Fate of Thiabendazole and Chlorpropham Residues in Extruded Potato Peels

Mary E. Camire, Rodney J. Bushway,* Jianxin Zhao, Brian Perkins, and Lance R. Paradis

Department of Food Science and Human Nutrition, 5736 Holmes Hall, University of Maine, Orono, Maine 04469-5736

Potato peels from potato processing facilities have potential as a food ingredient, but the possibility of contamination with post-harvest pesticides may limit their usage as a source of dietary fiber. Peels produced by steam peeling were twin-screw extruded in an attempt to reduce the concentrations of two common chemicals applied to tubers in storage prior to processing. Extruded and nonextruded peels were analyzed for the fungicide thiabendazole and the sprout inhibitor chlorpropham (CIPC) by high-performance liquid chromatography. Two barrel temperatures (104 and 143 °C) and three feed moistures (31, 33.5, 36%, dry basis) were studied. Peels contained 86.56 ppm thiabendazole and 33.12 ppm CIPC (dry basis) prior to extrusion. Extrusion cooking under these conditions did not significantly destroy either thiabendazole or chlorpropham.

Keywords: *Thiabendazole; chlorpropham; extrusion; potato peels*

INTRODUCTION

Utilization of potato peelings from potato processing has been limited largely to cattle feed, although some peels are fermented to ethanol or used as an ingredient in snack foods. Steam peeling as performed by frozen potato manufacturers results in potato peels containing approximately 50% dietary fiber (dry basis), primarily insoluble fiber (Camire et al., 1993). Potato peels may thus have value as a source of concentrated dietary fiber which could be added to fiber-depleted foods such as snacks or baked foods.

Although peels do not contain phytates (Toma et al., 1979), as do cereal brans, glycoalkaloids and protease inhibitors are present. These natural toxicants may be reduced by processing, but another toxicological concern is the possible presence of agrochemicals. After harvest a variety of chemicals are applied to potato tubers to prevent sprouting and mold. The post-harvest chemicals must be applied at high concentrations to be effective. No information on processing effects on the fungicide thiabendazole (TBZ) (Figure 1) in potatoes is available. Mondy and co-workers (1992, 1993) reported that cooking reduces levels of the popular sprout inhibitor isopropyl *N*-(3-chlorophenyl)carbamate, also known as chlorpropham or CIPC (Figure 2), but they did not study extrusion or other commercial processes. The United States tolerances for TBZ and CIPC residues in foods are 10 and 50 ppm, respectively (Hartley and Kidd, 1987).

Commercial production of a fiber supplement from potato peels must consider the presence of agrochemicals and their subsequent fate due to processing. The objective of this study was to quantitate TBZ and CIPC in potato peels and to determine the effects of extrusion cooking upon these two agrochemicals.

MATERIALS AND METHODS

Materials. Netted Gem (Russett Burbank) potatoes were commercially steam-peeled for 18–20 s at approximately 15 g/cm^2 and 180 °C eight months after the 1990 harvest. Peels were deep frozen for transport from a potato processing plant to the University. Tubers were gassed with chlorpropham in storage; the exact technique is proprietary. Further preparation of peels prior to extrusion is shown in Figure 3.

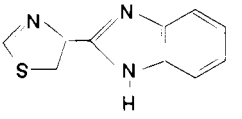

Figure 1. Thiabendazole.

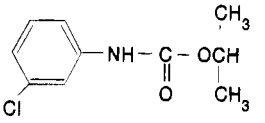

Figure 2. Chlorpropham.

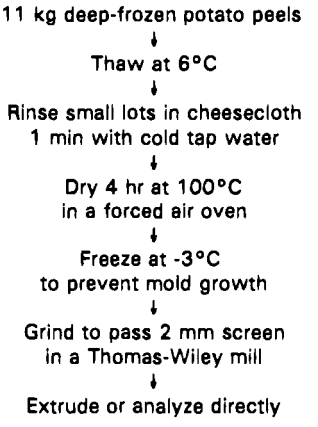

Figure 3. Preparation of potato peels obtained by commercial steam peeling.

Standards of each compound, thiabendazole and chlorpropham, were obtained from U.S. EPA Standards (Research Triangle Park, NC) with reported purity of 97.9 and 99.8%, respectively. Other reagents and solvents used were HPLC grade (VWR, Boston, MA).

Extrusion. Extrusion conditions have been reported previously (Arora et al., 1992; Camire et al., 1993). A Werner-Pfleiderer ZSK-30 laboratory scale twin screw extruder was used to process the peels. Two barrel temperatures (104 and 143 °C) and three feed moistures (31, 33.5, and 36%, dry basis) were studied as experimental factors.

* Author to whom correspondence should be addressed [telephone (207) 581-1626; fax (207) 581-1636].

0021-8561/95/1443-0495$09.00/0 © 1995 American Chemical Society

Table 1. Potato Peel Extrusion Processing Conditions[a]

barrel temp (°C)	feed moisture (% dry basis)	melt temp (°C)	die pressure (kPa)	torque (%)	peel moisture[b] (%)
104	31	132	1206	56	6.20
104	33.5	132	1068	53	7.00
104	36	127	1137	51	6.90
143	31	149	620	50	5.70
143	33.5	151	689	50	5.90
143	36	148	551	45	5.60

[a] From Arora et al., 1993. Average of duplicate extrusion runs. [b] Dry basis after extrusion, drying at 112 °C for 15 min, and grinding to pass a 2 mm sieve.

Pesticide Extraction. Duplicate extrusion runs were commingled for analyses. Thirty milliliters of a mixture of tetrahydrofuran (UV grade)–water–acetonitrile–acetic acid (50:30:20:1) was added to 2 g of dried, ground peels in a 50 mL polypropylene centrifuge tube. Samples were then homogenized (Polytron, Kinematic CH-6010, Switzerland) for 2 min at medium speed. After the Polytron probe was washed with extraction solution, additional solvent was added to make 50 mL. Tubes were centrifuged at 10000*g* for 10 min and the supernatant used directly for HPLC analyses. Six extractions were made for each commingled sample.

High-Performance Liquid Chromatography (HPLC) Determination of Thiabendazole. The method developed by Bushway et al. (1994) was employed. Ten microliters of the extract was injected into the following HPLC system: a Valco E-60 injector (Houston, TX); a Waters 510 isocratic pump (Milford, MA) with flow rate 1.0 mL/min through an Ultracarb 5μ 30 ODS column (Phenomenex, Torrance, CA) with a solvent system of 250 mL of water, 130 mL of acetonitrile, 35 mL of methanol, and 0.1 mL monoethanolamine and a Waters 470 fluorescence detector (set at 305 nm excitation and 345 nm, attenuation, 8; gain 100; and filter 1,5,s).

HPLC Determination of CIPC. A modified procedure developed by Wilson et al. (1982) was used. Five microliters of extract was injected into the following HPLC system: a Valco E-60 injector; a Hewlett-Packard (HP) 1050 isocratic pump (Avondale, PA) (flow rate of 1.0 mL/min); a Phenomenex Ultremex C_{18} 3 μ column with a solvent system of methanol–acetonitrile–water (35:35:30); a HP 1040 photodiode array detector with a flow cell and computer upgrade. The detector was set at 236 nm and 0.04 absorbance units full scale.

Statistical Analyses. Peak height was used for quantitation of thiabendazole and peak area for CIPC. Extruded peels were compared with barrel temperature and feed moisture as factors using the SYSTAT analysis of variance (ANOVA) program (Evanston, IL). Residues in extruded and nonextruded peels were compared as a one-way ANOVA with Fisher's least significant difference test for mean comparison at $p \leq 0.05$.

RESULTS AND DISCUSSION

During extrusion, melt temperature (temperature of the material within the extruder barrel immediately before the die) was about 30 °C higher than barrel temperature for samples extruded at 104 °C and die pressure was also higher (Table 1). Only slight increases in mass temperature were observed for peels extruded at 143 °C. Although viscosity of the mass was not determined, the higher barrel temperature most likely reduced viscosity within the barrel. Low viscosity materials are less subject to shear during extrusion, thus the temperature increase for 104 °C peels was likely due to friction. Torque was somewhat higher at 104 °C.

Thiabendazole Residues. Potato peels contained approximately 85 ppm of thiabendazole residues on a dry weight basis. This value is considerably higher than the United States tolerance of 10 ppm in fresh foods.

Table 2. Thiabendazole Residues in Nonextruded and Extruded Potato Peels[a]

barrel temp (°C)	feed moisture (% dry basis)	mean[b] (ppm)	SD (ppm)	CV (%)
not extruded		86.56 bc	3.51	4.05
104	31	91.13 c	6.92	7.59
104	33.5	92.88 c	7.89	8.49
104	36	93.45 c	12.25	13.11
143	31	86.65 bc	4.81	5.55
143	33.5	86.99 bc	7.10	8.16
143	36	82.70 ab	3.90	4.71

[a] Means followed by different letters are significantly different ($p \leq 0.05$, Fisher's least significant difference test) on a dry weight basis. [b] $N = 6$.

Table 3. Chlorpropham Residues in Nonextruded and Extruded Potato Peels[a]

barrel temp (°C)	feed moisture (% dry basis)	mean[b] (ppm)	SD (ppm)	CV (%)
not extruded		33.12 a	4.75	14.34
104	31	32.36 a	6.63	20.49
104	33.5	31.40 a	4.17	13.28
104	36	32.39 a	3.64	11.24
143	31	35.46 a	4.67	13.17
143	33.5	33.99 a	5.20	15.30
143	36	35.03 a	5.74	16.39

[a] Means followed by different letters are significantly different ($p \leq 0.05$, Fisher's least significant difference test) on a dry weight basis. [b] $N = 6$.

No significant differences in thiabendazole content were found between extruded and nonextruded potato peels (Table 2). However, peels extruded at 143 °C and 36% had a significantly lower ($p \leq 0.05$) thiabendazole level than those extruded at 104 °C. Among extruded peels, barrel temperature significantly affected thiabendazole content, but feed moisture content and temperature–moisture interaction had no effect. Since dried peels are not likely to be consumed directly, but as an ingredient in a foods product, the Acceptable Daily Intake of 0.3 mg of thiabendazole/kg of body weight would not be exceeded.

Chlorpropham Residues. Peels averaged 33 ppm of chlorpropham residues on a dry basis. The United States tolerance is 50 ppm for raw potatoes. Extrusion cooking under the parameters used in this study did not significantly reduce chlorpropham concentration (Table 3).

Even though these extruded peels contained a much lower CIPC level than the tolerance, chlorpropham, unlike thiabendazole, concentrations vary with season, application method, and with time after application. For example, Idaho Russet Burbank potatoes peeled three months after harvest had no detectable chlorpropham (unpublished findings). Therefore, it is also possible that some potato peels may have much higher CIPC levels.

In summary, under the extrusion conditions studied here, thiabendazole and chlorpropham are not reduced. Furthermore, since these chemicals are used in high amounts on potatoes, it would have been desirable to have observed significant degradation. Thus, additional studies are necessary to determine whether higher barrel temperatures might breakdown these post-harvest pesticides, particularly since CIPC decomposes at 150 °C.

ACKNOWLEDGMENT

Maine Agricultural and Forest Experiment Station external publication 1872. Paul Dean of McCain Foods, Ltd., Florenceville, NB, provided the potato peels used in this study. Tom Yang, Ann Barrett, and Jack Briggs of the U.S. Army RD&E Center, Natick, MA, graciously arranged for the use of the extruder and assisted with sample extrusion.

LITERATURE CITED

Arora, A.; Zhao, J.; Camire, M. E. Physical properties of extruded potato peels. *J. Food Sci.* **1993**, *58*, 335–337.

Bushway, R. J.; Young, B. E. S.; Paradis, L. R.; Perkins, L. B. Determination of thiabendazole in fruits and vegetables by competitive inhibition enzyme immunoassay. *J. Assoc. Off. Anal. Chem. Int.* **1994**, *77*, 1243–1248.

Camire, M. E.; Zhao, J.; Violette, D. A. *In vitro* binding of bile acids by extruded potato peels. *J. Agric. Food Chem.* **1993**, *41*, 2391–2394.

Hartley, D.; Kidd, H. *The Agrochemical Handbook*, 2nd ed.; The Royal Society of Chemistry: Nottingham, 1987.

Mondy, N. I.; Sharada, D.; Munshi, C. B.; Wurm, C. M. Effect of storage time, temperature, and cooking on isopropyl N-(3-chlorophenyl) carbamate levels in potatoes. *J. Agric. Food Chem.* **1992**, *40*, 197–199.

Mondy, N. I.; Wurm, C. M.; Munshi, C. B. Moist and dry heat reduce isopropyl N-(3–chlorophenyl) carbamate (CIPC) residue in potatoes. *J. Food Sci.* **1993**, *58*, 132–133, 163.

Toma, R. B.; Orr, P. H.; D'Appolonia, B.; Dintzis, F. R.; Tabekhia, M. M. Physical and chemical properties of potato peel as a source of dietary fiber in bread. *J. Food Sci.* **1979**, *44*, 1403–1407, 1417.

Wilson, A. M.; Bushway, A. A.; Bushway, R. J. Determination of CIPC in fruit and vegetables by HPLC. *J. Agric. Food Chem.* **1982**, *29*, 746–748.

Received for review July 26, 1994. Accepted November 23, 1994.[⊗]

JF940424A

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1995.