DIONEX

Application Note 272

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Faster Yet Sensitive Determination of *N*-Methylcarbamates in Rice, Potato, and Corn by HPLC

INTRODUCTION

The *N*-methylcarbamates and the *N*-methylcarbamoximes are among the most widely used pesticides in agriculture. Because these pesticides may create health problems—including issues impacting the central nervous and reproductive systems—concerns over the presence of carbamate residues in water, crops, and food products have promoted increased awareness and testing for these compounds.

For the detection of carbamate residues in environmental waters, the United States Environmental Protection Agency (U.S. EPA) provides guidelines for monitoring the presence of carbamate pesticides and related compounds in raw surface water using EPA Method 531.2.[1] This method uses high-performance liquid chromatography (HPLC) with fluorescence detection (FD) following postcolumn derivatization to enhance method sensitivity and selectivity compared to UV absorbance detection. Dionex has published detailed methods that are consistent with EPA Method 531.2.[2-4]

For the detection of carbamate residues in food matrices, sample preparation is key for a sensitive determination. Several methods currently exist for the extraction from a variety of different food matrices, such as using a solid-phase extraction (SPE) column,[5,6] accelerated solvent extraction (ASE),[7,8] liquid-liquid extraction,[9] and cloud-point extraction (CPE).[10] The work shown here uses a two-step sample preparation method that first uses a salting-out extraction to extract the target analytes, then a dispersive solid-phase extraction (dSPE) to remove sugars, lipids, organic acids, sterols, proteins, and pigments. Similar methods are now available, such as AOAC 2007.01 Method[11] by the Association of Official Analytical Chemists (AOAC) in the United States, and the European equivalent, EN 15662.[12]

This study describes a faster yet sensitive method for the determination of carbamates (those specified in EPA Method 531.2) in rice, potato, and corn (maize). The sample preparation method uses a salting-out extraction step with acetonitrile, NaCl, and $MgSO_4$; and a dSPE cleanup step using primary secondary amine (PSA) resin to extract the carbamates and remove interfering substances from these crop samples. The separation is performed on an Acclaim® Carbamate column with detection by a FLD-3400RS fluorescence detector. The chromatography method is based on a reversed-phase separation of the carbamates with subsequent derivatization by *o*-Phthalaldehyde (OPA) followed by FD.

EQUIPMENT

Dionex UltiMate® 3000 HPLC system including:

- HPG-3400A Pump with SRD-3400 Solvent Rack with Degasser
- WPS-3000 Autosampler
- TCC-3000 Thermostatted Column Compartment
- FLD-3400 Fluorescence Detector

Chromeleon® Chromatography Data System (CDS) software Version 6.80 SR9

Pickering PCX 5200 Derivatization Instrument, Pickering Laboratories, Inc. CA, U.S.A.

Mettler Toledo AL204 Laboratory Balance, Mettler Toledo (Shanghai) Co., Shanghai, China

Anke TDL 80-2B centrifuge, Anting Scientific Instrumental Factory, Shanghai, China

Anke TDL 16B centrifuge, Anting Scientific Instrumental Factory, Shanghai, China

IKA MS1 Minishaker, IKA Works, Guangzhou, China

Note:

Prior to the use of HPLC and Pickering PCX 5200 Derivatization Instruments, use pure methanol to wash the system.

The pressure limit of the Pickering PCX 5200 Derivatization Instrument needs to be increased to 350 bar to prevent shutdown during derivatization.

For more details on using the Pickering PCX 5200 Derivatization Instrument, see AN 96.[3]

REAGENTS AND STANDARDS

Deionized water, Milli-Q® Gradient A10, Millipore Corporation

Methanol (CH_3OH), Fisher

Acetonitrile (CH_3CN), Fisher

Potassium dihydrogen citrate ($KC_6H_7O_7$), 98%, Fluka

Sodium thiosulfate ($Na_2S_2O_3$), 98%, Fluka

Sodium hydroxide solution, (NaOH), 50%, Fluka

Boric acid, 99.5%, Fluka

o-Phthalaldehyde (OPA, $C_8H_6O_2$), 99%, Pickering

β-Mercaptoethanol, 99%, SCRC, China

Magnesium sulfate ($MgSO_4$), analytical grade, SCRC, China

Sodium chloride (NaCl), analytical grade, SCRC, China

Primary secondary amine (PSA) Bonded Silica, Supelco

Activated carbon, SCRC, China

EPA Method 531.2 Carbamate Pesticide Calibration Mixture, Restek, 100 µg/mL (P/N 257974)

4-Bromo-3,5-dimethylphenyl-*N*-methylcarbamate standard (BDMC), Restek, 100 µg/mL (P/N 32274)

PREPARATION OF REAGENTS AND STANDARDS

Reagent Water

Use deionized water from a Milli-Q Gradient A10, 18 MΩ-cm resistivity or better.

Preserved Reagent Water

Dissolve 4.6 g of potassium dihydrogen citrate and 40 mg of $Na_2S_2O_3$ in a 50 mL beaker with reagent water, transfer this solution to a 500 mL volumetric flask, and bring to volume with reagent water. Prior to use, filter the solution through a 0.45 µm filter.

Stock Standard Carbamates Calibration Mixture

Pipet 10 µL of EPA 531.2 carbamate calibration mixture (100 µg/mL) into a 1 mL vial and add 990 µL of methanol. The concentration for each carbamate in the stock standard mixture is 1.0 µg/mL.

1-Naphthol is naturally fluorescent. It may assist in troubleshooting postcolumn chemistry issues because it will be the only peak present in a chromatogram when the postcolumn system is not functioning properly.

Stock Standard of BDMC (Surrogate Analyte, SUR)

Pipet 10 µL of BDMC (100 µg/mL) into a 1 mL vial and add 990 µL of methanol. The concentration of the stock standard solution is 1.0 µg/mL.

Working Standard Solutions for Calibration

Prepare five working standard solutions by adding the quantities of carbamate mixture stock standard solutions listed in Table 1 to 25 mL volumetric flasks. Add 50 µL of the stock standard solution of BDMC into each flask. Bring to volume with preserved reagent water.

Sodium Hydroxide Hydrolysis Reagent (Postcolumn Reagent 1)

Sodium hydroxide, 0.2%: Dilute 4 mL of 50% w/w NaOH solution to 1 L with reagent water. The concentration of the hydrolysis solution can dramatically affect the analyte response. Filter and degas with nitrogen just before use.[1]

OPA Reagent (Postcolumn Reagent 2) for Postcolumn Derivatization

To prepare boric acid buffer: dissolve 3.0 g of boric acid in approximately 800 mL of reagent water in a 1 L volumetric flask. Add 1.2 mL of a 50% (w/w) NaOH solution. Bring the volume to 1.0 L with reagent water. Filter and degas prior to preparation of postcolumn reagent 2.

Dissolve 100 mg of OPA in 5–10 mL of methanol and add to 1 L of boric acid buffer, then add 1 mL of 2-mercaptoethanol. This solution is postcolumn reagent 2.[1] To review the postcolumn chemistry and see a diagram of the postcolumn system configuration, see EPA Method 531.2.[1]

SAMPLES AND SAMPLE PREPARATION

Three kinds of crop samples—rice, potato, and dried and fresh corn—were purchased from a market located in Zhangjiang High-Tech Park, Shanghai.

Mill the samples to powder or mash using a food processor. Put an accurately weighed ~5 g of milled sample into a clean 15 mL centrifuge tube, then add 5.0 mL of acetonitrile and 10 µL of 1 µg/mL BDMC (SUR). After 1 min of vortexing, add ~2 g $MgSO_4$ and ~0.5 g NaCl, then vortex for 1 min. Centrifuge for 10 min (rpm 3000), pipet 1.00 mL of supernatant into a 1.5 mL centrifuge tube, then add ~100 mg $MgSO_4$ and ~50 mg PSA. After 1 min of vortexing followed by 5 min of centrifugation (10,000 rpm), pipet 100 µL of supernatant to a 1.5 mL vial, then add 900 µL of preserved reagent water. Vortex this sample for a few seconds prior to analysis by HPLC.

Table 1. Preparation of Calibration Curve Standards

Stock Standard of Carbamate Mixture (µg/mL)	Volume of Stock Standard of Carbamate Mixture (µL)	Stock Standard of BDMC (SUR) (µg/mL)	Volume of Stock Standard of BDMC (SUR) (µL)	Final Volume of Calibration Standard (mL)	Final Concentration of Carbamate Standard (µg/L)	Final Concentration of BDMC (SUR) (µg/L)
1.0	6.25	1.0	50.0	25	0.25	2.0
	12.5				0.50	
	25.0				1.00	
	50.0				2.00	
	200				8.00	

CONDITIONS

Guard Column: Acclaim Carbamate, 3.0 × 10 mm, 3 µm, P/N 072929 (Use Holder V2, P/N 069580)

Analytical Column: Acclaim Carbamate, 3.0 × 150 mm, 3 µm, P/N 072926

Column Temp.: 50 °C

Mobile Phase: Methanol–water, in gradient (Table 2)

Flow Rate: 0.9 mL/min

Inj. Volume: 50 µL

Postcolumn Reagent 1: 0.2% NaOH, first reaction coil at 100 °C

Postcolumn Reagent 2: OPA regent, second reaction coil at room temperature

Flow Rate of Reagent 1 and 2: 0.3 mL/min

Fluorescence: Excitation: 330 nm
Emission: 465 nm
Data Collection Rate: 5
Response Time: 4
Sensitivity: 7
Lamp Mode: High Power
PMT (Photomultiplier Tube): Pmt1
Filter Wheel: 280 nm

Table 2. Gradient for the Separation of Carbamates

Time (min)	Flow Rate (mL/min)	Methanol (%)	H_2O (%)
-4	0.9	14	86
0		14	86
2		20	80
8		40	60
13.6		70	30
16		70	30

RESULTS AND DISCUSSION

Sample Preparation

The sample preparation uses two steps. One extraction step that is based on partitioning using salting-out extraction involving equilibrium between aqueous and organic layers, and then a second step, dSPE, that involves further cleanup using various combinations of salts and porous sorbents.

Acetonitrile was used because it is a good solvent for carbamates, and NaCl was used for the salting-out extraction. To remove residual water, $MgSO_4$ was used. The authors chose PSA for the dSPE step to remove sugars and fatty acids, and also because it was reported to be a good choice for the determination of carbamate and organophosphorus pesticides in fruits and vegetables.[13]

Effect of Water in Extracts

The presence of water in the extract may affect the adsorptivity of PSA in the dSPE step, resulting in poor removal of coextracted interferences.[13] The experiments showed that the more residual water in the extract, the more coextracted interferences were left after dSPE with PSA. A simple way to resolve this problem is to add enough $MgSO_4$ to remove the residual water as completely as possible. Therefore, use two additions of $MgSO_4$ during sample preparation.

Determining the Amount of PSA for Sample Preparation

Enough PSA is required to absorb as much of the co-extracted interferences as possible. Therefore, the effects of PSA on the determination of crop samples spiked with carbamate standards were investigated. Experiments showed that there was no significant difference for peak area of each carbamate after dSPE using 50 and 100 mg of PSA, respectively. Thus, use 50 mg of PSA for the dSPE sample preparation step.

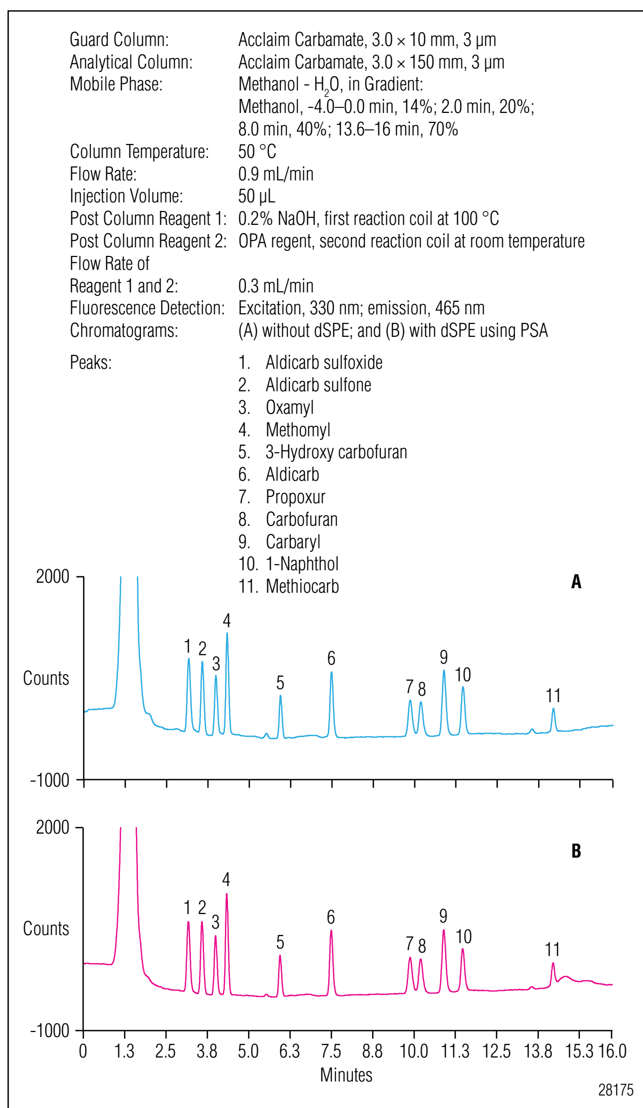

Figure 1. Chromatograms of extracts of carbamate standard-spiked rice samples (2 µg/L each) after acetonitrile and salt-out extractions (A) without and (B) with dSPE using PSA.

Choice of Sorbent

For some crop samples, such as rice, the coextracted substances were sufficiently removed after acetonitrile and salt-out extractions, and hence the dSPE cleanup step was not required. As shown in Figure 1, there is no significant difference between the chromatograms of the extracts of carbamate standard-spiked rice samples obtained by acetonitrile and salt-out extractions with and without using dSPE.

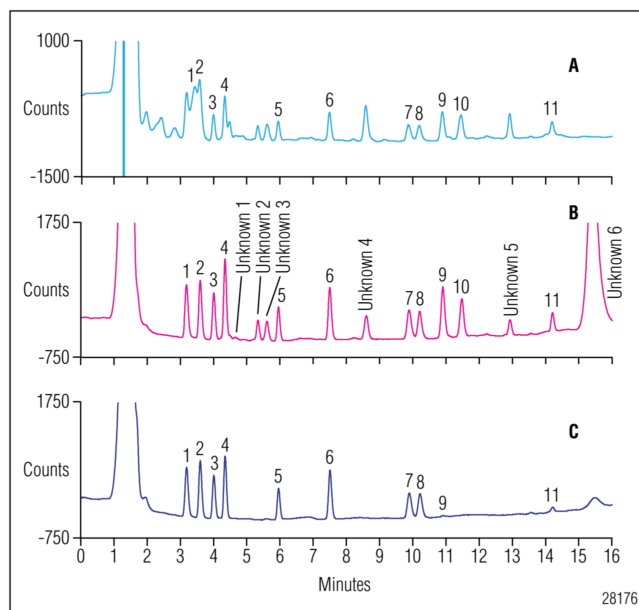

Figure 2. Chromatograms of extracts of carbamate standard-spiked corn samples (2 µg/L each) after acetonitrile and salt-out extractions (A) without and with dSPE using (B) PSA and (C) activated carbon. Other conditions are the same as in Figure 1.

For other crop samples, such as corn and potato, experiments demonstrated that after acetonitrile and salt-out extractions, coextracted interferences were still present in the extracts. Figure 2(A) shows a chromatogram of the extract of a carbamate standard-spiked corn sample obtained by acetonitrile and salt-out extractions. The coextracted interferences with retention times 3 ~ 5 min may interfere with the determination of aldicarb sulfoxide, aldicarb sulfone, oxamyl, and methomyl (peaks 1 to 4). Use dSPE with PSA or activated carbon to try to remove these interferences. As shown in Figure 2(B), after dSPE with PSA, good separation of these carbamates was observed. This can be attributed to the efficient removal of these interferences by PSA treatment. When using activated carbon instead of PSA, better removal of interferences was obtained. As shown in Figure 2(C), the coextracted substances with retention times 3 ~ 5 min were removed, and the unknown peaks in Figure 2(B) were removed as well; however, carbaryl (peak 9) and 1-naphthol (peak 10) were lost, and methiocarb (peak 11) was not fully recovered after dSPE with activated carbon, demonstrating that they were absorbed by activated carbon.

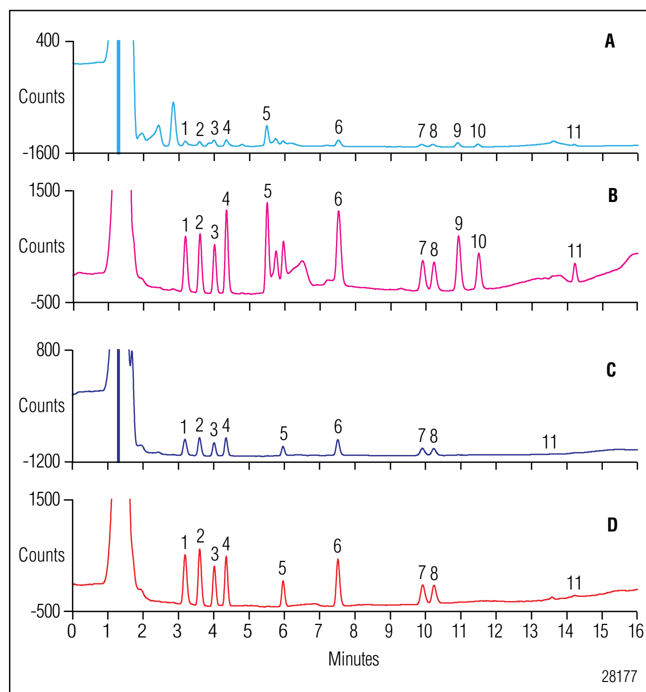

Figure 3. Chromatograms of extracts of carbamate standard-spiked potato samples (2 µg/L each) after acetonitrile and salt-out extractions (A) without and with dSPE using (B) PSA, (C) activated carbon, and (D) mixture of PSA and activated carbon (1:1, w/w). Other conditions are the same as in Figure 1.

Figure 3(A) shows a chromatogram of an extract of a potato sample obtained by acetonitrile and salt-out extractions and spiked with carbamate standards. It appears that large amounts of coextracted polar substances with retention times 1 ~ 2 min may interfere with the determination of carbamates (i.e., there are low responses for the carbamates). After dSPE with PSA, as shown in Figure 3(B), much higher responses were observed; however, the presence of the substances with retention times 5 ~ 7 min probably interfere with the determination of 3-hydroxycarbofuran (peak 5).

When using activated carbon, as shown in Figure 3(C), these coextracted interferences were removed, but the polar substances with retention times 1 ~ 2 min still remained and resulted in low responses of all carbamates.

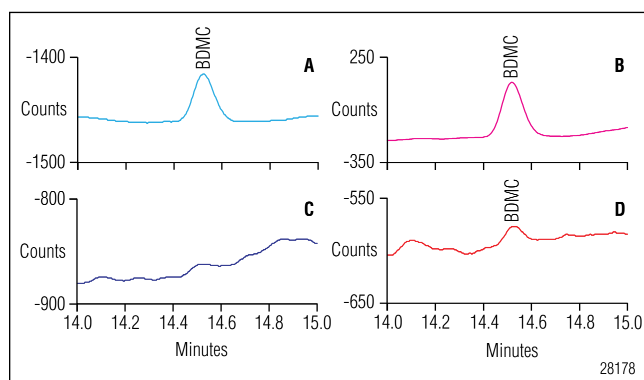

Figure 4. Chromatograms of BDMC (SUR) after acetonitrile and salt-out extractions (A) without and with dSPE using (B) PSA, (C) activated carbon, and (D) mix of PSA and activated carbon (1:1, w/w). Other conditions are the same as in Figure 1.

As with the corn samples, carbaryl (peak 9) and 1-naphthol (peak 10) were lost, and methiocarb (peak 11) exhibited poor recovery after dSPE with activated carbon. If the carbamates, except for those absorbed by activated carbon, were the target analytes, the mixture of PSA and activated carbon would be a better choice (Figure 3[D]).

The mixed sorbent treatment removed most of the interferences and the analyte responses were good. Unfortunately, the carbamate BDMC, whose addition was specified in EPA Method 531.2[1] as an SUR for quantification, was also absorbed completely by activated carbon (Figure 4). Therefore, only PSA was used for dSPE for all samples in this study (Table 3).

Effect of Sample Dilution

Experiments showed that the peak shapes of aldicarb sulfoxide, aldicarb sulfone, oxamyl, and methomyl (peak 1 ~ 4) were asymmetrical when the extract (extracted by acetonitrile) was injected directly, which can be attributed to the significant difference of solvent strength between the sample solvent (acetonitrile) and mobile phase (methanol–water). To acquire ideal peak shape, the extract was diluted with preserved reagent water (see the section on Preparation of Reagents and Standards). Accordingly, the injection volume was increased to 50 µL to maintain the detection limits.

Table 3. Peak Areas of Carbamates in Crop Samples Spiked with Carbamate Standards (2 µg/L for each), after dSPE Using Different Amounts of PSA												
Carbamate	Peak Area (Counts*min)											
	Rice			Corn (Maize)						Potato		
				Dried			Fresh					
	PSA 50 mg	PSA 100 mg	Difference (%)	PSA 50 mg	PSA 100 mg	Difference (%)	PSA 50 mg	PSA 100 mg	Difference (%)	PSA 50 mg	PSA 100 mg	Difference (%)
Aldicarb sulfoxide	121.3	127.2	4.9	125.9	128.7	2.2	128.9	138.5	7.5	123.7	127.2	2.8
Aldicarb sulfone	115.0	117.3	2.0	117.3	116.7	-0.5	123.0	128.1	4.1	109.8	116.6	6.2
Oxamyl	87.30	98.21	12	100.3	97.11	-3.2	105.8	108.6	2.6	95.33	103.5	8.6
Methomyl	138.9	157.3	13	135.3	150.6	11	145.9	156.4	7.2	153.5	162.0	5.5
3-Hydroxy carbofuran	57.30	63.81	11	66.42	67.47	1.6	67.28	70.86	5.3	65.34	68.03	4.1
Aldicarb	106.9	118.7	11	120.0	123.7	3.1	123.1	133.7	8.6	111.1	126.8	14
Propoxur	70.28	75.01	6.7	78.08	74.39	4.7	77.58	84.89	9.4	73.14	79.67	8.9
Carbofuran	62.44	69.14	11	68.36	69.55	1.7	74.53	80.85	8.5	68.46	72.67	6.1
Carbaryl	113.5	126.5	11	124.4	123.1	1.0	129.6	137.7	6.2	121.3	134.0	10
1-Naphthol	86.46	61.96	-28	104.0	45.73	-56	137.6	120.4	-12.5	99.22	89.02	-10
Methiocarb	32.01	36.81	15	34.68	34.68	0.0	34.37	38.16	11	36.23	41.20	14

*Note: The difference was calculated by using the following equation: Difference = $(A_{100\text{ mg of PSA}} - A_{50\text{ mg of PSA}}) / A_{50\text{ mg of PSA}}$

$A_{100\text{ mg of PSA}}$ stands for the average of peak area (n = 7) of each carbamate obtained by using 100 mg of PSA in dSPE, and $A_{50\text{ mg of PSA}}$ stands for that obtained by using 50 mg of PSA.

Separation and Reproducibility

Figure 5 illustrates good separation of the carbamates listed in EPA Method 531.2 using the Acclaim Carbamate column, which is designed for the baseline separation of these carbamates. Resolution (R_s) for all peaks is ≥1.5.

Reproducibility of the separation method was estimated by making seven replicate injections of a calibration standard with a concentration of 8.0 µg/L for each carbamate. The RSD value of each carbamate was ≤0.07% for retention time and ≤3.0 % for peak area.

The reproducibility of the sample preparation method was evaluated by making injections of carbamate standard-spiked crop samples from five separate sample preparations. The value of relative standard deviation (RSD) of each carbamate for peak area was ≤7.0 %, demonstrating sufficient reproducibility for the sample preparation method.

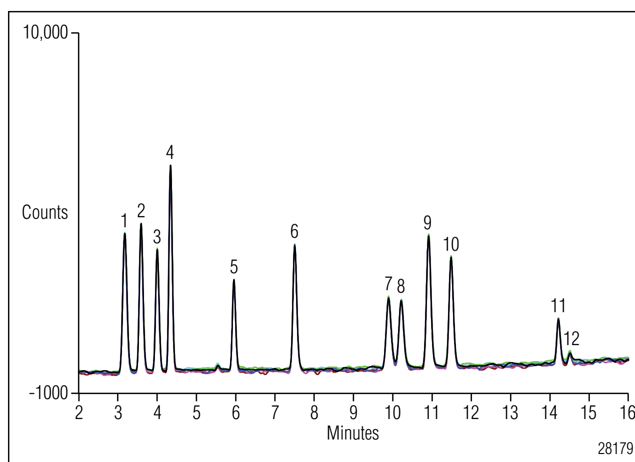

Figure 5. Overlays of chromatograms of seven consecutive injections of carbamate standards (8 µg/L each). Other conditions are the same as in Figure 1.

Table 4. Method Linearity Data and Method Detection Limits (MDL)				
Carbamate	Regression Equation	r^2	MDL	
			In Well-Prepared Sample Solution µg/L	Equivalent in the Original Sample µg/Kg
Aldicarb sulfoxide	$A = 2.4522\ c - 0.0994$	0.9971	0.08	0.8
Aldicarb sulfone	$A = 2.2352\ c - 0.0862$	0.9973	0.07	0.7
Oxamyl	$A = 1.7381\ c - 0.0523$	0.9972	0.06	0.6
Methomyl	$A = 2.7759\ c - 0.0117$	0.9975	0.09	0.9
3-Hydroxycarbofuran	$A = 1.2364\ c - 0.0627$	0.9965	0.09	0.9
Aldicarb	$A = 2.0374\ c + 0.0498$	0.9977	0.10	1.0
Propoxur	$A = 1.3220\ c + 0.0094$	0.9978	0.09	0.9
Carbofuran	$A = 1.2588\ c - 0.0315$	0.9973	0.04	0.4
Carbaryl	$A = 2.5121\ c - 0.0995$	0.9973	0.09	0.9
1-Naphthol	$A = 1.9981\ c + 0.0008$	0.9979	0.11	1.1
Methiocarb	$A = 0.6360\ c + 0.0069$	0.9976	0.09	0.9

Note: The single-sided Student's test method (at the 99% confidence limit) was used for determining MDL, where the standard deviation (SD) of the peak area of seven injections is multiplied by 3.50 to yield the MDL.

Linearity and Detection Limits

Calibration linearity for the determination of carbamates by this method was investigated by making seven replicate injections of serial standard solutions of carbamates at five different concentrations from 0.25 to 8 µg/L.

Detection limits of carbamates were calculated using the equation:

$$\text{Detection limit} = S t_{(n-1,\ 1-\alpha = 0.99)}$$

The symbol S represents Standard Deviation (SD) of replicate analyses, n represents number of replicates, and $t_{(n-1,\ 1-\alpha = 0.99)}$ represents Student's value for the 99% confidence level with n – 1 degrees of freedom. Seven replicate injections of extract of rice sample spiked with 2 µg/L of carbamate standard mixture were used to determine the minimum detection limits. Table 4 summarizes the calibration and MDL data, showing excellent method linearity and sensitivity.

Rice, Potato, and Corn Sample Analysis

Figure 6 shows the chromatograms of rice, potato, and fresh corn samples; the related data is summarized in Table 5, showing satisfactory spike recovery for each carbamate. No detectable levels of carbamates were found in rice and potato samples.

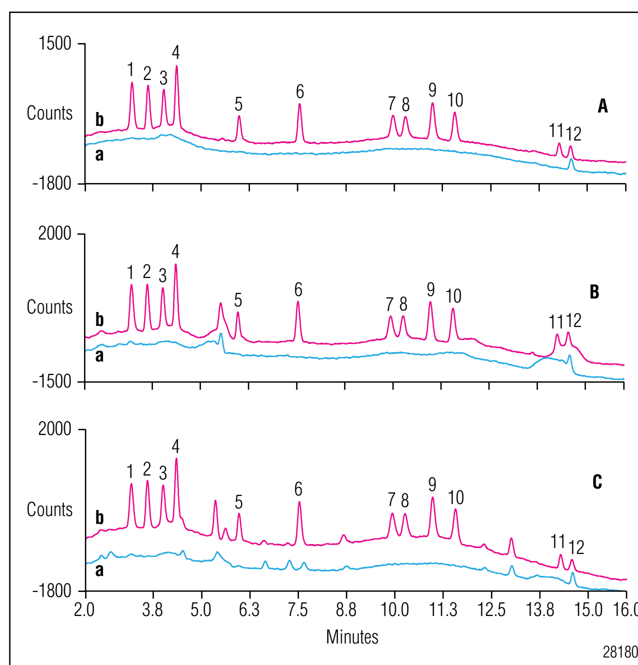

Figure 6. Overlays of chromatograms of crop samples spiked with 2.0 µg/L of BDMC (SUR, peak 12), and the same samples spiked with a carbamate standard mixture with 2.0 µg/L for each carbamate. Chromatograms, (a) crop samples, (b) carbamate standard-spiked crop samples; samples, (A) rice, (B) potato, and (C) fresh corn (maize). Other conditions are the same as in Figure 1.

Table 5. Crop Sample Analysis													
Carbamate	Rice				Potato				Fresh Corn (Maize)				
	Detected (µg/L)	Added (µg/L)	Found (µg/L)	Recovery (%)	Detected (µg/L)	Added (µg/L)	Found (µg/L)	Recovery (%)	Detected (µg/L)		Added (µg/L)	Found (µg/L)	Recovery (%)
									By FD	Confirmed by MS			
Aldicarb sulfoxide	ND*		1.81	90	ND		1.87	94	0.10	ND		1.82	91
Aldicarb sulfone	ND		1.72	86	ND		1.81	90	ND	Detected		1.88	94
Oxamyl	ND		1.82	91	ND		1.99	99	ND			2.05	102
Methomyl	ND		1.78	89	ND		2.06	103	ND			1.77	89
3-Hydroxy-carbofuran	ND	2.0	1.68	84	ND	2.0	1.98	99	ND	Detected	2.0	1.74	87
Aldicarb	ND		1.85	93	ND		1.97	98	0.29	Detected		1.73	87
Propoxur	ND		1.87	93	ND		1.96	98	ND			2.06	103
Carbofuran	ND		1.87	93	ND		1.88	94	ND			1.89	95
Carbaryl	ND		1.68	84	ND		1.77	89	ND			1.85	92
1-Naphthol	ND		1.58	79	ND		1.85	93	ND			1.80	90
Methiocarb	ND		1.79	90	ND		1.97	94	ND			1.95	97

Note: ND = not detected

When the fresh corn sample was analyzed, two small peaks with retention times near that of aldicarb sulfoxide (peak 1) and aldicarb (peak 6) were found and labeled, as the two carbamates with concentrations were 0.10 and 0.29 µg/L, respectively (Figure 6[C]).

A complicated matrix may sometimes yield false positives for carbamates. An efficient way to determine if the peaks are carbamates is by using mass spectrometry (MS) detection. Based on the LC-MS method described in Reference 14, LC-MS results revealed that the peak with retention time near peak 1 was not aldicarb sulfoxide, and the one near peak 6 was aldicarb with estimated concentration of 0.30 µg/L, which is similar to the concentration determined using FD.

The EPA's August 2010 risk assessment indicates that aldicarb no longer meets the Agency's rigorous food safety standards and may pose unacceptable dietary risks, especially to infants and young children. The Agency is initiating action to terminate uses of aldicarb, and also plans to revoke aldicarb tolerances. Bayer CropScience plans to stop marketing aldicarb worldwide by 2014.[15] Therefore, simpler, efficient, and sensitive methods for the determination of aldicarb in soil, crops, environmental water, and food products are desired. Additionally, although aldicarb sulfone (peak 2) and 3-hydroxycarbofuran (peak 5) were not found in the fresh corn sample using FD, they were detected using LC-MS.

CONCLUSION

This testing describes an effective method for the determination of carbamates in rice, potato, and corn on an UltiMate 3000 HPLC system with an Acclaim Carbamate column and FD following postcolumn derivatization. Acetonitrile extraction and dSPE cleanup using a PSA was used to isolate the carbamates and remove the interference substances from the crop samples prior to HPLC analysis. The prepared samples yielded accurate results using the method described here.

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