

**Analytical method for mancozeb in surface and drinking water matrices**

**Reports:** ECM: EPA MRID No.: MRID 50452901. Budgeon, Jr., A.D. 2017. Method Validation for Analysis of Mancozeb in Surface and Drinking Waters. Analytical Method No.: JRFA AU-274R0. Laboratory Project ID AU-2017-07. Report prepared by JRF America, Inc., Audubon, Pennsylvania; and sponsored and submitted by Mancozeb Task Force, c/o McDermott, Will and Emery, Washington, D.C.; 169 pages (including 2 blank, non-numerated pages). Final report issued September 25, 2017.

ILV: EPA MRID Nos. 50774406/50661201. Khanvilkar, T, 2018. Independent Laboratory Validation of an Analytical Method for the Determination of Mancozeb in Surface and Drinking Water by LC-MS/MS Analysis. Laboratory Project ID: JRF Study No. 228-2-14-18969. Report prepared by Jai Research Foundation, Gujarat, India; and sponsored and submitted by Mancozeb Task Force, c/o McDermott, Will and Emery, Washington, D.C.; 56 pages. Final report issued July 31, 2018.

**Document No.:** MRIDs 50452901 & 50774406 & 50661201 (a reprint of 50774406)

**Guideline:** 850.6100


**Statements:** ECM: The study was conducted in accordance with the USEPA FIFRA Good Laboratory Practice (GLP) standards (40 CFR Part 160; p. 3 of MRID 50452901). Signed and dated No Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4). The authenticity statement was included with the Quality Assurance statement (p. 4).

ILV: The study was conducted in accordance with OECD and Indian GLP standards, which are considered to be comparable to EPA FIFRA GLP standards (p. 3; Appendix 6, pp. 55-56 of MRID 50774406). Signed and dated No Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4; Appendix 6, pp. 55-56). The authenticity statement was included with the Quality Assurance statement (p. 4).

**Classification:** This analytical method is classified as supplemental. The specificity of the method was not supported by ILV representative chromatograms. Communications between the ILV and ECM/Study Monitor were not detailed in the ILV. The number of trials required to validate the method was not reported. The LOD was not reported in the ILV.

**PC Code:** 014504

**EFED Final Reviewer:** Mohammed Ruhman, Ph.D.,  
Senior Scientist

Signature: 

Date: 06/15/2020

Lisa Muto, M.S.,  
Environmental Scientist

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Date: 01/31/2019

**CDM/CSS-Dynamac JV Reviewers:**

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Environmental Scientist

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Date: 01/31/2019

*This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel. The CDM/CSS-Dynamac Joint Venture role does not include establishing Agency policies.*

## Executive Summary

The analytical methods, JRFA Analytical Method No. AU-274R0, is designed for the quantitative determination of mancozeb in surface and drinking water at the LOQ of 0.1 µg/L using LC/MS/MS. The LOQ is less than the lowest toxicological level of concern in water for each analyte. Due to the hydrolytic instability of mancozeb, mancozeb was methylate and quantified as dimethyl-EBDC. The ECM and ILV validated the method using characterized surface and drinking water matrices. The number of ILV trials required to validate the method was not reported; however, the reviewer assumed that the method was validated for water in the first trial with insignificant modifications to the analytical instrumentation and parameters. Communications between the ILV (JRFI) and ECM (JRFA) were not detailed. All ILV and ECM data was satisfactory regarding accuracy, precision, reproducibility and linearity for both analytes at the LOQ and 10×LOQ. The specificity of the method was not supported by ILV representative chromatograms since chromatograms were provided without fortification labels; ECM representative chromatograms were satisfactory.

**Table 1. Analytical Method Summary**

Analyte(s) by Pesticide	MRID		EPA Review	Matrix	Method Date (dd/mm/yyyy)	Registrant	Analysis	Limit of Quantitation (LOQ)
	Environmental Chemistry Method	Independent Laboratory Validation						
Mancozeb	50452901 <sup>1</sup>	50774406 <sup>2</sup> & 50661201 <sup>3</sup>		Water	25/09/2017	Mancozeb Task Force, c/o McDermott, Will and Emery	LC/MS/MS	0.1 µg/L

1 In the ECM, the surface water (Sample ID 202302; pH 7.6; 147 mg/L as CaCO<sub>3</sub> hardness; 484 ppm total dissolved solids) obtained from Skippack Creek in Collegeville, Pennsylvania (coordinates 40.150077, -75.447406) and drinking water (Sample ID 25791 Drinking Water; pH 6.2; <1 mg/L as CaCO<sub>3</sub> hardness; 1.0 ppm total organic carbon; 66 ppm total dissolved solids), Aquafina bottled water, were used in the study (pp. 15-16; Appendix VIII, pp. 162-163 of MRID 50452901). The water samples were characterized by Agvise Laboratories, Northwood, North Dakota.

2 In the ILV, the surface water (pH 8.19; 122 mg/L as CaCO<sub>3</sub> hardness; <1.0 ppm total organic carbon) obtained from the Daman Ganga River near N.H. No. 8 (near Jai Research Foundation, Gujarat, India) and drinking water (pH 7.37; 12 mg/L as CaCO<sub>3</sub> hardness; 8.849 ppm total organic carbon) obtained from Jai Research Foundation, Gujarat, India were used in the study (p. 12 of MRID 50774406). The water samples were characterized by Jai Research Foundation, Gujarat, India, under JRF S. N°: RES-2-14-19682.

3 MRID 50661201 was also submitted; however, MRID 50661201 was a reprint of MRID 50774406.

**Citations for MRID 50774406 also refer to citations in MRID 50661201, since MRID 50661201 was a reprint of MRID 50774406.**

## **I. Principle of the Method**

Fortification solutions (1000 and 10 µg/L) were prepared for mancozeb in isopropanol:water (1:1, v:v) and dimethyl-ethylenebisdithiocarbamate (dimethyl-EBDC) in acetonitrile (p. 18 of MRID 50452901). Calibrations solutions of dimethyl-EBDC (0.05-2.50 µg/L) were prepared in matrix for analyte quantification (pp. 18-19).

Water samples (5.00 mL) were fortified and mixed with 0.25 mL of 2.0mM EDTA/ 10mM ammonium formate solution via vortex for 45 seconds (p. 19; Appendix II, Figure 56, p. 90 of MRID 50452901). The pH was adjusted to 8-10, if necessary. The samples were methylated by adding 10 µL of dimethyl sulfate and 10 µL of iodomethane. Samples were mixed via vortex for 45 seconds and then refluxed for 1 hour at 50-60°C in a heating block. Samples were cooled and filtered (0.45 µm). Samples were diluted with untreated control, if necessary, and then vialled for LC/MS/MS analysis.

The method cautioned that mancozeb samples should be analyzed as soon as possible after extraction due to degradation of mancozeb (Appendix VII, p. 125 of MRID 50452901).

Samples were analyzed using an Agilent 1290 series HPLC coupled to a Sciex API 6500 Q Trap mass spectrometer (pp. 20-21 of MRID 50452901). The LC/MS conditions consisted of a Kinetex Phenomenex C18 column (100 x 2.1 mm, 1.7 µm particle size; oven temperature ambient) with a mobile phase gradient of A) 5mM ammonium formate with 0.1% formic acid in HPLC-grade water and B) 0.1% formic acid in HPLC-grade methanol [percent A:B (v:v) at 0.00-1.00 min. 90:10, 2.00 min. 50:50, 3.00-5.5.0 min. 10:90, 6.00-8.00 min. 90:10] and ESI ionization MS detection in positive ion mode with MRM (TEM 520°C). Injection volume was 8 µL for mancozeb (as dimethyl-EBDC). Two ion transitions were monitored as follows (quantitative and confirmatory, respectively):  $m/z$  240.870→133.900 and  $m/z$  240.922→193.000 for mancozeb (as dimethyl-EBDC). Retention time was *ca.* 3.20 minutes (as dimethyl-EBDC; p. 19).

The ILV performed Analytical Method No. AU-274R0 as written, except for the insignificant modifications to the LC/MS/MS instrument and monitored MS transitions (pp. 13-18 of MRID 50774406). Samples were analyzed using a Shimadzu Nexera X2 coupled with a Qtrap 6500 MS. All LC/MS parameters were the same as the ECM, except for adjustments to the monitored MS transitions. Two ion transitions were monitored as follows (quantitative and confirmatory, respectively):  $m/z$  241.1→134.1 and  $m/z$  241.1→193.2 for mancozeb (as dimethyl-EBDC). Retention time was *ca.* 3.10 minutes for mancozeb (as dimethyl-EBDC; Appendix I, p. 36). A different LC column and mobile phase gradient was reported for the characterization of dimethyl-EBDC reference standard.

In the ECM and ILV, Limit of Quantification (LOQ) in water was 0.1 µg/L for mancozeb (pp. 13-14 of MRID 50452901; Tables 5-8, pp. 25-28 of MRID 50774406). In the ECM, the Limit of Detection (LOD) for water was calculated as 0.0193 µg/L for drinking water and 0.0132 µg/L for surface water. The LOD was not reported in the ILV.

## II. Recovery Findings

ECM (MRID 50452901): Mean recoveries and relative standard deviations (RSD) were within guideline requirements (mean 70-120%; RSD  $\leq$ 20%) for analysis of mancozeb in two water matrices at fortification levels of 0.1  $\mu\text{g/L}$  (LOQ) and 1.0  $\mu\text{g/L}$  (10 $\times$ LOQ; Appendix I, Tables 1-5, pp. 26-30). Analytes were identified and quantified using two ion transitions; performance data was comparable between the primary and confirmatory analyses. The surface water (Sample ID 202302; pH 7.6; 147 mg/L as  $\text{CaCO}_3$  hardness; 484 ppm total dissolved solids) obtained from Skippack Creek in Collegeville, Pennsylvania (coordinates 40.150077, -75.447406) and drinking water (Sample ID 25791 Drinking Water; pH 6.2;  $<1$  mg/L as  $\text{CaCO}_3$  hardness; 1.0 ppm total organic carbon; 66 ppm total dissolved solids), Aquafina bottled water, were used in the study (pp. 15-16; Appendix VIII, pp. 162-163). The water samples were characterized by Agvise Laboratories, Northwood, North Dakota.

ILV (MRID 50774406): Mean recoveries and RSDs were within guidelines for analysis of mancozeb in two water matrices at fortification levels of 0.1  $\mu\text{g/L}$  (LOQ) and 1.0  $\mu\text{g/L}$  (10 $\times$ LOQ; Tables 5-8, pp. 25-28). Analytes were identified and quantified using two ion transitions; performance data was comparable between the primary and confirmatory analyses. The surface water (pH 8.19; 122 mg/L as  $\text{CaCO}_3$  hardness;  $<1.0$  ppm total organic carbon) obtained from the Daman Ganga River near N.H. No. 8 (near Jai Research Foundation, Gujarat, India) and drinking water (pH 7.37; 12 mg/L as  $\text{CaCO}_3$  hardness; 8.849 ppm total organic carbon) obtained from Jai Research Foundation, Gujarat, India were used in the study (p. 12). The water samples were characterized by Jai Research Foundation, Gujarat, India, under JRF S. N $^{\circ}$ : RES-2-14-19682. The number of trials required to validate the method was not reported; however, the reviewer assumed that the method was validated for water in the first trial with insignificant modifications to the analytical instrumentation and parameters (pp. 8, 13-18).

**Table 2. Initial Validation Method Recoveries for Mancozeb in Water<sup>1,2</sup>**

Analyte	Fortification Level (µg/L)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
<b>Drinking Water</b>						
Quantitation ion transition						
Mancozeb	0.1 (LOQ)	7	69.3-86.4	79.4	6.14	7.7
	1.0	5	82.6-85.2	83.6	1.06	1.3
Confirmation ion transition						
Mancozeb	0.1 (LOQ)	7	71.0-78.8	75.7	3.12	4.1
	1.0	5	81.8-87.6	84.6	2.70	3.2
<b>Surface Water</b>						
Quantitation ion transition						
Mancozeb	0.1 (LOQ)	7	84.7-97.6	91.1	4.21	4.6
	1.0	5	73.7-75.7	74.6	0.87	1.2
Confirmation ion transition						
Mancozeb	0.1 (LOQ)	7	87.2-103	93.4	5.75	6.2
	1.0	5	72.0-77.0	74.5	1.85	2.5

Data (uncorrected recovery results; pp. 21-23; Appendix I, Tables 2-5, pp. 27-30) were obtained from Appendix I, Tables 1-5, p. 26-30 of MRID 50452901.

1 The surface water (Sample ID 202302; pH 7.6; 147 mg/L as CaCO<sub>3</sub> hardness; 484 ppm total dissolved solids) obtained from Skippack Creek in Collegeville, Pennsylvania (coordinates 40.150077, -75.447406) and drinking water (Sample ID 25791 Drinking Water; pH 6.2; <1 mg/L as CaCO<sub>3</sub> hardness; 1.0 ppm total organic carbon; 66 ppm total dissolved solids), Aquafina bottled water, were used in the study (pp. 15-16; Appendix VIII, pp. 162-163). The water samples were characterized by Agvise Laboratories, Northwood, North Dakota.

2 Two ion transitions were monitored for each analyte as follows (quantitative and confirmatory, respectively): *m/z* 240.870→133.900 and *m/z* 240.922→193.000 for mancozeb (as dimethyl-EBDC).

**Table 3. Independent Validation Method Recoveries for Mancozeb in Water<sup>1,2</sup>**

Analyte	Fortification Level (µg/L)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%) <sup>3</sup>	Relative Standard Deviation (%) <sup>4</sup>
<b>Drinking Water</b>						
Quantitation ion transition						
Mancozeb	0.1 (LOQ)	7	78.00-92.00	81.57	5.41	6.10
	1.0	5	91.10-99.60	96.36	3.28	3.42
Confirmation ion transition						
Mancozeb	0.1 (LOQ)	7	94.00-104.00	97.29	3.25	3.09
	1.0	5	96.60-99.50	98.60	1.14	1.12
<b>Surface Water</b>						
Quantitation ion transition						
Mancozeb	0.1 (LOQ)	7	85.00-101.00	94.00	4.93	5.32
	1.0	5	85.10-105.70	98.02	7.79	7.96
Confirmation ion transition						
Mancozeb	0.1 (LOQ)	7	97.00-109.00	103.29	3.59	3.88
	1.0	5	83.90-102.80	97.20	7.66	7.92

Data (uncorrected recovery results; p. 16) were obtained from Tables 5-8, pp. 25-28 of MRID 50774406 and DER Attachment 2.

- 1 The surface water (pH 8.19; 122 mg/L as CaCO<sub>3</sub> hardness; <1.0 ppm total organic carbon) obtained from the Daman Ganga River near N.H. No. 8 (near Jai Research Foundation, Gujarat, India) and drinking water (pH 7.37; 12 mg/L as CaCO<sub>3</sub> hardness; 8.849 ppm total organic carbon) obtained from Jai Research Foundation, Gujarat, India were used in the study (p. 12). The water samples were characterized by Jai Research Foundation, Gujarat, India, under JRF S. N°: RES-2-14-19682.
- 2 Two ion transitions were monitored for each analyte as follows (quantitative and confirmatory, respectively): *m/z* 241.1→134.1 and *m/z* 241.1→193.2 for mancozeb (as dimethyl-EBDC). These were similar to those of the ECM.
- 3 Standard deviations were reviewer-calculated since they were reported in units of concentration, not % applied. Rules of significant figures were followed.
- 4 RSD values were reported from the study report. Reviewer-generated RSDs varied from those reported in the study report; differences were assumed to be due to calculation methods.

### III. Method Characteristics

In the ECM and ILV, LOQ in water was 0.1 µg/L for mancozeb (pp. 13-14, 23 of MRID 50452901; Tables 5-8, pp. 25-28 of MRID 50774406). In the ECM, the LOQ was defined as the lowest analyte concentration in a sample at which the methodology has been validated (Appendix VII, p. 127 of MRID 50452901). Generally, for accurate quantitation, the response for an analyte peak should be no lower than four times the mean amplitude of the background noise in an untreated sample at the corresponding retention time. No LOQ calculations or justifications were reported ILV. In the ECM, the LOD was defined as the lowest analyte concentration detectable above the mean amplitude of the background noise in an untreated sample at the corresponding retention time. The LOD was also calculated from the data of the seven LOQ recovery samples, as described in "Assigning Values to Non-detected/Non-quantified Pesticide Residues in Human Health Food Exposure Assessments, Item 6047, U.S. EPA, March 23, 2000" (p. 13). The following equations were used (p. 23):

$$\text{LOD} = \text{Stdev}(\text{LOQ R1: LOQ R7}) \times t_{0.99}$$

The standard deviation is calculated using the following equation:

$$\text{Stdev}(\text{LOQ R1: LOQ R7}) = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$$

Where, Stdev is the sample standard deviation of the calculated concentrations of the seven LOQ samples; n is number of samples, and  $\bar{x}$  is the average calculated concentration; and  $t_{0.99}$  is the one-tailed t-statistic at the 99% confidence level for n-1 replicates and is equal to 3.143 for n=7 samples.

The calculated LODs were 0.0193 µg/L for drinking water and 0.0132 µg/L for surface water (pp. 13-14 of MRID 50452901). The LOD was not reported in the ILV.



**Table 4. Method Characteristics for Mancozeb in Water**

Analyte		Mancozeb (as dimethyl-EBDC)	
		Drinking Water	Surface Water
Limit of Quantitation (LOQ)		0.1 µg/L	
Limit of Detection (LOD)	ECM (calc)	0.0193 µg/L	0.0132 µg/L
	ILV	<b>Not reported</b>	
Linearity (calibration curve r and concentration range)	ECM	r = 0.99688248874 (Q) r = 0.99734175847 (C)	r = 0.99860608270 (Q) r = 0.99820878155 (C)
		0.050-2.5 ng/mL	
	ILV	r = 0.9975 (Q) r = 0.9994 (C)	r = 0.9978 (Q) r = 0.9984 (C)
		0.050-2.479 ng/mL	
Repeatable	ECM <sup>1</sup>	Yes at LOQ and 10×LOQ (two characterized water matrices)	
	ILV <sup>2,3</sup>		
Reproducible		Yes at LOQ and 10×LOQ	
Specific	ECM	Yes, matrix interferences were <5% of the LOQ (based on peak area). Baseline noise interference with LOQ integration and attenuation. A minor contaminant (RT <i>ca.</i> 3.39) was noted in Q chromatograms.	
	ILV	<b>Could not be determined.</b> <sup>4</sup> Matrix interferences appeared insignificant, and analyte peaks were well-defined; however, only one representative chromatogram without a fortification label was provided for each water matrix.	

Data were obtained from pp. 13-14, 23 (LOQ/LOD); Appendix I, Tables 1-5, pp. 26-30 (recovery results); Appendix II, Figure 1, p. 36; Appendix II, Figure 27, p. 62 (calibration coefficients); Appendix II, Figures 2-52, pp. 37-87 (chromatograms) of MRID 50452901; Tables 5-8, pp. 25-28 (LOQ and recovery results); p. 8; Tables 1-4, pp. 21-24 (calibration coefficients); Appendix I, pp. 30-39 (chromatograms) of MRID 50774406; DER Attachment 2.

1 In the ECM, the surface water (Sample ID 202302; pH 7.6; 147 mg/L as CaCO<sub>3</sub> hardness; 484 ppm total dissolved solids) obtained from Skippack Creek in Collegeville, Pennsylvania (coordinates 40.150077, -75.447406) and drinking water (Sample ID 25791 Drinking Water; pH 6.2; <1 mg/L as CaCO<sub>3</sub> hardness; 1.0 ppm total organic carbon; 66 ppm total dissolved solids), Aquafina bottled water, were used in the study (pp. 15-16; Appendix VIII, pp. 162-163 of MRID 50452901). The water samples were characterized by Agvise Laboratories, Northwood, North Dakota.

2 In the ILV, the surface water (pH 8.19; 122 mg/L as CaCO<sub>3</sub> hardness; <1.0 ppm total organic carbon) obtained from the Daman Ganga River near N.H. No. 8 (near Jai Research Foundation, Gujarat, India) and drinking water (pH 7.37; 12 mg/L as CaCO<sub>3</sub> hardness; 8.849 ppm total organic carbon) obtained from Jai Research Foundation, Gujarat, India were used in the study (p. 12 of MRID 50774406). The water samples were characterized by Jai Research Foundation, Gujarat, India, under JRF S. No: RES-2-14-19682.

3 The number of ILV trials required to validate the method was not reported; however, the reviewer assumed that the method was validated for water in the first trial with insignificant modifications to the analytical instrumentation and parameters (pp. 8, 13-18 of MRID 50774406).

4 Based on Appendix I, pp. 30-35, 38-39 of MRID 50774406.

#### IV. Method Deficiencies and Reviewer's Comments

1. The specificity of the method was not supported for mancozeb based on ILV representative chromatograms. Matrix interferences appeared insignificant, and analyte peaks were well-defined; however, only one representative chromatogram without a fortification label was provided for each water matrix (Appendix I, pp. 30-35, 38-39 of MRID 50774406). The representative chromatograms consisted of a quantitation and confirmation chromatogram of "extracted" mancozeb for each water matrix.
2. The communications between the ILV (Jai Research Foundation, Gujarat, India) and ECM (JRF America, Inc.) were not reported, summarized, or detailed in the ILV (pp. 8-9 of MRID 50774406). Communication should be provided to demonstrate that no collusion occurred between the ECM and ILV. The reviewer also believed that communications between the Study Director and Sponsor Monitor during validation should have been provided since both laboratories were part of Jai Research Foundation (JRF).
3. The number of ILV trials required to validate the method was not reported; however, the reviewer assumed that the method was validated for water in the first trial with insignificant modifications to the LC/MS/MS instrument and monitored MS transitions (pp. 8, 13-18 of MRID 50774406).
4. The reviewer noted that the analytical method (Budgeon, Jr., A.D. and A. Li. 2017. Analytical Method for the Determination of Mancozeb and ETU in Water. JRFA Method No.: AU-274R0. Report prepared by JRF America, Inc., Audubon, Pennsylvania; and sponsored by Mancozeb Task Force, c/o McDermott, Will and Emery, Washington, D.C.; 50 pages. Final report issued September 5, 2017) provided in Appendix VII, pp. 112-161, of the ECM MRID 50452901 contained the same recovery data as the main ECM report. Some additional justifications for the LOQ and LOD were found in this second ECM.
5. The ECM reported that mancozeb is a very unstable compound; when ionized by an ion-spray in high voltage, it provides poor reproducibility (p. 14 of MRID 50452901). Hence, it is required to transform the analyte into its methylated form, dimethyl ethylene bisdithiocarbamate (EBDC), for improved solubility, stability, and instrument sensitivity.
6. In the ECM, the mancozeb LOQ and 10×LOQ final water extracts were not stable after *ca.* one week of storage (storage conditions were not reported; pp. 20, 24; Appendix I, Tables 6-9, pp. 31-34 of MRID 50452901). The stock and fortification solutions were considered stable for up to 3 months. Dimethyl-EBDC stock solutions were considered stable for up to 6 months (p. 18 of MRID 50452901). Mancozeb stock and fortification solutions were to be stored in a freezer (*ca.* -20°C); EBDC stock and standard solutions were to be stored in a refrigerator (*ca.* 4°C).
7. Although matrix effects were studied in the ECM and determined to be insignificant (<20%) for both water matrices, matrix-matched standards were used per SANCO guidelines (p. 25; Appendix I, Table 10, p. 35 of MRID 50452901).

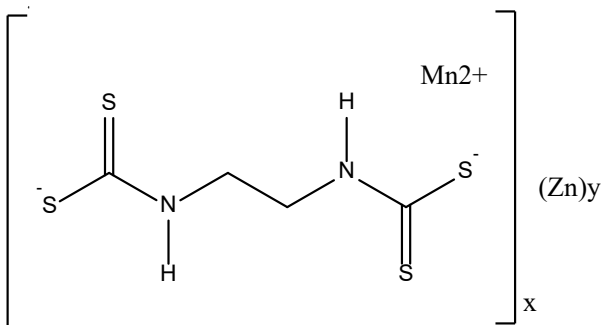
8. The estimations of the LOQ and LOD in ECM and ILV were not based on scientifically acceptable procedures as defined in 40 CFR Part 136 pp. 13-14, 23 of MRID 50452901; Tables 5-8, pp. 25-28 of MRID 50774406). In the ECM, the LOQ was defined as the lowest analyte concentration in a sample at which the methodology has been validated (Appendix VII, p. 127 of MRID 50452901). Generally, for accurate quantitation, the response for an analyte peak should be no lower than four times the mean amplitude of the background noise in an untreated sample at the corresponding retention time. No LOQ calculations or justifications were reported ILV. In the ECM, the LOD was defined as the lowest analyte concentration detectable above the mean amplitude of the background noise in an untreated sample at the corresponding retention time. The LOD was also calculated from the data of the seven LOQ recovery samples, as described in "Assigning Values to Non-detected/Non-quantified Pesticide Residues in Human Health Food Exposure Assessments, Item 6047, U.S. EPA, March 23, 2000" (p. 13). The following equations were used (p. 23):  $LOD = Stdev (LOQ R1: LOQ R7) \times t_{0.99}$ . See above for equation definitions. The LOD was not reported in the ILV. No calculations were reported to justify the LOQ for the method in the ECM and ILV. Detection limits should not be based on arbitrary values.
9. The time required to complete the method for a validation set of 15 samples was reported as 8 working hours for one chemist in the ECM (Appendix VII, p. 123 of MRID 50452901). This included the instrument analysis and data processing. The time required to complete the method for a validation set was not reported in the ILV.

## V. References

- U.S. Environmental Protection Agency. 2012. Ecological Effects Test Guidelines, OCSPP 850.6100, Environmental Chemistry Methods and Associated Independent Laboratory Validation. Office of Chemical Safety and Pollution Prevention, Washington, DC. EPA 712-C-001.
- 40 CFR Part 136. Appendix B. Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11, pp. 317-319.

**Attachment 1: Chemical Names and Structures****Mancozeb**

**IUPAC Name:** Zinc Manganese ethylenebis(dithiocarbamate)  
**CAS Name:** [[2-[(Dithiocarboxy)amino]ethyl]carbamdithioato(2-)- $\kappa S, \kappa S'$ ]manganese mixture with [[2-[(dithiocarboxy)amino]ethyl]carbamdithioato(2-)- $\kappa S, \kappa S'$ ]zinc  
**CAS Number:** 8018-01-7  
**SMILES String:** C(CNC(=S)[S-])NC(=S)[S-].C(CNC(=S)[S-])NC(=S)[S-].[Mn+2].[Zn+2]

**Dimethyl-EBDC**

**IUPAC Name:** Dimethyl Ethylenebis(dithiocarbamate)  
**CAS Name:** Not reported  
**CAS Number:** 20721-48-6  
**SMILES String:** Not found

