in batches of Florisil, determine the elution pattern in each laboratory prior to analysis.

Gas Chromatographic Analyses. Preliminary traces of each sample extract should be made before attempting to measure residue content. If high levels of captan residues are present, the extracts may require dilution with benzene. Dilution factors, as well as the level of interfering substances, can be determined by injecting 2-μl. aliquots of each extract into the gas chromatograph. Finally, the amount of residue can be determined by comparing the average peak area of a replicate series of three chromatograms with the standard curve.

RESULTS AND DISCUSSION

The gas chromatographic characteristics of captan were evaluated on columns packed with XE-60 (5% XE-60 on Gas-Chrom Q, 100- to 120-mesh), QF-1 (5% QF-1 on DMCS-treated Chrom G, 70- to 80-mesh) and DC-200 (10% DC-200 on Anachrom ABS 110- to 120-mesh). The peak height, symmetry, band width, and retention time of captan on each of these columns were dependent on the operating conditions of the gas chromatograph. Thus, for this study only one column, DC-200, was used for subsequent analyses. However, if samples of unknown history are to be analyzed, additional confirmatory evidence such as gas chromatography using a polar column, determination of p-value, or use of a more selective detector should be obtained.

The linearity of response to captan was measured over a range of 0.5 to 5 nanograms. The peak height, symmetry, band width, and column retention time of a 3-nanogram sample of captan are illustrated in Figure 1. In addition to the major captan peak, a small peak having a retention time of about 9 minutes was also evident. No attempt was made to identify this component as it was assumed to be either a minor impurity in the standard solution of captan or a decomposition product.

A negligible amount of interfering materials was found in untreated control samples of apricots, peaches, and tomatoes. A cleanup procedure was therefore not required. A typical gas chromatogram is shown in Figure 2.

Table I shows that the recovery values ranged from 86 to 105% when control samples were fortified with 1.0 p.p.m. of captan. Also, recoveries of captan from cottonseed extracts, which were purified by column chromatography, ranged from 80 to 100% at levels of 0.01 to 1.0 p.p.m., respectively.

To determine the reliability of the method, results obtained by both the gas chromatographic procedure and the resorcinol colorimetric technique (Ospenson *et al.*, 1964)

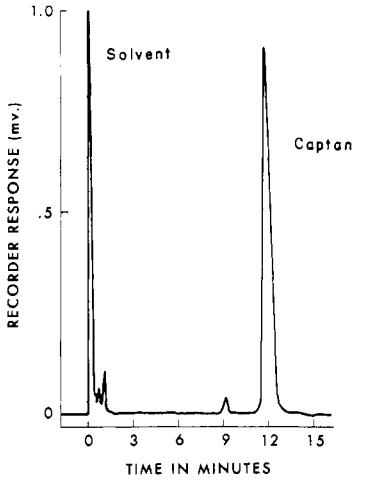

Figure 1. Gas chromatogram of captan

The curve reprsents 3 ng. of captan

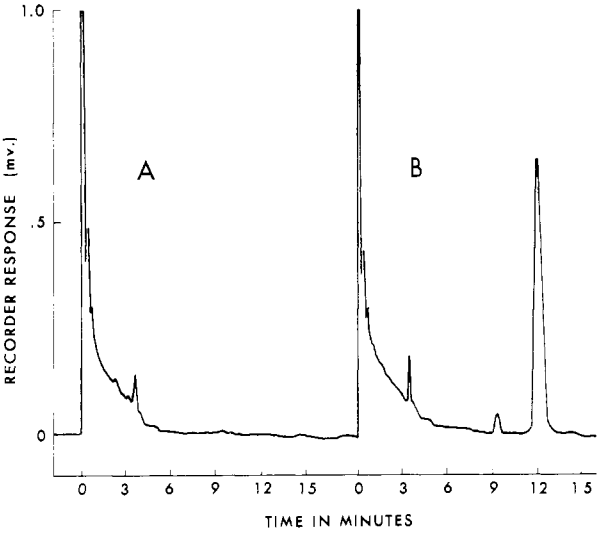

Figure 2. Gas chromatogram of apricot extract

A. Untreated control
B. Untreated control fortified with 1.0 p.p.m. captan

Table I. Recovery of Captan from Various Crops

Crop	P.P.M. Added	P.P.M. Found	Recovery, %	Av. Rec. %
Apricots	1.00	0.86	86	
	1.00	1.00	100	91
	1.00	0.88	88	
Peaches	1.00	0.86	86	
	1.00	0.98	98	91
	1.00	0.88	88	
Tomatoes	1.00	0.96	96	
	1.00	1.05	105	100
Cottonseed	1.0	0.96	96	
	0.1	0.093	93	87
	0.01	0.008	80	
Over-all av.				92

Table II. Determination of Captan Residues on Apricots Using Resorcinol-Colorimetric and Gas Chromatographic Procedures

Sample No.	Captan Residue Found, P.P.M.[a] Resorcinol-colorimetric procedure[b]	Gas chromatographic procedure[c]
1[d]	16.47	17.21
2[d]	16.47	17.21
3[e]	2.54	3.10
4[d]	7.64	7.60

[a] Application rate: 2 pounds of captan per 100 gallons of water; trees saturated to drip stage with hand sprayer.
[b] Average values of 3 determinations; figures uncorrected for an 83% recovery value.
[c] Average values of 3 determinations; figures uncorrected for a 91% recovery value.
[d] Fruit harvested 3 days after the last of 3 spray applications.
[e] Fruit harvested 6 days after the last of 2 spray applications.

were compared. Table II shows data obtained with apricots fortified with captan when the two procedures were used. From these data, it is apparent that the gas chromatographic procedure is as dependable as the colorimetric technique. The gas chromatographic procedure, however, offers several distinct advantages over the existing colorimetric procedure. For types of samples analyzed in this study, the procedure is more sensitive, requires less sample, and, with the exception of cottonseed, does not require cleanup of the extracts. In addition, pesticides used in combination with captan can be conveniently detected simultaneously (Kilgore and White, 1967).

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