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Residues of Maleic Hydrazide and Chlorpropham in Potato Chips

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Pesticide residue in foodstuffs can be a serious problem of hygienics. Maleic hydrazide (MLHD, l,2-dihydro-3,6-pyridazinedione, $C_4H_4N_2O_2$) is a common sprout inhibitor used on potatoes. No survey of MLHD residue has been reported in Japan because of the complication of the official analytical method. Chlorpropham (CIPC, l-methylethyl(3-chlorophenyl)- carbamate, $C_{10}OH_{12}ClNO_2$) is a common post-harvest chemical for sprout inhibition, and has been reported in the residue survey of potato and fried potato (Nagayama and Kikugawa 1992). There is no report of CIPC residue in potato chips in Japan.

In this study a simultaneous residue analytical method for two sprout inhibitors — MLHD and CIPC – in potato chips was established, and a market survey was carried out in Japan.

MATERIALS AND METHODS

The analytical standards of both MLHD and CIPC were supplied by Wako Pure Chemicals Inc. (Chuou, Ohsaka, Japan). MLHD was dissolved in methanol (MeOH); the working standard was dissolved in H_2O/MeOH (1+1). CIPC was dissolved in toluene and diluted with toluene for use as a standard. Florisil[PR] was also supplied by Wako Pure Chemicals Inc., and added 10v/w% of H_2O and shaken vigorously for 3 min, and left a few hours. Organic solvents and anhydrous Na_2SO_4 were the pesticide grade.

Samples of potato chips were purchased from the supermarkets in Nara, Japan, from Apr. 1994 to Mar. 1995.

The sample was weighed 15 g-raw, and added 15 g of anhydrous Na_2SO_4 and 150 mL of MeOH, and homogenized promptly with Polytron for 3 min. The homogenate was filtered with Toyo No.5A filter paper, and the residue was washed with 10 mL of MeOH for 3 times. The filtrate and the washings were joined and added 30 mL of acetonitrile and 150 mL of hexane, and shaken for 3 min. The lower layer was separated to cleanup for MLHD and CIPC measurement.

One third of the lower layer was evaporated, and the residue was dissolved in MeOH. The suspension was filtered with Toyo No.5A

filter paper, and the residue was washed with MeOH for a few times. The filtrate and the washings were put together into 10 mL test tube, and made up to 2.5 ml, and then H_2O was added to make up 5 mL. The test tube was added 2.5 mL of Hexane, and shaken vigorously for 3 min, and centrifuged (3000 rpm x 5 min). The lower layer was analyzed by liquid chromatography with diode array detector (LC-DAD) for free–MLHD measurement.

Two thirds of the lower layer were added 200 mL of 10% NaCl aq and 50 mL of hexane, and shaken for 3 min. The upper layer was washed by 50 mL of 10% NaCl aq for 3 times, and dehydrated with 25 g of anhydrous Na_2SO_4, and evaporated. The residue was dissolved in hexane, and loaded to Florisil column (10% hydrated, 3 g, 12 mmø). The column was eluted by 30 mL of diethyl-ethel/ hexane (1+9), and the eluate was evaporated. The residue was dissolved with toluene, and made up to 1 mL. This solution was offered to gas chromatography mass spectrometry (GC-MS) for CIPC detection.

The LC and GC analyses were carried out by following instruments and conditions. LC-DAD: Instrument; Waters 510, 712, 991, Column; Asahi Chemicals Inc. (Kawasaki, Kanagawa, Japan), Asahipak NH2P50 4.6 mmø x 250 mm, Mobile phase; (0.6% triethylamine + 0.2% H_3PO_4)aq : MeOH = 95 : 5, 0.6 mL/min, UV range; 200-400 nm, Quantify UV; 330 nm, Injection; 50 µL. GC-MS: Instrument; Hewlett-Packard 5890,5971, Column; Restek, RTX-200 0.20 µm x 0.18 mmø x 20 m, Oven temp.; 80°C(1 min)→ (10°C/min) →250°C, Injector; He, 50 kPa, 230°C, Injection; split (1:20), 3 µL, Ionization; EI, Quantify ion; m/e = 213, Qualify ion; m/e = 171, 154

RESULTS AND DISCUSSION

The development of analytical method was intended to simultaneous procedure for MLHD and CIPC. The bound form of MLHD in tobacco plant were reported MLHD D-glucoside (Frear and Swanson 1978), and MLHD- -D-glucoside (Tagawa et al. 1995). The official method decomposes all MLHD to hydrazine, and measures with spectrophotometer (AOAC 963.24). No residue survey was reported in Japan because of the complication of this method. On the other hand, free-MLHD is the major form in potato (Newsome 1980), and has been extracted with MeOH by King (1983), Vadukul (1991), and Cessna (1991). In this study the extraction from potato chips was also carried out with MeOH, which gave the sufficient recovery rates for both free-MLHD and CIPC. The extracted solution was added 20 v/v% acetonitrile for better separation with hexane layer to remove triglyceride.

The cleanup for MLHD was carried out by the partitioning in H_2O/MeOH/hexane (1+1+1). The anion exchange LC was adopted with the polymer-based NH2 column. The chromatogram of MLHD 50 ng is presented in Figure 1 A, and the injection of 5–500 ng-MLHD gave the response of direct proportion. The chromatogram of the sample that free-MLHD wasn’t detected is shown in Figure 1 B. The recovery rate and the detection limit of free-MLHD were 81 ± 5%,

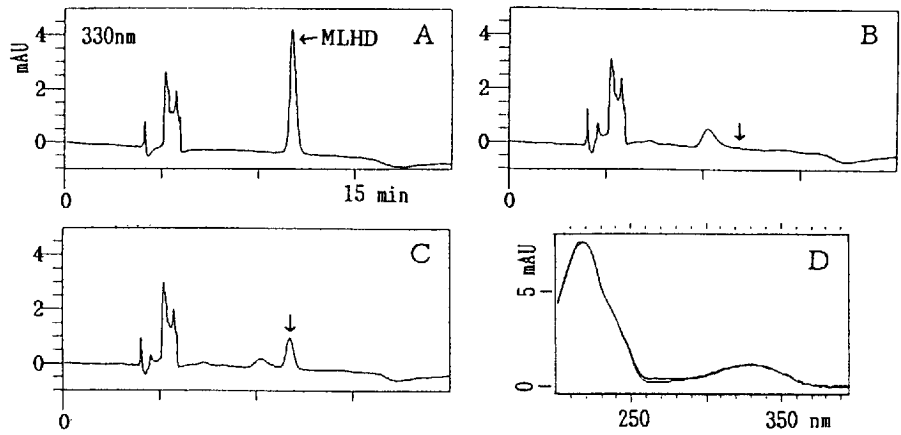

Figure 1. UV chromatograms and spectra of maleic hydrazide standard and test solutions from potato chips by LC-DAD
A; Standard (50 ng), B, C; Test solutions, D;
UV spectrum of the pointed peak of chromatogram C, which was overwritten with that of MLHD standard.

0.1 μg/g–raw respectively. The chromatogram of the sample that free–MLHD was detected is presented in Figure 1 C. The UV spectrum of the peak which hit MLHD is shown in Figure 1 D, and that of the standard is overwritten. The agreement of these spectra gave the identification of free-MLHD residue. The distribution of free–MLHD residues in potato chips on the market in Nara, Japan is presented in Figure 2. The detection rate of free-MLHD was 25% with the maximum amount of 0.3 μg/g–raw.

The cleanup for CIPC was carried out by hexane extraction and Florisil column chromatography. The recovery rate and the detection limit of CIPC were 79 ± 4%, 0.01 μg/g–raw respectively. The distribution of CIPC residues in potato chips on the market in Nara, Japan is presented in Figure 3. The detection rate of CIPC was 45% with the maximum amount of 0.11 μg/g–raw.

The CIPC residue level in fried potato was investigated by Nagayama and Kikugawa (1992) in Tokyo, Japan during 1988-89. The detection rate of CIPC was 70% with the residue level of 0.1–1 μg/g–raw. The CIPC residue level of potato chips in this study was one figure lower than that of Nagayama's in fried potato. Nagayama and Kikugawa (1992) also experimented the frying of frozen potato with soybean oil at 180°C for 4 min, and reported that CIPC was lost about 20% from potato, and the major part of the lost CIPC moved into soybean oil. As to potato chips, the translocation of CIPC to frying oil is expected to be more than that of fried potato. Ritchie et al. (1983) discussed that the residue rate of CIPC depends upon whether or not the frying oil has been used before. These considerations seem to be able to explain the difference of CIPC residue levels between fried potato and potato chips.

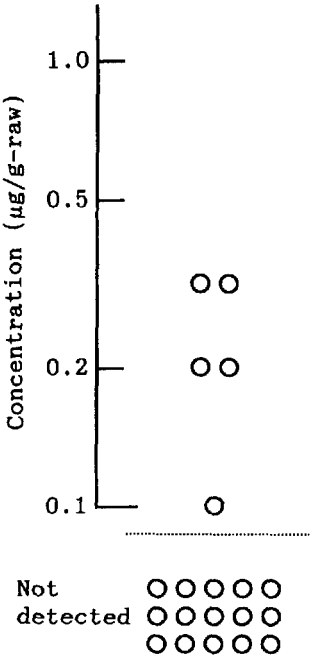

Figure 2. Distribution of free maleic hydrazide residues in potato chips

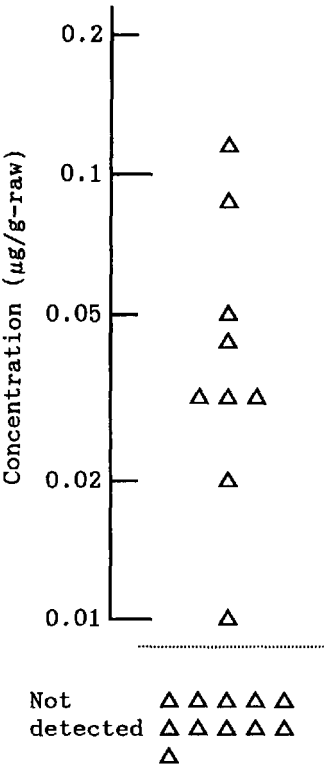

Figure 3. Distribution of chlor-propham residues in potato chips

There was no sample in which two sprout inhibitors were detected complexly, that is to say, the detection rate of anyone of them went up 70%. Japanese Ministry of Health and Welfare has not promulgated the tolerance for MLHD nor CIPC residue in potato chips. US-EPA has legislated the tolerance 160 ppm for MLHD residue in finished potato chips (40CFR185.3900). The residue amounts of free-MLHD in this survey were less than one-hundredth of the US tolerance.

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