

Analytical method for aldicarb, aldicarb sulfone, and aldicarb sulfoxide in water

Reports: ECM: MRID 49515901. Bianca, C. 2014. Method Validation of Aldicarb, Aldicarb Sulfone, and Aldicarb Sulfoxide in Three Water Types: Surface Water; Ground Water; and Drinking Water: Final Report. Project Number: AU/2014/03. Unpublished study prepared by JRF America. 193p.
 ILV: MRID 49515902. Rutt, D.; Budgeon, A. 2014. Independent Laboratory Validation of JRF America Analytical Method AU-269R0 “Analytical Method for Analysis of Aldicarb, Aldicarb Sulfone, and Aldicarb Sulfoxide in Three Water Types: Surface Water, Ground Water, and Drinking Water: Final Report. Project Number: AU/2014/09. Unpublished study prepared by JRF America. 169p.


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Guideline: 850.6100

Statements: The method validations were conducted in compliance with FIFRA GLP or UK GLP standards. Signed and dated No Data Confidentiality Claims, GLP Compliance, Quality Assurance, Certification of Authenticity, and Report Approval statements were provided for the ECM and ILV reports.

Classification: This analytical method is classified as **acceptable**. It was independently validated upon the first attempt.

PC Code: 098301

Primary Reviewer: Edmund Wong
 Environmental Chemist
Signature: 
Date: Jan. 13 2015

Secondary Reviewer: Gregory Orrick
 Environmental Scientist
Signature:
Date: Jan. 13, 2015

Executive Summary

This analytical method, AU-269R0, is designed for the quantitative determination of aldicarb, aldicarb sulfone, and aldicarb sulfoxide in three water types: surface water, ground water, and drinking water using LC-MS/MS (see Table 1). The method is quantitative for the analytes at the stated LOQ of 0.1 µg/L. The ILV was performed in the same laboratory facility that the method was developed; however, the study director, analysts, instruments, and chemicals were distinct from those of the initial validation. The independent laboratory was successful at validating the method. Although several ECM LOD and LOQ recoveries for Aldicarb Sulfone and Aldicarb Sulfoxide were either at baseline noise level or 2x the value, all mean recoveries were within the acceptable range of 70-110% and RSD ≤20% for LOQ and 10xLOQ in the primary and confirmatory analyses. The method is repeatable and reproducible.

Table 1. Analytical Method Summary

Analyte(s) by Pesticide	MRID		EPA Review	Matrix	Method Date	Registrant	Analysis	Limit of Quantitation (LOQ)
	Environmental Chemistry Method	Independent Laboratory Validation						
Aldicarb, Aldicarb Sulfone, & Aldicarb Sulfoxide	49515901	49515902	-	Water	10/15/14	AgLogic LLC	LC-MS/MS	0.1 µg/L

I. Principle of the Method

Fortified surface, ground or drinking water samples (10 mL) were vortexed, centrifuged and then analysed by LC-MS/MS in positive ion mode. The method quantifies residues of aldicarb, aldicarb sulfone, and aldicarb sulfoxide in water at the stated LOQ of 0.1 µg/L, 10xLOQ of 1.0 µg/L, and LOD of 0.05 µg/L. Each analyte were determined in surface, ground, and drinking water with primary and confirmatory analyses.

The ILV was performed in the same laboratory facility that the method was developed. To ensure impartiality and independence, the study director, analysts, instruments, chemicals, analytical standards, *etc.* were “distinct and operated separately and without collusion for the validation portion.” The study director and analysts had no prior experience using the method. One attempt per matrix was performed during the course of the ILV.

II. Recovery Findings

Initial Validation Method Recoveries for Analytes in Surface, Ground, and Drinking Water

Primary analysis mean recoveries and relative standard deviations (RSD) were within guideline requirements (aldicarb mean 102-105%, RSD ≤20%; aldicarb sulfone mean 101-109%, RSD ≤20%; aldicarb sulfoxide mean 103-107%, RSD ≤20%) for LOQ and 10xLOQ samples.

Meanwhile, confirmatory mean recoveries of LOQ and 10xLOQ were 102-105% for aldicarb, 97-107% for aldicarb sulfone, and 102-106% for aldicarb sulfoxide. RSD of all analytes in confirmatory analysis were ≤20%.

Table 2. Initial Validation Method Recoveries for Analytes in Surface Water

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Aldicarb	Primary Transition (m/z 208 → 88.6)					
	0.1 µg/L	7	93.4-110	102	5.9	5.7
	1 µg/L	5	101-108	104	2.6	2.5
	Confirmatory Transition (m/z 208 → 115.7)					
	0.1 µg/L	7	94-110	102	7.1	7.0
	1 µg/L	5	101-107	102.6	2.5	2.4
Aldicarb Sulfone	Primary Transition (m/z 240 → 75.5)					
	0.1 µg/L	7	81.5-115	103	11.3	11
	1 µg/L	5	104-118	108.8	5.4	5.0
	Confirmatory Transition (m/z 240 → 86)					
	0.1 µg/L	7	89.6-116	105	9.0	8.6
	1 µg/L	5	104-109	106.6	1.8	1.7
Aldicarb Sulfoxide	Primary Transition (m/z 207 → 88.5)					
	0.1 µg/L	7	91.7-117	104	9.2	8.9
	1 µg/L	5	105-110	107	2.0	1.9
	Confirmatory Transition (m/z 207 → 68.5)					
	0.1 µg/L	7	85-117	102	10.7	10.5
	1 µg/L	5	104-110	106.2	2.3	2.1

Table 3. Initial Validation Method Recoveries for Analytes in Ground Water

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Aldicarb	Primary Transition (m/z 208 → 88.6)					
	0.1 µg/L	7	102-109	105	2.5	2.4
	1 µg/L	5	103-105	104	0.8	0.8
	Confirmatory Transition (m/z 208 → 115.7)					
	0.1 µg/L	7	101-110	104	3.2	3.1
	1 µg/L	5	101-105	103	1.5	1.4
Aldicarb Sulfone	Primary Transition (m/z 240 → 75.5)					
	0.1 µg/L	7	101-112	107	3.4	3.2
	1 µg/L	5	104-110	107	2.6	2.4
	Confirmatory Transition (m/z 240 → 86)					
	0.1 µg/L	7	87.9-107	98	7.9	8.0
	1 µg/L	5	105-108	106	1.1	1.1
Aldicarb Sulfoxide	Primary Transition (m/z 207 → 88.5)					
	0.1 µg/L	7	101-110	105	3.3	3.2
	1 µg/L	5	101-106	103	2.3	2.2
	Confirmatory Transition (m/z 207 → 68.5)					
	0.1 µg/L	7	90.4-109	102	7.0	6.9
	1 µg/L	5	100-109	104	3.7	3.6

Table 4. Initial Validation Method Recoveries for Analytes in Drinking Water

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Aldicarb	Primary Transition (m/z 208 → 88.6)					
	0.1 µg/L	7	101-108	104	2.6	2.5
	1 µg/L	5	101-109	105	2.9	2.8
	Confirmatory Transition (m/z 208 → 115.7)					
	0.1 µg/L	7	102-109	105	2.4	2.2
	1 µg/L	5	100-106	103	2.6	2.5
Aldicarb Sulfone	Primary Transition (m/z 240 → 75.5)					
	0.1 µg/L	7	93-112	101	6.0	6.0
	1 µg/L	5	98.6-108	102	3.5	3.4
	Confirmatory Transition (m/z 240 → 86)					
	0.1 µg/L	7	85.3-108	97	7.9	8.2
	1 µg/L	5	102-109	106	2.9	2.7
Aldicarb Sulfoxide	Primary Transition (m/z 207 → 88.5)					
	0.1 µg/L	7	97.8-112	106	4.4	4.2
	1 µg/L	5	101-107	104	2.3	2.2
	Confirmatory Transition (m/z 207 → 68.5)					
	0.1 µg/L	7	97.8-113	106	5.4	5.1
	1 µg/L	5	102-110	106	3.3	3.1

Independent Validation Method Recoveries for Analytes in Surface, Ground, and Drinking Water

Primary analysis mean recoveries and relative standard deviations (RSD) were within guideline requirements (aldicarb mean 100-106%, RSD \leq 20%; aldicarb sulfone mean 93.4-106%, RSD \leq 20%; aldicarb sulfoxide mean 93.5-106%, RSD \leq 20%) for LOQ and 10xLOQ samples.

Meanwhile, confirmatory mean recoveries of LOQ and 10xLOQ were 100-106% for aldicarb, 89.4-107% for aldicarb sulfone, and 91-101% for aldicarb sulfoxide. RSD of all analytes in confirmatory analysis were \leq 20%.

Table 5. Independent Validation Method Recoveries for Analytes in Surface Water

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Aldicarb	Primary Transition (m/z 208 \rightarrow 88.6)					
	0.1 μ g/L	5	85.2-110	101	10.5	10.3
	1 μ g/L	5	92.6-107	102	5.8	5.7
	Confirmatory Transition (m/z 208 \rightarrow 115.7)					
	0.1 μ g/L	5	78.4-110	100	12.5	12.5
	1 μ g/L	5	86.8-113	103	10.2	9.9
Aldicarb Sulfone	Primary Transition (m/z 240 \rightarrow 75.5)					
	0.1 μ g/L	5	72.5-104	93.4	12.5	13.4
	1 μ g/L	5	89.7-103	95.9	5.0	5.2
	Confirmatory Transition (m/z 240 \rightarrow 86)					
	0.1 μ g/L	5	82.6-95.9	89.4	5.3	5.9
	1 μ g/L	5	88.2-104	93.7	6.2	6.7
Aldicarb Sulfoxide	Primary Transition (m/z 207 \rightarrow 88.5)					
	0.1 μ g/L	5	92.8-103	96.7	4.1	4.2
	1 μ g/L	5	86.2-97.9	93.5	4.5	4.9
	Confirmatory Transition (m/z 207 \rightarrow 68.5)					
	0.1 μ g/L	5	88.6-101	96.9	5.5	5.7
	1 μ g/L	5	87.1-109	101	8.6	8.5

Table 6. Independent Validation Method Recoveries for Analytes in Ground Water

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Aldicarb	Primary Transition (m/z 208 \rightarrow 88.6)					
	0.1 μ g/L	5	89.1-110	101	8.0	7.9
	1 μ g/L	5	89.7-112	100	8.9	8.9
	Confirmatory Transition (m/z 208 \rightarrow 115.7)					
	0.1 μ g/L	5	97.7-110	103	6.2	6.0
	1 μ g/L	5	96.1-113	106	6.3	5.9
Aldicarb Sulfone	Primary Transition (m/z 240 \rightarrow 75.5)					
	0.1 μ g/L	5	99.4-110	105	4.3	4.1
	1 μ g/L	5	89-104	98.1	6.2	6.3
	Confirmatory Transition (m/z 240 \rightarrow 86)					
	0.1 μ g/L	5	103-110	107	3.1	2.9
	1 μ g/L	5	98.4-109	105	3.9	3.7

Aldicarb Sulfoxide	Primary Transition (m/z 207 → 88.5)					
	0.1 µg/L	5	93.9-107	98.3	5.2	5.3
	1 µg/L	5	93.2-109	100	5.8	5.8
	Confirmatory Transition (m/z 207 → 68.5)					
	0.1 µg/L	5	72.9-107	92.6	13.4	14.5
	1 µg/L	5	77.3-110	91.9	12.2	13.3

Table 7. Independent Validation Method Recoveries for Analytes in Drinking Water

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Aldicarb	Primary Transition (m/z 208 → 88.6)					
	0.1 µg/L	5	98-110	106	5.2	4.9
	1 µg/L	5	90.7-110	102	7.6	7.4
	Confirmatory Transition (m/z 208 → 115.7)					
	0.1 µg/L	5	92.6-110	106	8.4	8.0
	1 µg/L	5	9.31-107	100	5.8	5.8
Aldicarb Sulfone	Primary Transition (m/z 240 → 75.5)					
	0.1 µg/L	5	100-109	106	6.7	6.3
	1 µg/L	5	95.4-110	103	6.9	6.7
	Confirmatory Transition (m/z 240 → 86)					
	0.1 µg/L	5	97.6-108	104	3.9	3.8
	1 µg/L	5	99.4-110	100	6.7	6.7
Aldicarb Sulfoxide	Primary Transition (m/z 207 → 88.5)					
	0.1 µg/L	5	95.1-111	106	6.7	6.3
	1 µg/L	5	96.2-103	102	5.0	4.9
	Confirmatory Transition (m/z 207 → 68.5)					
	0.1 µg/L	5	83-103	91	7.5	8.2
	1 µg/L	5	88.2-113	98.9	11.1	11.2

III. Method Characteristics

The LOD was considered to be a concentration equivalent to 50% of the stated LOQ (0.1 µg/L), which is 0.05 µg/L for aldicarb, aldicarb sulfone, and aldicarb sulfoxide. In some cases, the LOD was lowered to 24% of the LOQ (0.024 µg/L) dependent upon the sensitivity, linear range, and conditions of the LC/MS/MS system. The stated LOQ was determined as the lowest fortification concentration with adequate accuracy (mean recoveries within 70-120%) and precision (RSDs ≤20%).

The LOD and LOQ values were >10x the baseline noise in the control samples for aldicarb in surface, ground, and drinking water. However, the LOD was <1x the baseline noise in drinking water samples for aldicarb sulfone. The LOQ was about 2x baseline noise for surface, ground and drinking water for aldicarb sulfone. For aldicarb sulfoxide, the LOD was 2x the baseline noise in drinking water samples, while the LOQ was >4x baseline noise for surface, ground, and drinking water.

The method was reproducible for all analytes in surface, ground, and drinking water at the stated LOQ of 0.1 µg/L.

Table 4. Method Characteristics

	Aldicarb	Aldicarb Sulfone	Aldicarb Sulfoxide
Limit of Quantitation (LOQ)	0.1 µg/L	0.1 µg/L	0.1 µg/L
Limit of Detection (LOD)	0.05 µg/L	0.05 µg/L	0.05 µg/L
Linearity (calibration curve r^2 and concentration range)	$r^2 = 0.995$ (0.05 – 1.0 µg/L)	$r^2 = 0.995$ (0.05 – 1.0 µg/L)	$r^2 = 0.995$ (0.05 – 1.0 µg/L)
Repeatable	Yes (RSD <20%)	Yes (RSD <20%)	Yes (RSD <20%)
Reproducible	Yes	Yes	Yes
Specific	Yes	Yes	Yes

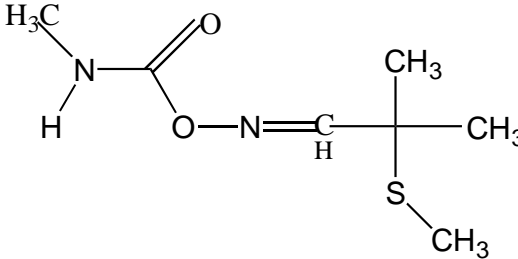
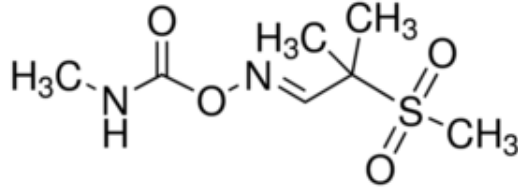
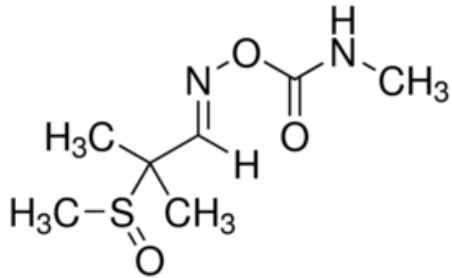
IV. Method Deficiencies and Reviewer's Comments

In the ECM, for aldicarb sulfone, the LOD was at the baseline noise level in drinking water samples, while the LOQ was about 2x baseline noise for surface, ground and drinking water. For aldicarb sulfoxide, the LOD was calculated as 2x the baseline noise in drinking water samples. However, mean recoveries for all analytes (aldicarb, aldicarb sulfone, and aldicarb sulfoxide) were within the acceptable range of 70-120% and RSD ≤20% in surface, ground, and drinking water.

No other major deficiencies with the method were found.

Attachment 1: Chemical Names and Structures

Table 1. Aldicarb, Aldicarb Sulfone, and Aldicarb Sulfoxide. ^A

Code Name/ Synonym	Chemical Name	Chemical Structure
Aldicarb	<p>IUPAC: 2-methyl-2(methylthio)propionaldehyde O-(methylcarbamoyl)oxime</p> <p>CAS No.: 116-06-3</p> <p>Formula: C₇H₁₄N₂O₂S</p> <p>MW: 190.26 g/mol</p> <p>SMILES: C(C)(C)(C=NOC(=O)NC)SC</p>	
Aldicarb Sulfone	<p>IUPAC: [(E)-(2-methyl-2-methylsulfonylpropylidene)amino] N-methylcarbamate</p> <p>CAS No.: 1646-88-4</p> <p>Formula: C₇H₁₄N₂O₄S</p> <p>MW: 222.26 g/mol</p> <p>SMILES: CC(C)(/C=N/OC(=O)NC)S(=O)(=O)C</p>	
Aldicarb Sulfoxide	<p>IUPAC: (E)-(2-methanesulfinyl-2-methylpropylidene)amino N-methylcarbamate</p> <p>CAS No.: 1646-87-3</p> <p>Formula: C₇H₁₄N₂O₃S</p> <p>MW: 206.263 g/mol</p> <p>SMILES: CNC(=O)O\N=C\C(C)(C)S(C)=O</p>	

^A MW means "molecular weight".