Analytical method for assessing potential dermal exposure to captan, using whole body dosimetry, in small vegetable production units in Argentina

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Abstract: An analytical method has been developed that can be used to determine the potential dermal exposure (PDE) of workers to the pesticide captan in small-scale horticultural production units. The methodology is based on the whole body dosimetry technique, using a cotton coverall and cotton gloves as sampling media, with protective clothing worn beneath the cotton media to protect the operator. The quantitative determination of captan was done by gas chromatography-electron capture detector (GC-ECD), with the analytical method validated by measuring limits of detection and quantification, linear ranges, sample recovery and precision. Special emphasis is placed on factors that affected the stability of captan during chromatographic determination. The data generated for potential dermal exposure are presented separately for mixing/loading and application activities. These data are compared with values obtained with visible tracers using a similar field technique. Margin of safety (MOS) values are also calculated for the agricultural procedures studied.

Keywords: captan; potential dermal exposure; periurban agriculture; GC-ECD

1 INTRODUCTION

Measurement of potential dermal exposure (PDE) is a key component of pesticide risk assessment, providing vital information on the quantity of a chemical substance contaminating uncovered body regions and clothing worn by pesticide handlers; in this sense, the margin of safety (MOS) formula has been proposed as a fast and simple indicator of risk,[1] comparing the acceptable exposure of a product with the quantity absorbed from exposure, plus a certain safety factor.

In the last 40 years, exposure to chemicals via the dermal route has received a great deal of attention. In the particular case of agricultural workers, this is partially explained by the fact that agriculture has seen an increasing use of pesticides during this period and it has become a central production activity throughout the world.[2] Although the determination of dermal exposure of these workers has been studied for several years, developing relationships between the PDE and different variables such as the type of crop, crop size, application technique, weather conditions, personal protective equipment, etc., is a relatively recent idea.[3] All these variables should be analyzed to allow the development of efficient predictive contamination scenarios and adequate labourer legislation.

The use of pesticides is usually regulated through official risk assessment, which includes – at least – hazard identification and risk characterization.[4] In developed countries, another issue evaluated is the exposure assessment for pesticide handlers. For example, EU countries, by establishing exposure data requirements, do not allow a pesticide to be authorized unless there are specific data or adequate model predictions to show that in normal use the operator exposure levels would be below the acceptable operator exposure level (AOEL). In Argentina, although improvements to the phytosanitary product registration process have occurred in the last 10 years, no occupational exposure data are required to obtain a commercial license for a pesticide.

The labourer's exposure situation is particularly delicate in small-scale production units. Buenos Aires is surrounded by a 'green belt' consisting of 14 districts with a total area of 18 000 ha with diverse and complex economic activities. One of these activities is periurban horticulture (agricultural practice in areas close to urban concentrations). The district of Moreno (Fig. 1) was selected as the research zone. In this area, horticulture has been developed principally by Bolivian immigrants in small production units (less than 5 ha) under poor working conditions (lack of education,

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(*Received 10 May 2005; revised version received 24 November 2005; accepted 22 December 2005*)
DOI: 10.1002/ps.1232

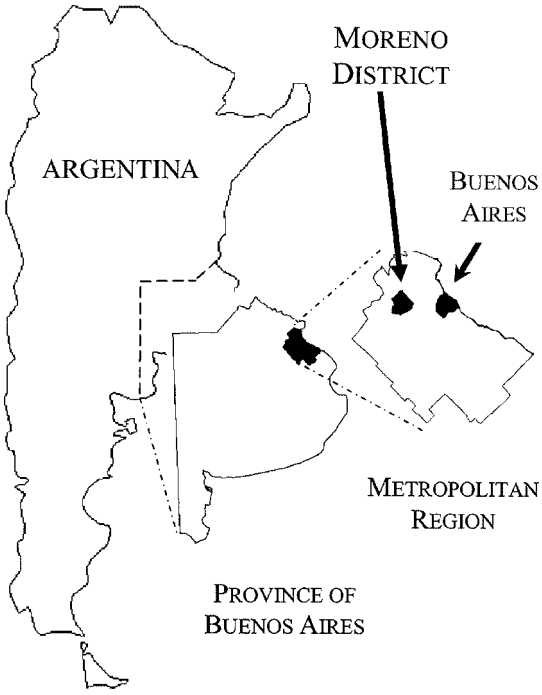

Figure 1. Location of the Moreno district in Argentina.

low technology, manpower dependent). Although many of them have become Argentine citizens, they have remained a closed community for many years, with their own particular horticultural traditions and practices. In recent years they have received technical support from the local government which prompted them to form an associative production system. The total production area covers 550 ha, with 64 production units and 250 workers. The main crops are tomato, lettuce, Swiss chard, onion, beet, maize and strawberry.

The working conditions of this community are very different from those in extensive agriculture, the prevalent mainstream production in Argentina. As a consequence of the social and economic vulnerability of this group, it is important to estimate the PDE of these workers, in order to evaluate the potential risk posed by pesticides, because their general PDE cannot be readily extrapolated from the existing national literature.

Therefore, the decision was made to determine the PDE of what was considered to be the most exposed group of workers, the pesticide applicators. The fungicide captan, *N*-(trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide, CAS RN [133-06-2], was selected for these studies. The EPA has recently determined that captan is 'not likely to be a human carcinogen at dose levels that do not cause cytotoxicity and regenerative cell hyperplasia' and 'not likely to be carcinogenic to humans via the dermal exposure route' owing to the very low dermal penetration of captan.[5]

In general terms, the interpretation of data for PDE is a complex task, as a consequence of the variability of multiple factors that affect this parameter. For example: crop height and separation between rows, application technique and volume, application time, temperature, humidity, wind speed and direction.[6]

In the particular case of captan, a factor that could greatly affect the accuracy of the PDE measurements is the analytical methodology applied. Most analytical chromatographic methods involve capillary gas chromatography with electron capture detection[7] or mass-spectrometry detector.[8] Alternatively, HPLC methods with electrochemical detection[9] and polarographic[10] methods have been reported.

The present work sets out the preliminary results for the PDE of pesticide applicators in small-scale and low-technology production units, developing the analytical methodology for the determination of the fungicide captan by gas chromatography-electron capture detection (GC-ECD). Critical variables affecting sensitivity and recovery of captan are discussed and compared with those given in previous reports. The GC-ECD data are compared with values obtained using dye tracers.

2 EXPERIMENTAL METHODS

2.1 Sites

All the field experiments were done in a small production unit in the Moreno district between June (winter) and December (summer) (Fig. 1). The selected site was a small maize field 45 m long and 12 m wide. The maize crop height was between 1.7 and 2.0 m, and rows were separated by 0.8 m. In all experiments, ambient temperature was between 18 and 29 °C, relative humidity was 50–60% and the wind velocity did not exceeded 14 km h^{-1}.

2.2 Reagents and materials

Solid captan (reference material, 97.2% purity) was dissolved in acetone (110 mg L^{-1}) as a primary stock solution. Other working solutions were prepared by dilution. Acetone (Aberkon pesticide grade) used for extraction was distilled prior to use and chromatographically checked as suitable for use under GC-ECD conditions. The captan commercial formulation used in field trials was an 850 g kg^{-1} wettable powder (Tomen-Chemiplant•).

For the dye tracer experiments, a concentrated solution was prepared using 10.00 g of Brilliant Blue No. 1 (C.I. 42090, Warner Jenkinson•) and 1.70 g of surfactant (Triton XL-100 – Amersham), dissolved in water (500 mL). This provided a suitable concentration for spraying when diluted with water in a 20 L backpack. A primary stock solution of 100 mg L^{-1} tracer in water was used to prepare all calibration solutions.

Silanized glass wool (Perkin-Elmer•) was used in the GC injector stability studies.

2.3 Instrumentation

All chromatographic analysis was performed on a Perkin-Elmer (Norwalk, CT, USA) AutoSystem XL gas chromatograph with an Autosampler automatic

injector, equipped with ECD, and a fused silica capillary column (PE-5, 100% methylpolysiloxane• stationary phase, 30 m length, 0.25 mm i.d. and 0.025 mm film thickness).

For the tracer studies a double-beam Perkin-Elmer Lambda 20 UV/VIS spectrophotometer was used.

2.4 Chromatographic conditions

The GC-ECD operating conditions for PDE determinations were as follows. Injector temperature 60–260 °C, ballistic; ECD temperature 350 °C; oven temperature 80 °C for 1 min, then 40 °C/min to 260 °C, and holding for 4 min; injection volume 5 μL; carrier gas nitrogen at 30 psi head pressure, split ratio 10:1; ECD auxiliary flow 40 mL min^{-1}. For thermal decomposition studies, either the oven temperature or the injector temperature was held steady at different values, with all other parameters as given above.

2.5 Sampling method and field procedure

The potential dermal exposure was measured using the whole body dosimetry technique.[3] Cotton fabric was selected for the following reasons:

- high absorption of water-based spray mixture;
- low retention of captan when extracted with acetone;
- high cost and low commercial availability of other materials, such as Sontara®.

As there were no 100% cotton coveralls commercially available, one was designed and manufactured in-house; for this, a series of different commercially available cotton materials were tested in the laboratory for water retention and pesticide recovery (data not shown). Coveralls were manually washed with water prior to use to remove fabric sizing. Two different operators performed the spray applications under normal working conditions (one application per day).

The operator was dressed with protective equipment (30 cm high rubber boots, a Tyvek coverall and latex gloves) over which the absorbent media were worn: the cotton overall with hood, cotton gloves and a half-face respiratory mask with two 2.2 g pads of cotton-wool as filter material. The operator also wore goggles.

The operator prepared an initial dispersion of either captan formulation or specially prepared dye concentrate in water and diluted it up to the total volume of the sprayer – a Jasco 20 L lever-operated knapsack, 60 cm lance with a single nozzle (Jasco JD-12P model), working pressures typically between 45 and 70 psig (310 and 480 kPa gauge) – in the usual way. After preparing the knapsack for spraying, the cotton gloves were exchanged for a clean set; if any contamination of the coverall was observed, this was also changed. The operator started spraying following his usual technique, with no other instructions. The application time was typical for small plot treatments, usually between 15 and 20 min, at an application rate of 60–80 L h^{-1}, being short enough to avoid overexposure and/or runoff of the spray mix from the suit. The application was done with both an upward and downward technique, spraying from ground level to shoulder height, walking along one row and returning along the next one. Halfway through the procedure, a 10–20 mL tank sample was sprayed into a bottle for further analysis. After the application was finished, the air filters and gloves were removed and placed in individual plastic bags. The facemask plus the filter were swabbed with a damp tissue and bagged for rinsing in the laboratory. Then the cotton coverall was taken off and hung up to dry in the shade. The Tyvek coverall was checked for stains that could indicate penetration of the cotton suit.

Duplicate blanks as well as captan and tracer recovery samples were prepared at the laboratory. The spiking volume used for this was roughly equivalent to the volume expected to contaminate one lower arm section.

2.6 Analysis

In the laboratory the cotton suit was cut into pieces, as indicated in Fig. 2, and then extracted. When measuring captan, coveralls, gloves and swabs were extracted not later than 5 h after the field trial. The pieces were placed in glass (450 mL) or polypropylene

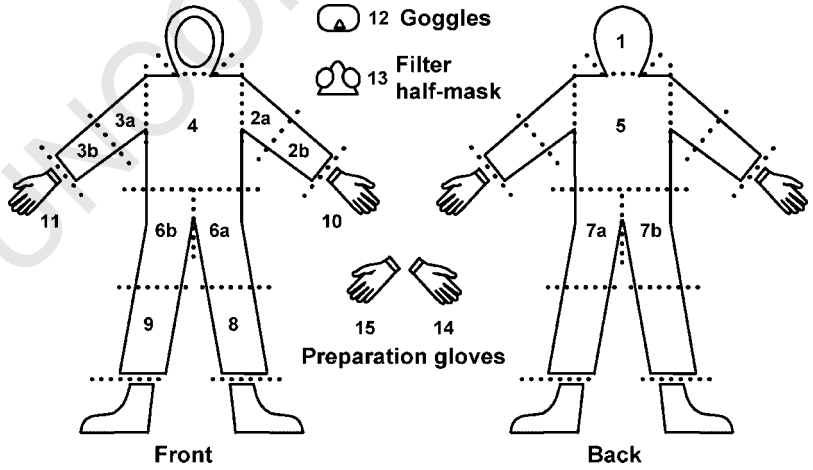

Figure 2. Coverall cutting scheme.

(1 L) containers and extracted using different volumes of acetone, standardized according to the amount of sampling material in each flask. The containers were shaken for 20 min in a rotary shaker at room temperature. A 1 mL fraction of each extract was sealed into a GC vial and stored in a refrigerator until analysis (not more than 1 day).

For the coloured dye tracer studies, the same procedure was followed, using distilled water instead of acetone in the extraction step. A sample of 2–3 mL of each extract was filtered through a 0.45 µm pore syringe filter (mixed cellulose esters) directly into a 1 cm glass cuvette, its absorbance was measured at 629 nm using water as a blank and the tracer concentration was calculated for each sample. Calibration was done once for each set of samples, in the range 0.05–15 µg L^{-1}.

2.7 Calculation of potential dermal exposure

The concentration of tracer or pesticide in each extract and its volume were used to calculate the amount deposited on each coverall part. The concentration of the sprayed mixture was determined by analysis of the tank sample. Both values were combined with the duration of each experience, thus giving a time rate value for the potential dermal exposure. The results are presented (see Table 2) as volume of sprayed liquid per unit of time (i.e. mL h^{-1}) for each body part. Data for facemask and goggles were not included in the 'total' PDE value for easy comparison with other published values. Data for gloves used during the preparation of the spray mix are also expressed separately, but as total amount (mg) and not time rate, as this step is not time dependent.

In the event of more than one 20 L tank being applied in a day, it could be more convenient to express PDE as mg of captan per complete mixing/loading/application procedure, so the total PDE is simply the product of the single PDE and the number of applications.

3 RESULTS AND DISCUSSION

3.1 GC-ECD methodology for captan determination. Validation of the GC methodology

3.1.1 Stability of captan on the cotton cloth matrix

There are various factors that may affect the stability of captan. In the first place, the influence of the cotton material matrix was studied in order to determine the maximum acceptable time period during which the samples could be stored without decomposition. Pure samples in acetone were stable for several days at 4 °C (data not shown), whereas the product absorbed on the cotton rapidly decomposed. Figure 3 presents captan recovery from cotton cloth extracted with acetone at the 5 mg L^{-1} level, as a function of storage time at two different temperatures. In the first case, cotton pieces fortified with pure captan were stored at 20 °C, while a second set of material was stored at 4 °C.

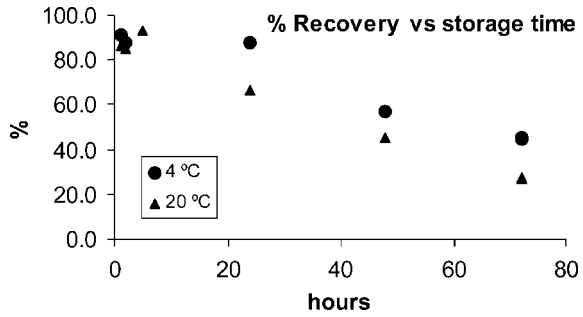

Figure 3. Captan recovery from the cotton matrix for laboratory samples spiked at 5 mg L^{-1} as a function of time at 4 °C and 20 °C.

In both cases, decomposition is evident, the rate at 4 °C ($t_{1/2}{}^{4\,°C} = 65$ h) being lower than at 20 °C ($t_{1/2}{}^{20\,°C} = 45$ h). It was therefore decided that captan samples should not be kept at room temperature for more than 5 h before extraction, in order to reduce degradation.

Another critical factor is the thermal stability of captan in the gas phase at high temperatures. It is well known that this fungicide thermally degrades, separating its trichloromethylthio and tetrahydrophthalate moieties, producing tetrahydrophthalimide and phosgene. It has been reported that, when captan was analyzed via GC, decomposition mainly occurred in the column when oven temperatures exceeded 210 °C.[8]

Therefore, work was done to evaluate the thermal stability of captan at the critical hot points of the chromatographic system – column and injector – as well as the influence of the silanized glass wool. For this, measurements were made of the area of the signal obtained with:

- different oven temperatures in isothermal runs;
- different injector temperatures;
- different amounts of glass wool in the injector.

The results are summarized in Table 1.

As can be seen from Table 1, column temperature was an important factor associated with the stability of captan. The relative area was at its maximum at 200 °C and decreased at higher temperatures, as indicated in the literature, but with a very unfavourable area/height ratio at all temperatures, as well as very low selectivity. It was not possible to obtain captan with reasonable retention times below 180 °C. Therefore, the selected temperature program for the method, as described in Section 2, was a compromise between selectivity and thermal stability.

Captan can also be thermally degraded at the injector, where two factors play a major role. The first one is the injector temperature itself. It can be seen from Table 1 that, when the injector temperature is reduced, the relative area increases. However, in spite of greater areas occurring at 150 and 100 °C, the method intermediate precision was found to be very poor (<20%). Therefore, ballistic temperature programming was tried, providing improved thermal stability with reasonable precision (see Section 3.1.6).

Table 1. Captan thermal decomposition at the column and the injector

T_{oven} (°C)	Relative area[a]	Area/ height[b]	$T_{injector}$ (°C)	Relative area[c]	Mass• of glass wool (mg)	Relative area[d]
250	1.000	7.0	300	1.000	**Used: 0.9**	**1.000**
225	1.364	7.8	250	1.013	1.6	0.602
200	1.413	8.7	200	1.035	3.1	0.483
Program	**0.78**	**2.0**	150	1.551	4.6	0.245
–	–		100	1.709	7.3	0.154
–	–		**Ballistic**	**1.312**	–	–

[a] Signal area$^{T_{oven}}$/signal area$^{250\,°C}$ for a 10 mg L^{-1} captan sample.
[b] Area/height of the recorded peak in the chromatogram.
[c] Signal area$^{T_{inj}}$/signal area$^{300\,°C}$ for a 10 mg L^{-1} captan sample.
[d] Signal area^{mass}/signal area$^{0.9\,mg}$ for a 1 mg L^{-1} captan sample.

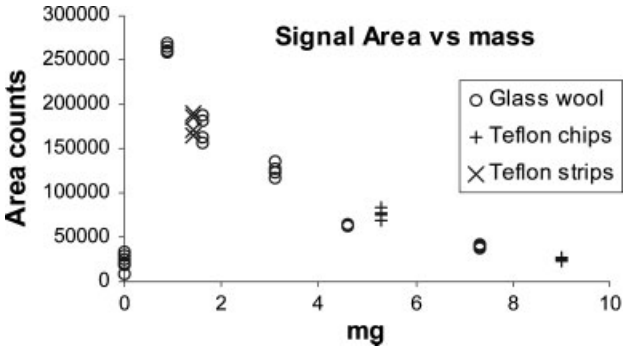

Figure 4. Captan thermal decomposition as a function of the mass of liner material.

Another factor that affected captan half-life at the injector was the amount of inert material in the liner. As can be seen from Table 1, when 5 µL of a captan solution (1 mg L^{-1}) was injected with different masses of silanized glass wool in the quartz liner, a sevenfold area reduction was observed when the amount of material was increased in the same proportion, indicating a direct relationship between captan degradation and glass wool content of the liner. When no glass wool was used, results were highly variable, although all values were very low, presumably owing to vaporization problems. Apparently, the effect is independent of the added material because, when Teflon® (chips and thin strips) was used instead of glass wool, the same phenomenon was observed (Fig. 4).

3.1.2 Selectivity

Chromatographic conditions were optimized so as to separate captan from thiophanate methyl, hexythiazox, deltamethrin and zineb. These were the agrochemical products most commonly used in combination (tank mix) with captan.

3.1.3 Limit of detection (LD) and limit of quantification (LQ)

The LD was calculated as the standard deviation of a 0.5 mg L^{-1} sample analyzed 10 times, and multiplied by the corresponding *t* factor. The LQ was determined as three times the LD. In this way the LD for captan was 0.075 mg L^{-1} and the LQ was 0.23 mg L^{-1}.

3.1.4 Linear ranges

The captan response was linear between 2 and 50 ng, with R^2 better than 0.999. A calibration curve was constructed between 2.5 ng (5 µL injected, 0.5 mg L^{-1}) and 25 ng (5 µL injected, 5 mg L^{-1}), with R^2 better than 0.999.

3.1.5 Recoveries

Recovery analysis was carried out by spiking and analyzing pieces of cotton fabric (20 × 20 cm) under the same extraction conditions as the clothing sections. The study was carried out at two concentrations of captan: 50 mg L^{-1} and 5 mg L^{-1}, and recoveries were between 83.7 and 107.6%.

3.1.6 Precision

The precision was studied following two different operators injecting 3 times each day during 6 different days. The variation of precision versus captan concentration was 20.7% (at the 0.5 mg L^{-1} level), 6.0% (at 5 mg L^{-1} level) and 6.5% (at the 50 mg L^{-1} level) expressed as percentage variation, and calculated as the standard deviation of all injections at each level.

3.2 Validation of the spectrophotometric methodology

3.2.1 Recoveries

In order to study the recovery of the dye from the different materials used, samples of cotton fabric (4), gloves (2), paper tissues (2) and cotton wool (2) were spiked with known amounts of Brilliant Blue and extracted as described in Section 2.6, giving final concentrations of 7–10 mg L^{-1}. Calculated recoveries were 103–109% for cotton cloth, 99% for gloves, 105% for tissues and 108% for cotton wool.

3.2.2 Linear range

Calibration was done in the range 0.05–15 mg L^{-1} for Brilliant Blue dye. In this range the response was linear, with R^2 correlation better than 0.998.

3.2.3 Variation of critical parameters

Pesticide formulations are diluted with groundwater for application. In the Moreno district this water tends to be hard, with an average value of 250 mg

$CaCO_3\ L^{-1}$ from the nine sites sampled. Because of this, three parameters that could affect tracer recoveries were studied: Ca^{2+} concentration, Mg^{2+} concentration and pH. No appreciable effect of these variables on Brilliant Blue recovery from cotton fabric was detected.

3.3 PDE results

As stated before, the PDE is a property that fluctuates greatly depending on multiple factors. One of the most important factors is operator experience. In Table 2, PDE using captan and coloured tracers is presented for two different operators: A, an experienced older person, and B, a young and practically inexperienced worker. Comparing both captan and coloured tracer PDE for operators A and B, similar results were found: the inexperienced operator was 13–17 times more contaminated than the more experienced one. These results could be explained by the different application techniques used by the two labourers: applicator A walked backwards, avoiding the pesticide spray, as opposed to applicator B, who walked forwards into the spray, also causing him to come into contact with recently sprayed leaves and stalks.

When evaluating PDE with captan, the most contaminated area for both operators was the right leg (parts 6b + 7b + 9, Table 2), corresponding to approximately 45% of total exposure to the fungicide. This can be attributed to the fact that the knapsack has the pump handle on the left side, obliging the operator to hold the spray gun with the right hand; therefore, the spray was closer to the right leg. Also, any leaks in the connection between the hose and the spray lance were practically over the right leg.

Considering the upper body, the sections most contaminated were the arms (2 and 3), with 23% of the total exposure, and the back (5), with 7.3% of the total exposure. Back contamination was particularly high for the inexperienced operator and was partly caused by sprayer tank leaks as a consequence of incorrect assembling and checking of the equipment before use.

Other important contaminated sections were the hands (10 and 11), with 10% of total PDE. It is interesting to note that hand contamination is more significant in the inexperienced operator, with higher levels on the right hand, possibly as a consequence of holding the spray gun, combined with a certain disregard of minor leaks. The PDE due to the preparation stage (mixing and loading) was also evaluated, using a different pair of gloves (Table 2, 14 and 15); it was found that in general these operations caused exposure levels lower than the application, approximately 5.5%, although in the first experience

Table 2. Potential dermal exposure expressed in mL h^{-1} for application of captan on a small maize plantation

	Potential dermal exposure (mL h^{-1})						
	Captan				Coloured tracers		
	Replicate number				Replicate number		
Section	1 Op. A[a]	2 Op. B[b]	3 Op. B	Mean –	1 Op. A	2 Op. B	Mean –
1	0.77	0.22	0.10	0.36	0.37	37.50	18.94
2a	0.39	20.09	2.41	7.50	0.72	2.83	1.78
2b	0.35	8.62	2.40	3.79	0.71	3.41	2.06
3a	0.36	1.90	14.61	5.62	1.78	40.99	21.39
3b	0.36	2.61	14.68	5.88	1.37	14.4	7.89
4	1.90	5.39	3.70	3.66	3.63	199.01	101.32
5	<DL	11.45	10.49	7.31	0.93	49.16	25.05
6a	1.00	7.76	5.11	4.62	4.68	15.97	12.31
7a	1.23	5.21	0.96	2.47		3.97	
6b	1.09	54.44	17.46	24.33	2.01	109.37	65.80
7b	0.94	8.52	2.44	3.97		20.21	
8	1.1	6.02	1.91	3.01	4.42	20.40	12.42
9	1.33	22.22	27.25	16.93	3.09	56.58	29.83
10	0.38	1.93	5.87	2.73	3.58	8.75	6.17
11	0.40	12.15	9.23	7.26	2.98	71.31	37.15
Total	11.60	168.53	118.72	99.62	30.27	653.86	342.07
12	<DL	<DL	<DL	–	NM	1.01	–
13	<DL	0.03	0.06	0.03	0.09	1.55	0.82
14[c]	0.84 (0.37)	0.66 (0.28)	0.02 (0.01)	0.51 (0.22)	NM	0.03 (0.01)	–
15[c]	11.46 (5.02)	3.47 (1.48)	0.05 (0.02)	4.99 (2.17)	NM	0.06	–

[a] Op. A: experienced operator.
[b] Op. B: inexperienced operator.
[c] Expressed as equivalent mL of spray mix (mg of captan).
[d] NM = not •measured.

the right glove registered a high value. As this is a single-event operation, it cannot be expressed as mL of spray mix per unit time. In order to have some basis of comparison, the data are presented as the equivalent amount of spray mix that would have resulted in this amount of substance, and also as mg of the pure substance involved (captan or dye).

The PDE was also measured with coloured tracers instead of the fungicide with the same operators on the same crop, in order to compare both methodologies. The results are presented in Table 2. It is interesting to note that the exposure pattern is similar using the two methods. In one case (using dye), high contamination was found on the hood and neck of the inexperienced operator, coinciding with the lid of the knapsack not having been screwed on properly; on another occasion (not reported here), operator B suffered an accidental disconnection of the hose, splashing a large volume of liquid over himself (this is not unusual according to the same operator).

Using the mean value of 99.6 mL h^{-1} (Table 2) and taking into account the measured fungicide concentration during the application process, 40 mg h^{-1} was the mean value for the mass of captan deposited on the applicator's clothing. This could be taken as a low estimate, considering that the dye studies, which included 'habitual' accidents (replicate 2, colour tracer, Table 2), gave higher values for PDE (653.9 mL h^{-1}).

The PDE values where no accidents occurred showed variations between 11.6 and 158.6 mL h^{-1}. The corresponding value for the coloured tracer study (38.4 mL h^{-1}) indicates that both methodologies gave comparable values. This is additional evidence of the validity of the captan measurements.

As a comparison, Machado-Neto *et al.*[11] reported PDE values of 95.7 mL h^{-1} for application of paraquat to maize (100 cm height) with knapsack sprayers, not considering the feet. These values resulted in the same order as the present mean values (99.6 mL h^{-1}) for the same crop using the same application technique.

In addition, the safety of these procedures may be assessed by the use of the margin of safety (MOS), as presented by Machado-Neto,[1] defined as follows:

$$\mathrm{MOS} = \mathrm{AE}/(\mathrm{AF} \times \mathrm{DE} \times \mathrm{SF})$$

where AE = acceptable exposure, AF = absorption factor, DE = dermal exposure and SF = safety factor. Thus, a value of MOS ≥ 1 would indicate safe working conditions, whereas a value of MOS < 1 would mean unsafe conditions.

In the particular situation of these sprayers working in small plots, they rarely apply more than one backpack (20 L) per day, so the MOS formula was adapted to describe the situation for a single application. The individual factors considered were:

- AE = NOAEL × average body weight, for which the following values were used: NOAEL (rats, three generations)[5] = 12.5 mg kg^{-1} d^{-1}; average human body weight 70 kg.
- AF, which considers the inhaled fraction (1% of DE[1]) and dermal absorption (0.4% per hour over an 8 h period[5]), represented by a factor of $(0.01 + 0.004 \times 8) = 0.042$. Clothing protection is not included, because the normal workwear varies from a simple sweatshirt and shorts to long-sleeved shirts, sweaters and trousers, so the worst case was considered.
- DE = PDE (mg of captan) resulting from the present study for one complete procedure with a 20 L tank (mixing/loading/application), including body and preparation gloves (sections 14 and 15).
- SF = 100 to account for intra- and interspecies variability.

Thus, the margin of safety formula under the conditions studied is

$$\mathrm{MOS} = 12.5\,\mathrm{mg\,kg^{-1}\,d^{-1}} \times 70\,\mathrm{kg}/(0.042 \times \mathrm{PDE} \times 100)$$

The MOS as presented here would represent the safety of a single application of captan under local conditions, including mix, load and spray tasks. For evaluating more than one application daily, the PDE is multiplied by the number of applications, and the MOS should be divided by this number to estimate the total daily MOS. Results for total PDE to captan (mg) for each individual experience and the resulting MOS are presented in Table 3.

Table 3. Total exposure to captan and MOS (per person per application)

	Replicate number		
	1	2	3
Total exposure to captan (mg)[a]	7.6	23.0	14.0
MOS per application[b]	27.4	9.1	14.9

[a] Calculated as PDE (mL h^{-1}) × concentration of spray mix (mg mL^{-1}) × duration (h).
[b] Calculated as MOS = 12.5 mg kg^{-1} d^{-1} × 70 kg/(0.042 × PDE × 100).

4 CONCLUSIONS

It can be concluded that this whole body dosimetry method developed for estimating PDE (using a cotton overall as the main sampling element and a Tyvek undergarment for protection) is simple and easy to use, and can be easily combined with different analytical techniques for determination of the applied product.

A gas-chromatographic analytical method for captan quantification has been validated on critical parameters: sample stability, selectivity, LD, LQ, linear ranges, recoveries and precision. The influence of column and injector temperatures was

evaluated. An unexpected factor (the amount of injector liner material) was identified and evaluated.

The experimental results show that the total PDE measured using coloured tracers is roughly of the same magnitude as the values obtained with captan, indicating that both methods give similar results. The use of coloured tracer has an additional advantage: it gives a very obvious indication of contamination, easily understood by any person, thus providing a simple and effective instruction tool.

As can be seen in Table 2, PDE during spraying is higher for operator B than for operator A. Using captan, operator B is one order of magnitude more exposed than operator A. The same tendency was observed using tracers: operator B is approximately 15 times more exposed than A. Taking into account that both used the same backpack and sprayed the same crop under similar conditions, these differences could be assigned to the different application techniques employed: operator A is a well-trained, experienced worker while operator B is a young untrained person.

In the mixing and loading stage, the contamination of hands is rather low, compared with that resulting from the actual spraying; furthermore, there is no significant difference between operators for this task, which could be attributed to the fact that the mixing and loading operation is not time dependent. These results suggest that the application stage is the task contributing most towards dermal exposure of these operators to the agrochemical products. This is due to the application techniques employed and to malfunction/leaks or misuse of the equipment. Thus, operator experience is an important factor affecting pesticide exposure in small-scale agricultural units. Simple training actions (such as clear instructions for assembly and leak tests, simulated accidents, etc.) could be useful for reducing the exposure of workers to pesticides in this type of situation.

Furthermore, when these PDE values are considered together with the toxicological data for this particular fungicide, the resulting MOS values indicate that the spray procedures evaluated can be considered safe, as they represent a fraction of the acceptable exposure.

ACKNOWLEDGEMENTS

The authors wish to thank the Instituto de Desarrollo Económico Local de la Municipalidad de Moreno and agricultural workers of the Moreno district for their kind cooperation. The captan standard was courtesy of SENASA, and the Triton X-100 surfactant was courtesy of CIPEIN–CITEFA. This work has been financially supported by the Universidad Nacional de General Sarmiento.

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