Waters[®] Alliance[™] LC/MS System



LC/MS Application Notes: Carbamates I: Instrument Optimization Eric H. Block, Waters Corporation, Milford, MA

Instrumental ConditionsLinearity and SensitivityPrecision and AccuracyRepresentative SpectrumRepresentative
ChromatogramKey Words:
N-methyl Carbamates
Endocrine Disruptors
Post-column

The analysis of N-methyl Carbamates has received renewed interest in light of their implication as potential endocrine disruptors. In this study, instrumental conditions were examined and optimized for the analysis of a 10-component standard mixture without the use of pre-column derivatization.

Linearity, sensitivity, precision, and accuracy were evaluated using positive electrospray ionization. The method was demonstrably linear, accurate and precise for all 10 analytes. Instrumental limits of detection and quantitation were determined to be approximately 10 pg and 25 pg on-column, respectively.

These results show the feasibility of using LC/MS as a viable alternative to current post-column derivatization methodologies.

Derivatization

Instrumental Conditions

HPLC

- Waters Alliance LC/MS System
- Symmetry[®] C₁₈ column (1mm x 150 mm) with Acetonitrile/Water gradient
 - Microbore column provides complete resolution of underivatized components

Mass Spectrometer

- Waters ZMD Detector (4000 amu mass range); positive electrospray
 - Full-scan acquisition provides molecular weight information
 - Figure 1 shows representative spectrum of 3-OH Carbofuran
 - Selected Ion Recording (SIR) acquisition for quantitation
 - Provides discrete chromatographic channels for each analyte and increases specificity
 - Cone voltage programming optimizes signal for each compound
 - Figure 2 shows overlaid chromatograms of a 10-component mixture

Linearity and Sensitivity

Linearity was assessed from triplicate analysis of a series of calibration standards (5-1000 ng/mL). In a separate experiment, instrumental LOD and LOQ were determined from 5 replicate injections of a standard mixture (50 pg each analyte on-column). Figure 3 shows a representative calibration curve for Aldicarb; Figure 4 is the chromatogram of 50 pg of Aldicarb on-column overlaid on a blank. The following table summarizes the linearity and sensitivity for all analytes.

	Coefficient of		
	determination	LOD	LOD
Aldicarb Sulfoxide	0.9969	0.8 ng/mL	2.6 ng/mL
Aldicarb Sulfone	0.9982	1.8 ng/mL	6.1 ng/mL
Oxamyl	0.9990	0.7 ng/mL	2.2 ng/mL
Methomyl	0.9959	1.6 ng/mL	5.5 ng/mL
3-OH Carbofuran	0.9970	0.4 ng/mL	1.4 ng/mL
Aldicarb	0.9963	0.2 ng/mL	0.5 ng/mL
Propoxur	0.9967	1.7 ng/mL	5.5 ng/mL
Carbofuran	0.9981	0.9 ng/mL	3.0 ng/mL
Carbaryl	0.9994	0.3 ng/mL	1.1 ng/mL
Methiocarb	0.9995	0.4 ng/mL	1.4 ng/mL

Precision and Accuracy

Five replicate injections of a 5 ng/mL standard solution were made. Precision is defined as the percent coefficient of variation of the calculated concentrations. Accuracy is defined as the percent difference from theoretical of the mean calculated concentration.

	Mean (ng/mL)	S.D.	% C.V.	% Diff.	
Aldicarb Sulfoxide	7.48	0.259	3.5	49.6	
Aldicarb Sulfone	6.32	0.606	9.6	26.4	
Oxamyl	6.68	0.217	3.2	33.6	
Methomyl*	5.50	0.548	10.0	10.0	
3-OH Carbofuran	6.80	0.141	2.1	36.0	
Aldicarb	7.36	0.055	0.7	47.2	
Propoxur	4.90	0.552	11.3	-2.0	
Carbofuran*	3.98	0.299	7.5	-20.5	
Carbaryl	6.26	0.114	1.8	25.2	
Methiocarb	5.70	0.141	2.5	14.0	

*n=4

Figure 1. Background-subtracted full-scan ESI⁺ spectrum of 3-OH Carbofuran





Figure 2. Composite SIR Chromatograms from a 10-component standard mix

Figure 3. Aldicarb calibration curve; 5-1000 ng/mL

Compound 6 name: Aldicarb (m/z 208) Coefficient of Determination: 0.996271Calibration curve: 3635.57 * x + -25066.7Response type: External Std, Area Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



Figure 4. Overlaid SIR chromatograms of Aldicarb (50 pg) and a blank injection

