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A Reproducible Method for the Extraction of Pesticide Residues from Fabrics

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Methods for analysis of pesticide residues in clothing of agricultural workers have either been unavailable or not standardized. Pesticide residue analysis has been the means of evaluation in both penetration and laundry-removal studies. The analytical methodology used by many researchers for the determination of pesticide residues in fabrics is based on procedures developed for the extraction of pesticide residues in agriculture crops. (ORLANDO et al. 1981, EASLEY et al. 1981, FINLEY and ROGILLIO 1969). The basic method is comprised of four major steps: solvent extraction, concentration of the extract, cleanup of the extract, and gas chromatograpic analysis. This method includes the use of two or three consecutive extractions for a total extraction time of 1 to 3 hrs. In addition to the excessive length of time involved in this method, the pesticide residue is diluted to a large solvent-to-residue ratio. Hence, a condensation step is required to reduce the solvent volume and yield residues in a detectable range.

The major purpose of this research was to determine if multiple extractions are required to extract pesticide from fabrics and secondly, to evaluate the length of time required to produce the most efficient recoveries. This paper describes a rapid procedure for the extraction of Captan® residues from fabrics which yields an extract ready for gas chromatographic analysis. The procedure was used to evaluate the recover of Captan® from nine fabric variations.

MATERIALS AND METHODS

Analytical quality Captan® standard of 99.0% purity was obtained from the Pesticide Quality Assurance Laboratory, Environmental Protection Agency, Research Triangle Park, NC. Ten milligrams (corrected for % purity) of primary standard were dissolved in 1 ml of toluene and diluted to a volume of 50 ml with iso-octane. Working standards were prepared by dilution of the stock solution to 2 µg/ml (2 ng/µl); 0.5 µg/ml (0.5 ng/µl); and 0.1 µg/ml (100 pg/µl). These solutions were injected into the gas chromatograph, using aliquots ranging from 1 to 5 µl. A standard curve was constructed by plotting the average area of four injections against the amount injected. The linear range of the detector was was measured over a range of 100 pg/µl to 20 ng/µl.

The fabrics used in the study are characterized in Table 1. All fabric types, with the exception of Tyvek® and gauze, were prewashed to remove manufacturing residues and sizing. Analysis blanks, conducted without pesticide fortification, consisted of one complete cycle of extraction and gas chromatographic analysis to assure that there were no interfering compounds on the fabrics prior to the fortification process. No detectable pesticide residues or any other extractable components and/or additives that could interfere with analysis were obtained from the fabric blanks.

Table 1. Fabric Characteristics

FABRIC	WEIGHT gm/m^2	THICKNESS[a] (mils)	FABRIC COUNT[b] Warp/Filling
100% COTTON DENIM Burlington S/1885	543.8	41	66/48
100% COTTON DENIM Burlington S/1549	361.7	34	68/40
100% COTTON KNIT Standard Knitting S/9909	153.4	20	32/22
50/50 COT/POLY KNIT Standard Knitting S/9904	129.2	15	32/32
100% COTTON CHAMBRAY West Point Pepperell S/36-011	167.8	20	74/54
GORE-TEX® RIPSTOP/TRICOT NYLON W. L. Gore	122.7	13	N/A
GORE-TEX® POLYESTER TRICOT W. L. Gore	95.5	10	N/A
TYVEK® Dupont S/1445A	48.2	10	N/A
100% COTTON GAUZE (eleven layers)	270.6	42	N/A

(a) Determined according to standard procedure ASTM Method D1777.
(b) Determined according to standard procedure ASTM Method D1910.

All solvents used were Burdick and Jackson distilled-in-glass solvents, suitable for pesticide residue analysis. Preliminary experimentation using several solvents (iso-octane, toluene, benzene, ethyl acetate and hexane) showed that hexane was the most efficient extracting solvent. Hexane also produced the most acceptable chromatogram when evaluated on the gas chromatograph.

A Varian 3700 Gas Chromatograph equipped with an electron capture detector was used for the analysis. The gas chromatograph was connected to a CDS 111 Integrator which was programmed to compute retention time and area counts.

The chromatograph was equipped with a 0.318 cm ID X 1.83 m glass column packed with a 4% SE-30/OV 210 on a GC Q mesh. The carrier gas was nitrogen; 40 ± 0.2 ml/min. Operating temperatures were column oven at 220°C, inlet 250°C and detector 300°C. Multiple injections of Captan® standards were injected onto the column until a constant response was obtained. Subsequent injections of sample were 2 µl or greater using a 10-µl Hamilton syringe.

For the recovery study three samples for each fabric variation were fortified with a known amount of Captan® standard solution. A representative sample of contaminated fabric was prepared for analysis by the following procedures: (1) a 3X3 in. fabric sample was placed in the bottom of a 250-ml Erlenmyer flask using a steril glass rod; (2) 1 ml of pesticide stock solution (200 g/ml) was pipetted onto the center of each fabric sample and the flask rotated to fully saturate the fabric sample; and (3) the fabric sample was allowed to dry in the flask at room temperature. This took from 45 min to 1 hr.

The pesticide fortified fabrics were extracted by the following procedure: (1) 50 ml of hexane were added to each flask and the flask was stoppered with a glass stopper; (2) the stoppered flask was placed on a Burrell® Wrist-Action shaker and agitated for 15 min, 30 min, or 1 hr; (3) 10 ml of the extract were removed from the flask and transferred to a sample bottle; and (4) the remaining extract was decanted by pouring off the extracting solvent using a sterile glass rod to retain the fabric sample in the flask.

For the second and third extractions 50 ml of hexane were added and steps 1 through 4 repeated. Then 10 ml of the second and third extractions were removed from the flask and all three extraction samples were stored in separate vials.

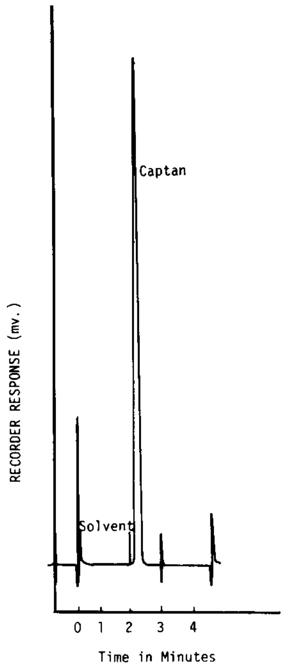

Figure 1. Gas Chromatogram of Captan® Standard Solution (4 ng of Captan®)

External standard procedures were used to quantify the % recovery from pesticide fortified fabrics. Known amounts of Captan® standards (in the range being evaluated) were injected before and after every four injections of fabric extracts. If the standard differed more than 1% from the original calibration curve, the gas chromatograph was recalibrated. The CDS-111 Integrator was programmed for external standard procedures. The detector's response to the standard solutions, measured in peak areas, was ratioed to the peak areas produced by the fabric extracts. The results were recorded in $\mu g/cm^2$.

RESULTS AND DISCUSSION

The peak height, symmetry, band width and column retention time of a 4 ng sample of Captan® are illustrated in Figure 1. The electron capture GC response for the Captan® standard solutions, in the absence of fabric extracts, were linear within the range of 100 pg to 20,000 pg.

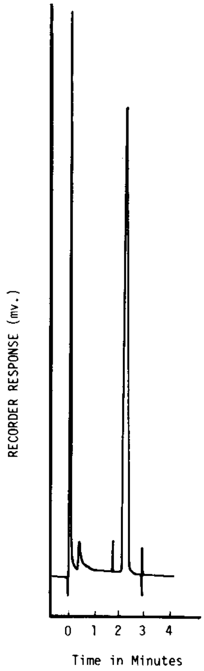

Figure 2. Gas Chromatogram of fortified fabric extract (2 ml injection of a 1 µg/ml spike)

In addition to the major Captan® peak, a small peak having a retention time of approximately 1.5 min was also evident. No attempt was made to identify this component as it was assumed to be due to the detergent (Liquid All®) which was used in the prewashing of the fabrics. This impurity appeared in all extracts of the fabrics with the exception of Tyvek® and 100% cotton gauze, which had not been prewashed. With the exception of the detergent peak, negligible amounts of interfering materials were found in the fabric extracts of all nine fabrics and the fabric extracts were analyzed directly.

Part of this study involved evaluation of the length of time required to effeciently extract fabric samples; 15 minute extractions vs 30 min extractions vs 1 hr extractions were analyzed. The fabrics denim, chambray, Gore Tex® and Tyvek® were used. The fabrics were fortified with 200 mg/ml of Captan® standard solution. After air-drying, one set of fabric samples was extracted for 1 hr, a second set for 30 min, and a third set for 15 min. The analysis of the extracts showed that the % recoveries were not statistically different for all fabric types for the 30 min and 1 hr extractions. However, analysis of the extracts from the 15 min extractions produced lower recoveries in some cases, in the range of 89 to 97%. Therefore, all subsequent extractions involved the use of 30 min extractions.

To determine the number of extractions required to obtain approximately 100% extraction efficiencies, nine fabric variations (3 samples/fabric type) were fortified with 1 ml of Captan® standard stock solution and then subjected to two consecutive 30 min extraction procedures. The extracts were each analyzed by gas chromatography. Recovery values from the first extraction ranged from 96 to approximately 100% with a mean value of 98% (Table 2).

Table 2: Recovery of Captan® From Fabrics

FABRIC	EXTRACT 1		EXTRACT 2		
	RECOV'D (P.P.M.)	RECOV'Y %	RECOV'D (P.P.M.)	RECOV'Y %	TOT RECOV'D %
100% Cotton Knit					
Mean	3.99	100	0.12	3	103
S.D.	0.04		0.02		
50/50 Cot/Poly Knit					
Mean	3.89	97	0.11	3	100
S.D.	0.08		0.02		
100% Cot Chambray					
Mean	3.83	96	0.04	1	97
S.D.	0.04		0.05		
100% Cot Denim(14oz)					
Mean	3.92	98	0.10	2	100
S.D.	0.11		0.00		
Gore Tex® (Nylon Tricot/Ripstop)					
Mean	3.91	98	0.03	2	100
S.D.	0.07		0.00		
Tyvek®					
Mean	3.85	96	0.03	1	100
S.D.	0.07		0.00	1	
100% Cot Denim(10oz)					
Mean	3.95	99	0.14	3	102
S.D.	.04		.04		
100% Cot Gauze					
Mean	4.04	101	0.27	6	107
S.D.	0.07		0.01		
Gore Tex® (Polyester Tricot)					
Mean	3.99	100	0.06	2	101
S.D.	0.02		.01		

Note: Fortification 4.00 ppm.

From these data it is apparent that one 30 min extraction was a reproducible and highly efficient procedure. Recoveries from the second extraction ranged from 1 to 3% for all fabrics with the exception of 100% cotton gauze, which averaged 6%. When analyzed on the gas chromatograph the third extract produced no detectable residues. It was concluded that residues were below the the detection limit of the GC system. It was noted during the decanting procedure that the fabrics which gave the higher percentage of residue in the second extract tended to retain more of the extracting solvent from the first extraction procedure. This may have been a result of a combination of factors including fabric construction, fabric weight and fabric thickness. This may be especially true with gauze, as multiple layers were used for the test sample compared to a single layer sample for the other fabrics.

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REFERENCES

EASLEY, C.B., LAUGHLIN, J.M., GOLD, R.E. and D.R. TUPY: Bull. of Environ. Contam. Toxicol. 27, 101 (1981).

FINDLEY, E.L. and J.R.B. ROGILLIO: Bull. Environ. Contam. Toxicol. 4, 6, 343 (1969).

MANUAL OF ANALYTICAL METHODS FOR THE ANALYSIS OF PESTICIDES IN HUMANS AND ENVIRONMENTAL SAMPLES. EPA-600, Health Effects Research Laboratory, Research Laboratory, Research Triangle Park, NC (1980).

ORLANDO, J., BRANSON, D., AYRES, G. and R. LEAVITT: J. Environ. Sci. Health B16, 5, 617 (1981).

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