

Alliance™ HPLC System Performance Enhanced Sensitivity for Monitoring Carbamate Pesticides in Drinking Water

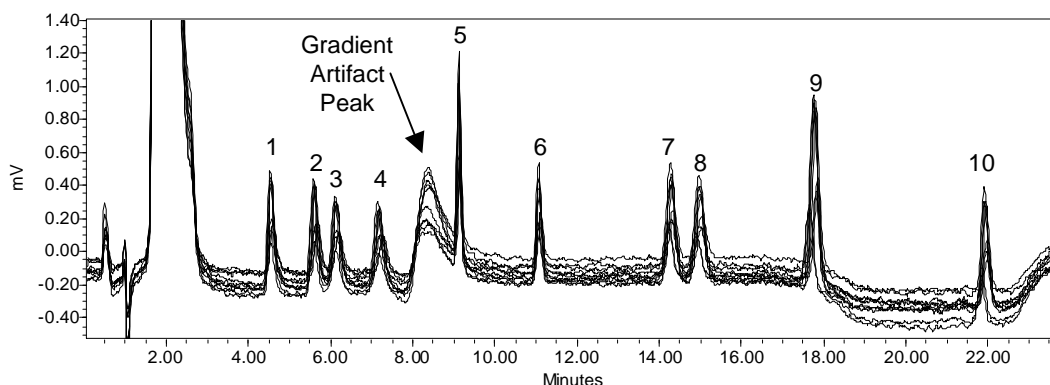
Increased Sensitivity Using Alliance System Sample and Solvent Management:

Carbamates are a class of compounds derived from carbamic acid and frequently used as commercial pesticides. The United States Environmental Protection Agency requires that drinking and raw source water be monitored for the presence of carbamate pesticides and related compounds using established EPA approved methods (EPA Method 531.1). Because the concentration of these substances in real samples may be in the low ppb, detection sensitivity can be significantly affected by the performance of the solvent and sample management system. Previous Waters® Performance PerSPECTives have demonstrated how the technology contained in the Waters Alliance™ HPLC System effectively increases detection sensitivity due to advancements in solvent and sample management (See WPP208 and WPP209). This Performance PerSPECTive will demonstrate the ability of the Alliance HPLC system to exceed the demanding EPA requirements for the analysis of carbamates.

Superior Retention Time Reproducibility of Base-line Resolved Compounds Increases Confidence in Collected Data:

EPA Method 531.1 for carbamate analysis recommends use of a reversed-phase HPLC column with a linear, binary gradient. Detection of the ten target analytes listed in Table 2 is obtained via post-column derivatization with fluorescence detection. The data presented below was collected using the Waters Alliance System for Carbamate Analysis consisting of a 2690 Separations Module, a Waters Post-Column Reagent Delivery System, a Waters Temperature Control System, Waters Carbamate Analysis Column and a Waters 474 Fluorescence Detector. The 2690 Separations Module was controlled by Waters Millennium®32 Chromatography Manager Software. Figure 1 shows the highly reproducible chromatography obtained when carbamate standards, at 0.5 ppb concentrations, are analyzed over several days using a nonlinear, ternary gradient. Note the baseline resolution of all peaks and the excellent retention time reproducibility obtained when this ternary, gradient method is performed on the Alliance System (calculated retention time standard deviation < 0.050 minutes for each peak).

Figure 1: Overlay of 10 Injections of 0.5 ppb Carbamate Standards Collected Over 8 Days



Experimental Conditions:

System: Waters Alliance System for Carbamate Analysis
Sample: Ten carbamate stds (See Table 2) at 0.5 ppb level
Injection: 400 µL
Column: Waters Carbamate Analysis Column (WAT035577) at ambient temperature
Post: OPA/NaOH @ 0.5 mL/min.
Eluents: A= HPLC grade water B= HPLC grade methanol C= HPLC grade acetonitrile
Flow: 1.5 mL/min.
Detector: Excitation Wavelength = 339 nm Emission Wavelength = 445 nm

Time (Min)	INIT	5.3	5.4	14	16.1	20	22	30
Flow (mls)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
% A	88	88	68	68	50	50	88	88
% B	12	12	16	16	25	25	12	12
% C	0	0	16	16	25	25	0	0
Curve		1	5	3	7	6	5	1

Detection at Levels Below EPA Method 531.1 Detection Limit:

Detection of regulated compounds at ever decreasing levels is a challenge faced by many water testing laboratories. The technology contained in the Waters Alliance System for Carbamate Analysis enables the detection of significantly lower levels of carbamates as indicated in Table 2. Compared to traditional HPLC systems that use linear, binary gradients, Waters new technology delivers an optimized ternary gradient which provides shortened analysis time for increased sample throughput and improved resolution of critical pairs, such as propoxur and carbofuran, for enhanced quantitative precision. In addition, the substitution of acetonitrile for methanol as recommended in the Alliance System ternary gradient protocol, **doubles the detection sensitivity for the last six analytes by reducing methanol-induced fluorescence quenching** (Waters Lab Highlights LAH 0435 6/90). As illustrated in Figure 2, superior resolution and detection of carbamates at concentrations < 0.5 ppb is easily accomplished using the described method performed on the Waters Alliance System for Carbamate Analysis.

Figure 2: Overlay of 0.5 ppb and 0.2 ppb Carbamate Standards Compared to Blank Injection

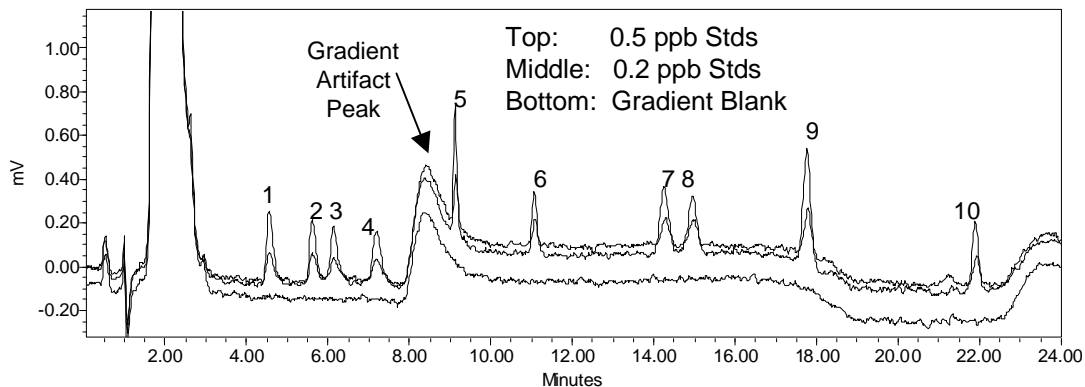


Table 2: EPA Method 531.1 Method Detection Limits Compared to Alliance System for Carbamate Analysis Results

Peak Number / Analyte	EPA Method Detection Limit	Alliance Method Detection Limit *
1) Aldicarb Sulfoxide	2.0 ppb	0.06 ppb
2) Aldicarb Sulfone	2.0 ppb	0.09 ppb
3) Oxamyl	2.0 ppb	0.15 ppb
4) Methomyl	0.5 ppb	0.06 ppb
5) 3-Hydroxycarbofuran	2.0 ppb	0.05 ppb
6) Aldicarb	1.0 ppb	0.09 ppb
7) Propoxur	1.0 ppb	0.12 ppb
8) Carbofuran	1.5 ppb	0.12 ppb
9) Carbaryl	2.0 ppb	0.10 ppb
10) Methiocarb	4.0 ppb	0.16 ppb

*Alliance System detection limits were determined as outlined in the [Environmental Protection Agency Federal Register, 40 CFR Ch.1 \(7-1-92 Edition\) Appendix B to Part 136-Definition and Procedure for the Determination of the Method Detection Limit- Revision 1.11](#). A spike level of 0.5 ppb in Reagent Water (pH 3.0) was used. Calculated data determined from 7 replicates analyzed on 3 separate days.

Summary:

- The exceptional solvent management capabilities of the Waters Alliance HPLC System provide pulse free solvent delivery for decreased flow fluctuation compared to traditional technologies. This generates smoother baselines for improved detection sensitivity and superior retention time reproducibility.
- The use of a ternary gradient method performed on the Alliance System for Carbamate Analysis provides increased sample throughput and improved resolution of critical pairs while also enhancing detection sensitivity and quantitative precision compared to the use of binary gradient HPLC methods for carbamate analysis.

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