CAPTAN (007)

EXPLANATION

Captan has been reviewed several times since the initial evaluation in 1965, most recently in 1984, 1986, 1987 and 1990. The 1987 Meeting had recommended that a detailed review of all aspects of the use of captan be carried out at the 1989 Meeting or as soon as possible. The 1990 JMPR reviewed the information currently available and recommended withdrawal of a number of MRLs and establishment of TMRLs for those commodities for which residue data were being generated.

On the basis of the 1990 JMPR recommendations the 1991 CCPR (ALINORM 91/24A, paras 73-76) agreed to propose the withdrawal of several CXLs and made the following MRLs temporary until 1992: apple, blueberry, peach, pear, strawberry and tomato, pending receipt of residue data and information on GAP; citrus fruits, pending the submission of residue data and information on GAP by Spain; dried grapes, pending the submission of residue data and information on GAP by the manufacturer.

The review by the FAO Panel was postponed from 1992 to 1993 owing to the work-load; the 1992 CCPR then rescheduled the review to 1994 because of the availability of data from one of the manufacturers (ALINORM 93/24, para 64).

One manufacturer provided a large amount of information, including details of GAP and data on residue trials, metabolism, processing, analytical methods and frozen storage stability. Many of the studies would normally be provided for an old compound when it is scheduled for periodic review. Captan is not strictly a periodic review compound, but the Meeting welcomed the opportunity to bring the critical supporting studies for captan up to date. The other manufacturer provided additional information on analytical methods, frozen storage stability and residue trials.

Information on GAP and residue trials was also supplied by Canada and Spain.

IDENTITY

ISO common name: captan

Chemical name

IUPAC: *N*-(trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide

CA: 3a,4,7,7a-tetrahydro-2-[(trichloromethyl)thio]-1*H*-isoindole-1,3(2*H*)-dione

CAS No.: 133-06-2
CIPAC No.: 40

Molecular weight: 300.6

Molecular formula: $C_9H_8Cl_3NO_2S$

Structural formula:

Synonyms/trade names: SR-406, Merpan, Vanicide 89, Orthocide

Physical and chemical properties

Pure active ingredient

Physical state:	colourless crystals
Melting point:	171-174°C
Vapour pressure:	1×10^{-5} Pascal
Henry's Law Constant:	6.2×10^{-9} atm m^3 mol^{-1}
Octanol/water partition coefficient:	P_{ow} 610 ± 90 at 25°C

Solubility:	water	5.1	mg/litre at 25°C
	acetone	30	g/litre at 20°C
	ethanol	2.9	g/litre at 20°C
	chloroform	78	g/litre at 20°C
	toluene	7.0	g/litre at 20°C

Technical material

Physical state:	white to buff-coloured solid, "nutty" odour
Melting point:	158-170°C
Thermal stability:	the technical material is stable for at least 12 months at ambient temperature. Half-life at 80°C exceeds 213 weeks.

Formulations

Captan is formulated as wettable powders (WP) containing 50%, 80% or 83% w/w ai; as an 80% w/w wettable granule (WG), and as a 50% w/v suspension concentrate (SC), either alone or in combination with other fungicides.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Metabolism studies on rats, lactating goats and laying hens were made available to the Meeting. Radiolabelled captan, both [*cyclohexene*-1,2-^{14}C] and [*trichloromethyl*-^{14}C], was used to trace the fate of the two parts of the captan molecule.

Abbreviations are used for some of the metabolites, as shown below.

THPI:	1,2,3,6-tetrahydrophthalimide
3-OH-THPI:	3-hydroxy-1,2,3,6-tetrahydrophthalimide
5-OH-THPI:	5-hydroxy-1,2,3,6-tetrahydrophthalimide
4,5-di-OH-HHPI:	4,5-dihydroxy-1,2,3,4,5,6-hexahydrophthalimide
THPAM:	6-carbamoyl-3-cyclohexene-1-carboxylic acid
THPI epoxide:	7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide

Metabolites were identified (Lappin and Havell, 1990) in rat excreta from rats dosed orally with [*cyclohexene*-1,2-^{14}C]captan at 10 mg/kg bw (single low dose), 500 mg/kg bw (single high dose), or 10 mg/kg bw (single dose after 14 daily unlabelled doses).

The major urinary metabolites were 3-OH-THPI (42%), 5-hydroxy-THPAM (20%), and THPI (10%). The major faecal metabolites were THPI (35%), 5-OH-THPI (27%), and 3-OH-THPI (11%). Captan itself was a minor component in the urine and low-dose faeces, and a major component in the high-dose faeces.

The material balance after dosing a lactating goat for 2 days with [*trichloromethyl*-^{14}C] captan equivalent to 55 ppm in the diet was investigated (Powell and Skidmore, 1993). 77.9% of the administered ^{14}C was recovered, with 43.3% in the expired air as $^{14}CO_2$, 19.8% in the gastro-intestinal contents, 8.0% in the urine and 4.6% in the faeces. Milk accounted for 0.18% of the administered dose and tissues for 1.37% (liver 0.82%). It is likely that some of the dose was expired as $^{14}CH_4$, because conversion of CO_2 to CH_4 can occur in the rumen.

Residues in the tissues, milk and excreta were measured in a lactating goat (54 kg) dosed orally by capsule 3 times daily for 3 days and once on the fourth day with [*trichloromethyl*-^{14}C] captan at the equivalent of 1.4 mg/kg bw/day, or 0.47 mg/kg bw/dose (Daun, 1988b). The feed intake was 0.7 kg per day. Milk and excreta were collected throughout; the animal was slaughtered for tissue collection approximately 4 hours after the final dose.

The faeces contained 20% of the administered dose and the urine 6.3%. Milk contained 1.5% and levels were still increasing slightly at the end of the experiment. The liver contained 0.57%, and other tissues less than 0.1%. A metabolite identified in the urine was thiazolidine-2-thione-4-carboxylic acid.

The material balance after dosing a single hen for 2 days with [*trichloromethyl*-^{14}C]captan at a rate equivalent to 10 ppm in the diet was investigated by Mathis and Skidmore (1993). 88.4% of the administered ^{14}C was recovered, with 49.9% in the excreta, 33.1% in the expired air as $^{14}CO_2$, and 5.4% in the carcase.

Tissue, egg and excreta residues were measured in laying hens, (a group of 10, each bird weighing 1.7-2.2 kg) dosed orally for 10 days by capsule with [*cyclohexene*-1,2-^{14}C]captan equivalent to 10 ppm captan in the diet (Renwick and Skidmore, 1993). The feed intake was a nominal 150 g/bird/day. Eggs and excreta were collected throughout, and birds were slaughtered 16 hours after the final dose for tissue collection.

Residues in the eggs quickly reached a plateau level, after 2 to 4 days (Table 1).

Table 1. Total ^{14}C residues, expressed as captan equivalents in eggs, from hens dosed orally for 10 days with [*cyclohexene*-1,2-^{14}C]captan equivalent to 10 ppm captan in the diet (Renwick and Skidmore, 1993).

	^{14}C residues as captan, mg/kg	
Day	**Egg yolk**	**Egg white**
1	0.24	0.43
2	0.55	0.72
3	0.65	0.81
4	0.70	0.78
5	0.75	0.81
6	0.75	0.76
7	0.79	0.83
8	0.78	0.78
9	0.74	0.76
10	0.83	0.84

Most of the dose was excreted, but small amounts were distributed in the tissues (Table 2).

Table 2. Distribution of ^{14}C in excreta, tissues and eggs of hens dosed for 10 days with [*cyclohexene*-1,2-^{14}C]captan equivalent to 10 ppm captan in the diet (Renwick and Skidmore, 1993).

Component	^{14}C as % of total dose
Excreta	86
Egg yolks	0.5
Egg whites	1.3
Liver	0.2
Kidneys	0.1
Peritoneal fat	0.02
Skin and subcutaneous fat	0.1
Leg muscle	0.5
Breast muscle	0.5
Cage washings and filter papers	1.5

THPI was by far the major metabolite in the tissues and eggs (Table 3), and accounted for most of the residue.

The proposed biotransformation pathway of captan in hens is shown in Figure 1. There is no particular target tissue for the residue. THPI residues (expressed as captan) were 0.5 mg/kg or less in the eggs and tissues at a feeding level of 10 ppm.

Table 3. Metabolite identity and distribution in excreta, tissues and eggs of hens dosed for 10 days with [*cyclohexene*-1,2-^{14}C]captan equivalent to 10 ppm captan in the diet (Renwick and Skidmore, 1993).

Metab	Excreta	Liver		Peritoneal fat		Muscle		Egg yolk		Egg white	
	Metab as % of ^{14}C	Metab as % of ^{14}C	Conc (as captan), mg/kg	Metab as % of ^{14}C	Conc (as captan), mg/kg	Metab as % of ^{14}C	Conc (as captan), mg/kg	Metab as % of ^{14}C	Conc (as captan), mg/kg	Metab as % of ^{14}C	Conc (as captan), mg/kg
THPI[1]	8.9	64	0.38	77	0.11	52	0.29	74	0.50	61	0.50
3-OH-THPI[2]	22.8	5.2	0.03	2.1	0.003	8.9	0.05	6.0	0.04	6.6	0.05
5-OH-THPI[3]	10.2	1.3	0.01	0.5	0.001	1.5	0.01	1.3	0.01	1.6	0.01
4,5-di-OH-HHPI[4]	1.3	0.1	0.001	0.4	0.001						
THPAM[5]	4.3					0.6	0.003				
THPI epoxide[6]	2.4					1.7	0.01	1.6	0.01		

[1] 1,2,3,6-tetrahydrophthalimide
[2] 3-hydroxy-1,2,3,6-tetrahydrophthalimide
[3] 5-hydroxy-1,2,3,6-tetrahydrophthalimide
[4] 4,5-dihydroxy-1,2,3,4,5,6-hexahydrophthalimide
[5] 6-carbamoyl-3-cyclohexene-1-carboxylic acid
[6] 7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide

The residues of metabolites in tissues and eggs were in good agreement when determined by chemical analysis and by ^{14}C measurement (Table 4).

Table 4. Comparison of an analytical enforcement method with ^{14}C measurement for the determination of captan metabolites in hens dosed for 10 days with [*cyclohexene*-1,2-^{14}C]captan equivalent to 10 ppm in the diet (Renwick and Skidmore, 1993).

SAMPLE	Enforcement method		^{14}C measurement
Metabolite	Metabolite, mg/kg	Captan equivs, mg/kg	Captan equivs, mg/kg
LIVER			
THPI	0.20	0.40	0.39
trans-3-OH-THPI	0.025	0.045	0.03
trans-5-OH-THPI	<0.01	<0.02	0.01
cis-3-OH-THPI	<0.01	<0.02	ND
cis-5-OH-THPI	<0.01	<0.02	ND
PERITONEAL FAT			
THPI	0.070	0.14	0.11
trans-3-OH-THPI	<0.01	<0.02	0.003
trans-5-OH-THPI	<0.01	<0.02	0.001
cis-3-OH-THPI	<0.01	<0.02	ND
cis-5-OH-THPI	<0.01	<0.02	ND
MUSCLE			
THPI	0.13	0.26	0.29
trans-3-OH-THPI	0.028	0.051	0.05
trans-5-OH-THPI	0.024	0.043	0.01
cis-3-OH-THPI	<0.01	<0.02	ND
cis-5-OH-THPI	<0.01	<0.02	ND

SAMPLE	Enforcement method		^{14}C measurement	
Metabolite	Metabolite, mg/kg	Captan equivs, mg/kg	Captan equivs, mg/kg	
WHOLE EGG			EGG YOLK	EGG WHITE
THPI	0.20	0.40	0.50	0.50
trans-3-OH-THPI	0.029	0.052	0.04	0.05
trans-5-OH-THPI	<0.01	<0.02	0.01	0.01
cis-3-OH-THPI	<0.01	<0.02	ND	ND
cis-5-OH-THPI	<0.01	<0.02	ND	ND

ND: not detected

Tissue, egg and excreta residues were measured in laying hens (groups of 4 and 6, each bird weighing approximately 1.7kg) dosed orally for 5 days by capsule with [*cyclohexene*-1,2-^{14}C]captan at a rate equivalent to 6.2 or 61 ppm in the diet, 0.5 or 5.0 mg/kg bw/day (Daun, 1988a). The feed intake was 120-150 g/bird/day. Eggs and excreta were collected throughout, and birds were slaughtered approximately 4 hours after the final dose for tissue collection.

The distribution of ^{14}C was investigated in the 0.5 mg/kg bw/day group. The faeces contained 67% of the dose. Egg yolks contained 0.31% and egg whites 0.74%. The distribution of the dose in the tissues was liver 0.56%, muscle 1.7%, kidneys 0.18%, fat 0.08%, skin 0.28%, gizzard 0.18%, ovaries and oviducts 1.4%, and heart 0.06%. In terms of concentration the ^{14}C was generally evenly distributed through the tissues, blood and organs. THPI was the major metabolite and generally accounted for most of the ^{14}C (Table 5).

Table 5. Identified metabolites in tissues and eggs from laying hens dosed for 5 days with 0.5 mg/kg bw/day *cyclohexene*-1,2-^{14}C]captan (Daun, 1988a). Metabolites are expressed as % of the total ^{14}C in the tissue or egg component.

Sample	3-OH-THPI + 5-OH-THPI as % of ^{14}C	THPI as % of ^{14}C
Egg yolk	26	59
Egg white	2.4	16
Liver	21	44
Kidney	22	38
Thigh muscle	17	60
Breast muscle	18	68
Fat	3.8	69

Tissue, egg and excreta residues were measured in laying hens (groups of 4 and 6, each bird weighing approximately 1.7kg) dosed orally for 5 days by capsule with [*cyclohexene*-1,2-^{14}C]captan at a rate equivalent to 10.6 or 69 ppm in the diet, 0.78 or 5.3 mg/kg bw/day (Daun, 1988c). The feed intake was 130 g/bird/day. Eggs and excreta were collected throughout, and birds were slaughtered approximately 4 hours after the final dose for tissue collection.

The distribution of ^{14}C was investigated in the 0.78 mg/kg bw/day group. The faeces contained 44% of the dose. Egg yolks contained 0.10% and egg whites 0.09%. The distribution of the dose in the tissues was liver 0.26%, muscle 0.14%, kidneys 0.13%, fat 0.01%, skin 0.04%, gizzard 0.05%, ovaries and oviducts 0.62% and heart 0.016%. In terms of concentration the ^{14}C expressed as captan ranged from 0.03 mg/kg in fat to 0.82 mg/kg in the kidneys. Attempts were made to characterize the ^{14}C

components in eggs and tissues. Much of the ^{14}C appeared to be incorporated into natural compounds, e.g. non-polar lipids.

Figure 1. Proposed biotransformation pathway of captan in hens.

Plant metabolism

Metabolism studies on tomatoes and lettuce were made available to the Meeting. Both [*cyclohexene*-1,2-^{14}C]captan and [*trichloromethyl*-^{14}C]captan were used, so that the fate of both parts of the molecule could be studied.

[*Cyclohexene*-1,2-^{14}C]captan was applied 4 times at 7-day intervals to <u>tomato</u> and <u>lettuce</u> plants at an application rate equivalent to 4.5 kg ai/ha, and the plants were harvested 3 hours after the final application (Chen, 1988b). The plants were separated into leaf, stem, root and tomato fractions.

The distribution of ^{14}C is summarized in Table 6.

In tomatoes, 89% of the ^{14}C was removed by an acetone wash, indicating that it was mostly a surface residue. When the tomatoes were separated into juice and pulp, 8.9% of the ^{14}C (captan equivalent 0.71 mg/kg) was present in the juice and 2.2% (captan equivalent 1.2 mg/kg) in the pulp. The residue did not move to the roots of lettuce or tomatoes, suggesting that it was largely immobile.

Metabolites were characterized by two-dimensional TLC, HPLC and mass spectrometry. The major residues were captan and THPI. Captan epoxide and THPI epoxide were also detected.

The metabolic pathways of captan in lettuce and tomatoes were N-S cleavage to form THPI and epoxidation of the cyclohexene double bond. The metabolite distribution is shown in Table 7.

Captan and THPI were measured in lettuce leaves by an enforcement analytical method for comparison with the ^{14}C measurements. The captan levels were 39 mg/kg (^{14}C) and 42 mg/kg (enforcement), and the THPI levels 4.2 mg/kg (^{14}C) and 1.5 mg/kg (enforcement).

When lettuce and tomato plants were treated with [*trichloromethyl*-^{14}C]captan, with similar rates and timing, as a companion experiment (Chen, 1988a) the trichloromethyl moiety was mainly released as $^{14}CO_2$. The distribution of the remaining ^{14}C in the plants is summarized in Table 8, with the metabolite distribution shown in Table 9.

In the tomatoes, 80% of the ^{14}C was removed by an acetone wash, indicating that it was mostly a surface residue. When the tomatoes were separated into juice and pulp 15% of the ^{14}C (captan equivalent 1.2 mg/kg) was present in the juice and 5.7% (captan equivalent 2.9 mg/kg) in the pulp.

The captan level in lettuce leaves measured by an enforcement method was 37.3 mg/kg, which agreed with the ^{14}C measurement of 37.5 mg/kg.

Table 6. Distribution of ^{14}C in tomatoes and lettuce from application of [*cyclohexene*-1,2-^{14}C]captan at a rate equivalent to 4.5 kg ai/ha, with plants harvested 3 hours after the final application (Chen, 1988b).

Plant part	Tomato plant			Lettuce plant	
	Wt. as % of plant wt.	^{14}C as % of total ^{14}C in plant	^{14}C mg/kg as captan	^{14}C as % of total ^{14}C in plant	^{14}C mg/kg as captan
Leaves	7.5	70	202	99.7	64
Stems	7	9.7	30		
Roots	21	0.2	0.21	0.3	0.30
Tomatoes	63	20	6.7		

Table 7. Metabolite distribution in tomatoes and lettuce from application of [*cyclohexene*-1,2-^{14}C]captan at a rate equivalent to 4.5 kg ai/ha, with plants harvested 3 hours after the final application (Chen, 1988b).

Compound	Tomato leaves and stems		Tomato fruit		Lettuce leaves	
	% of ^{14}C in leaves & stems	mg/kg, as captan	% of ^{14}C in fruit	mg/kg, as captan	% of ^{14}C in leaves	mg/kg, as captan
Captan	70	128	82	5.5	77	50
Captan epoxide	0.4	0.73	0.4	0.03	0.6	0.39
THPI	4.6	8.3	4.5	0.30	9.5	6.1
Other free metabs	6.9	13	5.2	0.35	4.3	2.8
Polar and conjugates	8.9	16	7.5	0.50	4.5	2.9
Unextractable	8.8	16	0.9	0.06	3.0	1.9

Table 8. Distribution of ^{14}C in tomatoes and lettuce from application of [*trichloromethyl*-^{14}C]captan at a rate equivalent to 4.5 kg ai/ha, with plants harvested 3 hours after the final application (Chen, 1988a).

Plant part	Tomato plant		Lettuce plant	
	^{14}C as % of total ^{14}C in plant	^{14}C mg/kg as captan	^{14}C as % of total ^{14}C in plant	^{14}C mg/kg as captan
Leaves	62	129	98.7	69
Stems	9.2	22		
Roots	0.2	0.20	1.3	1.3
Tomatoes	29	6.9		

Table 9. Metabolite distribution in tomatoes and lettuce from application of [*trichloromethyl*-^{14}C]captan at a rate equivalent to 4.5 kg ai/ha, with plants harvested 3 hours after the final application (Chen, 1988a).

Compound	Tomato leaves and stems		Tomato fruit		Lettuce leaves	
	% of ^{14}C in leaves & stems	mg/kg, as captan	% of ^{14}C in fruit	mg/kg, as captan	% of ^{14}C in leaves	mg/kg, as captan
Captan	81	93	77	5.3	76	52
Captan epoxide	0.3	0.34	0.2	0.14	0.3	0.21
Other free metabs	6.9	7.9	9.5	0.66	5.2	3.6
Polar and conjugates	4.8	5.5	10	0.72	4.6	3.2
Unextractable	7.2	8.3	3.3	0.23	14	9.4

Figure 2. Metabolic pathways of captan in plants.

Environmental fate in soil

The major compounds identified in the degradation of [*carbonyl*-^{14}C]captan in soil were CO_2, THPI and tetrahydrophthalamic acid (Pack, 1974). Captan was degraded very rapidly, with 99% of the initial 5 mg/kg in a sandy loam soil disappearing in 7 days. Table 10 lists the major products, their maximum concentrations, and the days on which the maximum concentrations were reached.

Table 10. Degradation products, their maximum concentrations and days after treatment when the maximum concentrations were reached when a sandy loam soil was treated with [*carbonyl*-^{14}C]captan at 5 mg/kg (Pack, 1974).

Product	Max. conc., mg/kg	% of initial dose	Day of max conc.
THPI	1.8	66	7
THPI epoxide	0.046	1.6	7
5,6-dihydroxyhexahydrophthalimide	0.021	0.62	37
Tetrahydrophthalamic acid	0.50	17	14
Tetrahydrophthalic acid	0.096	3.2	14

The degradation of captan in aerobic soil has also been studied with [*trichloromethyl*-^{14}C]captan (Pack and Verrips, 1988). Captan was degraded rapidly with a half-life of about 1 day when incubated in the soil at 25°C at an initial concentration of 5 to 6 mg/kg expressed on the dry weight. Carbon dioxide was rapidly eliminated, and was the only significant ^{14}C product. The soil was a sandy loam, pH 7.2, 1.2% organic matter, 12% clay, 30% silt, 58% sand, and with a cation exchange capacity of 7.7 meq/100 g.

Captan ([trichloromethyl-^{14}C]) was rapidly degraded in a laboratory study with aerobic sandy loam soil (Diaz and Lay, 1992). The half-life was less than 4 hours.

The sandy loam soil properties were pH 7.7, organic matter 0.70%, clay 11.8%. [*Trichloromethyl*-^{14}C]captan was added to the soil at 8.8 mg/kg. After 3 days and 28 days 59% and 81% respectively of the applied ^{14}C was recovered as CO_2. The experiment was also run with sterilized soil. In the sterile soil the ^{14}C recovered as CO_2 was 26% (3 days) and 39% (28 days) of that applied. Thiocarbonic acid was the other major product in the unsterilized soil; it accounted for 1.1% of the ^{14}C at day 14, and 0.63% at day 28.

Environmental fate in water/sediment systems

Lee (1989b) examined the hydrolysis of [*cyclohexene*-1,2-^{14}C]captan in sterile buffer solutions (2.2 mg/l) in a laboratory study. At 25°C the half-lives of captan were 11.7 hours, 4.7 hours and 8.1 minutes at pH 5, 7 and 9 respectively.

THPI was the major hydrolysis product identified at each pH. At pH 7 and pH 9 sodium *S*-tetrahydrophthalimido thiocarbonate was also produced.

In a companion study Lee (1989a) examined captan hydrolysis with the ^{14}C label on the trichloromethyl group. At 25°C the half-lives of captan were 18.8 hours, 4.9 hours and 8.3 minutes at pH 5, 7 and 9 respectively. Carbon dioxide was the major hydrolysis product.

Captan is not photo-degraded in aqueous solution (Pack, 1986). Captan was continuously exposed to artificial sunlight in sterile aqueous pH 5 buffer (1 mg/l captan) at 25°C, but there was no difference in the rate of degradation between irradiated and control (non-irradiated) samples.

The fate of [*cyclohexene*-1,2-^{14}C]captan in sediment-water systems under controlled laboratory conditions was studied by Travis and Simmons (1993). Captan was introduced to two water-sediment systems at an initial concentration of 1.2 mg/l. One system contained a clay loam sediment with a high organic matter content (21.5%) and the other a loamy sand with low organic matter (5.4%). Parallel sterile systems were also established to observe chemical as distinct from microbial activity. The systems were incubated at 20°C in the dark. The distribution of ^{14}C is shown in Table 11.

In the sterile systems CO_2 was not produced, but in the non-sterile systems approximately 50% of the applied ^{14}C had been mineralised to CO_2 after 90 days.

Captan disappeared very quickly, and was not detected by day 1 in either sterile or non-sterile systems. THPI was the initial product of hydrolysis. It declined to undetectable levels in the non-sterile systems by day 60 and to 36% and 64% of the applied ^{14}C in the sterile systems by day 90.

Three other compounds identified in the microbial non-sterile systems were THPAM (6-carbamoyl-3-cyclohexene-1-carboxylic acid), THPAL (3-cyclohexene-1,6-dicarboxylic acid) and THPI epoxide (7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide). All three reached maximum levels by day 14, and had declined to undetectable levels by day 59. The three were also detected in the sterile systems after 30 days incubation, showing that conversion of THPI to these compounds occurred in the absence of microbial activity.

Table 11. Distribution of ^{14}C as % of that applied in water-sediment systems incubated at 20°C in the dark after [*cyclohexene*-1,2-^{14}C]captan was introduced at 1.2 mg/l (Travis and Simmons, 1993).

Sample	Distribution of ^{14}C as % of applied ^{14}C									
	High organic matter system					Low organic matter system				
	Day 7	Day 30	Day 29 sterile	Day 90	Day 90 sterile	Day 7	Day 30	Day 29 sterile	Day 90	Day 90 sterile
$^{14}CO_2$	0.2	8.9	*ND*	53	*ND*	2.0	9.8	*ND*	49	*ND*
Surface water	53	42	*63*	1.7	*63*	75	72	*80*	2.4	*76*
Sediment, extractable	21	14.5	*32*	2.9	*22*	16	17	*15*	10.6	*16*
Unextracted	26	29	*6.7*	29	*15*	3.8	5.2	*1.1*	24	*0.5*

ND: not detected

METHODS OF RESIDUE ANALYSIS

Analytical methods

Methods have been developed for the determination of captan and THPI in crops, and for THPI and hydroxylated metabolites in animal commodities. The methods rely on gas chromatography for the final determination. Limits of determination are usually in the range 0.01 to 0.05 mg/kg.

A method (RM-1K-2) for the determination of captan and THPI in crops was reported by Fujie (1982). Because of the possible instability of captan in some crop matrices captan-treated crops should be analysed immediately after maceration and sub-sampling.

A small quantity of phosphoric acid is added to the macerated sample which is extracted with ethyl acetate. After filtration, the ethyl acetate fraction is washed with dilute phosphoric acid. An additional acetonitrile/hexane partition clean-up is introduced at this stage for oily crops. The extract is cleaned up further by gel-permeation chromatography. Captan and THPI are separated on a nuchar-silica gel column, and the captan extract is cleaned up further on a Florisil column.

Captan and THPI are determined by GLC using a flame-photometric detector in the sulphur mode for captan and an NP flame-ionisation detector for THPI.

Breault (1986) described a revision of method RM-1K-2, in which the use of a Coulson electrolytic conductivity detector allowed the elimination of the Florisil column clean-up step for all samples and the gel permeation step for non-oily crops. The Coulson detector was operated in the halogen mode for captan detection and in the nitrogen mode for THPI.

Iwata (1989) used similar methods for extraction and clean-up. The final determination was by GLC with a Coulson electrolytic conductivity detector operated in the halogen and nitrogen modes for captan and THPI respectively. Good recoveries from apples were demonstrated for both captan and THPI down to 0.05 mg/kg.

Graham (1986a) described a GLC method for the determination of captan, THPI, 3-OH-THPI and 5-OH-THPI in chicken tissues and eggs. Captan added to control samples of eggs and tissues was found to be quantitatively converted to THPI.

Egg and tissue samples are extracted with ethyl acetate after adding sodium chloride. Fatty samples are cleaned up with an acetonitrile-hexane partition, followed by a small silica gel column. The three compounds are determined by capillary GLC with a mass-selective detector. The two isomers of 5-OH-THPI are resolved into peaks. The limits of determination were THPI 0.02 mg/kg (equivalent to 0.04 mg/kg captan), 3-OH-THPI 0.03 mg/kg, and 5-OH-THPI 0.02 mg/kg (A) and 0.03 mg/kg (B). Recoveries were satisfactory, but could be variable at low levels.

Peterson (1991) described a GLC method for captan residues in fruit. The sample was extracted with ethyl acetate after ensuring a strongly acidic environment by adding a small amount of phosphoric acid, and the extract washed with aqueous phosphoric acid. The evaporated extract was cleaned up on a small silica column and analysed by capillary GLC with electron-capture detection. The limit of determination was 0.05 mg/kg. Jones (1991) reported details of a very similar method used for the determination of captan and THPI in crop samples in many of the supervised residue trials. Dry ice was used during the sample preparation to prevent the conversion of captan to THPI. The final determination was by GLC using electron-capture and mass-selective detectors for captan and THPI respectively.

Schlesinger (1992e) described a method for the determination of captan and THPI in non-oily crops such as lettuce, tomatoes, melons, apples, squash, potatoes, grapes and strawberries. The sample was extracted with ethyl acetate after addition of a small amount of phosphoric acid, and the extract washed with aqueous phosphoric acid. The ethyl acetate was evaporated and the residue taken up in hexane and cleaned up on a small Florisil column, eluting with dichloromethane containing 1% methanol. The solution was analysed for captan by GLC with electron-capture detection. THPI was cleaned up separately after the ethyl acetate extraction by extracting the ethyl acetate with pH 11.5

buffer solution, acidifying with phosphoric acid and extracting into dichloromethane. The dichloromethane was evaporated and the residue taken up in ethyl acetate for GLC analysis using a specific thermionic detector. The limits of determination for captan and THPI were 0.05 and 0.2 mg/kg respectively.

Davy (1989) described a method for the determination of the captan metabolites THPI, 3-OH-THPI and 5-OH-THPI in animal tissues and milk. The sample is macerated with acetone. The acetone is evaporated and the residue partitioned between hexane and acetonitrile to remove fat. The extract is cleaned up on a small silica column, and the metabolites derivatized with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide containing 10% trimethylchlorosilane. Determination is by GLC using a mass-selective detector. The 2 isomers of 5-OH-THPI are resolved into 2 peaks. Satisfactory recoveries were achieved for milk and animal tissues. Limits of determination were 0.01 mg/kg for milk and 0.05 mg/kg for animal tissues.

Wiebe *et al*. (1992) described a very similar method for the 5 metabolites THPI, *trans*-3-OH-THPI, *cis*-3-OH-THPI, *trans*-5-OH-THPI and *cis*-5-OH-THPI in animal tissues and milk. Limits of determination for both milk and tissues were 0.01 mg/kg.

Stability of pesticide residues in stored analytical samples

The stability of captan and its metabolites during frozen storage has been studied in crops and animal commodities. Captan itself is unstable in some matrices but the metabolites are generally stable. When captan breaks down in storage it generates THPI.

McKay (1990b) investigated the freezer storage stability of captan and THPI residues in a range of crops and processed commodities. The samples were directly fortified with known amounts of captan and THPI and stored in glass bottles with polyethylene-lined lids in the dark at -20 ± 10°C. Some samples with field-incurred residues were also included in the study (Table 12). Fortification of separate samples with captan and THPI provided information on the stability of THPI in frozen storage (Table 13).

Table 12. Residues of captan and THPI in field-treated commodities stored in a freezer at -20°C (McKay, 1990b).

Storage interval	Residues, mg/kg									
	Apple		Cucumber		Lettuce		Spinach		Strawberry	
	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI
0	2.7	0.095	1.05	0.12	13	0.22	32	2.7	8.7	0.24
3 months	2.8	0.11	0.43	0.22	8.8	0.43	34	9.9	6.7	0.36
6 months	2.8	0.12	0.55	0.28	8.1	0.72	30	7.6	6.4	0.41
14 months	2.9	0.13	0.39	0.34	7.4	0.58	32	12	6.4	0.50

Captan was adequately stable under frozen storage conditions in some commodities but in others it was degraded, presumably by released enzymes, to generate THPI. In a number of cases captan levels appeared to drop in the first months of storage, but were reasonably stable after that. THPI itself was reasonably stable in most matrices, so the total residue (captan + THPI expressed as captan) remains reasonably constant.

The stability of captan and THPI in whole and chopped or ground commodities was compared to see whether greater exposure to plant enzymes would accelerate the decomposition process (Table 14). Captan was more stable in the whole commodity samples.

In the evaluation of residue data the possible conversion of captan to THPI during sample storage needs to be considered, particularly in those cases where the proportion of THPI in the residue is substantial.

Table 13. Residues of captan and THPI in field-treated tomatoes and cherries, and in other commodities fortified with captan and THPI, stored at -20°C (McKay, 1990b).

Storage interval	Residues, mg/kg									
	Almond		Apple juice		Beet tops		Cherry		Maize grain	
	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI
Fortificn. level	0.50	0.50	0.48	0.24	0.48	0.48			0.50	0.50
0 month	0.38	0.44	0.41	0.24	0.55	0.69	21	0.26	0.38	0.44
1 month	<0.05	0.64	0.41	0.26	0.10	0.24	25	0.30	0.46	0.46
3 months	<0.05	0.36	0.58	0.15	0.19	0.32	19	0.35	0.080	0.41
6 months	<0.05	0.42	0.48	0.15	0.13	0.35	12	0.36	0.029	0.45
12 months							16	0.30		
15 months			0.31	0.28	<0.05	0.35				
	Potato tubers		Soya bean forage		Soya bean grain		Tomato			
Fortificn. level	0.48	0.24	0.52	0.52	0.48	0.24				
0 month	0.47	0.17	0.38	0.44	0.29	0.24	0.88	0.089		
1 month	0.32	0.14	0.38	0.39	0.21	0.21	0.40	0.22		
3 months	0.25	0.23	0.35	0.40	0.14	0.32	0.30	0.25		
6 months	0.27	0.24	0.22	0.22	0.12	0.21	0.28	0.35		
12 months							0.14	0.34		
15 months	0.14	0.25	0.36	0.38	0.041	0.10				
20 months							0.15	0.30		

Table 14. Residues of captan and THPI in commodities fortified with captan and THPI separately, then stored at -20°C (McKay, 1990b).

Storage interval	Residues, mg/kg											
	Captan	THPI	THPI	Captan	THPI	THPI	Captan	THPI	THPI	Captan	THPI	THPI
	Almond nuts, whole			Almond nuts, coarsely ground			Apples			Apple sauce		
Fortificn. level	0.50		0.50	0.50		0.50	0.50		0.50	0.50		0.50
0 month	0.41		0.44	0.50		0.38	0.52		0.42	0.47		0.43
1 month	0.27		0.36	0.21		0.38	0.41		0.44	0.40		0.37
2 months	0.42	0		0.33	0.065							
3 months	0.38	0	0.31				0.39		0.40	0.37		0.36
6 months	0.33	0.016	0.35				0.38		0.36	0.37		0.42
9 months	0.36	0	0.45				0.43		0.49	0.35		0.38

	Maize grain, whole		Maize grain, coarsely ground		Grape pomace, dry		Potato tubers	
Fortificn. level	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
0 month	0.40	0.46	0.44	0.40	0.41	0.42	0.46	0.45
1 month	0.13	0.35	0.053	0.36	0.35	0.36	0.37	0.40
2 months	0.15 0.20							
3 months	0.13 0.16	0.46			0.41	0.43	0.37	0.37
3.5 months	0.14 0.17	0.40						
6 months					0.38	0.38	0.37	0.35
8 months	0.19 0.15	0.40						
9 months					0.37	0.41	0.34	0.36
12 months	0.046 0.42	0.46						
	Raisins		Spinach, coarsely chopped by hand		Spinach, finely chopped in Hobart chopper		Sugar beet tops	
Fortificn. level	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
0 month	0.46	0.39	0.48	0.44	0.49	0.43	0.48 0	0.47
1 month	0.36	0.44	0.055	0.39	0.15	0.37	0.43 0.033	0.35
2 months			0.12 0.097					
3 months	0.37	0.53	0.14 0.16	0.47			0.46 0.098	0.42
6 months	0.42	0.49					0.42 0.42	0.37
8 months			0.057 0.27	0.36				
10 months	0.36	0.41						
12 months			0.031 0.36	0.47			0.33 0.11	0.33
	Tomato, whole fruit		Tomato, dry pomace		Tomato sauce		Wheat forage	
Fortificn. level	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
0 month	0.46	0.37	0.43	0.43	0.42	0.41	0.41 0	0.39
1 month	0.38	0.42	0.42	0.38	0.51	0.38	0.39 0.15	0.46
3 months	0.38	0.46	0.38	0.40	0.44	0.53	0.37 0.080	0.39
6 months	0.38	0.43	0.36	0.39	0.42	0.46	0.097 0.35	0.54
9 months	0.40	0.42	0.38	0.38	0.36	0.39		
12 months							0.043 0.18	0.35

Schlesinger (1992e) examined the frozen storage stability of captan and THPI in potatoes, tomatoes and melons. With fortification at 1 mg/kg and storage in plastic bags at -18°C for 11-13 months, the captan remaining was 65-67%, 72-74% and 74-84% of the initial level respectively. The corresponding values for THPI were 62-71%, 83-92% and 69-75%.

The storage stability of captan (recovered as THPI), THPI, 3-OH-THPI and 5-OH-THPI in eggs and chicken tissues was investigated by Graham (1986a). The metabolites were stable under the tested storage conditions (Table 15). Captan was very rapidly converted to THPI by eggs and tissues, and the THPI was shown to be stable.

Table 15. Storage stability of captan (recovered as THPI) and metabolite residues in fortified eggs and chicken tissues held at -20°C (Graham, 1986a). All fortifications were at 0.20 mg/kg.

Sample	Months storage	% of original remaining (% of captan remaining as THPI)			
		Captan	THPI	3-OH-THPI	5-OH-THPI
Eggs	10	91	76	82	61
Muscle	8	85	69	69	106
Liver	8	92	81	88	90
Gizzard	8	74	95	94	101
Fat	6	-	114	77	69
Skin	6	97	95	79	58

As part of a national survey of captan and metabolite residues in milk in the USA, Slesinski and Wilson (1992) reported the storage stability of residues in milk. The data were also reported by Wiebe (1992). The stability data for captan are summarized in Table 16. Clearly, captan is unstable in this situation; THPI is formed as captan disappears. Milk samples should be analysed for captan without delay. However, the absence of THPI is good evidence that captan was not present in a sample.

Table 16. Storage stability of milk samples fortified with captan at 0.40 mg/l and stored at -20 ± 10°C (Slesinski and Wilson, 1992; Wiebe, 1992).

Storage interval	Captan, mg/kg	THPI, mg/kg
Day 0	0.43, 0.40, 0.46	0.015, 0.018, 0.016
2 weeks	0.31, 0.33, 0.30	0.058, 0.056, 0.054
1 month	0.21, 0.21, 0.20	0.066, 0.062, 0.072
3 months	0.17, 0.19, 0.15	0.11, 0.098, 0.12
6 months	0.089, 0.099, 0.11	0.15, 0.12, 0.13

Wiebe (1992) also tested the stability in frozen storage of THPI, 3-OH-THPI and 5-OH-THPI residues in milk and bovine tissues, which were fortified with THPI alone or with the 4 other metabolites (*cis*- and *trans*-3-OH-THPI, and *cis*- and *trans*-5-OH-THPI) in combination and stored at -20 ± 10°C for 1 year. THPI was kept separate because of the theoretical possibility of enzymatic hydroxylation. The results (Table 17) show that the 5 metabolites have adequate stability in animal tissues and milk when stored at -20 ± 10°C.

Table 17. Storage stability of captan metabolites in bovine tissues and milk held at -20 ± 10°C for 1 year (Wiebe, 1992). Each reported value is the mean of 3 samples stored and analysed after the specified interval. All samples were fortified at 0.4 mg/kg.

Storage interval	% of fortified level remaining									
	THPI	*trans*-3-OH-THPI	*trans*-5-OH-THPI	*cis*-3-OH-THPI	*cis*-5-OH-THPI	THPI	*trans*-3-OH-THPI	*trans*-5-OH-THPI	*cis*-3-OH-THPI	*cis*-5-OH-THPI
	Unpasteurised milk (raw)									
Day 0	88	96	93	105	88					
2 weeks	86	101	95	100	90					
2.5 months	89	109	114	106	100					
6 months	89	90	97	91	98					
1 year	82	104	102	102	101					
	Beef kidney					Beef liver				
Day 0	77	89	88	88	74	65	63	55	73	51
2 weeks	86	98	113	98	92	78	75	68	86	64
4 months	74	69	73	74	66	78	67	58	75	54
8 months	67	71	102	76	74	73	65	63	74	59
1 year	74	90	88	88	80	76	75	64	81	62
	Beef muscle					Beef fat				
Day 0	87	80	83	83	81	82	100	100	103	85
2 weeks	87	93	89	93	90	78	76	76	80	64
4 months	78	81	69	66	73	80	84	92	86	80
8 months	78	85	79	82	77	94	95	126	85	90
1 year	86	81	73	80	65	82	75	76%	74%	61%

USE PATTERN

Captan is a broad-spectrum fungicide which has been widely used on food crops, seed crops and ornamentals for over 30 years. It is very useful against some of the most destructive fungal diseases such as Apple Scab and Botrytis Rots. Fungal pathogens have not developed resistance to captan as they have to many other commonly used fungicides. Captan can be used to prolong the usefulness of other important fungicides by helping to avoid resistance.

The registered uses of captan are summarized in Table 18. The intervals between applications are usually 7 days, but can vary from 5 to 21 days. The maximum number of applications may not be specified, but will depend on the extent of infection or weather conditions favouring disease development.

Table 18. Registered uses of captan on food crops.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Almond	Portugal	WP	foliar		0.15-0.20		14

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Almond	Spain	WP	foliar		0.13-0.26		10
Almond	USA	WP	foliar	2.2-4.9			30
Apple	Argentina	WP	foliar	7.0		2	14
Apple	Brazil	WP	foliar		0.11		1
Apple	Canada	WP	foliar		0.05-0.1		7
Apple	Chile	WP	foliar		0.14		1-10[3]
Apple	Ecuador	WP	foliar	0.80-1.2			15
Apple	Greece	WP	foliar		0.13	3+	15
Apple	Hungary	WP	foliar	1.0-1.5		2-3[1]	10
Apple	Israel	WP	foliar		0.13-0.25	4	7
Apple	Japan	WP	foliar		0.064-0.14		3
Apple	Mexico	WP	foliar		0.10-0.13		14
Apple	Netherlands	SC WP	foliar		0.21	10-12[1]	21
Apple	Netherlands	SC WP	foliar		0.05	10-12[1]	7
Apple	Poland	WP	foliar	1.5-2.3		8-10[1]	7
Apple	Portugal	WP	foliar		0.24	10	21
Apple	Portugal	WP	foliar		0.15-0.20		21
Apple	South Africa	WP	foliar		0.048		14
Apple	Spain	WP	foliar		0.13-0.15	4[1]	7
Apple	Turkey	WP	foliar		0.075	2+	3
Apple	UK	WP	post-harvest		0.10		
Apple	UK	WG	foliar	2.7		10-12[1]	7
Apple	Uruguay	WP	foliar		0.10-0.13	2	7
Apple	USA (California)	WP	foliar	2.2-3.4			21
Apple	USA	WP	foliar	2.2-3.4			14
Apple	USA	WP	post-harvest		0.15		
Apricot	Canada	WP	foliar		0.10-0.12		2
Apricot	Poland	WP	foliar	1.5-2.3			7
Apricot	Uruguay	WP	foliar		0.13		7
Apricot	USA	WP	foliar	1.6-2.7			7
Aubergines	Spain	WP	foliar FG[2]		0.13-0.21		
Avocado	Mexico	WP	foliar		0.13		14
Beans	Chile	WP	foliar	1.6			1
Beans, Broad	Ecuador	WP	foliar	0.80-1.2			15
Beans, Broad	Spain	WP	foliar FG		0.13-0.21		10
Beans	Poland	WP	foliar	0.6	0.1		7
Beans	Spain	WP	foliar FG		0.13-0.21		21
Blueberry	Canada	WP	foliar	1.6-1.8	0.18		2

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Blueberry	USA	WP	foliar	1.1-2.8			0
Blueberry	USA (California)	WP	foliar	1.1-2.8			4
Carrot	Mexico	WP	foliar		0.20		14
Celery	Japan	WP	foliar		0.14	3	21
Cherry, Sour	Canada	WP	foliar		0.1-0.13		5
Cherry, Sweet	Canada	WP	foliar		0.1-0.13		2
Cherry	Chile	WP	foliar		0.14		[3]
Cherry	Greece	WP	foliar		0.13	4	20
Cherry	Hungary	WP	foliar	1.0-1.5		2-3[1]	10
Cherry	Japan	WP	foliar		0.10	5	14
Cherry, Sour	Poland	WP	foliar	1.5-2.3			7
Cherry	Spain	WP	foliar		0.13-0.15	4	7
Cherry	USA	WP	post-harvest		0.15		
Cherry	USA (California)	WP	foliar	1.7-2.2			7
Cherry	USA	WP	foliar	2.2			0
Chick-peas	Spain	WP	foliar		0.13-0.21		10
Citrus	Brazil	WP	foliar		0.11		7
Citrus	Spain	WP	foliar		0.13-0.15		7 or 14
Citrus	Turkey	WP	foliar		0.15		3
Cucumber	Brazil	WP	foliar		0.10		1
Cucumber	Canada	WP	foliar	1.8-3.4			2
Cucumber	Japan	WP	foliar		0.10-0.20		1
Cucurbits	Mexico	WP	foliar		0.10-0.15		7
Garlic	Brazil	WP	foliar		0.11		7
Grape, wine	Argentina	WP	foliar	1.3		3	25
Grape, table	Argentina	WP	foliar	1.3		5	14
Grape	Brazil	WP	foliar		0.11		1
Grape	Canada	WP	foliar		0.10-0.13		7
Grape, table	Chile	WP	foliar	3.20		3-4[1]	1-20[3]
Grape, wine and pisco	Chile	WP	foliar	3.20		3-4[1]	30
Grape	Chile	WP	foliar		0.12	4	15
Grape	France	WP	foliar	1.8		7	45
Grape	France	SC	foliar	1.8-3.5		7-10	33-45
Grape	Greece	WP	foliar		0.13	3-4[1]	40
Grape	Hungary	WP	foliar	1.0-1.5		2-3[1]	10
Grape, wine	Hungary	WP	foliar	1.0-1.5		2-3[1]	30
Grape	Japan	WP	foliar		0.10	5	14
Grape	Mexico	WP	foliar		0.10-0.13	2	0
Grape, table	Portugal	WP	foliar		0.17		21
Grape, wine	Portugal	WP	foliar		0.17		42

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Grape, wine and table	Spain	WP	foliar		0.21-0.26		21
Grape, wine and table	Spain	WP	foliar		0.13-0.15	4[1]	21
Grape	Turkey	WP	foliar		0.15	2+	3
Grape	Uruguay	WP	foliar	0.64-1.2			21
Grape	USA	WP	foliar	1.1-2.2			14
Grape	USA (California)	WP	foliar	2.2		6-8	45
Kidney bean	Japan	WP	foliar		0.064-0.14	1	45
Leek	Spain	WP	foliar FG		0.13-0.21		10
Lettuce	Spain	WP	foliar FG		0.13-0.21		21
Lettuce	Turkey	WP	foliar		0.15		7
Mango	Mexico	WP	foliar		0.13-0.18		14
Melon	Brazil	WP	foliar		0.10		1
Melon	Portugal	WP	foliar		0.15-0.20		28
Nectarine	Chile	WP	foliar		0.14		1-15[3]
Nectarine	Greece	WP	foliar		0.13	4	20
Nectarine	Hungary	WP	foliar	1.0-1.5		2-3[1]	10
Nectarine	Spain	WP	foliar		0.13-0.15	4[1]	7
Nectarine	Uruguay	WP	foliar		0.13		7
Nectarine	USA (California)	WP	foliar	2.2-4.5			7
Nectarine	USA	WP	foliar	4.5			0
Olives	Spain	WP	foliar		0.13-0.21		10
Onion	Brazil	WP	foliar		0.11		7
Onion	Japan	WP	foliar		0.14		
Onion	Mexico	WP	foliar		0.13-0.15		14
Onion	Turkey	WP	foliar		0.15		7
Peach	Brazil	WP	foliar		0.11		1
Peach	Canada	WP	foliar		0.1-0.13		2
Peach	Chile	WP	foliar		0.14		1-15[3]
Peach	Greece	WP	foliar		0.13	4	20
Peach	Hungary	WP	foliar	1.0-1.5		2-3[1]	10
Peach	Poland	WP	foliar	1.5-2.3			7
Peach	Portugal	WP	foliar		0.15-0.20		7
Peach	Spain	WP	foliar		0.13-0.15	4	7
Peach	Turkey	WP	foliar		0.15	2+	3
Peach	Uruguay	WP	foliar		0.13		7
Peach	USA (California)	WP	foliar	2.2-4.5			7
Peach	USA	WP	foliar	4.5		8	0
Pear	Brazil	WP	foliar		0.11		1
Pear	Canada	WP	foliar		0.10		7
Pear	Chile	WP	foliar		0.14		1-10[3]

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Pear	Ecuador	WP	foliar	0.80-1.2			15
Pear	Greece	WP	foliar		0.13	3+	15
Pear	Hungary	WP	foliar	1.0-1.5	0.10-0.15	2-3[1]	10
Pear	Japan	WP	foliar		0.080-0.14		3
Pear	Mexico	WP	foliar		0.10-0.13		
Pear	Netherlands	WP	foliar		0.05	10-12[1]	7
Pear	Netherlands	SC WP	foliar		0.083-0.21	10-12[1]	21
Pear	Poland	WP	foliar	1.5-2.3		8-10[1]	7
Pear	Portugal	WP	foliar		0.15-0.20		21
Pear	South Africa	WP	foliar		0.048		14
Pear	Spain	WP	foliar		0.13-0.15	4[1]	7
Pear	Turkey	WP	foliar		0.075	2+	3
Pear	UK	WP	post-harvest		0.10		
Pear	UK	WG	foliar	2.7		10-12[1]	7
Pear	Uruguay	WP	foliar		0.10-0.13	2	7
Pear	USA	WP	post-harvest		0.15		
Peas	Spain	WP	foliar FG		0.13-0.21		10
Peppers	Ecuador	WP	foliar	0.80-1.2			15
Plum/ Prune	Canada	WP	foliar		0.10-0.13		2
Plum	Chile	WP	foliar		0.14		1-8[3]
Plum	Greece	WP	foliar		0.13	4	20
Plum	Hungary	WP	foliar	1.0-1.5		2-3[1]	10
Plum	Portugal	WP	foliar		0.15-0.20		7
Plum	Spain	WP	foliar		0.13-0.15	4[1]	7
Plum	Turkey	WP	foliar		0.10	2+	3
Plum	Uruguay	WP	foliar		0.13		7
Plum/ Prune	USA (California)	WP	foliar	2.2-3.4			7
Plum/ Prune	USA	WP	foliar	3.4			0
Pome fruit	Spain	WP	foliar		0.13-0.26		10
Potato	Brazil	WP	foliar		0.11		14
Potato	Ecuador	WP	foliar	0.80-1.2			15
Potato	Greece	WP	foliar		0.13		20
Potato	Mexico	WP	foliar		0.10-0.20		14
Potato	Portugal	WP	foliar		0.15-0.20		7
Potato	Spain	WP	foliar		0.13-0.21		10
Potato	Turkey	WP	foliar		0.18		7
Potato	Uruguay	WP	foliar	0.64-1.0			7
Raspberry	Canada	WP	foliar		0.10		2

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Raspberry	Netherlands	WP	foliar		0.13		4
Stone fruit	Chile	WP	foliar		0.14		
Stone fruit	Greece	WP	foliar		0.13		20
Stone fruit	Spain	WP	foliar		0.13-0.26		10
Strawberry	Canada	WP	foliar	2.2-3.4	0.22-0.34		2
Strawberry	Chile	WP	foliar	1.6-3.2		1-2[1]	2-15[3]
Strawberry	Ecuador	WP	foliar	1.2-1.6			15
Strawberry	Hungary	WP	foliar	1.3		3	10
Strawberry	Japan	WP	foliar		0.10	2	30
Strawberry	Mexico	WP	foliar	1.5-2.0	0.15-0.20		7
Strawberry	Netherlands	SC WP	foliar		0.13	2-4[1]	4
Strawberry	Netherlands	SC WP	foliar G[2]		0.13	2	14
Strawberry	Spain	WP	foliar FG	1.3	0.13-0.21	4	21
Strawberry	USA (California)	WP	foliar	1.7-3.4			2
Strawberry	USA	WP	foliar	1.7-3.4			0
Tomato	Brazil	WP	foliar		0.11		1
Tomato	Canada	WP	foliar FG	2.3-3.4			2
Tomato	Ecuador	WP	foliar	0.80-1.2		2[1]	15
Tomato	Greece	WP	foliar		0.13	3-4[1]	
Tomato	Hungary	WP	foliar	1.0-1.5		2-3[1]	5
Tomato	Israel	WP	foliar	1.3-2.5		3	11
Tomato	Japan	WP	foliar		0.064-0.14		1
Tomato	Mexico	WP	foliar	0.75-1.5	0.075-0.15		7
Tomato	Portugal	WP	foliar		0.15-0.20		7
Tomato	Spain	WP	foliar FG		0.13-0.21		10
Tomato	Spain	WP	foliar		0.13-0.15	4[1]	7
Tomato	Turkey	WP	foliar		0.15	2+	7
Tomato	UK	WG	foliar		0.25	3-4[1]	
Vine	Japan	WP	foliar		0.10	5	14
Witloof	Spain	WP	foliar		0.13-0.21		21

[1] Information not on label, but is part of GAP followed in country.
[2] G: glasshouse use. FG: field and glasshouse uses.
[3] Set on requirements of importing country.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data from supervised trials on citrus, apples, pears, cherries, peaches, nectarines, plums, grapes, blueberries, strawberries and tomatoes are summarized in Tables 19 to 28.

Table 19. Citrus. Spain.
Table 20. Apples. Argentina, Australia, Brazil, Canada, Chile, France, Israel, Japan,

	Netherlands, Portugal, South Africa, UK, USA.
Table 21.	Pears. Australia, Chile, South Africa, UK, USA.
Table 22.	Cherries. Japan, USA.
Table 23.	Peaches. Australia, Chile, Spain, USA.
	Nectarines. Chile, Spain, USA.
Table 24.	Plums. Chile, USA.
Table 25.	Grapes. Argentina, Chile, France, Germany, Japan, USA.
Table 26.	Blueberries. USA.
Table 27.	Strawberries. Australia, Belgium, Canada, Chile, Hungary, Spain, USA.
Table 28.	Tomatoes. Brazil, Canada, Greece, Israel, Mexico, USA.

Animal transfer studies on laying hens and dairy cows are also included in this section.

Where residues were not detected, they are recorded in the Tables as less than the limit of determination (LOD), e.g. <0.05 mg/kg. Results have generally been rounded to 2 significant figures or, near the LOD, to 1 significant figure. Residues in control samples are recorded in the Tables only in the few cases that they were detected above the LOD.

Most of the reported residues were adjusted for recovery. Recoveries were generally good, so the difference between adjusted and unadjusted results should not influence the interpretation.

In most of the trials samples were analysed for THPI as well as for captan, but in many cases THPI was undetectable or negligible. If captan, but negligible TPHI, residues are found it is good evidence that the captan residues were stable during sample storage. The captan and THPI residues in the same sample are recorded in most cases.

Where residues are recorded in pairs the two values were from duplicate plots.

In the US trials various sprayers were used, including CO_2 backsprayers, hand guns and tractor-mounted air-blast sprayers. Plot sizes for the orchard crops varied from 1 tree to 0.4 ha, but were usually 2-6 trees. Plots for aerial spraying were around 0.4 ha. Plots of grapes were 0.01-0.04 ha for ground application and 0.18 ha for aerial application, and of strawberries 15 m^2 - 0.02 ha for ground application and 1.2 ha for aerial application. Tomato plots ranged from 7 m^2 to 0.034 ha.

In the UK trials plot sizes for pears and apples were 2-10 trees, and captan was applied by orchard sprayer or mist blower. Plot sizes in the South African trials were 2-5 trees for apples and pears; application was by power sprayer with hand gun. A boom sprayer was used in the apple trials in The Netherlands where the plot size was 16 trees.

In Chile plot sizes were 5 trees in orchards and 5 vines of grapes. A motorised sprayer with hand gun was used in the trials. A mist blower was used in the strawberry trials, where the plot size was 112 m^2.

A motorised mist blower was used in the Australian trials, where plot sizes were 2 trees for orchard crops and 1 row of 70 m for strawberries.

In Brazil, a CO_2-powered spray was used to apply captan to tomato plots of 19-27 plants, while a knapsack was used in the apple trials (6 trees per plot).

In Spain a knapsack was used in the trials on peaches, nectarines and strawberries (plot size 204 plants).

A knapsack and a motorised mist blower were used in the German trials on grapes. The plot size, where recorded, was 30 vines.

Table 19. Residues of captan in citrus fruits from single foliar applications of WP formulations of captan in supervised trials in Spain. Underlined residues are from treatments according to GAP.

Country, year (Variety)	Application		Day	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl		Captan	
ORANGES					
Spain, 1988 (Navel)	7.8	0.15	0 7 14 21 28 42 56	0.42, 0.40 0.08, 0.10, 0.10 0.07, 0.11, 0.08 0.08, 0.12, 0.08 0.09, 0.14, 0.12 0.12, 0.14, 0.12 0.12, 0.15, 0.12	Spain, 8.10.91
Spain, 1989-90 (Navel)	7.8	0.15	0 14 22	0.92 0.44 0.32	Spain
Spain, 1990 (Navel)	7.8	0.15	0 14 22 28	0.68 0.38 0.32 0.10	Spain
Spain, 1991 (Valencia)	8.4	0.2	0 7 14 21 28	0.75, 0.75, 0.88 0.38, 0.36, 0.45 0.13, 0.39, 0.35 0.18, 0.35, 0.29 0.12, 0.20, 0.18	Spain
MANDARINS					
Spain, 1989-90 (Clementine)	7.8	0.15	0 14 22 28	1.2 0.48 0.38 0.13	Spain
Spain, 1989-90 (Satsuma)	7.8	0.15	0 14 22 28	1.6 0.48 0.37 0.15	Spain
Spain, 1989	7.5	0.15	0 0 7 7 14 14 21 21 28 28 49 49	Lab A: 0.80, 0.63, 0.72 Lab B: 0.37, 0.34, 0.40 Lab A: 0.68, 0.59, 0.62 Lab B: 0.25, 0.28, 0.25 Lab A: 0.55, 0.56, 0.52 Lab B: 0.20, 0.18, 0.24 Lab A: 0.57, 0.57, 0.55 Lab B: 0.15, 0.17, 0.22 Lab A: 0.48, 0.40, 0.36 Lab B: 0.19, 0.12, 0.15 Lab A: 0.15, 0.24, 0.28 Lab B: 0.13, 0.20, 0.11	Spain, 8-10-91

Table 20. Residues of captan and THPI in apples from foliar applications of captan in supervised trials in Argentina, Australia, Brazil, Canada, Chile, France, Israel, Japan, Netherlands, Portugal, South Africa, the UK and the USA. Post-harvest applications in the USA are also included. Underlined residues are from treatments according to GAP.

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Argentina	WP	7.0	0.17	2	14 14	0.005, 0.003, 0.004	0.013, 0.009, 0.007	R.7108
Australia, 1991 (Granny Smith)	WG		0.13	7 6 5	7 14 27	3.6 3.7 1.0		S38990 91-50
Australia, 1991 (Granny Smith)	WG		0.25	7 6 5	7 14 27	8.1 7.9 2.0		S38990 91-50
Brazil, 1992 (Gala)	WP		0.060	11	1 7	0.15 0.12	0.11 <0.05	RJ1419B
Brazil, 1992 (Gala)	WP		0.12	11	1 7	0.68 0.38	0.18 0.13	RJ1419B
Brazil, 1992 (Gala)	WP		0.24	11	1 7	1.2 0.31	0.20 0.18	RJ1419B
Brazil, 1992 (Gala)	SC		0.24	11	1 7	0.55 0.13	0.20 0.10	RJ1419B
Brazil, 1992 (Fuji)	WP		0.12	10	1 7	4.1 0.30	0.18 <0.05	RJ1419B
Brazil, 1992 (Fuji)	WP		0.24	10	1 7	5.2 0.45, c 0.13	0.19 <0.05	RJ1419B
Brazil, 1992 (Gala)	SC		0.060	11	1 7	0.06 <0.05	0.10 0.06	RJ1419B
Brazil, 1992 (Fuji)	SC		0.060	11	1 7	0.14 0.24	0.07 0.05	RJ1419B
Brazil, 1992 (Fuji)	SC		0.12	11	1 7	1.0 0.19	0.38 0.08	RJ1419B
Brazil, 1992 (Fuji)	SC		0.060	10	1 7	1.0 0.27	0.12 0.09	RJ1419B
Brazil, 1992 (Fuji)	SC		0.12	10	1 7	1.4 0.47	0.12 <0.05	RJ1419B
Brazil, 1992 (Fuji)	SC		0.24	10	1 7	1.7 0.54	0.15 <0.05	RJ1419B
Brazil, 1992 (Fuji)	WP		0.24	11	1 7	4.6 0.30, c 0.08	0.92 0.09	RJ1419B
Brazil, 1992 (Fuji)	WP		0.12	11	1 7	2.5 0.13	0.55 0.06	RJ1419B
Brazil, 1992 (Fuji)	SC		0.24	11	1 7	2.1 0.33	0.53 0.09	RJ1419B
Brazil, 1992 (Fuji)	WP		0.060	11	1 7	1.7 0.14	0.61 <0.05	RJ1419B

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Brazil, 1992 (Fuji)	WP		0.060	10	1 7	3.1 0.22	0.22 0.33	RJ1419B
Brazil, 1992 (Gala)	SC		0.12	11	1 7	0.44 0.11	0.11 0.05	RJ1419B
Canada, 1991 (Macintosh)	WP	3.0	0.10	10	6 13 20	3.5 3.9 1.7	0.09 0.08 <0.05	RJ1190B
Canada, 1991 (Macintosh)	WP	3.0	0.10	10	6 13 20	3.2 2.1 2.6	0.08 0.05 <0.05	RJ1190B
Canada, 1991 (Red Delicious)	WP	3.0	0.10	10	7 14 21	2.8, c 0.22 1.5, c 0.09 0.99, c 0.06	0.05 <0.05 <0.05	RJ1190B
Canada, 1991 (Macintosh)	WP	6.0	0.20	10	6 13 20	4.8 4.2 3.5	0.11 0.09 0.07	RJ1190B
Canada, 1991 (Macintosh)	WP	3.0	0.10	10	6 13	4.0 4.5	0.06 0.05	RJ1190B
Canada, 1991 (Idared)	WP	3.0	0.10	10	7 14 21	2.9 2.9 1.2	0.05 <0.05 <0.05	RJ1190B
Canada, 1991 (Macintosh)	WP	6.0	0.20	10	6 13 21	9.5 9.1 7.7	0.11 0.08 0.07	RJ1190B
Canada, 1991 (Macintosh)	WP	3.0	0.10	10	6 13 21	4.1 4.5 4.5	0.07 <0.05 <0.05	RJ1190B
Canada, 1991 (Idared)	WP	3.0	0.10	10	7 14 21	2.9 1.1 2.7	<0.05 <0.05 <0.05	RJ1190B
Canada, 1991 (Idared)	WP	6.0	0.20	10	7 14 21	6.5 2.3 5.4	0.09 0.08 0.08	RJ1190B
Canada, 1991 (Red Delicious)	WP	6.0	0.20	10	7 14 21	6.9 5.5 4.8	0.10 0.10 0.05	RJ1190B
Canada, 1991 (Red Delicious)	WP	3.0	0.10	10	7 14 21	4.2 3.3 2.8	0.06 <0.05 <0.05	RJ1190B
Chile, 1991 (Granny Smith)	WP	3.6	0.12	1	28 59	0.37 0.05	0.06 <0.05	RJ1302B
Chile, 1991 (Granny Smith)	WP	3.6	0.12	1	29 60	0.44 0.13	<0.05 <0.05	RJ1302B
Chile, 1991 (Granny Smith)	WP	3.6	0.12	1	28 59	0.46 0.15	<0.05 <0.05	RJ1302B
Chile, 1992 (Red King Oregon)	WP	2.2-3.8	0.18- 0.25	4	122	0.01, 0.04 0.02, <0.01	<0.1 (2) <0.1 (2)	R-6986
France, 1991 (Golden,	WP	1.5		10	31	0.60	<0.05	RJ1261B

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Ozark Gold)					40	0.37	<0.05	
France, 1991 (Golden, Ozark Gold)	WP	1.9		10	29 41	0.12 0.06	<0.05 <0.05	RJ1261B
France, 1991 (Golden, Ozark Gold)	WP	1.5		16	30 39	3.0 2.4	0.08 0.07	RJ1261B
Israel, 1991	WP	1.8-2.0	0.18	4	0 0 23 23 36 36 83 83	1.6, 1.6 2.4, 2.5 0.73, 0.85 0.90, 0.24 0.55, 0.17 0.50, 0.23 0.89, 0.74 0.78, 0.39 control[1]	0.25, 0.36 0.39, 0.41 0.56, 0.13 0.10, <0.1 <0.1, 0.1 0.22, <0.1 <0.1 (2) <0.1 (2) control[1]	CT/36/92
Israel, 1991	WP	3.6-4.0	0.36	4	0 0 23 23 36 36 83 83	2.0, 1.9 2.0, 2.2 0.82, 0.91 0.85, 0.64 0.57, 0.88 0.64, 0.14 0.64, 2.0 1.8, 4.9 control[1]	0.50, 0.20 0.31, 0.87 0.1, 0.1 <0.1 0.1, 0.35 <0.1 (2) <0.1 (2) <0.1 (2) control[1]	CT/36/92
Japan, 1991 (Fuji)	WP	8	0.13	8	14 21	7.2 5.3	0.32 0.29	RJ1185B
Japan, 1991 (Fuji)	WP	8	0.13	8	3 7 14 21	10 13 4.6 3.5	0.23 0.28 0.24 0.14	RJ1185B
Japan, 1991 (Fuji)	WP	8	0.13	8	14 21	3.8 3.0 c 0.09	0.32 0.44	RJ1185B
Netherlands, 1991 (Cox)	WP	1.0	0.50	16	0 0 14 21 21	3.1, 2.7, c 0.19 2.9, 3.0, c 0.35 1.1, 1.3, c 0.18 1.0, 0.34, c 0.06 0.48, 0.48, c 0.06	0.13, 0.11 0.09, 0.11 0.28, 0.15 0.11, 0.14 0.12, 0.13	RJ1115B
Netherlands, 1991 (Elstar)	WG	1.1	0.50	16	0 0 7 7 14 14 21 21	2.5, 1.3 1.3, 4.0 2.3, 2.4 1.0, 1.4 0.85, 1.1 0.86, 1.5 0.84, 0.56 0.66, 0.58	0.06, 0.05 0.05, 0.12 0.14, 0.14 0.13, 0.14 0.12, 0.10 0.13, 0.16 0.19, 0.11 0.17, 0.18	RJ1115B
Netherlands, 1991 (Elstar)	WP	1.0	0.50	16	0 0 7 7 14 14	1.4, 2.6, c 0.16 1.5, 2.6, c 0.12 0.67, 1.7 1.7, 1.1 0.88, 1.1 1.8, 1.4	0.05, 0.05 <0.05, 0.07 0.13, 0.22 0.20, 0.14 0.10, 0.09 0.16, 0.12	RJ1115B

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
					21 21	0.40, 0.54 0.55, 0.37	0.15, 0.15 0.14, 0.16	
Netherlands, 1991 (Elstar)	WG	0.96	0.50	16	0 0 7 7 14 14 21 21	2.7, 2.1 1.4, 2.8 0.99, 0.59 0.93, 1.2 1.2, 0.93 0.83, 0.90 1.0, 0.68 0.41, 0.38	0.06, 0.07 0.08, 0.08 0.11, 0.13 0.12, 0.11 0.11, 0.09 0.13, 0.16 0.23, 0.13 0.25, 0.13	RJ1115B
Netherlands, 1991 (Cox)	WG	1.1	0.50	16	0 0 14 14 21 21	1.2, 1.4 1.3, 1.3 0.55, 0.54 1.6, 1.7 0.31, 0.63 0.33, 0.77	0.12, 0.11 0.12, 0.09 0.13, 0.08 0.15, 0.16 0.14, 0.15 0.14, 0.22	RJ1115B
Netherlands, 1991 (Cox)	WG	0.96	0.50	16	0 0 14 14 21 21	1.8, 1.6 2.2, 1.8 0.38, 0.57 1.1, 0.60 0.18, 0.12 0.23, 0.26	0.13, 0.08 0.14, 0.13 0.08, 0.12 0.12, 0.11 0.09, 0.06 0.11, 0.11	RJ1115B
Portugal, 1991	WP	2.0-2.4	0.24	10	0 0 10 10 21 21	6.3, 5.1 6.7, 6.7 2.6, 2.5 4.4, 2.4 3.1, 2.9 3.2, 2.5	<0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2)	CT/37/92
South Africa, 1992 (Starking)	SC		0.15	2	0 4 8 16 32 59	4.3 5.0 1.0 1.2 2.1 1.2	0.09 0.14 0.07 0.13 0.06 0.06	RJ1416B
South Africa, 1992 (Starking)	SC		0.075	2	0 4 8 16 32 59	3.5 2.6 5.3 3.6 0.82 0.17	0.07 0.10 0.13 0.11 <0.05 <0.05	RJ1416B
South Africa, 1992 (Granny Smith)	SC		0.15	2	0 4 32 59	3.4 4.0 1.2 0.45	0.14 0.19 <0.05 <0.05	RJ1416B
South Africa, 1992 (Granny Smith)	SC		0.075	2	4 8 16 59	2.0 2.0 2.0 0.15	0.13 0.09 0.11 <0.05	RJ1416B
UK, 1990 (Cox)	WP	2.7		9	7 21	4.4 1.3	0.15 0.08	GB51-90-S291
UK, 1990 (Cox)	WG	2.7		9	7	4.3	0.13	GB51-90-S291

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
					21	1.8	0.09	
UK, 1990 (Cox)	WP	2.7		3	7	4.2	0.08	GB52-90-S291
UK, 1990 (Cox)	WG	2.7		8	12 26 39 53 67	3.7 1.0 0.70 0.54 0.11	0.11 <0.05 <0.05 <0.05 <0.05	GB52-90-S291
UK, 1990 (Cox)	WP	2.7		8	12 26 39 53 67	0.45 1.0 0.58 0.24 0.14	<0.05 <0.05 <0.05 <0.05 <0.05	GB52-90-S291
UK, 1990 (Cox)	WP	2.7		8	12 26 39 53 67	2.0 1.1 0.98 0.51 0.22	0.08 <0.05 0.06 <0.05 <0.05	GB52-90-S292
UK, 1990 (Cox)	WP	2.7		3	6 20 35	4.8 1.1 0.62	0.14 0.09 0.09	GB52-90-S292
UK, 1990 (Cox)	WG	2.7		8	12 26 39 53 67	2.2 0.85 0.87 0.37 0.21	0.07 0.07 0.07 <0.05 <0.05	GB52-90-S292
UK, 1990 (Cox)	WP	2.7		3	6	0.98	<0.05	GB52-90-S293
UK, 1990 (Cox)	WG	2.7		8	11 25 38	1.6 0.69 0.29	<0.05 <0.05 <0.05	GB52-90-S293
UK, 1990 (Cox)	WP	2.7		8	11 38	2.5 0.68	0.07 <0.05	GB52-90-S293
UK, 1991 (Cox)	WP	3.3		3	7 21 35	6.6 4.4 1.6	0.25 0.15 0.07	RJ1134B
UK, 1991 (Cox)	WG	3.4		10	0 14 28 42 56	1.3 0.72 0.33 0.11 0.15	0.07 <0.05 <0.05 <0.05 <0.05	RJ1134B
UK, 1991 (Cox)	WP	3.3		10	0 14 28 42 56	6.3 3.1 1.4 0.51 0.38	0.23 0.14 0.07 0.05 <0.05	RJ1134B
UK, 1991 (Cox)	WP	3.3		3	7 14 35	3.1 2.4 0.42	0.11 0.12 0.05	RJ1134B
UK, 1991 (Cox)	WG	3.4		10	0 14 28	4.6 0.91 c 0.06 0.58 c 0.07	0.33 <0.05 <0.05	RJ1134B

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
					42 56	0.37 0.18	<0.05 <0.05	
UK, 1991 (Cox)	WP	3.3		9	0 14 28 42 56	7.7 2.4 1.4 1.9 1.1	0.19 0.07 0.10 0.07 0.05	RJ1134B
UK, 1991 (Cox)	WG	3.4		9	0 14 28 42 56	4.9 2.5 2.6 0.98 0.31	0.21 0.14 0.09 <0.05 <0.05	RJ1134B
UK, 1991 (Cox)	WP	3.3		10	0 14 28 42 56	8.3 3.9 3.3 1.9 0.81	0.32 0.15 0.17 0.12 0.06	RJ1134B
UK, 1991 (Cox)	WP	3.3		3	7 14 35	9.7 4.2, 3.0	0.46 0.36 0.21	RJ1134B
USA (NY), 1986 (McIntosh)	WP	8×4.5 kg ai/ha + Po dip 0.15kg ai/hl			0	5.7, 5.9	0.16, 0.10	40189-803 (056131-C)
USA (WA), 1986 (Red Delicious)	WP	Po dip 0.15 kg ai/hl				4.0, 4.0	0.08, 0.09	40189-803 (056131-C)
USA (WA), 1986 (Red Delicious)	WP	8×4.5 kg ai/ha + Po dip 0.15 kg ai/hl			0	7.7, 7.0	0.35, 0.28	40189-803 (056131-C)
USA (NY), 1986 (McIntosh)	WP	Po dip 0.15 kg ai/hl				2.5, 3.3	0.07, 0.10	40189-803 (056131-C)
USA (VA), 1986 (Golden Delicious)	WP	4.5		8	0	1.4, 0.41	0.07, <0.05	40189-803 (056131-C)
USA (MI), 1986 (Jonathan)	WP	4.5		8	0 7 14	3.4, 3.9 1.7, 1.3 2.2, 0.64	<0.05 (2) <0.05 (2) <0.05 (2)	40189-803 (056131-C)
USA (NY), 1986 (McIntosh)	WP	4.5		8	0	4.7, 2.8	0.10, 0.09	40189-803 (056131-C)
USA (NY), 1986 (McIntosh)	WP	4.5		8	7 14	2.8, 2.5 2.8. 2.1	0.12, 0.12 0.23, 0.10	40189-803 (056131-C)
USA (NC), 1986 (Red Delicious)	WP	4.5		8	0	0.31, 1.5	0.06, 0.05	40189-803 (056131-C)
USA (WA), 1986 (Winter Banana)	WP	4.5		8	0	1.2, 5.2	0.37, 0.76	40189-803 (056131-C)
USA (WA), 1986 (Red Delicious)	WP	4.5		8	0	5.5, 5.1	0.23, 0.21	40189-803 (056131-C)
USA (WA), 1986 (Red Delicious)	WP	4.5		6	0	2.2, 2.3, 1.9	<0.05 (3)	40189-803
USA (WA), 1986 (Red Delicious)	WP	13		8	0	9.1, 5.5	0.40, 0.43	40189-803 (056131-C)
USA (WA), 1986 (Red	WP	4.5		7	7	5.2, 3.5	0.21, 0.20	40189-803

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Delicious)					14	2.2, 3.3	0.19, 0.28	(056131-C)
USA (WA), 1986 (Red Delicious)	WP	4.5		a 6	0	0.86, 0.74, 0.42	<0.05 (3)	40189-803
USA (CA), 1986 (Granny Smith)	WP	4.5		8	0	3.8, 4.9	0.08, 0.13	40189-803 (056131-C)
USA (WA), 1989 (Red Delicious)	WP	4.5		4 5 6 7	141 134 125 117	<0.05 0.13 0.10 0.59	<0.05 <0.05 <0.05 <0.05	15WA89-263
USA (CA), 1989 (Golden Delicious)	WP	4.5		4 5 6 7	138 136 125 116	0.13 0.15 0.12 0.44	<0.05 <0.05 <0.05 <0.05	17CA89-262
USA (MI), 1989 (Red Delicious)	WP	4.5		4 5 6 7	131 125 116 102	<0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	28MI89-260
USA (WV), 1989 (Rome Beauty)	WP	4.5		4 5 6 7	171 151 139 125	<0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	55WV89-261
USA (NY), 1989 (McIntosh)	WP	4.5		4 5 6 7	121 114 105 92	<0.05 <0.05 <0.05 0.08	<0.05 <0.05 <0.05 <0.05	56NY89-259

c: control sample. Po: post-harvest. a: aerial application.
[1] In trial CT/36/92 residues of captan and THPI were detected in control samples. Levels of captan ranged up to 0.5 mg/kg and higher; levels of THPI ranged up to 0.3 mg/kg. No residues were detected in 83-day control samples.

Table 21. Residues of captan and THPI in pears from foliar application of captan in supervised trials in Australia, Chile, South Africa, the UK and the USA, and post-harvest applications in the USA. Underlined residues are from treatments according to GAP.

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Australia (Vic), 1991 (Packham's Triumph)	WG		0.13	5 4 3	6 14 27	2.5 1.9 1.4		S38990 91-48
Australia (Vic), 1991 (Packham's Triumph)	WG		0.25	5 4 3	6 14 27	7.1 5.7 1.2		S38990 91-48
Chile, 1992 (Berry Box)	WP	3.6	0.12	1	26 57	<u>1.1</u> <u>0.10</u>	0.06 <0.05	RJ1303B
Chile, 1992 (Winter Nelly)	WP	3.6	0.12	1	30 61	<u>1.3</u> <u>0.31</u>	<0.05 <0.05	RJ1303B

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Chile, 1992 (Packams)	WP	3.6	0.12	1	28 60	1.0 0.21	0.05 <0.05	RJ1303B
South Africa, 1992 (Bon Chretien)	SC		0.15	2	32 40	0.69 0.74	<0.05 <0.05	RJ1417B
South Africa, 1992 (Bon Chretien)	SC		0.075	2	32 40	<0.05 <0.05	<0.05 <0.05	RJ1417B
South Africa, 1992 (Packham's Triumph)	SC		0.10	4	105 112	0.15 0.07	<0.05 <0.05	RJ1417B
UK, 1990 (Conference)	WP	2.7		3	7 20 34	1.5 0.94 0.23	<0.05 <0.05 <0.05	RJ1003B
UK, 1990 (Conference)	WP	2.7		8	37 51 65	1.5 0.54 0.15	<0.05 <0.05 <0.05	RJ1003B
UK, 1990 (Conference)	WG	2.7		8	12 26 37 51 65	1.7 1.5 0.74 0.24 0.12	<0.05 <0.05 <0.05 <0.05 <0.05	RJ1003B
UK, 1990 (Conference)	WP	2.7		3	7 21 35	7.0 2.4 1.2	0.18 0.10 <0.05	RJ1003B
UK, 1990 (Conference)	WP	2.7		9	7 21 35 49 63	7.3 3.1 1.4 0.73 0.18	0.14 <0.05 <0.05 <0.05 <0.05	RJ1003B
UK, 1990 (Conference)	WG	2.7		9	7 21 35 49 63	9.2 2.6 0.59 1.9 0.47	0.17 <0.05 <0.05 <0.05 <0.05	RJ1003B
UK, 1991 (Conference)	WP	3.3		9	0 14 28 42 56	10 2.6 1.7 0.81 0.33	0.36 0.11 0.05 <0.05 <0.05	RJ1171B
UK, 1991 (Conference)	WP	3.3		3	7 21 35	5.5 2.6 0.49	0.18 0.10 <0.05	RJ1171B
UK, 1991 (Conference)	WG	3.4		9	0 14 28 42 56	13 2.0 1.6 0.51 0.39	0.42 0.08 0.06 <0.05 <0.05	RJ1171B
UK, 1991 (Comice)	WG	3.4		10	0 14 28 42 56	4.8 1.2 0.62 0.36 0.50	0.17 <0.05 <0.05 <0.05 <0.05	RJ1171B

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
UK, 1991 (Comice)	WP	3.3		3	7 14 35	7.4 6.5 1.7	0.21 0.14 <0.05	RJ1171B
UK, 1991 (Comice)	WP	3.3		10	0 14 28 42 56	6.5 1.9 1.4 0.89 0.22	0.18 <0.05 <0.05 <0.05 <0.05	RJ1171B
USA (CA), 1986 (Bartlett)	WP	Po dip 0.15 kg ai/hl				4.7, 3.0	0.07, 0.06	40189-815 (056131-O)
USA (WA), 1986 (Bartlett)	WP	5×4.5 kg ai/ha + Po dip 0.15 kg ai/hl			0	11, 6.1	<0.05 (2)	40189-815 (056131-O)
USA (CA), 1986 (Bartlett)	WP	5×4.5 kg ai/ha + Po dip 0.15 kg ai/hl			0	2.6, 2.9	<0.05 (2)	40189-815 (056131-O)
USA (WA), 1986 (Bartlett)	WP	Po dip 0.15 kg ai/hl				11, 11	0.43, 0.31	40189-815 (056131-O)
USA (NY), 1986 (Bartlett)	WP	4.5		5	0 7 14	2.8, 1.8 1.6, 1.5 1.5, 1.4	<0.05 (2) <0.05 (2) 0.08, 0.11	40189-815 (056131-O)
USA (MI), 1986 (Bartlett)	WP	4.5		5	0	5.4, 5.7	<0.05 (2)	40189-815 (056131-O)
USA (WA), 1986 (Bartlett)	WP	4.5		5	0 7 14	4.3, 1.3 2.9, 2.9 1.3, 2.0	<0.05 (2) <0.05 (2) <0.05 (2)	40189-815 (056131-O)
USA (CA), 1986 (Bartlett)	WP	4.5		5	0	0.90, 1.6	<0.05 (2)	40189-815 (056131-O)

Po: post-harvest

Table 22. Residues of captan and THPI in cherries from foliar applications of WP formulations of captan in supervised trials in Japan and the USA, and post-harvest applications in US. Underlined residues are from treatments according to GAP.

Country, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Japan, 1991 (Satonishiki)		0.094	5	14 21	0.58 0.38	<0.05 <0.05	RJ1409B
Japan, 1991 (Satonishiki)		0.13	5	14 21	1.3 1.3	<0.05 <0.05	RJ1409B
USA (WA), 1987 (Lambert)	2.2		7	0	17, 19	0.22, 0.24	40189-808
USA (WA), 1987 (Lambert)	7×2.2 kg ai/ha +Po dip 0.15 kg ai/hl			0	35, 13	0.45, 0.20	40189-808
USA (WA), 1987 (Lambert)	Po dip 0.15 kg ai/hl				3.8, 14	0.09, 0.30	40189-808
USA (WA), 1987 (Lambert)	7×2.2 kg ai/ha +Po dip 0.15 kg ai/hl			10	25, 9.2	0.44, 0.35	40189-808
USA (WA), 1987 (Lambert)	Po dip 0.15 kg ai/hl				7.3, 5.8	0.15, 0.17	40189-808

Country, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
USA (WA), 1987 (Van)	2.2		7	0	<u>14</u>, <u>14</u>	0.14, 0.13	40189-808
USA (WA), 1987 (Van)	7×2.2 kg ai/ha +Po dip 0.15 kg ai/hl			0	2.1, 23	0.15, 0.34	40189-808
USA (WA), 1987 (Van)	Po dip 0.15 kg ai/hl				<u>15</u>, <u>14</u>	0.23, 0.24	40189-808
USA (MI), 1987 (Montmorency)	2.2		7	0	<u>9.6</u>, <u>10</u>	0.19, 0.18	40189-808
USA (NY), 1987 (Emperor Francis)	2.2		7	0	<u>11</u>, <u>10</u>	0.17, 0.15	40189-808

Po: post-harvest

Table 23. Residues of captan and THPI in peaches and nectarines from foliar applications of captan in supervised trials in Australia, Chile, Spain and the USA, and post-harvest treatments in the USA. Underlined residues are from treatments according to GAP.

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
PEACH								
Australia (Vic), 1991 (Golden Queen)	WG		0.25	5 4 3	6 14 27	11 4.8 3.7		S38990 91-51
Australia (Vic), 1991 (Golden Queen)	WG		0.13	5 4 3	6 14 27	4.7 2.8 1.5		S38990 91-51
Chile, 1992 (Pomona)	WP	2.9	0.14	1	27 50	<u>2.0</u>, <u>1.7</u> <u>0.25</u>, <u>0.27</u> c 0.08	0.06, 0.05 <0.05 (2)	RJ1356B
Chile, 1992 (E. Lady)	WP	2.9	0.14	1	24 46	<u>0.44</u>, <u>0.43</u> <u>0.32</u>, <u>0.34</u> c 0.07, c 0.22	<0.05 (2) <0.05 (2)	RJ1356B
Chile, 1992 (O'Henry)	WP	2.9	0.14	1	28 50	<u>1.0</u>, <u>0.24</u> <u>0.30</u>, <u>0.31</u>	<0.05 (2) <0.05 (2)	RJ1356B
Spain, 1991 (Spring Crest)	WP	7.5	0.15	1	10 20 28	<u>3.5</u> <u>3.5</u> <u>1.8</u>	<0.05 <0.05 <0.05	RJ1172B
Spain, 1991 (Spring Crest)	WP	6.3	0.13	1	10 20 28	<u>2.8</u>, c 0.08 <u>2.7</u> <u>1.8</u>	<0.05 <0.05 <0.05	RJ1172B
USA (GA), 1986 (Redskin)	WP	8×4.5 kg ai/ha + Po dip 0.15 kg ai/hl			0	131, 135	2.0, 2.4	40189-814 (056131-N)
USA (CA), 1986 (Fay Alberta)	WP	8×4.5 kg ai/ha + Po dip 0.15 kg ai/hl			0	38, 48	0.61, 0.56	40189-814 (056131-N)
USA (GA), 1986 (Redskin)	WP	Po dip 0.15 kg ai/hl				136, 144	1.7, 0.87	40189-814 (056131-N)
USA (CA), 1986 (Fay Alberta)	WP	Po dip 0.15 kg ai/hl				39, 27	0.50, 0.38	40189-814 (056131-N)
USA (WA), 1987 (Elberta)	WP	4.5		6	0	<u>5.8</u>, <u>3.0</u>	0.08, 0.07	40189-813

Country, year (Variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
					0	2.7, 2.9	0.07, 0.08	
USA (WA), 1987 (Elberta)	WP	4.5		a 6	0	3.6, 2.5, 4.3	<0.05 (3)	40189-813
USA (CA), 1987	WP	4.5		8	0	11, 12, 12	0.50, 0.33, 0.24	40189-814
USA (CA), 1987	WP	4.5		8	0	7.8, 6.9, 6.2	0.15, 0.16, 0.16	40189-814
USA (CA), 1987	WP	4.5		a 8	0	4.3, 0.80, 2.6	0.07, <0.05 (2)	40189-814
USA (MI), 1986 (Red Haven)	WP	4.5		8	0	5.6, 6.0	<0.05 (2)	40189-814 (056131-N)
USA (CA), 1986 (Fay Alberta)	WP	4.5		8	0	9.9, 14	0.08, 0.18	40189-814 (056131-N)
USA (NY), 1986 (Red Haven)	WP	4.5		8	0	7.7, 9.0	0.20, 0.42	40189-814 (056131-N)
USA (CA), 1986 (Fay Alberta)	WP	4.5		8	0	10, 2.9	0.30, 0.65	40189-814 (056131-N)
USA (SC), 1986 (Topaz)	WP	4.5		8	0	7.4, 3.4	<0.05 (2)	40189-814 (056131-N)
USA (GA), 1986 (Redskin)	WP	4.5		8	0	1.4, 2.0	<0.05 (2)	40189-814 (056131-N)
NECTARINE								
Chile, 1992 (Sun Sweet)	WP	2.9	0.14	1	31 53	0.16, 0.22 0.14, 0.10	<0.05 (2) <0.05 (2)	RJ1362B
Chile, 1992 (L.316)	WP	2.9	0.14	1	31 52	0.17, 0.30 0.16, 0.15	<0.05 (2) <0.05 (2)	RJ1362B
Chile, 1992 (Fiar Line)	WP	2.9	0.14	1	31 52	0.16, <0.05 0.14, 0.07	<0.05 (2) <0.05 (2)	RJ1362B
Spain, 1991 (Red Globe)	WP	1.9	0.15	1	10 20 28	0.77 0.47 0.18	<0.05 <0.05 <0.05	RJ1172B
Spain, 1991 (Red Globe)	WP	1.6	0.13	1	10 20 28	0.40 0.33 0.17	<0.05 <0.05 <0.05	RJ1172B
USA (CA), 1986 (Snow Queen)	WP	2.8		6	0	3.9, 2.7	0.12, 0.07	40189-813 (056131-M)
USA (CA), 1986 (Mike Grant)	WP	2.8		6	0	1.3, 1.5	0.06, <0.05	40189-813 (056131-M)
USA (CA), 1986 (Spring Red)	WP	2.8		6	0	2.2, 1.5	<0.05 (2)	40189-813 (056131-M)

a: aerial application. c: control sample. Po: post-harvest.

Table 24. Residues of captan and THPI in plums from foliar applications of WP formulations of captan in supervised trials in Chile and the USA. Underlined residues are from treatments according to GAP.

Country, year (Variety)	Application	Day	Residues, mg/kg	Ref.

	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Chile, 1992 (Roy Sum)	2.9	0.14	1	26 49	0.62, 0.66 <0.05 (2)	<0.05 (2) <0.05 (2)	RJ1299B
Chile, 1992 (Roy Sum)	2.9	0.14	1	27 48	0.07, 0.11 0.08, 0.05	<0.05 (2) <0.05 (2)	RJ1299B
Chile, 1992 (Angelino)	2.9	0.14	1	26 50	0.12, 0.55 0.06, <0.05	<0.05 (2) <0.05 (2)	RJ1299B
USA (CA), 1986 (Black Amber)	3.4		9	0	0.45, 0.14	<0.05 (2)	40189-816 (056131-P)
USA (CA), 1986 (Queen Ann)	3.4		9	0	0.42, 0.60	<0.05 (2)	40189-816 (056131-P)
USA (CA), 1986 (Queen Ann)	10		9	0	4.8, 3.8	<0.05 (2)	40189-816 (056131-P)
USA (MI), 1986 (Stanley)	3.4		9	0 7 14	3.5, 5.6 3.0, 3.4 2.2, 1.5	<0.05 (2) <0.05 (2) <0.05 (2)	40189-816 (056131-P)

Table 25. Residues of captan and THPI in grapes from foliar applications of captan in supervised trials in Argentina, Chile, France, Germany, Japan and the USA. Underlined residues are from treatments according to GAP.

Country, year (variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Argentina, 1992 (wine grapes)	WP	1.3	0.12	3	25 25	0.66, 0.58 0.74, 0.72	<0.01, 0.13 0.19, <0.01	R.7440
Argentina, 1992 (table grapes)	WP	1.2	0.094	5	14 14	0.77, 0.59 0.62	0.11, 0.32 0.20	R.7440
Chile, 1992 (Red Seedless)	WP	2.4		1	7 21	1.6 6.4, c 0.10	0.13 0.36	RJ1374B
Chile, 1992 (Thompson Seedless)	WP	2.4		1	7 21	2.4 6.1, c 0.09	0.23 0.11, c 0.07	RJ1374B
Chile, 1992 (Red Seedless)	WP	2.4		2	7 21	9.1 0.19	0.21 <0.05	RJ1374B
Chile, 1992 (Thompson Seedless)	WP	1.5-1.9	0.12	4	15	12, 18, 25	1.5, 1.2, 1.2	R-6986
France	SC	1.8	1.2	10	0 0 11 11 20 20 33 33	5.6, 5.4 2.5, 2.4 7.7, 5.5 4.8, 2.3 4.2, 1.6 2.2, 0.95 2.9, 2.8 1.1, 0.83	0.75, 0.59 0.43, 0.43 0.25, 0.56 0.37, 0.41 0.18, 0.19 0.26, 0.19 0.48, 0.61 0.23, 0.28	R.6904 (101/91)
France	SC	3.5	2.3	10	33 33	3.1, 3.0 4.4, 2.5	0.65, 0.64 1.3, 0.66	R.6904
France	SC	1.8	1.3	7	0 0 10 10 21 21 45	3.4, 1.6 3.3, 1.2 0.94, 2.1 1.9, 1.6 0.7, 1.4 1.3, 1.2 0.63, 0.53	1.7, 0.69 1.2, 0.84 1.0, 1.6 0.44, 0.72 0.45, 0.77 0.70, 0.60 0.33, 0.42	R.6904 (103/91)

Country, year (variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
					45	1.3, 0.54	0.80, 0.33	
France	SC	1.8	2.2	7	0 0 10 10 21 21 45 45	2.3, 2.4 2.3, 2.3 1.2, 1.2 2.4 1.5 0.29, 0.41 0.33, 0.46 0.09, 0.06 0.07, 0.05	0.26, 0.49 0.27, 0.33 0.14, 0.18 0.33, 0.16 0.25, 0.20 0.23, 0.27 0.45, 0.35 0.33, 0.29	R.6904 (102/91)
Germany, 1990 (Weissburgunder)	WP	2×1.8 +5×2.7 +1×3.6		8	30	3.6	0.23	RJ1154B
Germany, 1990 (Riesling)	WP	2×1.8 +3×2.7 +1×3.6		6	48 57	7.4 7.1	0.22 0.22	RJ1154B
Germany, 1990 (Riesling)	WP	2×1.8 +5×2.7 +1×3.6		8	28	15	0.35	RJ1154B
Germany, 1990 (Bacchus)	WP	2×1.8 +5×2.7 +1×3.6		8	28	8.3	0.19	RJ1154B
Germany, 1990 (Portugieser)	WP	2×1.8 +4×2.7 +1×3.6		7	34 42	1.1 1.4	0.09 0.08	RJ1154B
Germany, 1990 (Portugieser)	WP	2×1.8 +3×2.7 +1×3.6		6	49 55	1.1 0.93	0.10 0.08	RJ1154B
Germany, 1990 (Portugieser)	WP	2×1.8 +5×2.7 +1×3.6		8	28	1.7	0.14	RJ1154B
Germany, 1990 (Bacchus)	WP	2×1.8 +3×2.7 +1×3.6		6	50 55	0.93 2.8	<0.05 0.08	RJ1154B
Germany, 1990 (Weissburgunder)	WP	2×1.8 +3×2.7 +1×3.6		6	49 56	1.3 0.79	0.10 <0.05	RJ1154B
Germany, 1990 (Bacchus)	WP	2×1.8 +4×2.7 +1×3.6		7	36 43	4.4 7.0	0.17 0.24	RJ1154B
Germany, 1990 (Riesling)	WP	2×1.8 +4×2.7 +1×3.6		7	36 43	9.8 7.7	0.32 0.34	RJ1154B
Germany, 1990 (Weissburgunder)	WP	2×1.8 +4×2.7 +1×3.6		7	38 43	1.7 1.9	0.15 0.14	RJ1154B
Germany, 1990 (Portugieser)	WP	2×1.8 +4×2.7 +1×3.6		7	34 42	1.7 1.6	0.11 <0.05	RJ1160B
Germany, 1990 (Portugieser)	WP	2×1.8		8	28	2.8	0.08	RJ1160B

Country, year (variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
		+5×2.7 +1×3.6						
Germany, 1990 (Bacchus)	WP	2×1.8 +3×2.7 +1×3.6		6	55 50	1.5 2.4	0.08 0.14	RJ1160B
Germany, 1990 (Bacchus)	WP	2×1.8 +5×2.7 +1×3.6		8	28	6.5	0.26	RJ1160B
Germany, 1990 (Portugieser)	WP	2×1.8 +3×2.7 +1×3.6		6	49 55	1.6 0.85	<0.05 0.06	RJ1160B
Germany, 1990 (Bacchus)	WP	2×1.8 +4×2.7 +1×3.6		7	43 36	3.0 2.2	0.12 0.08	RJ1160B
Germany, 1991 (Kerner)	SG	2.3		8	0 10 21 26 33	2.3 1.1 0.70 0.54 0.46	<0.05 <0.05 <0.05 <0.05 <0.05	RJ1176B
Germany, 1991 (Dornfelder)	WP	2.3		8	0 10 21 29 35	6.3 2.7 2.3 2.2 2.2	0.10 <0.05 <0.05 0.05 0.06	RJ1176B
Germany, 1991 (Dornfelder)	SG	2.3		8	0 10 21 29 35	6.7 4.4 2.2 2.1 3.1	0.09 0.06 <0.05 <0.05 <0.05	RJ1176B
Germany, 1991 (Ortega)	WP	2.3		8	0 10 20 27 33	2.5 1.6 2.4 3.0 1.4	0.07 <0.05 0.05 <0.05 0.06	RJ1176B
Germany, 1991 (Ortega)	SG	2.3		8	0 10 20 27 33	2.9 3.3 2.4 2.2 2.9	0.08 0.07 0.05 0.05 0.08	RJ1176B
Germany, 1991 (Kerner)	WP	2.3		8	0 10 21 26 33	1.5 1.4 0.65 0.59 0.42	<0.05 <0.05 <0.05 <0.05 <0.05	RJ1176B
Germany, 1991 (Müller-Thurgau)	WP	2.3		8	0 10 21 26 35	6.0 3.0 2.0 2.1 1.3	0.06 <0.05 <0.05 <0.05 <0.05	RJ1176B
Germany, 1991 (Müller-Thurgau)	SG	2.3		8	0 10	2.9 3.1	0.07 0.06	RJ1176B

Country, year (variety)	Application				Day	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		Captan	THPI	
					21 26 35	2.2 2.6 1.8	<0.05 <0.05 <0.05	
Japan, 1991 (Kyohou)	WP	3.0	0.10	4	21	2.9	0.08	RJ1177B
Japan, 1991 (Kyohou)	WP	3.0	0.10	4	21	4.7	0.27	RJ1177B
Japan, 1991 (Kyohou)	WP	3.0	0.10	5	14	6.1	0.21	RJ1177B
Japan, 1991 (Kyohou)	WP	3.0	0.10	5	14	6.1	0.19	RJ1177B
Japan, 1991 (Kyohou)	WP	3.0	0.10	5	14 21	14 13	0.27 0.25	RJ1177B
Japan, 1991 (Kyohou)	WP	3.0	0.10	5	14 21	5.8 3.8	0.08 0.08	RJ1177B
Japan, 1991 (Kyohou)	WP	3.0	0.10	3	14 21	1.1 3.2, c 0.17	<0.05 0.06	RJ1177B
Japan, 1991 (Kyohou)	WP	3.0	0.10	3	14 21	12 11	0.24 0.15	RJ1177B
USA (WA), 1989 (Concord)	WP	2.2		2 3 4	76 67 57	0.07 0.17 0.24	<0.05 <0.05 <0.05	15WA89-303
USA (CA), 1989 (Thompson Seedless)	WP	2.2		2 3 4	136 118 104	0.17 0.94 0.10	<0.05 <0.05 <0.05	18CA89-301
USA (MI), 1989 (Concord)	WP	2.2		2 3 4	116 96 84	<0.05 <0.05 <0.05	<0.05 <0.05 <0.05	28MI89-305
USA (NY), 1987 (Catawba)	WP	2.2		a 6	0	3.5, 2.2, 2.1	0.07, <0.05 (2)	40189-811
USA (NY), 1987 (Catawba)	WP	2.2		6	0	8.0, 8.4, 8.0	0.21, 0.22, 0.25	40189-811
USA (NY), 1989 (Catawba)	WP	2.2		2 3 4	103 90 78	<0.05 <0.05 0.08	<0.05 <0.05 <0.05	56NY89-302
USA (PA), 1989 (Concord)	WP	2.2		2 3 4	90 80 73	<0.05 <0.05 <0.05	<0.05 <0.05 <0.05	57PA89-304

c: control sample

Table 26. Residues of captan and THPI in blueberries from foliar applications of WP formulations of captan in supervised trials in the USA. Underlined residues are from treatments according to GAP.

State, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
NJ, 1987 (Elliot)	2.8		6	1 3 5 7	11 15 7.1 7.1	0.09 0.14 0.06 0.21	3458
ME, 1987	2.8		4	21	0.55		3458

State, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
ME, 1987	2.8		10	0	8.4	0.15	3458
WA, 1987 (Jersey)	2.8		3 4 14	64 7 0	0.67 3.4 18	 <0.05 0.17	3458
MI, 1987	2.8		a 6	1 3 5 7	4.8 4.3 3.5 1.2	<0.05 <0.05 <0.05 <0.05	3458
MI, 1987	2.8		4	0 3 5 7 10	4.0 5.4 2.4 2.0 1.3	0.07 0.08 <0.05 <0.05 <0.05	3458
MI, 1987	2.8		a 3	7 8	3.3 2.8	<0.05 <0.05	3458
MI, 1987	2.8		a 3	0 3 5 7 10	1.7 2.0 0.50 0.31 0.50	 <0.05	3458
MI, 1987	2.2		4	0 3 5 7 10	8.3 5.5 6.5 2.6 1.8	0.12 0.08 0.06 0.07	3458
MI, 1987	2.8		8	0 3 5 7 10	8.2 6.9 6.8 6.1 3.6	0.11 0.09 0.10 0.05 <0.05	3458
MI, 1987	4.5		4	0 3 5 7 10	23 16 11 8.5 7.2	0.32 0.23 0.15 0.16 0.06	3458

a: aerial application.

Table 27. Residues of captan and THPI in strawberries from foliar applications of WP formulations of captan in supervised trials in Australia, Belgium, Canada, Chile, Hungary, Spain and the USA. Underlined residues are from treatments according to GAP.

Country, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Australia (Qld), 1991 (Promise)	6.0		5	1 2 3	20 12 12		S38990 91-49
Australia (Qld), 1991 (Promise)	3.0		5	1 2	6.9 6.6		S38990 91-49

Country, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
				3	7.9		
Belgium, 1991		0.12	8	0 4 7	2.0 2.1 1.1		RIC1800
Canada, 1982 (Redcoat)	1.8	0.27	1	0 1 2 5 10 14	2.4 1.8 0.87 1.3 0.93 0.31		Ritcey *et al.*, 1982a
Canada, 1983 (Redcoat)	3.4	0.50	1	0 1 2 5 10 15	4.1 4.1 3.0 0.91 0.76 0.26		Ritcey *et al.*, 1983a
Chile, 1991 (Chandler)	3.2		1	3 7	2.1, 3.0 2.9, 3.8	0.55, 0.73 0.39, 0.39, c 0.07	RJ1367B
Chile, 1991 (Pajaro)	3.2		1	3 7	3.3, 4.8 1.9, 2.7, c 0.07	0.46, 0.44 0.19, 0.25	RJ1367B
Chile, 1991 (Selva)	3.2		1	3 7	3.8, 3.3 3.4, 4.2	0.65, 0.67 0.22, 0.24	RJ1367B
Hungary, 1991	1.3	0.13	3	0 0 5 5 10 10 10	7.4, 6.9 5.1, 8.4 2.2, 3.2 2.2, 3.3 0.65, 0.83 0.79, 0.93 0.70, 0.88, 0.86	0.1, 0,1 <0.1, 0.1 <0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2) <0.1 (3)	CT/42/92
Spain, 1992 (Pajaro)	1.3	0.15	1	0 0 12 12 21 21	0.08, 0.17 0.24, 0.16 0.04, 0.01 0.01, 0.01 <0.01 (2) <0.01 (2)	1.2, 0.43 3.1, 1.5 0.09, 0.01 0.93, 0.15 0.01, <0.01 0.21, 0.15	FRESA SP 92
USA (FL), 1986 (Chandler)	3.4		6 7	0 0	1.6, 2.0 1.5, 2.6	0.14, 0.15 0.08, 0.19	40189-822 (056131-V)
USA (MI), 1986 (Holiday)	3.4		8	0	3.9, 3.0	0.50, 0.43	40189-822 (056131-V)
USA (NC), 1986 (Apollo)	3.4		8	0	7.2, 7.7	0.25, 0.30	40189-822 (056131-V)
USA (CA), 1986 (Tuft)	3.4		8	0	5.2, 4.8	0.52, 0.83	40189-822 (056131-V)
USA (CA), 1986 (Driscoll)	3.4		8	0	12, 11	1.4, 1.3	40189-822 (056131-V)
USA (CA), 1987 (Pajaro)	4.5		6	0	0.84, 0.60, 1.0	0.08, 0.08, 0.09	40189-822
USA (CA), 1987 (Pajaro)	4.5		6	0	13, 8.5, 6.4	0.61, 0.51, 0.42	40189-822
USA (CA), 1987 (Pajaro)	4.5		a 6	0	15, 13, 8.9	0.39, 0.69, 0.22	40189-822
USA (WA), 1986	3.4		7	0	3.6, 4.4	0.15, 0.22	40189-822

Country, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
							(056131-V)

a: aerial application. c: control sample.

Table 28. Residues of captan and THPI in tomatoes from foliar applications of WP formulations of captan in supervised trials in Brazil, Canada, Greece, Israel, Mexico and the USA. Underlined residues are from treatments according to GAP.

Country, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
Brazil, 1991 (Santa Clara S200)	2.2	0.24	8	1 7	0.27 0.18	0.16 0.10	RJ1435B
Brazil, 1991 (Santa Clara S200)	1.1	0.12	8	1 7	0.12 0.08	0.09 0.07	RJ1435B
Brazil, 1991 (Santa Clara S300)	2.2	0.24	8	1 7	0.64 0.29	0.13 0.08	RJ1435B
Brazil, 1991 (Santa Clara S300)	1.1	0.12	8	1 7	0.18 0.13	0.08 0.06	RJ1435B
Brazil, 1991 (Santa Clara S300)	2.2	0.24	8	1 7	0.81 0.57	0.31 0.21	RJ1435B
Brazil, 1991 (Santa Clara S300)	1.1	0.12	8	1 7	0.46 0.34	0.27 0.12	RJ1435B
Canada, 1982 (Heinz 2653M)	1.8	0.23	1	0 1 3 5 7 10 14	1.3 1.6 0.12 0.079 0.090 0.021 0.002		Ritcey *et al.*, 1982b
Canada, 1983	1.9	0.19	g 2	0 1 2 5 10 15	0.88 1.5 1.3 1.0 0.47 0.77		Ritcey *et al.*, 1983b
Canada, 1983	1.8	0.23	2	0 1 2 10 15	0.73 0.79 0.31 0.19 0.078		Ritcey *et al.*, 1983b
Canada, 1984	1.9	0.19	g 2	0 1 2 5 10 15	0.41 0.69 0.72 0.51 1.0 1.7		Ritcey *et al.*, 1984
Greece, 1991 (Troyan)	1.0	0.12	1	1 7 14 21	0.61 0.21 0.17 <0.05	<0.05 <0.05 <0.05 <0.05	RJ1189B

Country, year (Variety)	Application			Day	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Captan	THPI	
				28	0.13	<0.05	
Greece, 1991 (Rio Grande)	0.5	0.12	1	1 7 15 22 28	0.11, 0.43 0.07, 0.09 <0.05 (2) <0.05 (2) 1.4, 2.2 c 0.78, c 1.6	<0.05 (2) <0.05 (2) <0.05 (2) <0.05 (2) 0.21, 0.30 c 0.29, c 0.46	RJ1189B
Greece, 1991 (Troyan)	1.0	0.12	1	1 7 14 21 28	0.15 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	RJ1189B
Greece, 1991 (Star Pack)	0.5	0.12	1	1 7 15 22 28	0.38, 0.26 <0.05 (2) <0.05 (2) <0.05 (2) <0.05, 1.9, c 0.59	0.07, 0.07 0.08, 0.07 <0.05 (2) <0.05 (2) <0.05, 0.47, c 0.27	RJ1189B
Israel, 1991	1.3	0.63	3	0 0 4 4 11 11	0.11, 0.22 0.16, 0.35 0.13, 0.14 0.10, 0.08 0.05, 0.06 0.07, 0.10	0.1, 0.31 0.36, 0.37 0.1, 0.1 0.1, 0.1 0.1, 0.1 0.1, 0.1	CT/40/92
Israel, 1991	2.5	1.3	3	0 0 4 4 11 11	0.30, 0.23 0.51, 0.23 0.38, 0.10 0.21, 0.11 0.09, 0.18 0.35, 0.07	0.45, 0.51 0.68, 0.61 0.50, 0.23 0.29, 0.1 0.1, 0.28 0.29, 0.1	CT/40/92
Mexico, 1992 (Peto 2)	1.5		3	7 14	0.37 <0.05	0.18 <0.05	RJ1431B
Mexico, 1992 (Peto 2)	1.5		3	7 14	0.12 0.13	<0.05 0.13	RJ1431B
USA (TX), 1986 (Flori America)	4.2		4	0	1.4, 0.25	0.11, 0.10	40189-823
USA (MI), 1986 (A7814)	4.2		4	0 7 14	1.4, 1.4 0.88, 0.52 0.18, 0.16	0.10, 0.11 0.09, 0.08 0.08, 0.07	40189-823
USA (TX), (Flori Americana)	4.2		a 4	0	0.38, 0.53	0.08, 0.11	40189-823
USA (TX), (Flori Americana)	4.2		4	0	2.1, 0.51	0.32, 0.27	40189-823
USA (NY), 1986 (Heinz 1350)	4.2		4	0	1.5, 2.2	0.08, 0.08	40189-823
USA (CA), 1986 (Peto 19)	4.2		4	0	0.55, 0.48	0.06, 0.13	40189-823
USA (CA), 1986 (Peto 19)	13		4	0	0.86, 1.8	0.12, 0.15	40189-823
USA (FL), 1986 (Better Boy)	4.2		4	0	0.28, 0.43	0.09, 0.07	40189-823

a: aerial application c: control sample. g: glasshouse trial.

Animal feeding studies

Groups of 20 White Leghorn laying hens (each bird weighing 1.4-2.2 kg) were fed captan at nominal levels of 0, 1.5, 15, 45 and 150 ppm in the diet for 28 days (Graham, 1986b). Eggs were collected for analysis. On day 28 ten hens from each group were slaughtered for tissue collection. The remaining hens were placed on a residue-free diet and five from each group were slaughtered on day 31 and five on day 35. The birds consumed 100-120 g feed each per day.

The THPI residues are shown in Table 29. Captan added to control samples of eggs and tissues was found to be converted quantitatively to THPI, so that THPI represents captan residues in animal tissues. THPI residues in eggs reached a plateau after about 7-10 days. Over the wide range of feeding levels tested the ratio of the captan feeding level to the THPI levels in the eggs was about 40-50 at the plateau. The residues in eggs decreased quickly when the hens received a residue-free diet.

Other metabolites detected in eggs were 3-OH-THPI and 5-OH-THPI. Levels of these were lower than those of THPI but were similar to each other; their plateau levels in the eggs at the different feeding levels were <0.03 mg/kg at 1.5 ppm, 0.02-0.04 mg/kg at 15 ppm, 0.10-0.15 mg/kg at 45 ppm and 0.5-0.6 mg/kg at 150 ppm.

Table 29. THPI residues in eggs from hens dosed with captan at nominal levels of 1.5, 15, 45 and 150 ppm in the diet for 28 days (Graham, 1986b).

Day	THPI, mg/kg			
	Nom feed level 1.5 ppm	Nom feed level 15 ppm	Nom feed level 45 ppm	Nom feed level 150 ppm
1	0.02	0.16	0.56	1.2
4	0.03	0.24	0.76	2.7
7	0.03	0.31	0.96	2.5
10	0.04	0.34	0.98	2.5
14	0.04	0.35	1.0	2.6
21	0.04	0.34	1.1	3.0
28	0.05	0.36	1.0	2.9
32	<0.02	0.02	0.05	0.22
35	<0.02	<0.02	<0.02	<0.02

Residues in the tissues of hens slaughtered on day 28 are shown in Table 30. THPI residues were evenly distributed with no particular tissue as the main target. THPI levels in the tissues were 120-150 times lower than the nominal captan feeding levels. Residues of the hydroxy metabolites were somewhat lower than those of THPI.

Residues decreased rapidly when the birds were returned to a residue-free diet. THPI had disappeared from most tissues of the birds on the 150 ppm diet 3 days after withdrawal and was undetectable in all tissues after 7 days.

Table 30. THPI, 3-OH-THPI and 5-OH-THPI residues in tissues from hens dosed with captan at nominal levels of 1.5, 15, 45 and 150 ppm in the diet for 28 days (Graham, 1986b).

TISSUE	Residues, mg/kg											
	Nom feeding level, 1.5 ppm			Nom feeding level, 15 ppm			Nom feeding level, 45 ppm			Nom feeding level, 150 ppm		
	THPI	3-OH-THPI	5-OH-THPI	THPI	3-OH-THPI	5-OH-THPI	THPI	3-OH-THPI	5-OH-THPI	THPI	3-OH-THPI	5-OH-THPI
Muscle	<0.02	<0.03	<0.03	0.08	<0.03	<0.03	0.22	0.05	0.03	1.1	0.28	0.08
Liver	<0.02	<0.03	<0.03	0.11	<0.03	<0.03	0.24	0.04	0.03	1.1	0.19	0.08
Kidney	0.03	<0.03	<0.03	0.12	0.03	<0.03	0.29	0.05	0.03	1.3	0.21	0.09
Heart	<0.02	<0.03	<0.03	0.13	<0.03	<0.03	0.30	0.05	0.03	0.67	0.13	0.07
Gizzard	<0.02	<0.03	<0.03	0.07	<0.03	<0.03	0.19	0.03	<0.03	0.93	0.10	0.04
Fat	<0.02	<0.03	<0.03	0.04	<0.03	<0.03	0.10	<0.03	<0.03	0.30	<0.03	<0.03
Skin	<0.02	<0.03	<0.03	0.07	<0.03	<0.03	0.21	0.03	<0.03	0.72	0.12	0.10

Groups of 4 lactating Holstein dairy cattle (each animal weighing 490 to 740 kg) were fed technical captan in gelatin capsules at nominal levels of 0, 10, 30 and 100 ppm (dry-weight basis) in the diet for 29 days (Wiebe, 1991). Milk was collected for analysis. On day 29, three cows from each group were slaughtered for tissue collection within 3 hours after administration of the final dose. The remaining cows (one from each group) were placed on a residue-free diet and were slaughtered on day 36. Animals consumed 27 to 48 kg feed (fresh weight) each per day. There were no apparent effects on feed consumption, milk production, body weight, or general health of the animals.

Samples of milk and tissues were analysed for five captan metabolites: THPI, *trans*-3-OH-THPI, *trans*-5-OH-THPI, *cis*-3-OH-THPI, and *cis*-5-OH-THPI.

The residues of three of the metabolites in milk are shown in Table 31. Residues reached a plateau level very quickly, essentially by days 1-4, and residues disappeared rapidly when dosing was stopped. THPI and *trans*-3-OH-THPI were the predominant residues, but were approximately 500-1000 and 400-500 times lower than the captan levels in the diet respectively. Neither of the *cis*-isomers was detected in the milk.

Residues of the three metabolites in muscle, liver, kidney and fat from animals slaughtered on day 29 are shown in Table 32. THPI and *trans*-3-OH-THPI were again the predominant residues. No residues of any metabolite were detected in the tissues of animals slaughtered on day 36. The *cis*-isomers were not detected in any of the tissues, and are not recorded in the Table.

Residues of THPI and *trans*-3-OH-THPI in muscle, liver and kidney were generally 300-500 times lower than captan levels in the diet. Residues in the fat were even lower. *Trans*-5-OH-THPI was a very minor residue.

Table 31. Residues of captan metabolites in milk from cows dosed with captan at nominally 10, 30 and 100 ppm in the diet for 29 days (Wiebe, 1991).

Day	Residues, mg/kg								
	10 ppm feeding level			30 ppm feeding level			100 ppm feeding level		
	THPI	*trans*-3-OH-THPI	*trans*-5-OH-THPI	THPI	*trans*-3-OH-THPI	*trans*-5-OH-THPI	THPI	*trans*-3-OH-THPI	*trans*-5-OH-THPI
1	~0.01	0.02	<0.01	0.03	0.08	0.01	0.15	0.31	0.06
4	<0.01	0.02	<0.01	0.02	0.06	~0.01	0.16	0.25	0.04
7	~0.01	0.02	<0.01	0.03	0.06	~0.01	0.30	0.28	0.04
10	~0.01	0.02	<0.01	0.02	0.06	~0.01	0.19	0.18	0.03
14	~0.01	0.02	<0.01	0.03	0.06	~0.01	0.17	0.20	0.03
21	~0.01	0.02	<0.01	0.03	0.06	~0.01	0.20	0.21	0.03
28	~0.01	0.02	<0.01	0.03	0.06	<0.01	0.21	0.23	0.04
30	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.02	0.10	<0.01
32	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
35	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

~0.01 : residues at LOD in some animals and below LOD in others of the same group.

Table 32. Residues of captan metabolites in tissues from cows dosed with captan at nominally 10, 30 and 100 ppm in the diet for 29 days (Wiebe, 1991). Results are means of values from 3 animals.

TISSUE	Residues, mg/kg								
	10 ppm feeding level			30 ppm feeding level			100 ppm feeding level		
	THPI	*trans*-3-OH-THPI	*trans*-5-OH-THPI	THPI	*trans*-3-OH-THPI	*trans*-5-OH-THPI	THPI	*trans*-3-OH-THPI	*trans*-5-OH-THPI
Muscle	0.02	0.02	<0.01	0.06	0.06	0.01	0.24	0.18	0.04
Liver	0.02	~0.01	<0.01	0.12	0.04	<0.01	0.31	0.11	<0.01
Kidney	0.02	0.02	<0.01	0.09	0.09	0.02	0.25	0.27	0.07
Fat	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.07	0.02	<0.01

~0.01 : residues at LOD in some animals and below LOD in others of the same group.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Processing studies on apples, grapes, prunes and tomatoes were made available to the Meeting.

Captan and THPI residues were measured in apples and processed commodities by Riggle (1991a). The results are shown in Table 33.

Unwashed apples (25 kg) were crushed in a grinder and pressed to produce fresh juice. The resulting wet pomace was dried in a forced-air oven at 70-90°C for 2.5 to 4 hours to produce dry pomace. Residues were generally low in the fruit, but tended to concentrate in the pomace. Conversion of captan to THPI occurred when the pomace was dried.

Table 33. Residues of captan and THPI in apples and processed apple commodities from foliar applications of WP formulations of captan in supervised trials in the USA (Riggle, 1991a).

State, year (Variety)	Application, kg ai/ha	Day	Commodity	Residues, mg/kg	Ref.

				Captan	THPI	
CA, 1989 (Golden Delicious)	4×4.5	138	apples	0.14, 0.09	<0.05 (2)	17CA89-330
			juice	<0.05	<0.05	17CA89-330
			wet pomace	0.47	0.05	17CA89-330
			dry pomace	0.42	0.39	17CA89-330
CA, 1989 (Golden Delicious)	5×4.5	136	apples	0.15, 0.29	<0.05 (2)	17CA89-330
			juice	<0.05	<0.05	17CA89-330
			wet pomace	0.68	0.06	17CA89-330
			dry pomace	0.55	0.58	17CA89-330
CA, 1989 (Golden Delicious)	6×4.5	125	apples	0.30, 0.22	<0.05 (2)	17CA89-330
			juice	0.09	<0.05	17CA89-330
			wet pomace	0.74	0.07	17CA89-330
			dry pomace	0.55	0.64	17CA89-330
CA, 1989 (Golden Delicious)	7×4.5	116	apples	0.59, 0.16	<0.05 (2)	17CA89-330
			juice	0.16	<0.05	17CA89-330
			wet pomace	0.86	0.06	17CA89-330
			dry pomace	0.72	0.64	17CA89-330
NY, 1989 (Rome)	4×4.5	142	apples	<0.05 (2)	<0.05 (2)	56NY89-331
			juice	<0.05	<0.05	56NY89-331
			wet pomace	<0.05	<0.05	56NY89-331
			dry pomace	<0.05	<0.05	56NY89-331
NY, 1989 (Rome)	5×4.5	132	apples	<0.05 (2)	<0.05 (2)	56NY89-331
			juice	<0.05	<0.05	56NY89-331
			wet pomace	<0.05	<0.05	56NY89-331
			dry pomace	<0.05	<0.05	56NY89-331
NY, 1989 (Rome)	6×4.5	123	apples	<0.05 (2)	<0.05 (2)	56NY89-331
			juice	<0.05	<0.05	56NY89-331
			wet pomace	<0.05	<0.05	56NY89-331
			dry pomace	<0.05	<0.05	56NY89-331
NY, 1989 (Rome)	7×4.5	113	apples	<0.05 (2)	<0.05 (2)	56NY89-331
			juice	<0.05	<0.05	56NY89-331
			wet pomace	<0.05	<0.05	56NY89-331
			dry pomace	0.06	<0.05	56NY89-331

Captan wettable powder was applied 8 times to an apple orchard in the USA (WA) as a foliar spray to provide apples with field-incurred residues for processing (Smith, 1987b). Apples were washed, peeled, cored and trimmed, then crushed and pulped. Peels and cores were included in the pomace, which was dried at 53°C. The juice was treated with pectinase and heated to produce canned apple juice for analysis. The processing for juice and pomace was very similar to that shown for grapes in Figure 4. Results are shown in Table 34.

Captan residues were below the LOD in the juice. THPI was distributed in the juice and pomace. Captan was converted to THPI during the drying of the pomace.

Table 34. Captan and THPI residues in apples, pomace and juice from an apple orchard in the USA (WA) treated with captan at 8 × 4.5 kg ai/ha and at an exaggerated rate of 8 × 13 kg ai/ha, and harvested on the day of the final application for processing (Smith, 1987b). Field trial: 86639, year: 1986, variety: Red Delicious.

Application rate	Commodity	Captan, mg/kg	THPI, mg/kg
4.5 kg ai/ha	apples	5.5, 5.1	0.23, 0.21
	juice	<0.05	0.10
	wet pomace	2.1	1.9
	dry pomace	10	12
13 kg ai/ha	apples	9.1, 5.5	0.40, 0.43
	juice	<0.05	2.2
	wet pomace	7.8	3.5
	dry pomace	7.9	42

Apples treated with captan in trials in the USA (MI and WV) were processed according to Figure 3 (Iwata, 1992b). Residues of captan and THPI are shown in Tables 35 and 36.

Captan levels decreased on washing by an average of 42% (range 19-61%). Peeled, cored and sliced apples generally had no detectable residues of captan or THPI. These results are consistent with captan being a surface residue. Apple sauce, derived from the peeled, cored and sliced apples, did not contain detectable residues of captan, and only an occasional low residue of THPI.

Captan residues present in unclarified juice were converted to THPI, presumably when the juice was heated during the production of canned unclarified juice and canned clarified juice. Heating during the production of apple jelly also resulted in residues of THPI but not of captan. Captan was converted to THPI when the pomace was dried.

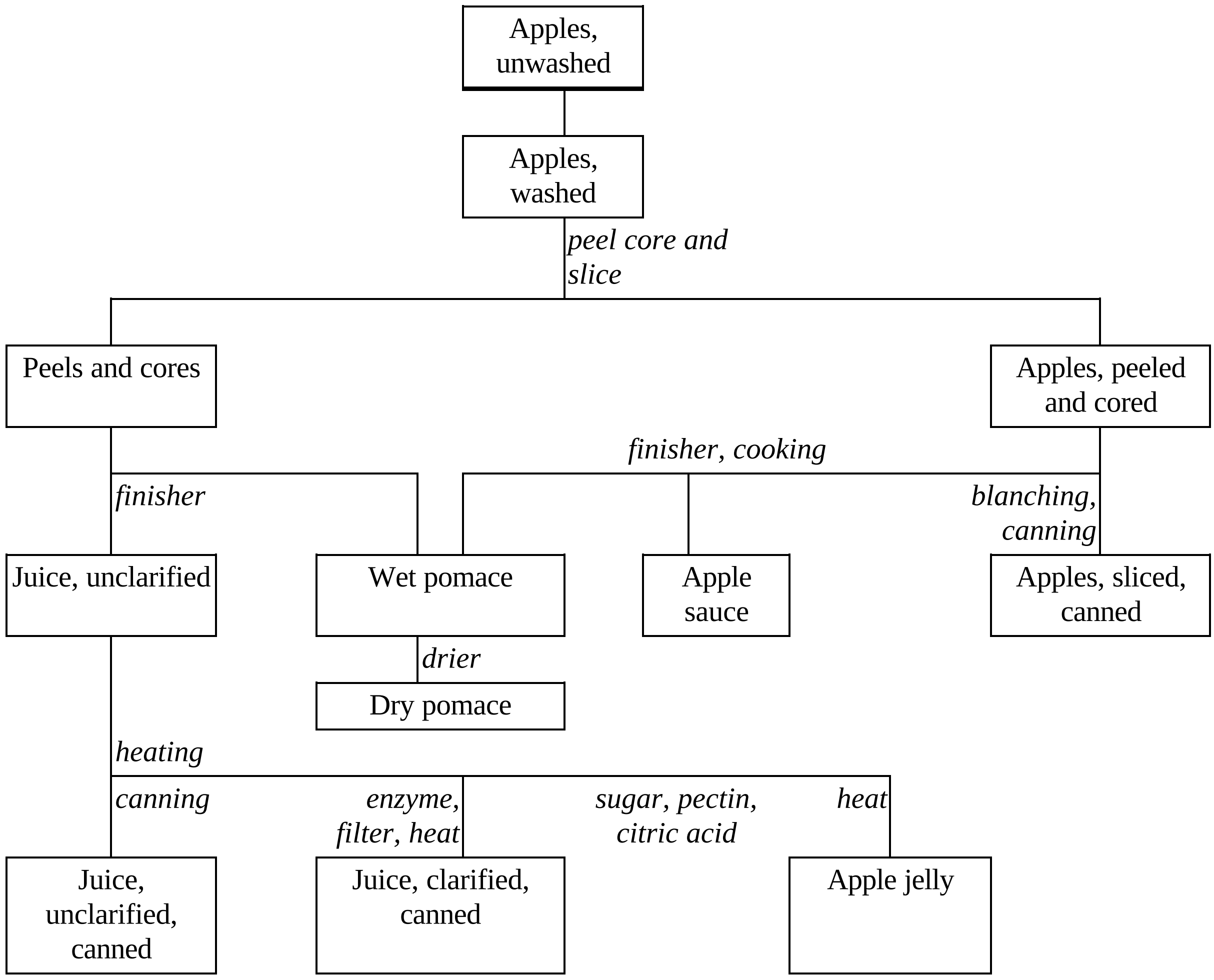


Figure 3. Apple processing (Iwata, 1992b).

Table 35. Residues of captan and THPI in apples and processed apple commodities after foliar applications of captan in supervised trials in the USA (MI) (Iwata, 1992b 28-MI-90-111). Captan WP was applied 10 times at 3.4 kg ai/ha to plots in an apple orchard (Yellow Delicious variety) and apples were harvested at maturity for processing. Approximately 90 kg of apples were processed in each trial.

Commodity	Residues, mg/kg									
	PHI 97 days		PHI 83 days		PHI 69 days		PHI 55 days		PHI 41 days	
	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI
apples, field	0.06	<0.05	0.15	<0.05	0.36	<0.05	0.40	<0.05	0.56	<0.05
apples, unwashed	0.06	<0.05	0.10	<0.05	0.19	<0.05	0.36	<0.05	0.44	<0.05
apples, washed	<0.05	<0.05	<0.05	<0.05	0.10	<0.05	0.29	<0.05	0.17	<0.05
apples, peeled cored sliced	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
apple sauce	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
baby food apple sauce	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
apple slices, canned	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
juice, unclarified	<0.05	<0.05	<0.05	<0.05	0.13	0.05	0.19	0.08	0.29	0.10

Commodity	Residues, mg/kg									
	PHI 97 days		PHI 83 days		PHI 69 days		PHI 55 days		PHI 41 days	
	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI
juice, unclarified, canned	<0.05	<0.05	<0.05	<0.05	<0.05	0.11	<0.05	0.18	<0.05	0.27
juice, clarified, canned	<0.05	<0.05	<0.05	<0.05	<0.05	0.08	<0.05	0.12	<0.05	0.18
apple jelly	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.08	<0.05	0.11
wet pomace	<0.05	<0.05	<0.05	<0.05	0.06	0.09	<0.05	0.15	0.07	0.21
dry pomace	0.05	0.08	<0.05	0.10	0.11	0.33	0.13	0.59	0.13	0.84

Table 36. Residues of captan and THPI in apples and processed apple commodities after foliar applications of captan in supervised trials in the USA (WV) (Iwata, 1992b, 54-WV-90-112). Captan WP was applied 10 times at 3.4 kg ai/ha to plots in an apple orchard (Spartan variety), and apples were harvested at maturity for processing. Approximately 80 kg of apples were processed in each trial.

Commodity	Residues, mg/kg									
	PHI 55 days		PHI 42 days		PHI 28 days		PHI 21 days		PHI 14 days	
	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI	Captan	THPI
apples, field	0.06	<0.05	0.09	<0.05	0.45	<0.05	0.87	<0.05	1.5	<0.05
apples, unwashed	<0.05	<0.05	0.22	<0.05	0.89	0.05	1.7	0.06	2.2	0.08
apples, washed	<0.05	<0.05	0.12	<0.05	0.55	<0.05	0.81	<0.05	1.5	0.07
apples, peeled cored sliced	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	<0.05
apple sauce	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07
baby food apple sauce	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07
apple slices, canned	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
juice, unclarified	<0.05	<0.05	0.06	0.09	0.28	0.11	1.1	0.27	2.3	0.26
juice, unclarified, canned	<0.05	<0.05	<0.05	0.13	<0.05	0.36	<0.05	0.98	<0.05	1.6
juice, clarified, canned	<0.05	<0.05	<0.05	0.07	<0.05	0.38	<0.05	1.0	<0.05	1.3
apple jelly	<0.05	<0.05	<0.05	0.05	<0.05	0.15	<0.05	0.42	<0.05	0.58
wet pomace	<0.05	<0.05	0.06	0.10	0.21	0.27	0.77	0.60	0.72	0.85
dry pomace	<0.05	<0.05	0.12	0.34	0.41	1.0	1.4	2.1	2.0	2.6

Specht (1992) described the fate of captan residues on apples (Golden Delicious) when processed according to normal domestic procedures. Apple sauce was produced by cooking apple pieces with water until soft and passing the soft apple through a strainer. Apple juice (warm) was produced from apple pieces placed in the sieve of a steam juice extractor. Pomace remained after the juice was drained. Apple juice (cold) was produced from apple pieces in a centrifugal juice extractor. The apple residue was taken as pomace. Slices of apple, without core, were dried in a desiccation apparatus to produce dried apple. Residue data are shown in Table 37.

Captan was converted to THPI during cooking to produce apple sauce or warm juice. In the production of cold juice captan and THPI partitioned into the pomace, with only minor residues remaining in the juice. Some of the captan residue was converted to THPI during the production of dried apples.

Table 37. Residues of captan and THPI in Golden Delicious apples after foliar applications of captan in supervised trials in Germany (1991), and in processed products after typical domestic procedures (Specht, 1992).

Application			Day	Commodity	Residues, mg/kg		Ref.
Form	kg ai/ha	No.			Captan	THPI	
WP	1.6	10	0 3 7 14 19	apples	3.1 2.7 4.1 2.7 1.6	0.52 0.44 0.61 0.47 0.23	91JH045E1
SG	1.6	10	0 3 7 14 19	apples	3.0 4.8 4.5 2.9 2.1	0.53 0.69 0.74 0.49 0.32	91JH045E1
WP	1.6	12	0 3 7 14 20	apples	2.7 5.0 2.0 1.5 1.7	0.30 0.42 0.14 0.12 0.17	91JH045B1
WP	1.6	12	14	apples, washed apple sauce juice (warm) pomace (juice warm) juice (cold) pomace (juice cold) dried apples	2.2 <0.01 <0.01 0.03 0.10 3.8 2.8	0.14 0.92 1.3 1.5 0.07 0.99 3.2	91JH045B1
SG	1.6	12	0 3 7 14 20	apples	2.8 4.4 2.8 1.8 1.4	0.31 0.31 0.17 0.21 0.11	91JH045B1
SG	1.6	12	14	apples, washed apple sauce juice (warm) pomace (juice warm) juice (cold) pomace (juice cold) dried apples	1.8 <0.01 <0.01 0.01 0.25 5.2 1.4	0.18 1.2 1.1 1.2 0.13 0.84 2.7	91JH045B1
WP	1.6	10	0 3 7 14 22	apples	2.3 2.2 2.0 1.0 0.95	0.24 0.26 0.53 0.27 0.21	91JH045Ext.2
WP	1.6	10	14	apples, washed apple sauce juice (warm) pomace (juice warm) dried apples	1.1 <0.01 <0.01 0.02 2.2	0.21 1.0 0.88 0.87 2.1	91JH045Ext.2

Application			Day	Commodity	Residues, mg/kg		Ref.
Form	**kg ai/ha**	**No.**			Captan	THPI	
SG	1.6	10	0	apples	3.8	0.50	91JH045Ext.2
			3		3.2	0.50	
			7		2.2	0.52	
			14		1.2	0.34	
			22		1.5	0.33	
SC	1.6	10	14	apples, washed	1.8	0.36	91JH045Ext.2
				apple sauce	<0.01	0.77	
				juice (warm)	<0.01	1.1	
				pomace (juice warm)	0.03	1.1	
				dried apples	2.0	1.8	

Captan and THPI residues were determined in grapes, juice and pomace in three supervised trials in the USA (two in California and one in New York). Residues were also measured in raisins in the California trials (Riggle, 1991b). The results are shown in Table 38. Fresh grapes (25-40 kg) were processed into juice and pomace, and 5-7 kg samples of field-dried grapes were processed into raisins and raisin waste.

Unwashed grapes were ground and the stems removed. The mash was pressed to produce juice and wet pomace.

Captan residues in the whole fruit were distributed into juice and pomace. Conversion of captan to THPI occurred during the processing and drying of the pomace. Captan residue levels in raisins were similar to those in the original fruit.

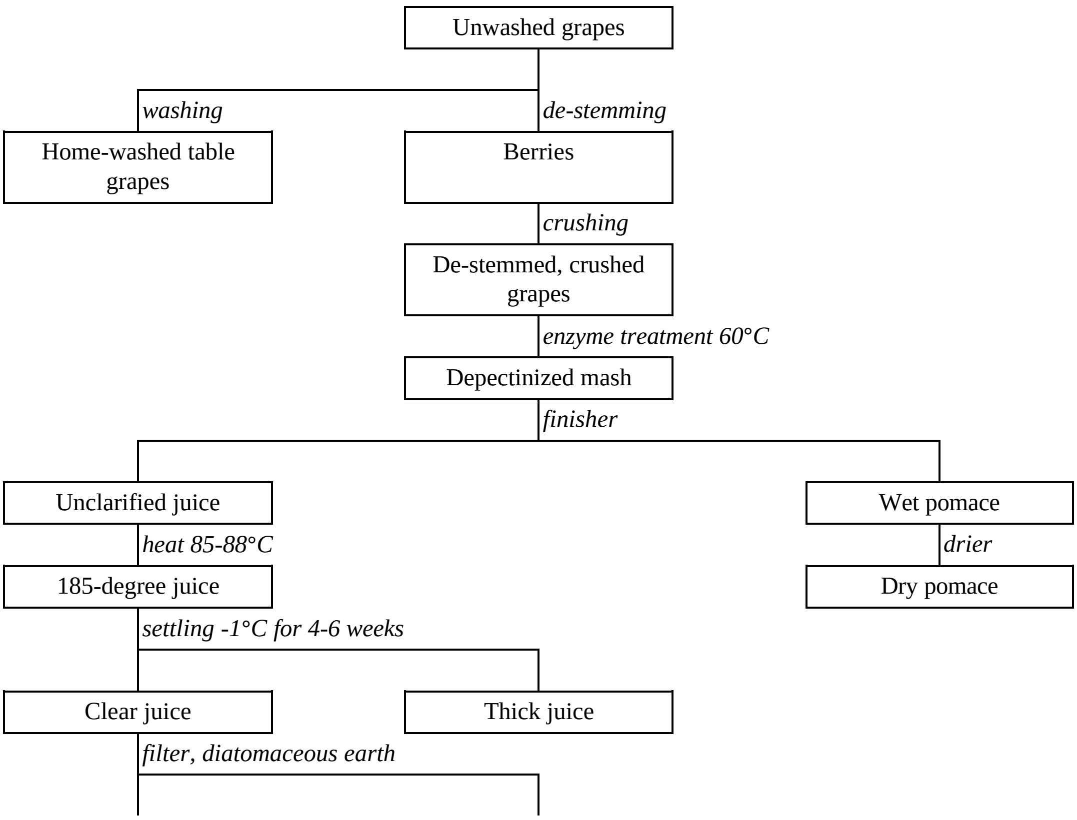
Table 38. Residues of captan and THPI in grapes and processed grape commodities after foliar applications of WP formulations of captan in supervised trials in the USA in 1989 (Riggle, 1991b).

State (Variety)	Application, kg ai/ha	Day	Commodity	Residues, mg/kg		Ref.
				Captan	THPI	
CA, 1989 (Thompson Seedless)	2×2.2	119	grapes	0.08, 0.07	<0.05 (2)	18CA89-334
			juice	<0.05	<0.05	18CA89-334
			wet pomace	0.09	<0.05	18CA89-334
			dry pomace	0.11	<0.05	18CA89-334
			raisin	0.08	<0.05	18CA89-334
			raisin waste	0.62	<0.05	18CA89-334
CA, 1989 (Thompson Seedless)	3×2.2	91	grapes	0.64, 0.38	<0.05 (2)	18CA89-334
			juice	0.51	0.12	18CA89-334
			wet pomace	0.46	0.06	18CA89-334
			dry pomace	0.22	0.12	18CA89-334
			raisin	0.61	0.06	18CA89-334
			raisin waste	13	0.20	18CA89-334
CA, 1989 (Thompson Seedless)	4×2.2	77	grapes	0.17, <0.05	<0.05 (2)	18CA89-334
			juice	0.10	0.07	18CA89-334
			wet pomace	0.17	<0.05	18CA89-334
			dry pomace	0.09	0.09	18CA89-334
			raisin	0.29	<0.05	18CA89-334
			raisin waste	5.8	0.10	18CA89-334
CA, 1989 (Thompson Seedless)	2×2.2	118	grapes	<0.05 (2)	<0.05 (2)	19CA89-336
			juice	<0.05	<0.05	19CA89-336
			wet pomace	<0.05	<0.05	19CA89-336
			dry pomace	<0.05	<0.05	19CA89-336
			raisin	<0.05	<0.05	19CA89-336
			raisin waste	0.09	<0.05	19CA89-336
CA, 1989 (Thompson Seedless)	3×2.2	98	grapes	0.07, <0.05	<0.05 (2)	19CA89-336
			juice	0.05	<0.05	19CA89-336
			wet pomace	0.09	<0.05	19CA89-336
			dry pomace	<0.05	<0.05	19CA89-336
			raisin	0.08	<0.05	19CA89-336
			raisin waste	0.30	<0.05	19CA89-336
CA, 1989 (Thompson Seedless)	4×2.2	84	grapes	0.11, 0.22	<0.05 (2)	19CA89-336
			juice	<0.05	0.09	19CA89-336
			wet pomace	0.12	<0.05	19CA89-336
			dry pomace	0.09	<0.05	19CA89-336
			raisin	0.19	<0.05	19CA89-336
			raisin waste	0.52	<0.05	19CA89-336
NY, 1989 (Aurora)	2×2.2	85	grapes	<0.05 (2)	<0.05 (2)	56NY89-335

State (Variety)	Application, kg ai/ha	Day	Commodity	Residues, mg/kg		Ref.
				Captan	THPI	
			juice	<0.05	<0.05	56NY89-335
			wet pomace	<0.05	<0.05	56NY89-335
			dry pomace	<0.05	0.07	56NY89-335
NY, 1989 (Aurora)	3×2.2	62	grapes	0.20, 0.08	<0.05 (2)	56NY89-335
			juice	<0.05	<0.05	56NY89-335
			wet pomace	0.19	<0.05	56NY89-335
			dry pomace	0.09	0.09	56NY89-335
NY, 1989 (Aurora)	4×2.2	50	grapes	0.32, 0.29	<0.05 (2)	56NY89-335
			juice	0.07	<0.05	56NY89-335
			wet pomace	0.31	0.09	56NY89-335
			dry pomace	0.29	0.39	56NY89-335

Concord grapes were treated in the USA (PA) with captan WP 6 times at 2.2 kg ai/ha and harvested 36 days after the final treatment for processing (Iwata, 1992a). The fresh grapes were processed in a manner simulating commercial procedures into juices, jelly and pomace (Figure 4).

Residues of captan and THPI in the processed grape commodities are shown in Table 39. Washing, as for direct consumption, reduced captan residues by about 23%. Captan residues were hydrolysed in the production of juice and during heating. The THPI which was formed was reasonably stable through the processes, and was evenly distributed among the juices and pomaces.



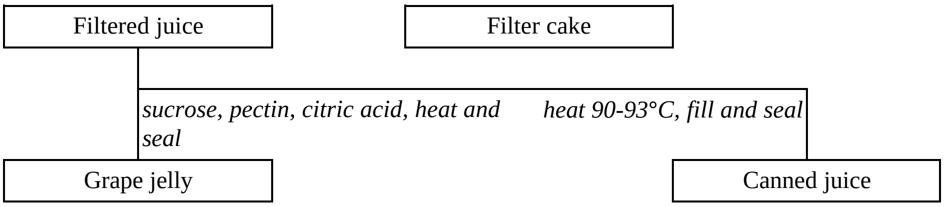


Figure 4. Grape processing (Iwata, 1992a).

Table 39. Captan and THPI residues in grapes and grape processed commodities. Vines were treated with captan WP 6 times at 2.2 kg ai/ha and grapes harvested 36 days after the final treatment (Iwata, 1992a). Processing was according to Figure 4.

Commodity	Captan, mg/kg	THPI, mg/kg
Grapes, field	0.44	<0.05
Grapes, processor	0.39	0.08
Home-washed table grapes	0.30	0.07
De-stemmed crushed grapes	0.06	0.18
Depectinized mash	<0.05	0.17
185-degree juice	<0.05	0.21
Clear juice	<0.05	0.14
Thick juice	<0.05	0.19
Filtered juice	<0.05	0.16
Filter cake	<0.05	0.18
Grape jelly	<0.05	0.08
Canned juice	<0.05	0.20
Wet pomace	<0.05	0.07
Dry pomace	<0.05	0.27

Captan wettable powder was applied as a foliar spray 9 times to a prune orchard, Stanley variety (a French Plum/Prunus) in the USA (MI) to provide prunes with field-incurred residues for drying (Smith, 1987h). The process includes a wash in cold water and drying in a bin drier at 74°C for 16 hours. The drying process concentrates the fruit 3.5-fold. Results are shown in Table 40.

Table 40. Captan and THPI residues in fresh fruit and dry prunes from a prune orchard in the USA (MI) treated with captan at 9 × 3.4 kg ai/ha and the prunes harvested on the day of the final application for drying (Smith, 1987h). Field trial: 86202, year: 1986, variety: Stanley.

Commodity	Captan, mg/kg	THPI, mg/kg
Prunes, whole fruit	3.5, 5.6	<0.05 (2)
Prunes, composites	2.6	<0.05
Dry prunes	0.59	5.2

Captan wettable powder was applied 4 times as a foliar spray to tomatoes in the USA (CA) to provide tomatoes with field-incurred residues for processing (Smith, 1987k). The process is shown in Figure 5 and the residues in Table 41.

Much of the captan appears to have been removed by the early washing and cleaning steps and the remainder largely converted to THPI during heating and drying.

Table 41. Captan and THPI residues in tomatoes and processed commodities from tomato crops in the USA (CA) treated with captan at 4 × 4.2 kg ai/ha and at an exaggerated rate of 4 × 13 kg ai/ha, and harvested on the day of the final application for processing (Smith, 1987k). Field trial: 86934, year: 1986, variety: Peto 19.

Application rate	Commodity	Captan, mg/kg	THPI, mg/kg
4.2 kg ai/ha	whole fruit	0.55, 0.48	0.06, 0.13
	wet pomace	0.10	0.09
	dry pomace	0.06	2.1
	puree	<0.05	0.23
	juice	<0.05	0.10
	ketchup	<0.05	0.44
13 kg ai/ha	whole fruit	0.87, 1.8	0.12, 0.15
	wet pomace	<0.05	0.14
	dry pomace	0.11	2.3
	puree	<0.05	0.38
	juice	<0.05	0.10
	ketchup	<0.05	0.60

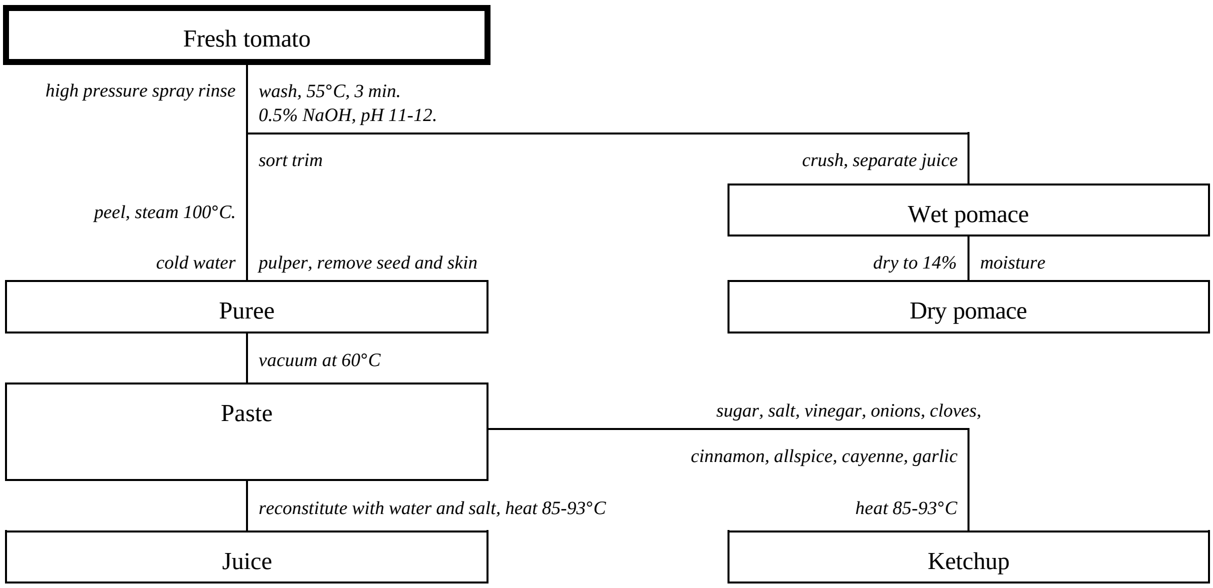


Figure 5. Tomato processing (Smith, 1987k).

Residues in the edible portion of food commodities

Captan is a surface residue. The level of residues found in processed commodities usually depends on the efficiency of washing and whether or not the skin is included in the process. Cooking and heating in juices or in the presence of water convert captan to THPI.

When apple juice was prepared from unpeeled apples captan residues in the juice were ½-¼ of those in the apples. When peeled apples were used and the juice was heated, captan residues were not detected (<0.05 mg/kg) in the juice from apples containing 5-9 mg/kg captan. The heating step converted some captan to THPI.

Captan levels in apples decreased by an average of 42% (range 19-61%) when the apples were washed in an industrial process. Captan was undetectable (<0.05 mg/kg) in juice, jelly, apple sauce and canned slices, all of which had been cooked or heated. THPI was produced if captan was present before heating.

In the simulated domestic processing of apples, captan residues in juice produced cold by a centrifugal juice extractor were 5% and 14% of the levels in the washed apples. When juice was produced by a method which included cooking, no captan was detectable (<0.01 mg/kg) in the juice from washed apples with captan levels of 1-2 mg/kg. Levels of captan in dried apple were generally similar to levels in the fresh apples; THPI was generated in the drying process.

Captan residues in grape juice were sometimes at similar levels to those in the grapes, and sometimes were reduced by a factor of 4-5. Residues in wet grape pomace and in the grapes were at similar levels. Captan residues in raisins were also similar to those in the grapes.

Washing grapes for direct consumption reduced captan residues by about 23%. In heating processes to produce grape juice, grape jelly and grape pomace captan residues were reduced to undetectable levels (<0.05 mg/kg). THPI was generated in the heating process.

In the production of dried prunes, captan levels decreased by a factor of 4-8. Captan was converted to THPI.

In tomato processing, early washing and cleaning steps removed captan, but it is not clear how much; captan residues in wet pomace were 4-20% or less of the levels in the tomatoes. Captan was not detectable (<0.05 mg/kg) in puree, juice or ketchup, which had been through a cooking stage. Cooking converted some captan to THPI.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Whole milk in the USA was surveyed in 1991 for residues of captan and 3 metabolites (Slesinski and Wilson, 1992). The design of the survey was intended to provide national estimates of the average yearly residues in milk as purchased by consumers, and involved collection of samples of whole milk from stores selected randomly across the USA.

All of the milk samples (224) were analysed for captan, THPI, 3-OH THPI and 5-OH THPI with validated limits of determination of 0.005 mg/kg. Considerable attention was paid to analytical recoveries, which were defined as adequate if 80% of the recoveries were between 70% and 120%, and all were between 60% and 130% at 0.01 mg/kg and higher, and between 50% and 150% at 0.005 mg/kg.

In all 224 samples the levels of captan and the three metabolites were below the limits of determination.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware that the following national MRLs had been established.

Country	MRL, mg/kg	Commodity
Argentina	15	aubergine, melon, pimento, pumpkin, tomato, watermelon,
	10	potato
Austria	10	vegetables
	2	grapes
	1	other fruits
	0.1	others
Belgium	10	berries
	3	apples, pears, small fruit, tomatoes
	2	beans, endive, leeks, lettuce, peas, stone fruit (cherries, prunes)
	0.1*	others
Brazil	25	apple, pear, garlic
	15	peach, tomato
	10	cucumber, onion
	2	grapes, melon, watermelon
	1	potato
Canada	5	apples, apricots, blueberries, cranberries, cherries, grapes, peaches, pears, plums, raspberries, strawberries, tomatoes
Denmark	3	berries + small fruits (raspberries, strawberries, red and black currants, gooseberries, wine etc.), other fruits, (banana, fig, kiwifruit, papaya, passion fruit etc.)
	0.1	asparagus, aubergine, beans, borecole, broccoli, Brussels sprouts, cabbage, carrots, cauliflower, celery, chervil, chives, citrus fruit, cucumber, early garden turnip, fennel, horseradish, leek, lettuce, onion, peas, potatoes, radish, red beet, spinach, squash, tomato, turnip-rooted celery, vipers grass
EU	3	berries and small fruit, grapes, pome fruit, tomatoes
	2	beans, broad-leaved endives, endives, leeks, lettuce, peas, stone fruit
	0.1	other products
France	3	berries, grapes, pome fruits (apples and pears), small fruits, tomatoes
	2	beans, chicory - salads, endives, leek, peas, stone fruits
	0.1	other fruits and vegetables
Germany	3	berry fruit, grapes, pome fruit, tomatoes
	2	beans, chicory, endive, leeks, lettuce, peas, stone fruit
	0.1	hops, others
Greece	3	berries, grapes, pome fruit, small fruit, tomatoes
Hungary	5	fruit, other vegetables, paprika, tomato
	2	cucumber, melon, wine/grape
Italy	3	berries, grapes, pome fruit, tomato
	2	beans, leaf greens, leeks, lettuce, peas, stone fruit

Country	MRL, mg/kg	Commodity
	0.1	other vegetable products
Japan	5	apple, cucumber, egg plant, tomato
Kenya	40	apples, cherries
	30	pears
	20	apricots
	15	citrus fruits, peaches, plums, rhubarb, tomatoes
	10	cranberries, cucumbers, raspberries, strawberries
	5	green beans, lettuce, marrow, peppers, raisins.
Malaysia	20	onions, potatoes
	15	coffee, tea
	10	leafy vegetables, non-leafy vegetables
Netherlands	5	raisins
	3	berries and small fruit (including currants and strawberries), tomato, top fruit (apple and pear)
	2	leaf vegetables (including lettuce and endive), leeks, pulse crops, stone fruit
	0.1	cereals, other fruit and nuts, other vegetables (including spinach)
Poland	3	soft fruit, tomato
	2	leeks, legumes, lettuce, stone fruit
	0.1	feedstuffs of plant origin
Spain	3	aubergine, berries, grapes, pome fruits, small fruits, tomato
	2	beans, chickpea, curly-leaved lettuce, endive, green bean, leek, lettuce, pea, stone fruit
	0.5	citrus
	0.1	all other vegetable products
Sweden	3	apples, berries (except cherries), grapes, pear, tomatoes
	2	apricot, beans, cherries, lettuce, nectarines, peaches, peas
	0.1	fruit and vegetables (except those listed), potatoes
Switzerland	3	fruit
Turkey	5	apples, citrus fruits, peaches, pears
	3	peppers, raisins, tomatoes
	2	grape
	1	cucumber, lettuce
	0.05	milk
USA	100	almond hulls[1], beets greens, cherries, lettuce, plums (fresh prunes), spinach
	50	apricots, celery, grapes, leeks, mangoes, nectarines, onions green, peaches, shallots,
	25	apples, avocados, beans succulent[1], beans dry[1], blackberries, blueberries, cantaloupe, cucumbers, dewberries, egg plants, garlic, honey dew melons, huckleberries, muskmelons, onions dry bulb, pears, peppers, pimento, potatoes[1], pumpkins, raspberries, strawberries, summer squash, tomatoes, watermelon, winter squash
	2	almonds[1], beets roots, broccoli, Brussels sprouts, cabbage, carrots, cauliflower, collards, corn sweet, cotton seed, kale, mustard greens, peas succulent, peas dry, rutabaga root, soya beans dry, soya beans succulent, turnip roots, turnip greens,
	0.25	taro (corm)
	0.05	cattle fat, cattle meat, hogs fat, hogs meat

[1] temporary * at or about the limit of determination

APPRAISAL

The 1987 JMPR had recommended that a detailed review of all aspects of the use of captan be carried out and the 1990 JMPR reviewed the information currently available and recommended withdrawal of a number of MRLs and the establishment of TMRLs for those commodities for which residue data were being generated.

Extensive supporting information, as well as residue trials data, was supplied to the Meeting. The available studies included fate in animals, plants, soils and sediments, analytical methods and frozen storage stability, animal transfer and fate of residues in processing. Residue trials data were available for citrus, apples, pears, cherries, peaches, nectarines, plums, grapes, blueberries, strawberries and tomatoes. The information was supplied by Canada, Spain and two manufacturers.

Metabolism studies with [^{14}C]captan on rats (cyclohexene-1,2 label), lactating goats (trichloromethyl label) and laying hens (cyclohexene-1,2 and trichloromethyl labels) were made available to the Meeting. An additional metabolism study on rats and goats (carbonyl label) was received at a late stage of the Meeting, and was not reviewed.

The following abbreviations are used for some of the captan metabolites.

THPI:	1,2,3,6-tetrahydrophthalimide
3-OH-THPI:	3-hydroxy-1,2,3,6-tetrahydrophthalimide
5-OH-THPI:	5-hydroxy-1,2,3,6-tetrahydrophthalimide
THPAM:	3-hydroxy-1,2,3,6-tetrahydrophthalamic acid

The major urinary and faecal metabolites identified in rats were THPI, 5-OH-THPI, 3-OH-THPI and THPAM.

When [*trichloromethyl*-^{14}C]captan was administered to goats and hens, CO_2 was the major metabolite.

Total ^{14}C residues in eggs rapidly reached a plateau (within 2-4 days) when [*cyclohexene*-1,2-^{14}C]captan was administered daily to laying hens. Most of the dose was excreted, but small amounts were distributed through the tissues. THPI was the predominant metabolite and accounted for 52-77% of the ^{14}C in the tissues, egg yolk and egg white. Minor metabolites identified in each of the tissues and eggs were 3-OH-THPI and 5-OH-THPI. Residues of metabolites in tissues and eggs were in good agreement when determined by chemical analysis and by measurement of ^{14}C.

Metabolism studies on tomatoes and lettuce were made available to the Meeting. Both [*cyclohexene*-1,2-^{14}C]captan and [*trichloromethyl*-^{14}C]captan were used (foliar application), so that the fate of both parts of the captan molecule could be studied.

In tomatoes, most of the ^{14}C was removed by an acetone wash, suggesting that residues were largely on the surface. The residues were not translocated to the roots of lettuce or tomatoes, indicating an immobile residue.

Metabolites in lettuce and tomatoes arose from N-S cleavage and epoxidation of the cyclohexene bond. Captan was the major component (70-82%) of the residue, with THPI and captan epoxide identified as minor parts of the total residue (<10%) in tomatoes, tomato leaves and stems, and lettuce leaves. Captan levels determined in lettuce leaves by an enforcement method and by ^{14}C measurement were in good agreement. THPI levels measured by the enforcement method were somewhat lower than by ^{14}C.

The major products identified in the degradation of [*carbonyl*-^{14}C]captan in soil were CO_2, THPI and tetrahydrophthalamic acid. Captan degraded was very rapidly with 99% of the initial 5 mg/kg in a sandy loam soil disappearing in 7 days.

[*Trichloromethyl*-^{14}C]captan was degraded rapidly with a half-life of about 1 day when incubated under aerobic conditions in a sandy loam soil (pH 7.2, 1.2% organic matter) at 25°C at an initial concentration of 5 to 6 mg/kg. Carbon dioxide was rapidly eliminated, and was the only significant ^{14}C product. In another similar study the half-life of captan was less than 4 hours.

At 25°C the half-lives of captan in sterile buffer solutions were 11.7 hours, 4.7 hours and 8.1 minutes at pH 5, 7 and 9 respectively. THPI was the major hydrolysis product identified at each pH. Captan was not photodegraded in sterile aqueous solution at pH 5; the rates of loss were the same in irradiated and non-irradiated samples.

The fate of [*cyclohexene*-1,2-^{14}C]captan was studied in sterile and non-sterile sediment-water systems under controlled laboratory conditions at 20°C in the dark. In the sterile systems CO_2 was not produced, but in the microbial systems after 90 days approximately 50% of the applied ^{14}C had been mineralised to CO_2. Captan disappeared very quickly in both sterile and non-sterile systems and was not detected by day 1. THPI was the initial product of hydrolysis.

Methods have been developed for the residue analysis of captan and THPI in crops, and for THPI and hydroxylated metabolites in animal commodities. The methods rely on gas chromatography for the final determination. Limits of determination are usually in the range 0.01 to 0.05 mg/kg. The methods employed to generate the residue data in the supervised trials were validated in terms of recoveries and interferences.

Captan is easily degraded by high pH or when exposed to some enzymes. Crops should be analysed without delay after maceration. Phosphoric acid is added at the extraction step to maintain acid conditions and enhance captan stability. Captan and THPI require different clean-up steps and different GLC conditions; the analyses in effect require parallel procedures after the extraction step.

The hydroxylated metabolites, 3-OH-THPI and 5-OH-THPI, must be silylated for determination by GLC. Limits of determination of 0.01 mg/kg and 0.05 mg/kg were achieved for milk and animal tissues respectively.

Extensive information on the stability of captan and THPI residues in frozen storage was provided for a range of commodities: almonds, almond nuts coarsely ground, almond nuts whole, apples, apple juice, apple sauce, beet tops, cherries, cucumbers, dry grape pomace, lettuce, maize grain, maize grain coarsely ground, maize grain whole, melons, potato tubers, raisins, soya bean forage, soya beans, spinach, spinach coarsely chopped, spinach finely chopped, strawberries, sugar beet tops, tomatoes, dry tomato pomace, tomato sauce, tomato whole fruit and wheat forage.

Captan residues remained at 70% or more of the initial concentration after storage at -20°C for the specified interval for the following commodities involved in the residue or processing trials: apples (14 months), cherries (12 months), strawberries (14 months), tomato whole fruit (9 months), apple juice (6 months), apple sauce (9 months), grape pomace (9 months), raisins (10 months), tomato dry pomace (9 months) and tomato sauce (9 months). Less than 20% of the initial captan residues remained in tomato matrix held at -20°C for 12 months. In those cases where captan was degraded, THPI was formed.

THPI itself was shown to be stable in frozen storage. The absence of THPI residues in a sample containing captan is good evidence that captan was stable during storage.

Captan was rapidly converted to THPI in eggs and chicken tissues; the THPI was shown to be stable. The other metabolites, 3-OH-THPI and 5-OH-THPI were also stable under the tested storage conditions (-20°C for 6 to 10 months). Captan was also unstable in milk, with about 50% disappearing in 1 month at -20°C. THPI, 3-OH-THPI and 5-OH-THPI were stable in bovine tissues and milk stored at -20°C for 1 year.

Captan is a broad-spectrum fungicide, widely used on food crops, seed crops and ornamentals. It is registered for use in many countries. Application rates are often in the 1-3 kg ai/ha range and high-volume spray concentrations are often 0.1-0.2 kg ai/hl.

Residue data from supervised trials were made available to the Meeting on citrus, apples, pears, cherries, peaches, nectarines, plums, grapes, blueberries, strawberries and tomatoes.

The Meeting considered a number of points which influence a decision on the definition of the residue.

In crops, captan is the major component of the residue at short intervals between application and harvest; THPI is usually a minor constituent. However, when the residue is older and lower THPI levels may be of the same order as those of the captan. The level of captan itself on a raw agricultural commodity is a good indicator of compliance with GAP, provided the sample is analysed without delay or stored correctly.

The main component of the residue in animal commodities is THPI, where it is the indicator compound.

When commodities are processed, particularly in cooking and heating operations, captan is converted to THPI.

Captan is converted to THPI during frozen storage of some types of sample. Satisfactory sample storage must be questioned when THPI levels in raw agricultural commodities, particularly in samples harvested at short intervals after captan application, constitute a considerable part of the total residue.

After considering these points the Meeting decided that, for enforcement purposes, the residue should be defined as captan alone. The residue definition will need reconsideration if MRLs are recommended for animal commodities or processed commodities.

Residue data recorded in the tables of supervised trials show the captan and THPI residues separately. In the following discussion of residue trials, the residues quoted are for captan.

Residue trial data on oranges and mandarins in Spain were made available to the Meeting. The use pattern was the same and the resulting residues were similar. No information was available on the storage conditions of the samples between harvest and analysis, or on the storage stability of captan residues in citrus. Also, in the absence of data on THPI residues it was not possible to decide whether captan residues had been stable during storage. The Meeting was unable to estimate a maximum residue level for captan in oranges or mandarins.

Residue trials on apples (according to GAP) were available from Argentina, Brazil, Canada, Chile, France, Japan, The Netherlands and the UK. The French and Netherlands data were evaluated against UK GAP. Residues in many trials were in the 0.5 to 5 mg/kg range, and two trials from Japan produced residues above this, at 7.2 and 13 mg/kg. Residues of 4.3, 4.4 and 4.8 mg/kg were produced in 3 UK trials. THPI was generally a minor part of the residue in the upper levels.

On the basis of the preponderance of the data the Meeting estimated a maximum residue level of 10 mg/kg for captan in apples to replace the previous recommendation (25 mg/kg T).

Residue trials on pears according to GAP for foliar applications were available from Chile and the UK. In three trials from the UK where captan was used at 2.7 kg ai/ha and the fruit were harvested at the official PHI, 7 days, residues in the 7 to 10 mg/kg range were recorded. THPI residues were low compared with those of captan. Two US post-harvest trials according to GAP (0.15 kg ai/hl) produced captan residues of 4.7 and 11 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg for captan in pears to replace the previous recommendation (25 mg/kg T).

Supervised trials on cherries were provided from Japan and the USA. When captan was used according to GAP in Japan (14 days PHI), residues up to 1.3 mg/kg were reported. Foliar application according to US GAP (2.2 kg ai/ha and PHI of 0 days) produced residues in the 10 to 20 mg/kg range. Post-harvest dipping according to US GAP (0.15 kg ai/hl) gave captan residues of 3.8 to 15 mg/kg.

The Meeting estimated a maximum residue level of 20 mg/kg for captan in cherries.

Data on Peaches were made available from trials in Australia, Chile, Spain and the USA. The highest residues in peaches from Chile and Spain were 2.0 mg/kg and 3.5 mg/kg respectively when captan was used according to the GAP of those countries. The majority of the captan residues from the US trials according to GAP (4.5 kg ai/ha and PHI of 0 days) were in the 2 to 10 mg/kg range, but in three of the 11 trials, residues were 10, 12 and 14 mg/kg. THPI was a minor part of the residue.

The Meeting estimated a maximum residue level of 15 mg/kg for captan in peaches to replace the previous recommendation (15 mg/kg T).

Trials on nectarines were available from Chile, Spain and the USA. The intervals between application and harvest in the Chile trials were much longer than the intervals permitted by the label. The spray concentrations in the Spanish trials were much lower than Spanish GAP. Captan residues up to 0.30 mg/kg and 0.77 mg/kg were reported in the trials from Chile and Spain respectively. Captan residues in the US trials were in the range 1.3 to 3.9 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg for captan in nectarines.

Residues in plums in Chile were similar to those in nectarines for similar conditions of use. In the US trials, application rates on plums were about 20% higher than on nectarines. The highest captan residues in each of three US trials were 0.45, 0.60 and 5.6 mg/kg. Captan is essentially a surface residue, and the Meeting decided that the nectarine data could be used to supplement the plum data in estimating a maximum residue level.

The Meeting estimated a maximum residue level of 5 mg/kg for captan in plums.

Extensive data on residues in grapes were provided from trials in Argentina, Chile, France, Germany, Japan and the USA. Residues in grapes from the Argentine trials were in the range 0.5 to 0.8 mg/kg. Three trials from Chile produced captan residues in the 5 to 10 mg/kg range. The fourth trial produced much higher residues, 12 to 25 mg/kg. In France the PHI is 33-45 days; the highest residue according to GAP was 4.4 mg/kg. THPI was the major part of the residue in some of these grape samples. If the THPI was formed during sample storage the original captan residues in these samples would have been somewhat higher.

There are no registered uses of captan on grapes in Germany, so the German trials were evaluated in terms of French GAP. A PHI of 30 days after a final application of 3.6 kg ai/ha was considered to be according to GAP. The majority of trials according to these conditions produced residues in the 1 to 5 mg/kg range, with three trials producing residues of 9.8, 7.4 and 7.0 mg/kg. In two trials where a PHI of 28 days was observed residues of 8.3 and 15 mg/kg were recorded.

Residues in four of the eight grape trials in Japan were in the 5 to 10 mg/kg range and in two exceeded 10 mg/kg (12 and 14 mg/kg). PHIs were very long in the US trials on grapes, so residues were low and did not influence the estimation of a maximum residue level.

The Meeting estimated a maximum residue level of 20 mg/kg for captan in grapes.

In nine blueberry trials in the USA according to GAP (1.1-2.8 kg ai/ha, PHI 0 days), residues in four were in the 5 to 10 mg/kg range and in two exceeded 10 mg/kg at 15 and 18 mg/kg.

The Meeting estimated a maximum residue level of 20 mg/kg for captan in blueberries to replace the previous recommendation (20 mg/kg T).

Data on trials according to GAP on strawberries were provided from Canada, Chile, Hungary and the USA. The highest residue from treatments according to GAP in the Canadian trials was 3.0 mg/kg. The highest residues in the three trials from Chile were 3.8, 4.2 and 4.8 mg/kg; THPI residues in these trials ranged up to 0.73 mg/kg (equivalent to 1.5 mg/kg captan). In Hungary the highest residue was 0.93 mg/kg. In the six US trials according to GAP (1.7-3.4 kg ai/ha and 0 days PHI) residues of captan in three were in the 2 to 5 mg/kg range, in two in the 5 to 10 mg/kg range, and residues in one exceeded 10 mg/kg. The highest captan residues in three separate US trials were 5.2, 7.7 and 12 mg/kg. If some of the THPI detected in the samples was formed during sample storage, the original captan levels would have been slightly higher.

The Meeting estimated a maximum residue level of 15 mg/kg for captan in strawberries to replace the previous recommendation (20 mg/kg T).

Supervised trials according to GAP on tomatoes were reported from Brazil, Canada, Greece, Israel and Mexico. Data were reasonably consistent from the different countries, with the majority of trials producing highest residues in the 0.2 to 1 mg/kg range. The highest residues in three trials were 1.7 and 1.3 mg/kg in Canada and 0.46 mg/kg in Brazil. Data from one trial in Greece were considered invalid because of excessive residues in control samples. If the THPI residues in samples from trials in Israel and Brazil were formed during sample storage the original captan levels would have been considerably higher.

The Meeting estimated a maximum residue level of 2 mg/kg for captan in tomatoes to replace the previous recommendation (15 mg/kg T).

Animal transfer studies with laying hens and dairy cattle were made available to the Meeting. Captan itself disappears quickly from animal commodities; THPI is the residue of interest.

In the study on laying hens THPI residues in eggs reached a plateau after about 7 to 10 days of daily captan administration. The ratio of captan feeding level to THPI levels in the eggs was about 40-50 at the plateau. THPI residues were evenly distributed in the tissues and levels were 120 to 150 times less than the captan feeding levels. THPI residues decreased rapidly in tissues and eggs when the hens received a residue-free diet.

When dairy cattle were dosed with captan, THPI residues in milk reached a plateau rapidly, within 1 to 4 days, at levels 500 to 1000 times lower than captan levels in the diet. Residues of the metabolite *trans*-3-OH-THPI in milk and tissues were similar to those of THPI. Residues of THPI in muscle, liver and kidney were generally 300 to 500 times lower than captan levels in the diet, and were even lower in fat. Residues disappeared quickly when dosing was withdrawn.

There are currently no recommendations for MRLs in animal feeds. If additional uses of captan lead to residues in feeds, the maximum residues in animal commodities should be estimated. The current animal transfer studies should provide the basis for an estimate. The Meeting also noted that the residue in animal commodities is not captan but THPI. Residues of THPI in animal commodities will generally not exceed 0.05 mg/kg when captan in the diet is in the parts per million range.

Processing studies on apples, grapes, prunes and tomatoes were made available to the Meeting.

Captan residues are on the surface, and washing the raw agricultural commodity as the initial step in processing removes some of the residue. Peeling apples removes most of the residue. Captan is converted to THPI in cooking or heating. The net result is that captan itself is not present in processed commodities such as apple sauce, canned apple slices, apple jelly, canned juice, tomato puree and tomato ketchup. The level of THPI residues depends on the captan levels present at the boiling or cooking step.

In the drying of prunes, where the process included a water wash and oven drying for 16 hours at 74°C, most of the captan was converted to THPI, and because of the removal of moisture the level of the total residue increased. The data suggest that the total residue (as captan) in dried prunes is approximately 3 times the level in the raw commodity.

Captan residues in raisins, where the process involved sun-drying of the grapes and subsequent removal of raisin waste, were on average 1½ times those in the grapes. Captan was not converted to THPI in the drying process. The Meeting noted that the captan levels in grapes (less than 1 mg/kg) used for the US processing trials were appropriate for the use pattern in the USA where raisins are produced. The estimated MRL for grapes was based on captan uses on grapes which were not used for raisin production.

Whole milk in the USA (224 samples) was surveyed in 1991 for captan, THPI, 3-OH-THPI and 5-OH-THPI residues to validated LODs of 0.005 mg/kg. In all 224 samples, captan and the three metabolites were below the limits of determination.

Information on national MRLs for captan was provided to the Meeting.

RECOMMENDATIONS

The residues shown below are recommended for use as MRLs.

Definition of the residue: captan.

Commodity		Recommended MRL (mg/kg)		PHI on which based, days
CCN	Name	New	Previous	
FP 0226	Apple	10	25 T	1-14
FB 0020	Blueberries	20	20 T	0
FS 0013	Cherries	20		0
FB 0269	Grapes	20		7-43
FS 0245	Nectarine	5		0
FS 0247	Peach	15	15 T	0
FP 0230	Pear	10	25 T	7
FS 0014	Plums (including Prunes)	5		0
FB 0275	Strawberry	15	20 T	0
VO 0448	Tomato	2	15 T	1-15

FURTHER WORK OR INFORMATION

Desirable

1. Current information on registered uses of captan on citrus in Spain (the available information was dated May 1991).

2. Details of Spanish trials on citrus (sample storage conditions, storage interval before analysis, storage stability data for captan residues in citrus). Reports should include author or study director, date and report numbers. Without trial identification numbers and document identification numbers it is sometimes difficult to know if reports are for different trials, or are progress reports for the same trial, or have been reviewed on previous occasions.

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