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ANALYSIS OF N-METHYL CARBAMATE PESTICIDES IN FOOD

BY HPLC WITH POST-COLUMN DERIVATIZATION AND FLUORESCENCE DETECTION

Carbamate pesticides are widely used around the world to protect agricultural produce. In addition, they are used in homes, gardens and industrial applications. The main route of exposure for people to N-Methyl Carbamates is through food pathways, so pesticide use in food crops is strictly regulated.

As part of FDA's pesticide monitoring program, individual lots of domestic and imported foods and feeds are sampled and tested for pesticide residues in order to enforce the tolerances set by the EPA. Methyl carbamates are separated using a reversed-phase column and then react with o-Phthalaldehyde and a mercaptan after hydrolysis to form a highly fluorescent derivative. This post-column reaction is the basis for EPA Method 531.2 and AOAC official Method 985.23.

The "QuEChERS" (Quick, Easy, Cheap, Effective, Rugged, and Safe) method is a single step sample extraction and salting out technique that is combined with dispersive SPE clean-up for multi-residue pesticide analysis. AOAC official Method 2007.01 utilizes QuEChERS extraction and clean-up for wide range of pesticides in food matrices. This method abstract demonstrates that dispersive SPE can be successfully used in combination with post-column derivatization and fluorescence detection for analysis of carbamates in food.

METHOD

Sample Preparation

Place 15 g (5 g for spices or other challenging matrices) of homogenized sample into 50 mL centrifuge tube and add 15 mL of 1% Acetic Acid in Acetonitrile (v/v). Mix well. Add one Q-sep packet (Cat. # 26238, Restek), containing 6.0 g Magnesium Sulfate and 1.5 g of Sodium Acetate, to the mixture and immediately shake or vortex for 1 min. Centrifuge for 1 min to separate solid material.

Take 1 mL of supernatant and place into Q-sep d-SPE tube and shake vigorously for 2 min. Use to clean-up samples containing fats and waxes, 50 mg PSA, 150 mg $MgSO_4$, and 50 mg C_{18} (Q-sep Cat # 26125, Restek). Use for intensely colored extracts, 50 mg PSA, 150 mg $MgSO_4$, 50 mg C_{18} and 50 mg graphitized carbon (Q-sep Cat # 26219, Restek). Centrifuge the tube for 1 min to separate the solid material, filter through 0.45 um filter and place into injection vial for HPLC analysis.

Analytical Conditions

Column: Carbamate Column
P/N 0846250 (250 x 4.6 mm), C_8, 5 um

Flow Rate: 1 mL/min

Column Temperature: 42 °C

Mobile Phase: see Table 1

TABLE 1 HPLC CONDITIONS

TIME (Min)	WATER, %	METHONAL, %
0	100	0
1	100	0
1.1	82	18
36	30	70
39	30	70
39.1	0	100
41	0	100
41.1	100	0
55	100	0

Post-Column Conditions

Post-column System: Pinnacle PCX or Vector PCX

Reactor 1: 100 °C, 0.5 mL

Reactor 2: Ambient, 0.1 mL

Reagent 1: Hydrolysis Reagent CB130 or CB130.2

Reagent 2: 100 mg of OPA, 2 g of Thiofluor
in 950 mL of CB910

Detection: FLD, Excitation 330 nm, Emission 465 nm

Injection Volume: 10-20 uL

TABLE 2. RECOVERIES OF N-METHYL CARBAMATES IN FOOD MATRICES					
SAMPLE	**APPLES**	**BANANA**	**GINGER POWDER**	**BROWN RICE**	**BLUEBERRIES**
Spike concentration	10 ng/g	10 ng/g	25 ng/g, contaminated with 62 ng/g of Carbofuran	25 ng/g	10 ng/g
Aldicarb Sulfoxide	99. 62%	109.39%	91.14%	87.07%	92.76%
Aldicarb sulfone	107.02%	98.35%	79.83%	81.82%	92.52%
Oxamyl	73.11%	73.25%	76.79%	80.76%	68.66%
Methomyl	98.46%	84.18%	83.07%	86.94%	115.38%
3-Hydroxycarbofuran	39.1%	0%	39.1%	100%	39.1%
Carbofuran	84.13%	106.95%	87.43%	72.07%	80.76%
Aldicarb	89.69%	99.81%	77.83%	87.15%	87.50%
Propoxur	101.51%	91.04%	72.39%	88.36%	86.54%
Carbofuran	103.41%	100.25%	96.99%	84.08%	89.17%
Carbaryl	76.20%	111.84%	81.83%	83.40%	82.19%
Naphthol	61.56%	82.30%	74.99%	75.81%	37.15%
Methiocarb	86.84%	93.10%	49.82%	88.41%	83.49%

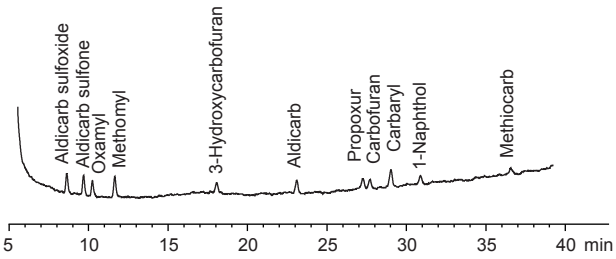

Fig 1. Banana sample spiked with 10 ng/g of carbamates

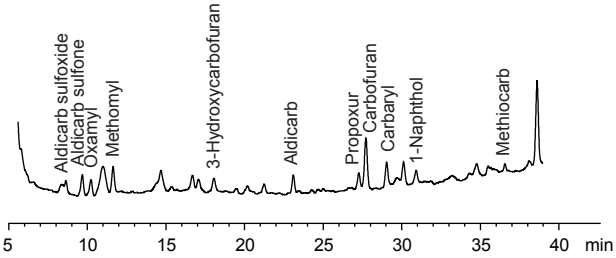

Fig 2. Ginger powder spiked with 25 ng/g of carbamates

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