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Incomplete Removal of the Pesticide Captan from Skin by Standard Handwash Exposure Assessment Procedures

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The dermal route of exposure is often the primary route of occupational exposure to pesticides, and several investigators have reported that over 60% of the total absorbed dose was contributed by the dermal route (Durham et al. 1972; Fenske and Elkner 1990). Although handwashing procedures to assess occupational dermal exposure have been standard practice for several decades (Durham and Wolfe 1962), the validity of these results are not typically addressed. As a significant quantity of pesticide may remain sorbed to the skin on the hands, handwashing procedures probably underestimate exposure. Moreover, for those pesticides that most sorb to skin, handwashing exposure assessment procedures result in the most significant underestimates of the physiologically relevant dose.

The purpose of this study was to determine the removal efficiency of the pesticide captan from participants' hands. Removal efficiency is defined here as the ratio of captan removed from the hand by handwashing to the total captan originally on the hand. Captan (3a,4,7,7a-Tetrahydro-2-(trichloromethyl)thio)-lH-isoindole-1,3(2H)-dione), CAS registry number 133-06-2, is a foliar fungicide used widely, and increasingly, in agricultural production, as well as in consumer pesticide products (Hayes and Laws 1991). It is classified as a probable human carcinogen (Group B2) by the U.S. Environmental Protection Agency, and it has been reported to cause contact dermatitis (Hayes and Laws 1991). This laboratory study demonstrates that removal of captan from hands by handwashing is incomplete, with only 68% of captan recovered from hands when handwashing was conducted one hour after hand contact with the pesticide.

MATERIALS AND METHODS

Removal efficiency of captan from hands by handwashing, both immediately and after one hour, was determined in the laboratory, following procedures detailed in a similar study on chlorpyrifos (Fenske and Lu 1994). To simulate occupational hand exposure to captan, participants grasped test tubes that had been spiked on their outer surface with a known quantity of captan in a wettable powder formulation. Following the hand contact, each test tube was then eluted (rinsed) with solvent to determine the quantity of captan not transferred to the hand. For one group of participants, each hand was immediately washed twice according to a well-defined handwash protocol (Fenske and Lu 1994). For a second group of participants, the handwashing procedure was conducted one hour following the controlled exposure. Handwashes were extracted with solvent and analyzed to determine the quantity of captan that could be removed from

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the hand. Elution efficiency and extraction efficiency were determined using spiked controls, and experimental results were corrected based on these determinations. The experimental method is described in detail below.

Removal efficiency from hands was calculated assuming mass balance, as represented in the equation below and illustrated in Figure 1. Captan that was neither left on the test tube nor recovered in the handwash was assumed, after elution and extraction efficiency corrections were made, to have remained sorbed to hands. A mass balance approach assumes that no degradation of captan occurred, which is supported by our observation of stability of captan levels over one hour in the handwash solution.

$$M_{spike} = M_{elute} + M_{wash} + M_{hand} \quad (1)$$

where:

M_{spike} = total mass of captan spiked onto test tube;

and

M_{elute} = mass of captan eluted from test tube following hand contact (non-transferred captan);

M_{wash} = mass of captan in handwash; and

M_{hand} = mass of captan remaining sorbed to skin on hands after the handwash procedure.

The removal efficiency of captan from hands by the handwashing procedure was defined as percent of the captan transferred to hands (i.e., not remaining on the test tube) that was observed in the handwash soiution. The removal efficiency can thus be expressed as follows:

$$\text{Removal efficiency (\%)} = \frac{M_{wash}}{M_{spike} - M_{elute}} \times 100 \quad (2)$$

To ready test tubes for hand contact, a solution of captan formulated as a 50% wettable powder in acetone (solubility approximately 20 mg/g) was prepared, and glass test tubes were spiked on the outside with 250 µl of the solution using a positive displacement micropipettor. This step is illustrated in Figure 2, part A. The tube was rotated during the spiking procedure to produce uniform coverage over the test tube's surface area of approximately 42 sq cm. The precise spike level was determined by spiking extraction solution controls with the same quantity of the same solution; the average total captan spiked on test tubes was 6.5 mg, at an area1 density of 0.15 mg/sq cm. Test tubes were allowed to dry under a fume hood for 10 minutes prior to contact with participants' hands. Additional tubes were prepared arid eluted to determine the quantity of pesticide applied for each experiment. The mass of captan eluted from these spiked test tubes was considered to be the mass available for transfer to participants' hands. Participants washed their hands with soap and water prior

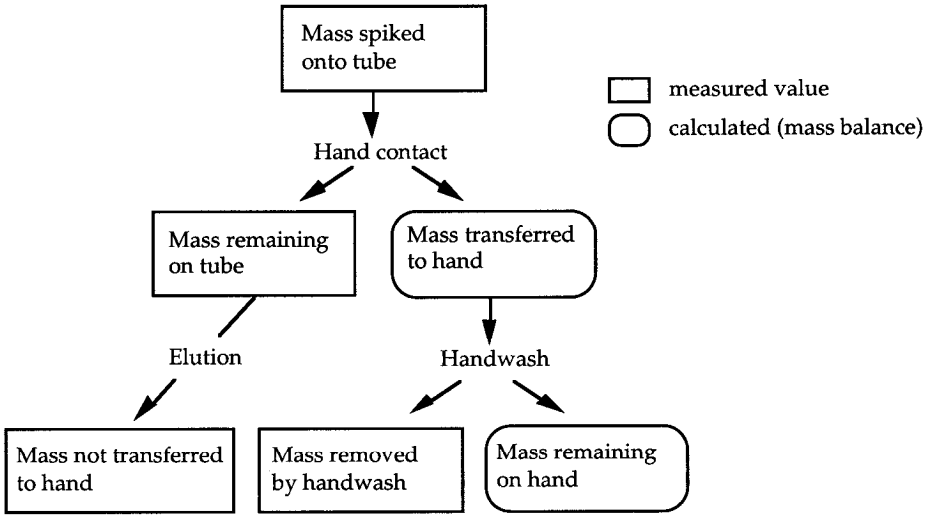

Figure 1. Mass balance for pesticide handwash removal experiment.

to the experimental exposure. The experiment was approved by the Rutgers University Institutional Review Board for the Protection of Human Subjects in Research, and all participants provided their informed consent.

For each observation, each participant grasped a spiked test tube firmly with one hand (as shown in Figure 2, part B) and slid the hand down the test tube; this was repeated 10 times per observation. A funnel and sample jar placed below the test tube ensured that any dislodged captan would be captured in the elution step. The participants then rubbed the fingers of the same hand against the palm to more evenly distribute the captan. After the initial six participants (n = 12 hands) were sampled at time = 0, a modified grasping procedure, which did-not alter the validity of the mass balance approach, was instituted in order to obtain more complete transfer of captan to hands. Participants under the modified procedure grasped the tube ten times while the technician rotated it in place. To maintain the prior total mass of captan transferred to the hands while following the modified procedure, the spike level was reduced from 7.4 mg to 5.6 mg for these participants. The modified grasping procedure was used for three participants (n = 6 hands) in the immediate handwash group, and for all six participants (n = 12 hands) in the group for which handwashing was conducted at time = 1 hr.

To measure the mass of pesticide that was not transferred to hands, each handled test tube was eluted twice, with 30 mL of toluene from a volumetric dispenser, over the funnel into the 4-0z jar, as shown in Figure 2, part C. The funnel was rinsed twice with 10 mL of toluene into the same sample jar (total sample volume = 80 mL). It was assumed that this solution contained all the captan that was not transferred from the test tube to the skin. The jar was capped and either analyzed immediately or frozen for later analysis.

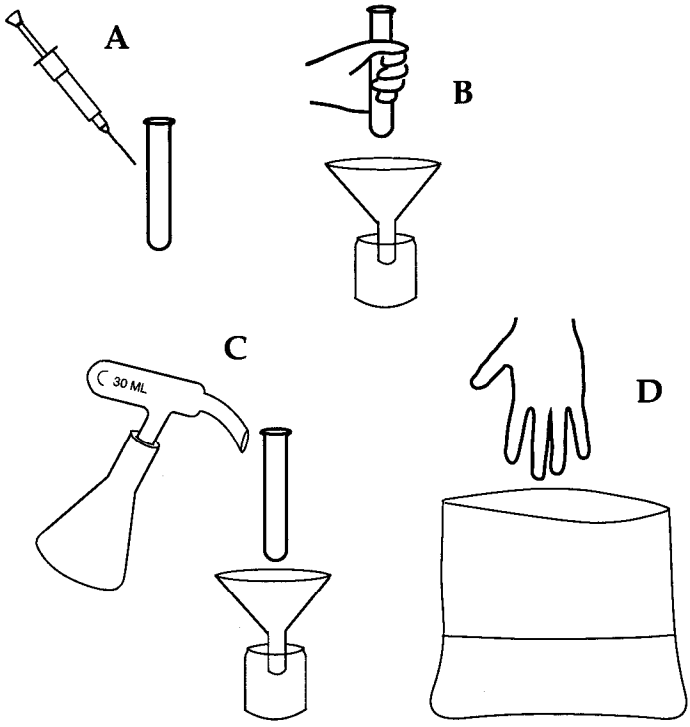

Figure 2. Schematic diagram of handwash removal efficiency experimental design. **A)** With a micropipettor, the pesticide captan in acetone solution is applied to the outside of a test tube and allowed to dry in a laboratory hood. **B)** Captan is transferred to the hand of the study participant; a funnel and sample jar capture any pesticide that falls off the tube. **C)** Pesticide remaining on the tube is removed by elution, i.e., two rinses of the test tube using 30 mL toluene from a volumetric dispenser for each rinse, plus two rinses of the funnel, each using 10 mL toluene. **D)** Hand is washed twice in 250 mL of 10% isopropanol/distilled water with vigorous shaking for 30 sec. in a polyethylene bag. Captan is then extracted from the handwash solution with toluene and a saturated sodium chloride/distilled water solution. Handwash removal efficiency is then calculated based on equations (1)

Each hand was washed twice using separate polyethylene bags (31 x 25 cm) containing 250 mL of the handwash solution (10% isopropanol in distilled water), as illustrated in Figure 2, part D. The hand was shaken by the technician for 30 sec. The two samples were poured immediately into a 1 L jar; the 500 mL solution was mixed thoroughly, and a 60 mL aliquot removed into a 4-oz jar and frozen prior to analysis. A 2 mL aliquot was dispensed into a previously prepared extraction solution and extracted as described below. At the end of the experiment participants washed their hands with soap and water to further remove residual pesticide. For nine participants (n = 18 hands), handwash samples were collected immediately (within 2 minutes of the initial hand contact with captan) following hand exposure, and for six different participants (n = 12 hands), samples were collected after one hour. To separately determine the removal contribution of each 30-sec handwash, the two handwashes were stored and analyzed separately for a subset of six participants.

Table 1. Elution efficiency of captan from test tubes(mean and coefficient of variation).

Captan in spiked controls (mg)	Captan from eluted spiked tubes (mg)	N	Elution efficiency[a] (%)	CV (%)
13.6	12.9	6	94.5	0.2
11.4	10.9	6	95.7	1.3
Mean elution efficiency		**12**	**95.1**	

[a] Elution efficiency is defined as the ratio of the mass recovered from the rinse solution to the mass originally applied to the test tube.

Table 2. Extraction efficiency of captan from handwash solution (mean and coefficient of variation).

Captan in spiked extraction solution (mg)	Captan in extraction solution, after handling as handwash sample (mg)	N	Extraction efficiency (%)[a]	CV (%)
1.27	1.20	3	94.4	2.4
2.51	2.26	9	90.0	4.4
3.80	3.21[b]	3	84.4	2.9

[a] A trend of reduced extraction efficiency with increased spike level was observed (linear regression $p<0.003$, $r^2=0.51$)

[b] Because the mass of captan extracted from these extraction efficiency samples was most similar in value to the average experimental handwash mass of 3.2 mg, the corresponding extraction efficiency value (84.4%) was used to adjust the experimental data.

For each sample, 2 mL of the handwash solution was extracted with 10 mL toluene and 2 mL saturated sodium chloride solution in distilled water. Samples were shaken under the same conditions for 90 minutes, and the solvent layer was collected after five minutes. Captan was analyzed with a Varian 3700 gas chromatograph equipped with an electron capture detector, a Varian auto injector and a Spectraphysics integrator. Duplicate 1 µL injections were conducted for all samples. Samples for which the coefficient of variation of replicate injections was >5% were rerun. The limit of detection was 0.16 ng/µL.

The elution and extraction efficiencies were assessed using spiked controls. Elution efficiency was determined by spiking six test tubes with two applications of 250 µL of the acetone solution of captan; each test tube was rinsed twice (eluted) with 30 mL toluene from a volumetric dispenser. Both rinses were collected in an 8-oz sample jar. Triplicate controls were produced by spiking the captan solution directly into sample jars containing 60 mL of toluene.

To assess extraction efficiency, 500 mL of the handwash solution in polyethylene bags was spiked; the bags were then closed and shaken for 30 sec, the solution was split into three sample jars, and an aliquot from each jar was extracted as were the handwash samples. Extraction efficiency controls were prepared by adding the pesticide formulation directly into the extraction solution. To independently assess the effect of the polyethylene bag on extraction efficiency, a similar determination of handwash extraction efficiency was made by spiking

Table 3. Captan handwash removal efficiency (means and coefficients of variation) for time = 0 and time = 1 hr.

Time[a] (hr)	N[b]	Total spike (mg)	Captan transferred to hand[c] (mg)	Captan removed from hand (mg)	Handwash removal efficiency[d]			
					2 washes (%)	CV (%)	1st wash only (%)	CV (%)
0	12	7.43	4.37	3.81	90.7	22	78.1[e]	--
0	6	5.62	5.25	4.10	77.8	18	67.1	22
1	12	5.88	5.62	3.85	68.4	7	58.9[e]	--

[a] Time between skin contact and handwashing.
[b] N = number of hands.
[c] An imroved protocol for transfer of pesticide to hands (described in Materials and Methods) was used for the second and third set of participants represented in this table.
[d] Removal efficiency is the mean ratio of captan removed from the hand by handwashing to the total captan originally transferred to the hand.
[e] These numbers were calculated based on the ratio of removal in the first wash to removal after two washes; washes were analyzed separately only for the second set of participants for hand residence time = 0.

handwash solution in jars, shaking the jars, following the extraction procedure, and comparing to extraction efficiency controls.

RESULTS AND DISCUSSION

Results of the elution efficiency determination (shown in Table 1) indicate that solvent rinsing of spiked test tubes produced nearly complete pesticide removal with a high degree of precision. An average of 95.1% of the captan was eluted, and this value was used to correct the experimental handwash removal data reported here in Table 3.

Results of the extraction efficiency determination are shown in Table 2; the data are suggestive of a trend of lower extraction efficiency for higher concentrations. Because the handwash recovery mass of 3.21 mg seen for the third group of extraction efficiency samples was closest to the average handwash removal values of 3.2 mg seen in the experimental data, the corresponding extraction efficiency value of 84.4% was used to correct the experimental data. The comparison of extraction efficiency in jars as compared to polyethylene bags suggested that 99% of extraction losses were attributable to the bags themselves.

Experimental handwash removal efficiency results are shown in Table 3. Removal of 77.8% of the captan transferred to hands was achieved in the group for whom handwashing was conducted immediately; efficiency was reduced to 68.4% after one hour's residence on the hand. Data for the subset of participants for whom the two serial handwashes were analyzed separately indicated that 86% of the removed captan was removed in the first handwash, and the remainder was removed in the second handwash. The proportions of removal and hand sorption of captan at time = 0 and time = 1 hr are illustrated in Figure 3.

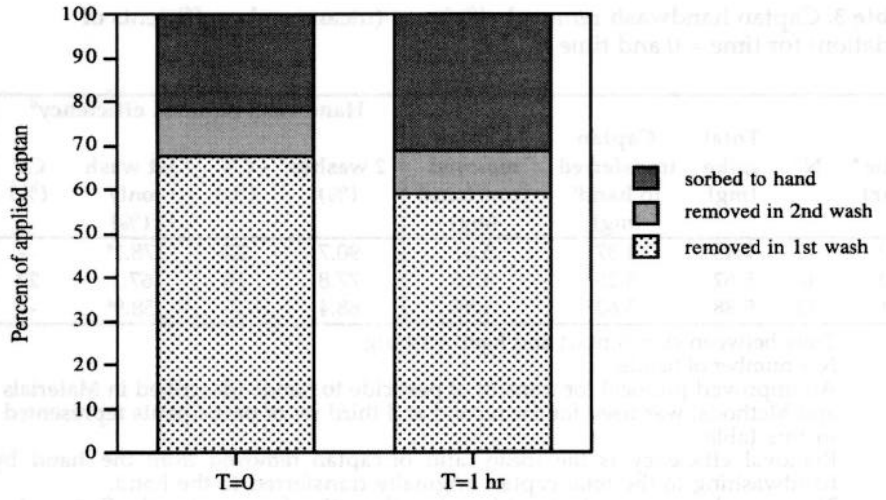

Figure 3. Removal and hand sorption of captan for time = 0 and time = 1 hr.

Occupational hand exposures to captan in peach harvesting have been reported at rates of approximately 10 to 20 mg/hr for each hand, resulting from work in orchards where dislodgeable foliar residues averaged 6.4 µg/sq cm (Fenske et al. 1989). Thus, although this laboratory experiment delivered an exposure that is considerably higher per surface area (0.15 mg/sq cm on the test tube surface) than reported captan leaf residues, workers' many contacts with pesticide-bearing surfaces and longer duration of exposure make these experimental exposures (5 mg per hand, one-time exposure) substantially lower than an orchard worker's potential hourly hand exposure.

A laboratory study on handwash removal of the pesticide chlorpyrifos demonstrated that removal was significantly lower (43% at time = 0 and 23% at time = 1 hr) than that of captan in this study (Fenske and Lu 1994). The differences can be explained in large part by 1) the much greater lipophilicity of chlorpyrifos, as represented by the log octanol/water partition coefficients of the two pesticides: log K_{ow} = 4.96 for chlorpyrifos and log K_{ow} = 2.35 for captan (Howard 1991); and 2) the differences in formulations, captan being formulated as a wettable powder while the chlorpyrifos formulation used was a liquid concentrate with an emulsifying agent.

Factors that have been reported to affect the removal of a particular pesticide from hands by handwash procedures include characteristics of the pesticide, its formulation, the specific handwash solution and handwashing procedures, use of gloves, and the complicated dynamics of pesticide loading and skin sorption (Fenske and Lu 1994). Furthermore, skin characteristics, the anatomical site of exposure, occlusion of the applied dose, and co-exposures or post-exposures to aqueous, alcohol, or solvent solutions all affect skin sorption of pesticides. (Wester and Maibach 1985). In the absence of experimental data on exposure to a given pesticide as measured with handwash procedure, models based on comparison to reported scenarios and the use of pesticide physical and chemical constants can be used to predict approximate removal efficiency. In spite of current gaps in scientific knowledge and empirical information for handwash

removal, it remains clear that interpretation of handwash exposure assessment values must take into consideration incomplete removal of pesticides by handwashing techniques.

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