Analytical method for captan in water

Reports: ECM: EPA MRID No. 51613101. Thom, M., 2005. Validation of an Analytical Method for Determination of Captan in Drinking Water and Surface Water. Study ID: 20041453/01-RVW. Report prepared by GAB Biotechnologie GmbH & GAB Analytik (GmbH), Niefern-Oschelbronn, Germany; sponsored and submitted by Makhteshim Agan of North America, Inc. (dba ADAMA) in Raleigh, North Carolina; Study ID: 20041453/01-RVW. 29 pages. Final report issued April 27, 2005.

ILV: EPA MRID No. 51725001. Trivedi, P. 2021. Independent Laboratory Validation of an Analytical Method for the Determination of Residues of Captan in Drinking Water and Surface Water by GC-MS. Report prepared by Jai Research Foundation, Department of Chemistry, Valsad, Gujarat, India; sponsored and submitted by Adama Makhteshim Ltd, Raleigh, North Carolina and UPL NA Inc., King of Prussia, Philadelphia; JRF Study Number: 228-2-13-29211. UPL Study Number: UPL/2021/0595. Adama Reference Number: 000109249. 101 pages. Final report issued November 2, 2021.

ILV: EPA MRID No. 52658401. Trivedi, P. 2025. Independent Laboratory Validation of an Analytical Method for the Determination of Residues of Captan in Drinking Water and Surface Water by GC-MS, Jai Research Foundation, India. Laboratory report number: 228-2-13-29211; November 02, 2021. *Amended Final Report I: July 29, 2025.*

Document No.: MRIDs 51613101 & 51725001/52658401

Guideline: 850.6100

Statements: ECM: This study was conducted in accordance with Principles of Good Laboratory Practice (GLP) Chemical Act, Federal Republic of Germany and OECD Principles of GLP. Signed and dated No Data Confidentiality and GLP statements were provided (pp. 2-3, 6, and 8 of MRID 51613101). Two Quality Assurance statements were provided (pp. 4 and 7 of MRID 51613101). The first Quality Assurance statement reported that the study was not subject to an audit by the Quality Assurance unit. A second signed and dated Quality Assurance statement reported the type of information and the date of audit activities.

ILV: The study was conducted in accordance OECD Series on Principles of GLP and Compliance monitoring (ENV/MC/CHEM(98)17, 1998; p. 3 of MRID 51725001/52658401). Signed and dated No Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4). A statement of the authenticity of the study report was not included.

Classification: This analytical method is classified as **Supplemental**. Since the reported method LOQ was not based on scientifically acceptable procedures defined

	in 40 CFR Part 136, the reported LOQ is the lowest level of method validation (LLMV) rather than LOQ. The specificity of the method for captan was not supported by ECM representative chromatograms due to baseline background noise and matrix interference at 10x LOQ-level. In the ECM, 10x LOQ recoveries were corrected by observed matrix effects.	
PC Code:	081301	
EFED Final Reviewer:	He Zhong, Ph.D. Biologist	Signature: HE ZHONG Digitally signed by HE ZHONG Date: 2025.09.11 13:30:54 -04'00' Date: 9/11/2025
CDM/CSS-Dynamac JV Reviewers:	Summer Piantes, M.S., Environmental Scientist	Signature: Summer Piantes Date: 06/14/2022
	Lisa Muto, M.S., Environmental Scientist	Signature: Lisa Muto Date: 06/16/2022

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

Executive Summary

This analytical method, GAB Biotechnologie GmbH & GAB Analytik GmbH 20041453/01-RVW, is designed for the quantitative determination of captan at the LOQ of 0.1 µg/L in water using GC/MS. The captan LOQ is less than the lowest toxicological level of concern in water for eastern oyster NOAEC (1.1 µg ai/L). Since the reported method LOQ was not based on scientifically acceptable procedures defined in 40 CFR Part 136, the reported LOQ is the lowest level of method validation (LLMV) rather than an LOQ. Based on the performance data submitted by the ILV and ECM, the LLMV was equivalent to the ECM reported method LOQ for captan in water (0.1 µg/L). An amended ILV (MRID 52658401) submitted in September 2025 (MRID 52658401), which confirmed that the ECM has been validated independently, without communication with the method developer.

The ILV validated the method, GAB Biotechnologie GmbH & GAB Analytik GmbH 20041453/01-RVW, as written, except for minor modifications to optimize the instrumentation used in the ILV. These modifications included: 1) changing the GC instrumentation and 2) changing the length of the GC column. The ILV did not state the number of trials required to validate the ECM method; however, only one set of results were reported in the ILV. The reviewer assumed that the ILV validated the method in the first trial; no updated ECM is required based on the ILV modifications. The ECM and ILV test matrices were characterized drinking and surface water matrices. The ECM reported the use of drinking water as “tap” water. The ILV did not report the use of the drinking water source.

All ILV and ECM data regarding repeatability, accuracy, precision, and linearity were satisfactory for captan at 0.1 µg/L and 1 µg/L. The specificity of the method for captan was not supported by ECM representative chromatograms since baseline noise and matrix interferences were observed for captan. The ECM reported that corrections were made to residue concentrations related to these matrix interferences, but the details of the corrections were not discussed. The chromatograms provided in the ECM were incomplete and difficult to read. An updated ECM is required to: 1) address the matrix interferences, including corrections made in response to the matrix interference and 2) provide a more comprehensive set of representative legible chromatograms.

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						
Captan	51613101[1]	51725001[2] 52658401		Water	27/04/2005	Makhteshim Agan of North America, Inc. (dba ADAMA)	GC/MS	0.1 µg/L

1 In the ECM, the specific source of the surface water was reported as river water from the "Nagold" at Werderbrücke, Pforzheim, Germany. The source of the drinking water was reported as tap water from GAB Analytik, Pforzheim, Germany (p. 13 of MRID 51613101). The surface water matrix had the following characteristics: pH (at 20ºC) 8.22; conductivity 708 µS/cm; total hardness 15.6 mmol/L; dissolved organic carbon 3.62 mg C/L. The drinking water matrix had the following characteristics: pH (at 20ºC) 7.75; conductivity 442 µS/cm; total hardness 13.4 mmol/L; dissolved organic carbon 0.86 mg C/L (p. 13 of MRID 51613101). The water characterization was performed by CIP Pforzheim. The water characterization report was not provided.

2 In the ILV, the specific source of the surface water was reported as river water from the Daman Ganga River, Vapi, Valsad, Gujarat, India. The source of the drinking water was reported as tap water from "JRF Golghar, JRF Vapi" in Valsad, Gujarat, India (p. 12 of MRID 51725001). The surface water matrix had the following characteristics: pH (at 20ºC) 7.48; conductivity 175 µS/cm; total hardness 0.79 mmol/L; dissolved content 6.97 mg/L. The drinking water matrix had the following characteristics: pH (at 20ºC) 7.14; conductivity 639 µS/cm; total hardness 3.54 mmol/L; dissolved content 8.06 mg/L (p. 12 of MRID 51725001). The water characterization was performed by Pollucon Lab in Surat, Gujarat, India. The water characterization report was not provided.

I. Principle of the Method

Water samples (500 mL) fortified with concentrations of LOQ-level (0.1 µg/L) or 10x LOQ-level (1.0 µg/L; p. 14 of MRID 51613101) were mixed with 0.2 mL of acetic acid and homogenized for half a minute using a magnetic stirrer then applied to a Bond Elut PPL polymer styrene divinylbenzene solid phase extraction (SPE) cartridge (200 mg, 3 mL) preconditioned with 3 mL of acetone and 2 x 3 mL of demineralized water. Water samples were attached to the SPE manifold with PTFE connectors and passed through the cartridges at one to two drops per second. After complete sampling, the cartridges were dried by sucking air through the manifold for 5 minutes. Volumetric flasks (2 mL) were placed under the cartridges and captan was eluted with each 2.5 mL of acetone. The solvent was evaporated to dryness using a gentle nitrogen

stream and reconstituted in 1 mL of n-hexane. Citral (10 µL) was added to the sample and analyzed by gas chromatography coupled with a mass spectrometric detection (GC/MS; pp. 11, 14-15 of MRID 51613101).

Stock solutions of (1000 µg/mL) were prepared in acetone. Three dilutions containing 100, 10, and 1 µg/mL were prepared in acetone (p. 13 of MRID 51613101). Details of stock solution and dilutions preparation were not reported in the ECM. All standard solutions were stored in a refrigerator at nominally 4ºC. Water matrix samples were stored in a refrigerator at nominally 4ºC (p. 13 of MRID 51613101).

Fortification solutions of water samples were prepared at concentrations of 0.1 µg/L and 1 µg/L. The LOQ-level samples (0.1 µg/L) were prepared by fortifying 500 mL water samples with 50 µL of the 1 µg/mL standard solution with acetone. The 10x LOQ-level samples (1 µg/L) were prepared by fortifying 500 mL water samples with 50 µL of the 10 µg/mL standard solution with acetone (pp. 14 and 17 of MRID 51613101).

Samples were analyzed using an Agilent HP 6840N gas chromatograph (GC) system coupled to an Agilent 5973 N mass selective quadrupole detector in selective ion monitoring (SIM) mode (p. 15 of MRID 51613101). The following GC conditions were used: Varian CP-Sil 8 CB Low Bleed/MS (DB-5 equivalent) column (*ca.* 15 m x 0.25 mm i.d., 0.25 µm film thickness), carrier gas of helium1 mL/min, injection volume of 2 µL pulsed splitless at 200 ºC, 150 kPa for 1 min, temperature program of 90ºC, 20ºC/min to 130ºC, 10ºC/min to 195ºC, 5ºC/min to 205ºC, 30ºC/min to 310ºC, hold 5 min, *ca.* retention time of 9.6 min. The following MS/MS conditions were used: 70 eV positive (ionizer temperature 230°C), transfer line 280ºC, quadrupole 150ºC, and selective ion monitoring (SIM, p. 15 of MRID 51613101). Three SIM masses (*m/ z*= 264, 266, and 114) were monitored for captan.

The independent laboratory performed the ECM as written, with the following modifications: 1) The equipment used differed from the equipment in the ECM. An Agilent 7890B GC system coupled to a Mass Hunter 5977-A-MSD mass selective quadrupole detector in selective ion monitoring (SIM) mode (pp. 11 and 18 of MRID 51725001). 2) An HP 5 MS column (30 m x 0.25 mm x 0.25 µm film thickness) was used. The column used in the ECM was (*ca.* 15 m x 0.25 mm i.d., 0.25 µm film thickness). 3) The expected retention time was *ca.* 11.8 min. The carrier gas, the temperature program, the carrier gas, and the injection volume, pressure, and flow rate column specifications, the column temperature, the injection volume, and flow rate were the same as used in the ECM. The MS/MS parameters were the same as used in the ECM. No updated ECM is required based on the ILV modifications.

The Limit of Quantification (LOQ) for captan in surface water and groundwater was reported as 0.1 µg/L in the ECM and the ILV (pp. 11, 18, and 20 of MRID 51613101; pp. 8-9, 19, and 21 of MRID 51725001). The Limit of Detection (LOD) for captan in surface water and drinking water was reported as 0.03 µg/L in the ECM and ILV (p. 11 of MRID 51613101; pp. 8-9, and 19 of MRID 51725001).

Since the LOQs were not based on scientifically acceptable procedures defined in 40 CFR Part 136, the reported LOQs are the lowest levels of method validation (LLMVs) rather than LOQs.

II. Recovery Findings

ECM (MRID 51613101): Mean recoveries and relative standard deviations (RSDs) met requirements (mean 70-110%; RSD ≤20%) for surface water and drinking water matrix samples were fortified with captan at the LOQ (0.1 µg/L) and 10×LOQ (1 µg/L; pp. 11, 18, and 20, Table 1, p. 17 of MRID 51613101). Two untreated control samples, five samples for each matrix and each fortification level were analyzed (Tables 3-4, pp. 21-22, Figures 3-6, pp. 25-28). Reagent blank analyses were not reported in the ECM. LOQ recoveries were not corrected, but 10x LOQ recoveries were corrected by observed matrix effects (pp. 16, 19).

Performance data for the quantification ion (*m/z* = 264) and qualifier ions (Q1 [*m/z* = 266] and Q2 [*m/z* = 114]) were evaluated. The ECM reported residues of captan were less than 30% of the LOQ in the control samples blanks (p. 17, Figures 3-4, pp. 25-26 of MRID 51613101); however, the ECM noted "minor interferences" in qualifier ion chromatograms (*m/z* = 114).

In the ECM, the specific source of the surface water was reported as river water from the "Nagold" at Werderbrücke, Pforzheim, Germany. The source of the drinking water was reported as tap water from GAB Analytik, Pforzheim, Germany (p. 13 of MRID 51613101). The surface water matrix had the following characteristics: pH (at 20ºC) 8.22; conductivity 708 µS/cm; total hardness 15.6 mmol/L; dissolved organic carbon 3.62 mg C/L. The drinking water matrix had the following characteristics: pH (at 20ºC) 7.75; conductivity 442 µS/cm; total hardness 13.4 mmol/L; dissolved organic carbon 0.86 mg C/L (p. 13 of MRID 51613101). The water characterization was performed by CIP Pforzheim. The water characterization report was not provided.

ILV (MRID 51725001): Mean recoveries and RSDs met requirements for surface water and drinking water matrix samples were fortified with captan at the LOQ (0.1 µg/L) and 10×LOQ (1.0 µg/L; pp. 8-9, 19-20, Tables 16-21, pp. 29-34 of MRID 51725001). Two control sample, one reagent blank, and five samples for each matrix and each fortification level were analyzed for captan (p. 17 of MRID 51725001). One quantification ion (*m/z* = 264) and two qualifier ions (*m/z* = 266 and *m/z* = 114; p. 18 of MRID 51725001). Performance data for the quantification and qualifier ions were comparable. Captan was less than 30% of the LOQ in the reagent blank and control samples.

In the ILV, the specific source of the surface water was reported as river water from the Daman Ganga River, Vapi, Valsad, Gujarat, India. The source of the drinking water was reported as "drinking" water from "JRF Golghar, JRF Vapi" in Valsad, Gujarat, India (p. 12 of MRID 51725001). The surface water matrix had the following characteristics: pH (at 20ºC) 7.48; conductivity 175 µS/cm; total hardness 0.79 mmol/L; dissolved content 6.97 mg/L. The drinking water matrix had the following characteristics: pH (at 20ºC) 7.14; conductivity 639 µS/cm; total hardness 3.54 mmol/L; dissolved content 8.06 mg/L (p. 12 of MRID 51725001). The water characterization was performed by Pollucon Lab in Surat, Gujarat, India. The water characterization report was not provided.

The method was validated by the ILV in the surface water matrix and the drinking water matrix with modifications to the analytical method (see Reviewer's Comment #6). The ILV validated the method no matrix suppression or enhancement was observed (p. 21 of MRID 51725001). The

ILV did not state the number of trials required to validate the ECM method; however, only one set of results were reported in the ILV. The reviewer assumed that the ILV validated the method in the first trial; no updated ECM is required based on the ILV modifications.

Table 2. Initial Validation Method Recoveries for Captan in Water[1,2]

Analyte	Fortification Level (µg/L)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)[3]	Relative Standard Deviation (%)
Surface (river) water						
Quantitation ion (*m/z* = 264)						
Captan	0.1 (LOQ)	5	85-97	93	5	5
	1 (10x LOQ)	5	75-95	86	8	9
Drinking (tap) water						
Quantitation ion (*m/z* = 264)						
Captan	0.1 (LOQ)	5	67-99	86	13	15
	1 (10x LOQ)	5	75-103	93	11	12

Data (LOQ recoveries were not corrected, but 10x LOQ recoveries were corrected by observed matrix effects; pp. 16, 19) were obtained from Table 1, p. 17 of MRID 51613101). Since the LOQ was not based on scientifically acceptable procedures defined in 40 CFR Part 136, the reported LOQ is the lowest level of method validation (LLMV) rather than an LOQ.

1 Three ions were monitored (one quantitation and two qualifier ions, respectively): Q *m/z* = 264, Q 1 *m/z* = 266, Q 2 *m/z* = 114. (p. 15 of MRID 51613101). However, recoveries were not reported for the qualifier ions.

2 The specific source of the surface water was reported as river water from the "Nagold" at Werderbrücke, Pforzheim, Germany. The source of the drinking water was reported as tap water from GAB Analytik, Pforzheim, Germany (p. 13 of MRID 51613101). The surface water matrix had the following characteristics: pH (at 20ºC) 8.22; conductivity 708 µS/cm; total hardness 15.6 mmol/L; dissolved organic carbon 3.62 mg C/L. The drinking water matrix had the following characteristics: pH (at 20ºC) 7.75; conductivity 442 µS/cm; total hardness 13.4 mmol/L; dissolved organic carbon 0.86 mg C/L (p. 13 of MRID 51613101). The water characterization was performed by CIP Pforzheim. The water characterization report was not provided.

3 Standard deviations were reviewer-calculated (see DER Excel Attachment) based on data provided in the study report because standard deviations were not calculated by the study authors. Rules of significant figures were followed.

Table 3. Independent Validation Method Recoveries for Captan in Water[1,2]

Analyte	Fortification Level (µg/L)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Surface (river) water						
Quantitation ion (*m/z* = 264)						
Captan	0.1 (LOQ)	5	83.03-88.42	84.64	2.17	2.56
	1 (10x LOQ)	5	80.48-91.18	85.45	4.06	4.75
Qualifier ion 1 (*m/z* = 266)						
Captan	0.1 (LOQ)	5	89.87-95.12	91.39	2.15	2.35
	1 (10x LOQ)	5	83.88-88.3	86.21	1.69	1.96
Qualifier ion 2 (*m/z* = 114)						
Captan	0.1 (LOQ)	5	83.11-88.50	86.16	2.47	2.87
	1 (10x LOQ)	5	88.75-98.63	93.96	3.87	4.12
Drinking water						
Qualifier ion (*m/z* = 264)						
Captan	0.1 (LOQ)	5	84.16-87.58	85.65	1.32	1.54
	1 (10x LOQ)	5	84.20-90.84	87.15	2.78	3.19
Qualifier ion 1 (*m/z* = 266)						
Captan	0.1 (LOQ)	5	90.92-94.11	92.33	1.25	1.35
	1 (10x LOQ)	5	90.3-92.1	88.61	2.92	3.30
Qualifier ion 2 (*m/z* = 114)						
Captan	0.1 (LOQ)	5	84.42-95.01	88.51	4.17	4.71
	1 (10x LOQ)	5	95.15-106.3	99.00	4.28	4.32

Data (uncorrected recovery results; p.18 of MRID 51725001) were obtained from pp. 8-9, 19-20, Tables 16-21, pp. 29-34 of MRID 51725001. Since the LOQ was not based on scientifically acceptable procedures defined in 40 CFR Part 136, the reported LOQ is the lowest level of method validation (LLMV) rather than an LOQ.

1 Three ions were monitored (one quantitation and two qualifier ions, respectively): Q *m/z* = 264, Q 1 *m/z* = 266, Q 2 *m/z* = 114 (pp. 8-9, 18, Appendix 1, pp. 44-85 of MRID 51725001).

2 The specific source of the surface water was reported as river water from the Daman Ganga River, Vapi, Valsad, Gujarat, India. The source of the drinking water was reported as "drinking" water from "JRF Golghar, JRF Vapi" in Valsad, Gujarat, India (p. 12 of MRID 51725001). The surface water matrix had the following characteristics: pH (at 20ºC) 7.48; conductivity 175 µS/cm; total hardness 0.79 mmol/L; dissolved content 6.97 mg/L. The drinking water matrix had the following characteristics: pH (at 20ºC) 7.14; conductivity 639 µS/cm; total hardness 3.54 mmol/L; dissolved content 8.06 mg/L (p. 12 of MRID 51725001). The water characterization was performed by Pollucon Lab in Surat, Gujarat, India. The water characterization report was not provided.

III. Method Characteristics

The Limit of Quantification (LOQ) for captan in surface water and drinking water was reported as 0.1 µg/L in the ECM and the ILV pp. 11, 18, and 20 of MRID 51613101: pp. 8-9, 19, and 21 of MRID 51725001). The Limit of Detection (LOD) for captan in surface water and drinking water was reported as 0.03 µg/L in the ECM and ILV (p. 11 of MRID 51613101; pp. 8-9, and 19 of MRID 51725001).

In the ECM and the ILV, the LOQ was justified as the lowest analyte concentration in a sample at which the methodology has been validated and a mean recovery of 70-110% with a relative standard deviation of ≤20% has been obtained (p. 18 of MRID 51613101; p. 92 of MRID 51725001). The estimated LOQ was taken as 0.1 µg/L. The ILV did not explicitly state the justification for the LOQ in the MRID text; however, the study was conducted in accordance with the Study Plan included as Appendix 2 (p. 86 of MRID 51725001). The Study Plan defined the LOQ as the lowest analyte concentration which meets the validation criteria.

The LOD in the ECM was defined as 30% of the LOQ (p. 11 of MRID 51613101). The LOD in the ILV was reported as the lowest level of calibration (pp. 8-9 and 92, Table 13, p. 26 of MRID 51725001).

Since the LOQs were not based on scientifically acceptable procedures defined in 40 CFR Part 136, the reported LOQs are the lowest levels of method validation (LLMVs) rather than LOQs.

Table 4. Method Characteristics –Water[1,2]

		Captan
Limit of Quantitation (LOQ)*	ECM	0.1 µg/L (ppb) [SW and GW]
	ILV	
Limit of Detection (LOD)	ECM	0.03 µg/L (ppb) (30% LOQ) [SW and GW]
	ILV	0.03 µg/L (ppb) (lowest calibration concentration) [SW and GW]
Linearity (calibration curve r and concentration range)	ECM[3,4]	r = 0.999 (Q *m/z* = 264, Q 1 and Q 2 not reported)[5]
		Calibration Range: 0.03 to 1.5 µg/L
	ILV	r = 0.998 (Q *m/z* = 264, Q 1 *m/z*=266, Q 2 *m/z*=114)[5]
		Calibration Range: 0.03 to 1.5 µg/L
Repeatable	ECM	Yes for 0.1 µg/L (LLMV) and 1 µg/L (10x LLMV) in one characterized surface water matrix and one characterized drinking (tap) water matrix where n = 5.
	ILV[6]	Yes for 0.1 µg/L (LLMV) and 1.0 µg/L (10x LLMV) in one characterized surface water matrix and one characterized drinking water matrix where n = 5.
Reproducible		Yes for 0.1 µg/L (LLMV) and 1 µg/L (10x LLMV) in tested water matrices.
Specific	ECM[7]	**No**, the baseline noise in control samples and fortification samples which interfered with captan peak interferences. Matrix effects were reported up to 20%. The 10x LOQ-level samples were corrected for the matrix interference.
	ILV[8]	Yes, matrix interferences were <20% (based on matrix effects study).

Data obtained from pp. 11, 18, and 20 (LOQ/LOD); Table 1, p. 17 (recovery data); p. 18, Appendix B: Figures 1-2, pp. 23-24 (calibration); Table 2, p. 19 (matrix effects), Figures 3-6, pp. 25-28 (chromatograms) of MRID 51613101; pp. 8-9 and 19 (LOQ/LOD); pp. 8-9, 19-20, Tables 16-21, pp. 29-34 (recovery data); pp. 8-9, Tables 13-15, Figures 1-3, pp. 26-28 (calibration curves); Tables 1-12, pp. 23-25 (matrix effects); Appendix 1, pp. 42-99 (chromatograms) of MRID 51725001.

Q = quantitative ion; Q 1 = Qualifier ion 1; Q 2 = Qualifier ion 2; SW = Surface water; DW = Drinking water.

* Since the LOQs were not based on scientifically acceptable procedures defined in 40 CFR Part 136, the reported LOQs are the lowest levels of method validation (LLMVs) rather than LOQs. The lowest concentration tested with sufficiently accurate and precise recoveries is the LLMV.

1 Three ions were monitored (one quantitation and two qualifier ions, respectively): Q *m/z* = 264, Q 1 *m/ z*=2 66, Q 2 *m/z* = 114. (p.15 of MRID 51613101, and pp. 8-9, 18, Appendix 1, pp. 44-85 of MRID 51725001).

2 In the ECM, the specific source of the surface water was reported as river water from the "Nagold" at Werderbrücke, Pforzheim, Germany. The source of the drinking water was reported as tap water from GAB Analytik, Pforzheim, Germany (p. 13 of MRID 51613101). The surface water matrix had the following characteristics: pH (at20ºC) 8.22; conductivity 708 µS/cm; total hardness 15.6 mmol/L; dissolved organic carbon 3.62 mg C/L. The drinking water matrix had the following characteristics: pH (at 20ºC) 7.75; conductivity 442 µS/cm; total hardness 13.4 mmol/L; dissolved organic carbon 0.86 mg C/L (p. 13 of MRID 51613101). The water characterization was performed by CIP Pforzheim. The water characterization report was not provided. In the ILV, the specific source of the surface water was reported as river water from the Daman Ganga River, Vapi, Valsad, Gujarat, India. The source of the drinking water was reported as "drinking" water from "JRF Golghar, JRF Vapi" in Valsad, Gujarat, India (p. 12 of MRID 51725001). The surface water matrix had the following characteristics: pH (at 20ºC) 7.48; conductivity 175 µS/cm; total hardness 0.79 mmol/L; dissolved content 6.97 mg/L. The drinking water matrix had the following characteristics: pH (at 20ºC) 7.14; conductivity 639 µS/cm; total hardness 3.54 mmol/L; dissolved content 8.06 mg/L (p. 12 of MRID 51725001). The water characterization was performed by Pollucon Lab in Surat, Gujarat, India. The water characterization report was not provided.

3 The ECM calibration used n-hexane and thus was not a matrix-matched calibration (p. 15 of MRID 51613101).

4 The ECM reported chromatograms for only calibration level (50 ng/mL).

5 The ECM and ILV study authors reported coefficients of determination (R^2). The reviewer converted the reported R^2 values to Calibration coefficients (r) (p. Appendix B, p. 23 of MRID 51613101; (pp. 8-9, Tables 13-15, Figures 1-3, pp. 26-28 of MRID 51725001; see DER Excel Attachment).

6 The ILV validated the method, JRS Study No. 228-2-13-29211, as written with minor modifications to the equipment and length of the column used in the GC system (p. 18 of MRID 51725001). The ILV did not state the number of trials required to validate the ECM method; however, only one set of results were reported in the ILV. The reviewer assumed that the ILV validated the method in the first trial; no updated ECM is required based on the ILV modifications.

7 There was baseline noise interfering with peak identification and integration (Figures 3-6, pp. 25-28 of MRID 51613101). The captan peak in chromatograms for qualifier ion 2 (*m/*z = 114) was particularly difficult to identify and quantify. In addition, each of the chromatograms included showed two unidentified peaks at *ca.* 10.3 minutes. The ECM should be updated to address the interference from baseline noise and explain the unidentified peaks.

8 In the ILV, an unidentified peak that appeared at a retention time *ca.* 11.5 min in solvent blank and control samples was also visible in fortification sample chromatograms. The peak for captan appeared at a retention time *ca.* 11.8 min. The peak at *ca.* 11.5 min appeared to be independent of the captan peak (Appendix 1 pp. 42-99 of MRID 51725001).

IV. Method Deficiencies and Reviewer's Comments

1. Since the reported method LOQ of the ECM and ILV were not based on scientifically acceptable procedures defined in 40 CFR Part 136, the reported LOQ of the ECM and ILV are the lowest level of method validation (LLMV) rather than LOQs (p. 18 of MRID 51613101; p. 92 of MRID 51725001). The lowest concentration tested with sufficiently accurate and precise recoveries is the LLMV.

2. The submitted ILV MRID 51725001 was conducted to develop and validate a confirmatory method for captan analysis in water using drinking water and surface water matrices. The ILV was based on the ECM with some insignificant modifications. The use of drinking water source (e.g. tap, finished, or well water) was not addressed as a test matrix in the ILV.

3. The specificity of the ECM for captan was not supported by ECM representative chromatograms since there was baseline noise interfering with peak identification and integration (Figures 3-6, pp. 25-28 of MRID 51613101). The captan peak in chromatograms for qualifier ion 2 (*m/*z = 114) was particularly difficult to identify and quantify. In addition, each of the chromatograms included showed two unidentified peaks at *ca.* 10.3 minutes. The ECM should be updated to address the interference from baseline noise and explain the unidentified peaks.

   In the ILV, matrix effects were less than 20% (Tables 1-12, pp. 23-25 of MRID 51725001). An unidentified peak that appeared at a retention time *ca.* 11.5 min in solvent blank and control samples was also visible in fortification sample chromatograms. The peak for captan appeared at a retention time *ca.* 11.8 min. The peak at *ca.* 11.5 min appeared to be independent of the captan peak (Appendix 1 pp. 42-99 of MRID 51725001).

4. The ECM included an incomplete set of chromatograms. The ECM only included one chromatogram for calibration, one control sample for each matrix (drinking water and surface water), and one LOQ-level chromatogram for each matrix. The chromatograms that were included are difficult to read. The ECM should be updated to include a complete set of clear, legible chromatograms.

5. It could not be determined if the ILV was conducted independently from the ECM since the ILV did not include a discussion or summary regarding communications between the

performing laboratory (JRF) and the study sponsors (Adama and UPL). This deficiency was corrected by an amended ILV (MRID 52658401) submitted in September 2025, which confirmed that the ECM has been validated independently, without communication with the method developer.

6. The ECM study report noted that matrix interferences were present at 16% and 20% in tap water and surface water matrix-matched standards, respectively, versus solvent-based standards for the 500 ng/mL reference solution (p. 19 of MRID 51613101). The ECM stated that the 10x LOQ-level concentrations were corrected by matrix effects; however, only solvent-based calibration standards were reportedly used for quantification (pp. 15-16, 19). The ECM did not provide details of how the matrix-effect correction was applied, and the reviewer could not determine the method of correction from the provided equation due to lack of raw data. Per the guideline, recovery results should not be corrected (OCSPP 850.6100 (d)(2)(iv)). The ECM did not include chromatograms for the 10x LOQ-level analyses; therefore, the reviewer could not verify the nature and extent of matrix interferences.

7. The ILV made the following modifications to the ECM (GAB Biotechnologie GmbH & GAB Analytik Study ID: 20041453/01-RVW): 1) The equipment used differed from the equipment in the ECM. An Agilent 7890B GC system coupled to a Mass Hunter 5977-A-MSD mass selective quadrupole detector was used (pp. 11 and 18 of MRID 51725001). 2) An HP 5 MS column (30 m x 0.25 mm x 0.25 µm film thickness) was used. The ECM used a Varian CP-Sil 8 CB Low Bleed/MS (DB-5 equivalent) column *ca.* 15 m x 0.25 mm x 0.25 µm film thickness (p. 15 of MRID 51613101).

   The analytical modifications included the following: 1) changing the GC instrumentation and 2) changing the column brand and length. Overall, the ILV method (JRF Study Number: 228-2-13-29211) was a suitable version of the ECM.

8. Two amendments to the final study plan dated October 7 and October 25, 2021, respectively, are included in Amendment 2 (Appendix 2, pp. 97-98 of MRID 51725001). The Amendment sent on October 7, 2021 related the GC injection volume that was specified in the ECM, but was missed during finalization of the Study Plan (p. 97 of MRID 51725001). The Amendment sent on October 25, 2021 corrected the molecular weight of captan and verified that the calibration range would be consistent with that presented in the ECM (from 30% of the LOQ to 20% above the highest level; p. 98 of MRID 51725001). These amendments were sent by Dr. Purushottam Trivedi, the JRF Study Director, to the Study Sponsors Chaitali Roy, the representative for Adama, and Roy Russell, the representative for UPL. The Study Sponsors approved these amendments on October 8 and 10, 2021 for the first amendment and October 26, 2021 for the second amendment. The ILV reported the start of the experiment on October 1, 2021 and the end of the experiment on October 26, 2021. Therefore, the approval of these amendments to the study plan was conducted within period of the experiment.

9. The determinations of the LOD and LOQ in the ECM and ILV were not based on scientifically acceptable procedures as defined in 40 CFR Part 136 (pp. 11, 18, and 20 of

MRID 51613101; pp. 8-9, 19, and 21 and MRID 51725001). In the ECM and the ILV, the LOQ was justified as the lowest analyte concentration in a sample at which the methodology has been validated and a mean recovery of 70-110% with a relative standard deviation of ≤20% has been obtained (p. 18 of MRID 51613101; p. 92 of MRID 51725001). Detection and quantitation limits should not be based on the arbitrarily selected lowest concentration in the spiked samples.

Since the LOQs were not based on scientifically acceptable procedures defined in 40 CFR Part 136, the reported LOQs are the lowest levels of method validation (LLMVs) rather than LOQs.

10. The ECM reported that stock solutions were prepared in acetone (p. 13 of MRID 51613101). The ECM did not report details of preparation of calibration solutions. Solvent-based calibrations were used in the ILV (p. 24 of MRID 51725001).

11. The ECM and ILV did not report the time requirement for analysis of a batch of samples.

12. In the ECM, surface sample extracts were stored up to 5 days with less than 5% degradation (p. 19 of MRID 51613101). The ILV reported extract stability of up to 18 days and stock solution stability of up to 26 days when refrigerated (2-8ºC; pp. 9 and 21 of MRID 51725001).

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.

USEPA. 2012. *Environmental Chemistry Method Guidance*. Memorandum From D. Brady to Environmental Fate and Effects Division. December 20, 2012. Environmental Fate and Effects Division. Office of Pesticide Programs. Office of Chemical Safety and Pollution Prevention. U.S. Environmental Protection Agency. Available at: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/environmental-chemistry-methods-guidance-pesticides.

40 CFR Part 136. Appendix B. Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11, pp. 344-347, and Revision 2; 2015 and 2016.

Attachment 1: Chemical Names and Structures

Captan

IUPAC Name: N-(trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide
CAS Name: 3a,4,7,7a-Tetrahydro-2-[(trichloromethyl)thio]-1H-isoindole-1,3(2H)-dione
CAS Number: 133-06-2
SMILES String: O=C(N(SC(Cl)(Cl)Cl)C(=O)C1CC=CC2)C12