Analytical method for dimethoate and omethoate in water

Reports:	**ECM:** The ECM is Appendix 10.3 of the ILV report (see below). Grote, C. and K.G. Schmitt. 2000. Method for Determination of Dimethoate and Omethoate in Water using GC/MS. Method 480/0. Unpublished study performed by BASF Aktiengesellschaft. **ILV:** Grote, C. 2000. Validation of Analytical Method No. 480/0 GC/MS Determination of Dimethoate and Omethoate in Tap Water and Surface Water. Unpublished study performed by BASF Aktiengesellschaft, Limburgerhof, Germany; sponsored by Dimethoate Task Force (DTF), Ingelheim, Germany; and submitted by Cheminova A/S, Lemvig, Denmark. Laboratory Study Code: 58222; Dimethoate Task Force Document No. 525-005.
Document No.:	MRID **46276301**
Guideline:	OCSPP 850.6100
Statements:	The study was conducted per Appendix 1 to § 19a, Section 1, Chemikaliengesetz of 25 July 94 (Official Bulletin/Federal Republic of Germany, 11994, P. 1703) GLP standards (p. 3 of study report). Signed and dated Data Confidentiality, GLP Compliance, Quality Assurance, and Authenticity Certification statements were provided for the ILV (pp. 2-5). The ECM was included as an appendix to the ILV.
Classification:	This analytical method is classified as unacceptable because it is incomplete. No data associated with the ECM was provided. Two distinct data sets should be provided and the ILV should validate the ECM. It appears that one of the primary authors of the ILV is the the author for the ECM. Refer also to **Section IV** for additional comments. Portions of this study submission may be used in the future to support a complete submission to satisfy the ECM/ILV data requirement for dimethoate. However, since the primary author is the same for both the ECM and ILV, one other acceptable evaluation of the method will need to be submitted to completely satisfy the data requirement.
PC Code:	035001

Reviewer:	José L. Meléndez EPA Reviewer	**Signature:** José Luis Meléndez **Date:** June 9, 2014
Final Reviewer:	Gabe Rothman EPA Reviewer	**Signature:** Gabe Rothman **Date:** June 9, 2014

Executive Summary

This analytical Method No. 480/0, GC/MS Determination of Dimethoate and Omethoate in Tap Water and Surface Water, is designed for the quantitative determination of dimethoate and its oxon derivative omethoate in tap and surface water using GC/MS (see **Table 1**). The method is quantitative for dimethoate and omethoate at the stated LOQ of 0.05 µg/L (for both dimethoate and omethoate). The LOQ is lower than the lowest toxicological level of concern in water. It is stated that the ILV was conducted according to the method with no deviations.

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						
Dimethoate	46276301[1]	46276301		Water	12/19/00	Cheminova A/S	GC/MS	0.05 µg/L
Omethoate	46276301[1]	46276301		Water	12/19/00	Cheminova A/S	GC/MS	0.05 µg/L

1 The ECM was appended to the ILV under MRID 46276301 (**Appendix 10.3**).

I. Principle of the Method

A method for the analysis of dimethoate and omethoate in tap and surface waters was described. An aliquot of 500 g of water is extracted using a preconditioned solid phase extraction column (SPE, activated charcoal). Dimethoate and omethoate are eluted from the sorbent using 3x2.5 mL of dichloromethane: methanol (80:20, v/v). The solvent is reduced to about 0.3 mL through evaporation (vacuum rotary evaporation at 30ºC), the flask is rinsed with 3x0.3 mL acetone, transferred to a 2 mL vial, evaporated using a stream of nitrogen at 30ºC, and the test substance is dissolved in acetone (volume depends on the expected concentration). Analysis is conducted by injecting 1 µL into a GC/MS for the analysis for dimethoate and omethoate (pp. 45-47 of study report). A flow chart of the method was provided (p. 49 of the report, **Attachment 2**). No deviations from the technical procedure were reported. Tap water was obtained from from the water pipe in Li 445 Agricultural Center Limburgerhof (wells from Mutterstadt, Schifferstadt and Waldsee, pH 7.46-7.88) and surface water was obtained from a lake in the palatine forest Jsenach-Weiher (pH 6.99, DOC=2.7 mg/L) (Germany). Examples MS graphs, chromatograms and data for the calibration curves were provided (pp. 25-35). The dimethoate and omethoate peaks were separated and distinguishable.

II. Recovery Findings

The study does not provide a full dataset for the ECM. Two distinct sets of data should be submitted. The ILV should fully validate the ECM. According to the ECM, spiked tap water at 0.05 ug/kg (both analytes), gave recoveries of 93 and 109% for dimethoate and 85 and 87% for omethoate (p. 50 of study report).

Table 2. Initial Validation Method Recoveries for Dimethoate and Omethoate in Water[1]

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
[Analyte x]	LOQ	NP	NP	NP	NP	NP
	10x LOQ	NP	NP	NP	NP	NP

1 Not performed. No results were reported in the method (ECM) provided in the **Appendix 10.3**.

For the ILV, several of the recoveries were above the recommended range (70-120%), with the exception of dimethoate in tap water. For omethoate in surface water at 0.5 µg/L, the RSD was not within the recommended range (≤20%).

Table 3. Independent Validation Method Recoveries for Dimethoate and Omethoate in Tap Water

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Dimethoate	0.05 µg/L	5	93.4-118	106.4	9.6	9.0
	0.5 µg/L	5	82.2-103	91.9	8.9	9.7
	5.0 µg/L	5	85.0-99.0	92.0	5.7	6.2
Omethoate	0.05 µg/L	5	101-**126**	112.1	9.4	8.4
	0.5 µg/L	5	73.6-**127**	103.6	19.2	18.6
	5.0 µg/L	5	87.0-102	96.3	5.8	6.0

Refer to the Attachment 3 for data. **Bolded and shaded** values are outside the recommended range of 70-120%.

Table 3. Independent Validation Method Recoveries for Dimethoate and Omethoate in Surface Water

Analyte	Fortification Level (units)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Dimethoate	0.05 µg/L	5	94.3-**129**	109.5	12.6	11.5
	0.5 µg/L	5	82.0-104	91.5	10.2	11.2
	5.0 µg/L	5	81.8-98.9	89.0	7.9	8.8
Omethoate	0.05 µg/L	5	93.2-**132**	114.5	14.7	12.8
	0.5 µg/L	5	70.3-**142**	109.0	26.0	**23.9**
	5.0 µg/L	5	80.4-112	96.6	11.3	11.7

Refer to the Attachment 3 for data. **Bolded and shaded** values are outside the recommended range of 70-120% or ≤20%.

III. Method Characteristics

The limit of detection for both analytes was set at 0.05 ng. It was "defined as the absolute amount of analyte injected into the GC/MS instrument using the lowest standard of the calibration curve." The LOQ is 0.05 µg/kg water for both analytes. This method for LOD/LOQ determination is not considered scientifically acceptable. The linearity was considered satisfactory ($r^2 \geq 0.995$).[1]

[1] This criterion is consistent with Superfund analytical methods for inorganic analytes at http://www.epa.gov/superfund/programs/clp/download/ism/ism1nfg.pdf (accessed June 4, 2014).

Table 4. Method Characteristics

	Dimethoate	Omethoate
Limit of Quantitation (LOQ)	0.05 µg/L	0.05 µg/L
Limit of Detection (LOD)	0.5 ng[1]	0.5 ng[1]
Linearity (calibration curve r^2 and concentration range)	r^2 = 0.9971 0.05-0.70 µg/L	r^2 = 0.9960 0.05-0.70 µg/L
Repeatable	No[2]	No[2]
Reproducible	NP	NP
Specific	Yes	Yes

Data obtained from p. 47 of study report and Attachment 2. NP=Not performed.
1 The limit of detection is defined by the absolute amount of material injected in the GC/MS (p. 21).
2 Several of the recovery values were above 120% and for omethoate in surface water, at 0.5 µg/L, the RSD was above 20%.

IV. Method Deficiencies and Reviewer's Comments

1. In the ECM, the example untreated tap water showed a concentration of 0.059 ppb of dimethoate (*i.e.*, it is apparent that dimethoate was an interference in that sample, p. 55).

2. In the ILV example chromatograms for reagent blanks were not provided; however, matrix blank example chromatograms were provided, showing no interfering peaks. It is stated that the spiked samples were corrected for matrix blank (p. 16 of study report). Elsewhere, it is said that there were no interfering peaks.

3. The LOD and LOQ were not defined by scientifically acceptable methods. Actual detection limits were based on the arbitrarily selected lowest concentration in the spiked samples. LOQ are often calculated as the mean matrix blank value plus 3 times the standard deviation and 10 times the standard deviation, respectively. 40 CFR Part 136, Appendix B lists some scientifically accepted procedures for estimating detection limits.

4. An ILV was not performed and documented in a report separate from the ECM report. A statement was not provided to confirm that the scientists who developed the original ECM differed from those who performed the ILV. The ILV was not independent. One of the authors of the ILV is the author of the ECM. If the laboratory that conducted the validation belonged to the same organization as the originating laboratory, the analysts, study director, equipment, instruments, and supplies of the two laboratories must have been distinct and operated separately and without collusion. The analysts and study director of the ILV must have been unfamiliar with the method both in its development and subsequent use in field studies. This is an issue that renders the ECM/ILV unacceptable.

5. For the ILV, the method recoveries did not meet OCSPP Guideline 850.6100 criteria for precision and accuracy (mean recoveries for replicates at each spiking level between 70% and 120% and RSDs ≤20%) at the stated LOQ and at higher concentrations. Several of the recoveries were above 120% recovered and RSD was above 20% for omethoate in surface water at 0.5 µg/L.

V. References

U.S. Environmental Protection Agency. 2012. Ecological Effects Test Guidelines, OCSPP (formerly OPPTS) 850.6100, Environmental Chemistry Methods and Associated Independent Laboratory Validation. Office of Chemical Safety and Pollution Prevention, Washington, DC. EPA 712-C-001 (January 2012).

U.S. Environmental Protection Agency. 2012. OCSPP Memorandum from D. Brady: Environmental Chemistry Method Guidance, December 20, 2012. Office of Chemical Safety and Pollution Prevention, Office of Pesticide Programs, Environmental Fate and Effects Division. Washington, DC.

Attachment 1: Chemical Names and Structures

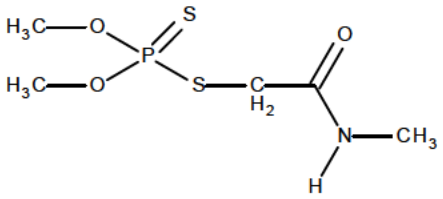
Dimethoate

IUPAC Name: O,O-Dimethyl S-methylcarbamoylmethyl phosphorodithioate

CAS Name: O,O-Dimethyl S-[2-(methylamino)-2-oxoethyl]phosphorodithioate

CAS Number: 60-51-5

SMILES String: O=C(NC)CSP(OC)(OC)=S



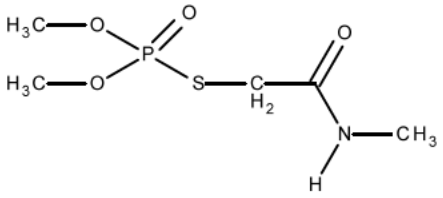
Omethoate

IUPAC Name: O,O Dimethyl S-[2-methylamino)-2-oxoethyl]phosphorothioate

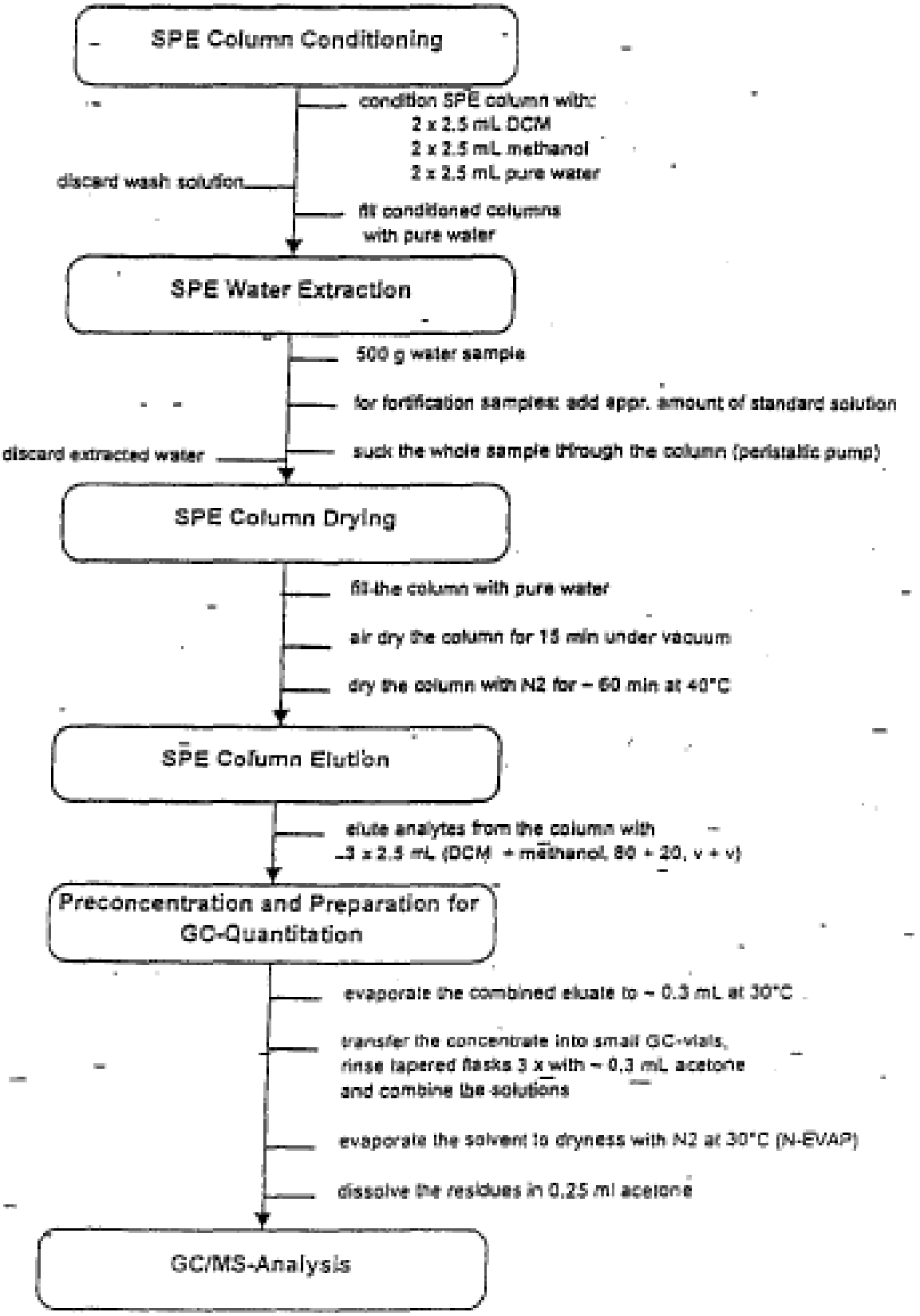
CAS Name: *O,O*-dimethyl *S*-[2-(methylamino)-2-oxoethyl] phosphorothioate

CAS Number: 1113-02-6

SMILES String: CNC(=O)CSP(=O)(OC)OC



Attachment 2: Flow Chart (from study report, p. 49)



Attachment 3: Calculations

Chemical: Dimethoate
PC Code: 035001
MRID: 46276301
Guideline: 850.6100

Environmental Chemistry Method/Independent Laboratory Validation

Recoveries of Dimethoate at Three Fortification Levels

	Tap Water			Surface Water		
Fortific.	0.05	0.5	5.0	0.05	0.5	5.0
Analyte	0.025	0.25	2.5	0.025	0.25	2.5
Added	0.025	0.25	2.5	0.025	0.25	2.5
(µg)	0.025	0.25	2.5	0.025	0.25	2.5
	0.025	0.25	2.5	0.025	0.25	2.5
	0.025	0.25	2.5	0.025	0.25	2.5
Analyte	0.02334	0.2471	2.417	0.02848	0.2558	2.561
Found	0.02520	0.2135	2.237	0.02525	0.2713	2.487
(µg)	0.02701	0.2055	2.124	0.02687	0.3176	2.416
	0.02789	0.2248	2.475	0.03159	0.1841	2.398
	0.02955	0.2581	2.244	0.02790	0.2662	2.174
Recover.	93.36	98.84	96.68	113.92	102.32	102.44
(%)	100.80	85.40	89.48	101.00	108.52	99.48
	108.04	82.20	84.96	107.48	**127.04**	96.64
	111.56	89.92	99.00	**126.36**	73.64	95.92
	118.20	103.24	89.76	111.60	106.48	86.96
Average	106.4	91.9	92.0	112.1	103.6	96.3
Std. Dev.	9.6	8.9	5.7	9.4	19.2	5.8
RSD	9.0	9.7	6.2	8.4	18.6	6.0
Max.	118	103	99.0	**126**	**127**	102
Min.	93.4	82.2	85.0	101	73.6	87.0

Overall Average	100.4	Overall max.	**127**
Std. Dev.	12.5	Overall min.	73.6
RSD	12.4		

Registrant-reported values were rounded to four significant figures in the report.
Data were obtained from pp. 17 and 19 of study report.
Bolded and shaded values are outside the recommended values (70-120%).

Chemical: Dimethoate
PC Code: 035001
MRID: 46276301
Guideline: 850.6100

Environmental Chemistry Method/Independent Laboratory Validation

Recoveries of Omethoate at Three Fortification Levels

	Tap Water			Surface Water		
Fortific.	0.05	0.5	5.0	0.05	0.5	5.0
Analyte	0.025	0.25	2.5	0.025	0.25	2.5
Added	0.025	0.25	2.5	0.025	0.25	2.5
(µg)	0.025	0.25	2.5	0.025	0.25	2.5
	0.025	0.25	2.5	0.025	0.25	2.5
	0.025	0.25	2.5	0.025	0.25	2.5
Analyte	0.02358	0.2510	2.473	0.02330	0.2574	2.797
Found	0.02663	0.2059	2.044	0.02696	0.2933	2.502
(µg)	0.02703	0.2051	2.049	0.03015	0.3552	2.363
	0.02726	0.2210	2.388	0.03304	0.1758	2.398
	0.03235	0.2602	2.170	0.02964	0.2814	2.010
Recover.	94.32	100.40	98.92	93.20	102.96	111.88
(%)	106.52	82.36	81.76	107.84	117.32	100.08
	108.12	82.04	81.96	**120.60**	**142.08**	94.52
	109.04	88.40	95.52	**132.16**	70.32	95.92
	129.40	104.08	86.80	118.56	112.56	80.40
Average	109.5	91.5	89.0	114.5	109.0	96.6
Std. Dev.	12.6	10.2	7.9	14.7	26.0	11.3
RSD	11.5	11.2	8.8	12.8	**23.9**	11.7
Max.	**129**	104	98.9	**132**	**142**	112
Min.	94.3	82.0	81.8	93.2	70.3	80.4

Overall Average	101.7	Overall max.	**142**
Std. Dev.	16.9	Overall min.	70.3
RSD	16.6		

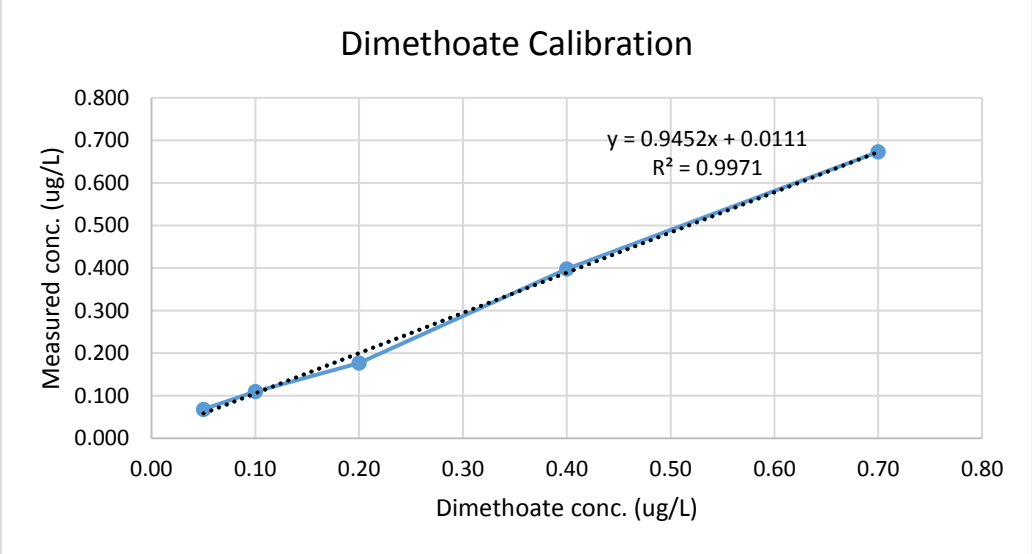
Registrant-reported values were rounded to four significant figures in the report.
Data were obtained from pp. 18 and 20 of study report.
Bolded and shaded values are outside the recommended values (70-120%).
Redline and shaded value is outside the recommended range (≤20%).

Chemical: Dimethoate
PC Code: 035001
MRID: 46276301
Guideline: 850.6100

Environmental Chemistry Method/Independent Laboratory Validation

Dimethoate Calibration

Dimethoate conc. (µg/L)	Measured conc. (µg/L)
0.05	0.068
0.10	0.110
0.20	0.177
0.40	0.398
0.70	0.673
Slope	0.945
R^2	0.9971



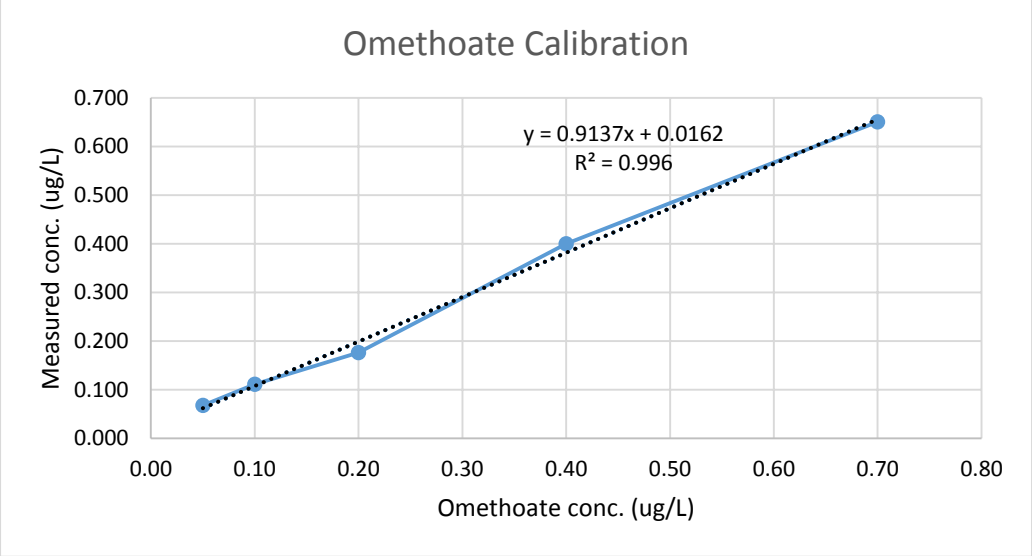
Data were taken from pp. 27-31 of study report.

Chemical: Dimethoate
PC Code: 035001
MRID: 46276301
Guideline: 850.6100

Environmental Chemistry Method/Independent Laboratory Validation

Omethoate Calibration

Omethoate conc. (µg/L)	Measured conc. (µg/L)
0.05	0.068
0.10	0.111
0.20	0.176
0.40	0.400
0.70	0.651
Slope	0.914
R^2	0.9960



Data were taken from pp. 27-31 of study report.