

# 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. 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 reacted 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. To clean-up samples containing fats and waxes, 50 mg PSA, 150 mg MgSO<sub>4</sub>, and 50 mg C<sub>18</sub> (Q-sep Cat # 26125, Restek). To clean-up intensely colored extracts, 50 mg PSA, 150 mg MgSO<sub>4</sub>, 50 mg C<sub>18</sub> 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 μm filter and place into injection vial for HPLC analysis.

### Analytical Conditions

**Column:** Carbamate Column  
P/N 0846250 (250 x 4.6 mm), C8, 5 μm

**Guard Column:** Reversed-phase guard cartridge,  
P/N 18ECG001

**Flow Rate:** 1 mL/min

**Column Temperature:** 42 °C

**Mobile Phase:** see Table 1

**Injection Volume:** 10-20 μL

### Post-Column Conditions

**Post-Column System:** Onyx PCX, Pinnacle PCX or Vector PCX

**Reactor 1:** 100 °C, 0.5 mL

**Reactor 2:** Ambient, 0.1 mL

**Reagent 1:** Hydrolysis Reagent CBI30 or CBI30.2

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

**Detection:** FLD, Excitation 330 nm, Emission 465 nm

Table 1. HPLC Conditions

Time	Water %	Methanol %
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

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; sample is contaminated with 62 ng/g of Carbofuran	25 ng/g	10 ng/g
Aldicarb Sulfoxide	99.6%	109.4%	91.1%	87.1%	92.8%
Aldicarb Sulfone	107.0%	98.4%	79.8%	81.8%	92.5%
Oxamyl	73.1%	73.3%	76.8%	80.8%	68.7%
Methomyl	98.5%	84.2%	83.1%	86.9%	115.4%
3-Hydroxycarbofuran	84.1%	107.0%	87.4%	72.1%	80.8%
Aldicarb	89.7%	99.8%	77.8%	87.2%	87.5%
Propoxur	101.5%	91.0%	72.3%	88.4%	86.5%
Carbofuran	103.4%	100.3%	97.0%	84.1%	89.2%
Carbaryl	76.2%	111.8%	81.8%	83.4%	82.2%
Naphthol	61.6%	82.3%	75.0%	75.8%	37.2%
Methiocarb	86.8%	93.1%	49.8%	88.4%	83.5%

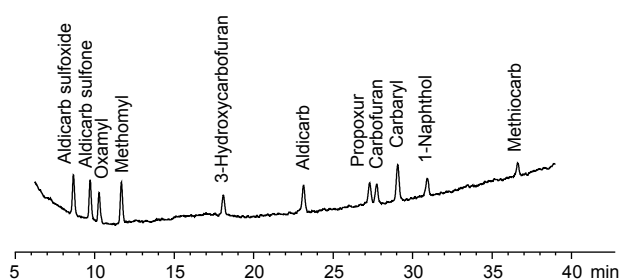


Fig 1. Carbamates standard solution, 5 ng/mL

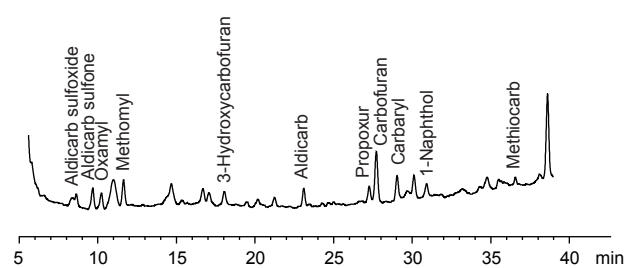


Fig 3. Ginger powder spiked with 25 ng/g of carbamates

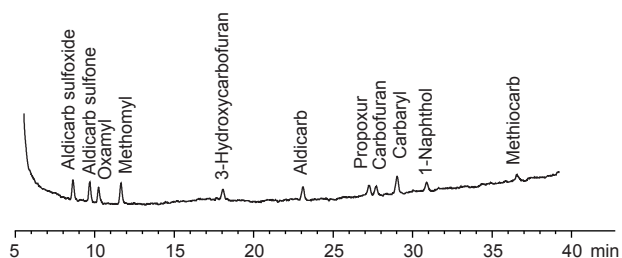


Fig 2. Banana sample spiked with 10 ng/g of carbamates

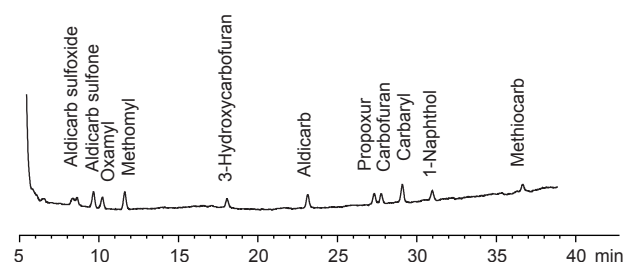


Fig 4. Brown rice sample spiked with 25 ng/g of carbamates