SUMMARY

(In accordance with 40 CFR Part 152, this summary is available for public release after registration)

STUDY TITLE

Analytical Method and Validation for the Determination of Impurities in 1,3-Dichloropropene Technical Grade Material – Method NA-AM-98-081.00 Extension

DATA REQUIREMENT

U.S. EPA OPPTS Test Guideline 830.1800
SANCO/3030/99 rev.4

STUDY DIRECTOR/AUTHOR

Rose M. Nelson

STUDY COMPLETED ON

July 6, 2015

PERFORMING LABORATORY

Dow AgroSciences LLC
9330 Zionsville Road
Indianapolis, Indiana 46268

LABORATORY STUDY ID

DAS-AM-G-14-50

SUMMARY

NA-AM-98-081.00, a gas chromatography (GC) method, was validated for the determination of an additional impurity in 1,3-dichloropropene technical grade material. The accuracy, precision, and linearity of the method have been shown to be acceptable.

STUDY TITLE

Analytical Method and Validation for the Determination of Impurities in 1,3-Dichloropropene Technical Grade Material – Method NA-AM-98-081.00 Extension

DATA REQUIREMENT

U.S. EPA OPPTS Test Guideline 830.1800
SANCO/3030/99 rev.4

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LABORATORY STUDY ID

DAS-AM-G-14-50

STATEMENT OF DATA CONFIDENTIALITY CLAIMS

Information claimed confidential has been removed to a confidential attachment.

Company: Dow AgroSciences LLC

Company Agent: Jim Baxter

Title: Regulatory Manager

Signature: J.P. Baxter

Date: 23 April 2015

STATEMENT OF COMPLIANCE WITH GOOD LABORATORY PRACTICE STANDARDS

STUDY TITLE: Analytical Method and Validation for the Determination of Impurities in 1,3-Dichloropropene Technical Grade Material – Method NA-AM-98-081.00 Extension

Study Initiation Date: 16-February-2015

All phases of this study were conducted according to the following Good Laboratory Practice Standards, except that the test substance was obtained from a commercial supplier, and the GLP status is unknown.

United States Environmental Protection Agency
Title 40 Code of Federal Regulations Part 160
FEDERAL REGISTER, August 17, 1989

J.P. Baxter — 12 June 2015
Jim Baxter — Date
Co-Sponsor
Dow AgroSciences LLC

[signature] — 21. of. 2015
Shun Kawaguchi — Date
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Rose M Nelson — July 6, 2015
Rose Nelson — Study Completion Date
Study Director
Dow AgroSciences LLC

Dow AgroSciences Quality Assurance Unit
Good Laboratory Practice Statement Page

Study ID: DAS-AM-G-14-50

Title: Analytical Method and Validation for the Determination of Impurities in I, 3 dichloropropene Technical Grade Material - Method NA-AM-98-081.00 Extension

Study Initiation Date: 16-Feb 2015 **Study Completion Date:** 6-Jul-2015

GLP Quality Assurance Inspections

Date of GLP Inspection(s)	Date Reported to the Study Director and to Management	Phases of the Study which received a GLP Inspection by the Quality Assurance Unit
12-Feb-2015	12-Feb-2015	Protocol Review
24-Feb-2015	25-Feb-2015	Recovery
30-Jun-15	30-Jun-15	Raw Data and Final Report

QUALITY ASSURANCE STATEMENT:

The Quality Assurance Unit has reviewed the final study report and has determined that the report reflects the raw data generated during the conduct of this study.

Debra Stefanek 6-Jul-2015

Debra Stefanek
Dow AgroSciences, Quality Assurance

Date

SIGNATURES

Rose M Nelson — July 6, 2015

Rose Nelson
Study Director
Dow AgroSciences LLC

Brandi Thomas — 21-April-2015

Brandi Thomas
Reviewer
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Annette Brown — 21-April-2015

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STUDY PERSONNEL

Study Title: Analytical Method and Validation for the Determination of Impurities in 1,3-Dichloropropene Technical Grade Material – Method NA-AM-98-081.00 Extension

Study Director / Analyst: Rose Nelson

TABLE OF CONTENTS

I. INTRODUCTION

NA-AM-98-081.00, a gas chromatography (GC) method, was validated for the determination of an additional impurity in 1,3-dichloropropene technical grade material. The accuracy, precision, and linearity of the method have been shown to be acceptable.

This report includes the OPPTS 830.1800 Enforcement Analytical Method for this additional impurity. The details for the analysis of the impurity in 1,3-dichloropropene TGAI are included in the Confidential Attachment of this report.

Study Title: Analytical Method and Validation for the Determination of Impurities in 1,3-Dichloropropene Technical Grade Material – Method NA-AM-98-081.00 Extension

Guidelines Reference OPPTS 830.1800 Enforcement Analytical Method for Impurities
(Information found in the Confidential Attachment under Cross Reference Number 1)

CONFIDENTIAL ATTACHMENT

STUDY TITLE

Analytical Method and Validation for the Determination of Impurities in 1,3-Dichloropropene Technical Grade Material – Method NA-AM-98-081.00 Extension

DATA REQUIREMENT

U.S. EPA OPPTS Test Guideline 830.1800
SANCO/3030/99 rev.4

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STUDY COMPLETED ON

July 6, 2015

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LABORATORY STUDY ID

DAS-AM-G-14-50

Cross Reference Number 1 This cross reference number noted on a place holder page is used in place of the indicated page reference.

Deleted Pages: Are attached immediately behind this page.

Page	Reason for Deletion	FIFRA Reference
9	Process Impurities Identified	§10(d)(1)(A)

TABLE OF CONTENTS – Confidential Attachment

I. ABSTRACT

This report describes the validation extension of NA-AM-98-081.00, a gas chromatography (GC) method for the determination of 1,1,2-trichloroethane (1,1,2-TCE) in 1,3-dichloropropene technical grade active ingredient (TGAI). NA-AM-98-081.00 was validated using a gas chromatography (GC) method with a DB-1701 60 m x 0.32 mm x 1 µm column and a thermal conductivity detector (TCD). Concentrations were determined using external standard calibration.

The results for range of precision, recovery, linearity, limit of quantitation (LOQ) and limit of detection (LOD) are presented below.

Parameter		**Result**
Method Precision (n = 10)	Avg wt %	0.037
	% RSD	3.3
	Horwitz RSD_r	4.4
	RSD Acceptable?	Yes
System Precision (n = 6)	Average wt%	0.036
	% RSD	2.9
Accuracy (n = 8)	Equivalent Wt % range	0.0108 to 1.05
	Avg % Recovery	105
Linearity (n = 8)	mg/mL range	0.0527 to 5.19
	Equivalent Wt.%	0.0108 to 1.05
	Coefficient of Determination (r^2)	0.9999
LOQ	Average recovery %	110
	Average wt %	0.012
	% RSD	2.9
	Horwitz RSD_r	5.2
	RSD Acceptable?	Yes
	Signal to noise	10
LOD	Average wt%	0.006
	Signal to noise	5

II. INTRODUCTION

A. Scope

The gas chromatography method described in this report is applicable for the determination of 1,1,2-trichloroethane (1,1,2-TCE) in 1,3-dichloropropene technical grade active ingredient (TGAI) and is an extension of method NA-AM-98-081.00.

This report reflects what was actually performed during the course of this study and includes all amendments and/or deviations to the protocol.

B. Principle

Sample preparation involves adding 2 mL of 1,3-dichloropropene to a 5 mL volumetric flask and diluting to volume with ethyl acetate. Sample solutions are then analyzed using a gas chromatography system, a DB-1701 60 m x 0.32 mm x 1 µm column and thermal conductivity detection. Sample quantitation is by external standard calibration using peak areas.

III. MATERIALS AND METHODS

A. Equipment

1. Analytical balance: capable of measuring to 0.1 mg: Mettler Toledo AT201
2. Gas Chromatography System: Agilent model 6890 equipped with a split/splitless inlet, thermal conductivity detector and autosampler
3. Data acquisition and processing system: Agilent EZChrom Elite data system
4. Column: DB-1701 60 m x 0.32 mm x 1 µm
5. Autosampler vials and caps: 2 mL with screw caps
6. Miscellaneous laboratory glassware and syringes

B. Reagents and Standards

1. Test Substances

   Test substances were received from Aldrich. Additional information for the test substances is as follows:

Chemical Name	Test Substance / Lot Number	Purity	Reference	Recertification Date
1,1,2-trichloroethane	Aldrich lot 28896MMV	96.8%	Aldrich CofA	March 7, 2015
1,1,2-trichloroethane	Aldrich lot MKBG8560V	99.9%	Aldrich CofA	March 27, 2017

Note: Lot 28896MMV was used for interference evaluation, precision and stability. Lot MKBG8560V was used for recovery, linearity, and LOD/LOQ.

The following test substances were used for the evaluation of interferences only:

Common Name (X#)	Chemical Name	Test Substance / Lot Number	Purity	Reference	Recertification Date
A	1,2-Dichloropropane	AGR277102	99%	FAPC13-000368	12-Aug-2017
B (X12314033)	2-Chloro-2-methylpentane	AGR238091	97%	FAPC12-000686	30-Aug-2017
C (X11719553)	2-Chloro-1,5-hexadiene	TSN030278-0001	96%	FAPC14-000510	2-Aug-2016
D (X139475)	2-Chloro-4-methylpentane	TSN106505	98%	FAPC14-000511	11-Aug-2018
E (X11842830)	2-Chloro-2,3-dimethylbutane	TSN028018-0001	100%	FAPC13-000375	12-Aug-2017
F (X11373675)	3-chloro-1,5-hexadiene	TSN303599	77%	FAPC14-000228	24-Aug-2016
G (X11742495)	3-Chloro-2-methylpentane	TSN303946	83%	FAPC14-000501	14-Aug-2016
H	1,3-dichloropropane	AGR238090	99.5%	FAPC12-000685	30-Aug-2017
I (X166920)	1,2,2-trichloropropane	TSN301451	97%	FAPC13-000365	02-Aug-2015
J	Cis-1,3,3-trichloropropene	AGR238088	94%	FAPC13-000366	03-Aug-2017
K-cis K-trans (X11731281)	Cis /Trans-2-chloro-3-(chloromethyl)oxirane	TSN307901	91%	FAPC14-000594	14-Aug-2015
L	Trans-1,3,3-trichloropropene	AGR238086	86.2%	FAPC11-000021	23-Aug-2015
M (X191117)	3,3-dichloro-1-propene	TSN030579-0001	97%	FAPC12-000717	22-Aug-2015
O (X11656878)	5-chloro-1-hexene	TSN106329	99%	FAPC13-000407	23-Aug-2015
P (X11661609)	(Z)-1-chloro-1,5-hexadiene	TSN304464	97%	FAPC13-000001	21-Aug-2015
N (X11656876)	4-chloro-4-methyl-1-pentene	TSN303759	92%	FAPC14-000506	29-Aug-2015
R (X11726078)	1-chloro-1-methylcyclopentane	TSN303032	97%	FAPC14-000505	15-Aug-2015
Q (X11726086)	3-chloro-1-methylcyclopentane	TSN303341	97%	FAPC14-000502	14-Aug-2016

2. Reference Substances

The reference substances were obtained from Aldrich. Additional information on the reference substances is presented below:

Chemical Name	Test Substance / Lot Number	Purity	Reference	Recertification Date
1,1,2-trichloroethane	Aldrich lot # 28896MMV	96.8%	Aldrich CofA	7-March-2015
1,1,2-trichloroethane	Aldrich lot # MKBG8560V	99.9%	Aldrich CofA	27-March-2017

3. Test Systems

Common Name (X#)	Chemical Name	Test Substance / Lot Number
1,3-dichloropropene (X191573)	1,3-dichloropropene	TSN304815
1,3-dichloropropene (X191573)	1,3-dichloropropene	1400861-46

4. Ethyl Acetate: EMD (min 99.9%)

C. Safety

Each analyst was acquainted with potential hazards of the reagents, products and solvents before beginning laboratory work. Sources of information included: material safety data sheets, literature and other related data. Disposal of reagents, reactants, and solvents were in compliance with local, state and federal laws and regulations.

D. Analytical Procedures

1. Preparation of calibration solutions:

A solution of the reference substance was prepared in duplicate by accurately weighing approximately 50 mg into a 50-mL volumetric flask (weight recorded to the nearest 0.1 mg) which was partially filled with ethyl acetate. The flask was then diluted to the mark with ethyl acetate and mixed well.

2. Calibration procedure:

The calibration solutions were injected at least twice into the gas chromatograph, using the conditions summarized in Section III.E, and the response factors were calculated using the equations given in Section III.F. The average of the response factors was used for calibration.

3. Sample Preparation and Analysis:

   Using a volumetric pipet, 2 mL of 1,3-dichloropropene was added to a 5 mL volumetric flask which was diluted to volume with ethyl acetate and mixed well. Weights of the 1,3-dichloropropene were recorded to the nearest 0.1 mg. Samples were mixed well and analyzed using the conditions given in Section III.E.

4. Preparation of Precision samples:

   Five precision samples were prepared and analyzed on each of two days as detailed in section III.D.3. Freshly prepared standards were prepared for each day's analysis. Single injections of the precision samples were made. The first five precision samples were re-analyzed three days after preparation to evaluate stability of the analytes in the prepared samples. One of the precision samples (Precision day 1-1) was used to evaluate system precision by injecting a total of six times.

5. Preparation of Recovery samples:

   Eight recovery (accuracy) samples were prepared by adding varying amounts of the test substance to the test system (TSN304815) in 5 mL volumetric flasks and diluting to volume with ethyl acetate. The total weight of the test substances and the test system was approximately 2400 mg (Table III). The solutions were shaken to dissolve and mixed well.

6. Preparation of Linearity samples:

   The linearity of 1,1,2-trichloroethane was determined using the recovery samples.

7. Preparation of Samples for the Evaluation of Interferences:

   Test Substances: Test substance samples were prepared by adding 20 µL of each test substance to individual 20 mL aliquots of ethyl acetate.

   Solvent Blank: The solvent blank was prepared by transferring ethyl acetate into an autosampler vial.

   Test System: A 2 mL aliquot of TSN304815 was added to a 5 mL volumetric flask which was diluted to volume with ethyl acetate and mixed well (Recovery 0A).

8. Evaluation of Limit of Quantitation (LOQ) and Limit of Detection (LOD):

   The signal to noise ratio was determined from the analysis of the lowest recovery sample and a sample spiked at a target concentration of 0.005% 1,1,2-trichloroethane.

Samples were analyzed using the conditions given in Section III.E. The accuracy and precision of the analysis at these levels were evaluated.

E. Instrumental Conditions

The following analytical conditions describe the analysis of samples for 1,1,2-trichlorethane in 1,3-dichloropropene technical grade active ingredient (TGAI).

Column:	DB-1701 60 m x 0.32 mm x 1µm	
Inlet temperature:	150°C	
Split ratio:	38:1	
Injection volume:	2 µL	
Column flow:	Constant flow at 1.9 mL/min Helium	
Column temperature:	40°C hold for 2 minutes, 5°C/minute to 80°C, hold for 7.5 minutes 5°C/minute to 110°C, hold for 1 minutes 25°C/minute to 270°C, hold for 0 minutes	
Detector:	TCD	
Detector temperature:	280°C	
Detector flow rate:	Reference Flow (Helium): 15 mL/min Make-up (Helium): 5 mL/min	
Run Time:	30.9 minutes	
Integrator:	Agilent EZChrom Elite	
Retention Times:	1,1,2-trichloroethane	~ 19.3 min

Approximate time to prepare and analyze a sample: 4 hours

F. Methods of Calculation

1. Calculation of the concentration of 1,1,2-trichloroethane in the calibration solutions:

$$Concentration_{(TCE)} = Wt_{(TCE)} \times Purity_{(TCE)}/DF$$

where:

$Concentration_{(TCE)}$	= Concentration of 1,1,2-trichloroethane in the calibration standard solution, mg/mL
$Wt_{(TCE)}$	= Weight of 1,1,2-trichloroethane reference substance added to the calibration solution, mg
$Purity_{(TCE)}$	= Purity of the 1,1,2-tricloroethane reference substance, expressed as a decimal
DF	= Dilution factor for standard solution (50 mL)

The following is an example calculation for 1,1,2-trichloroethane in Standard 201401677-5A calibration solution:

$$\text{Concentration}_{(TCE)} = 49.7 \text{ mg} \times 0.968/50 \text{ mL} = 0.962 \text{ mg/mL}$$

where:

$\text{Concentration}_{(TCE)}$ = Concentration of 1,1,2-trichloroethane in the calibration standard solution, mg/mL
$\text{Wt}_{(TCE)}$ = 49.7 mg
$\text{Purity}_{(TCE)}$ = 96.8% = 0.968
DF = 50 mL

2. Calculation of the response factor for 1,1,2-trichloroethane in the calibration solutions:

$$\text{Rf}_{(TCE)} = \frac{\text{Concentration}_{(TCE)}}{\text{A}_{(TCE)}}$$

where:

$\text{Rf}_{(TCE)}$ = Response factor for 1,1,2-trichloroethane
$\text{Concentration}_{(TCE)}$ = Concentration of 1,1,2-trichloroethane in the standard solution, mg/mL
$\text{A}_{(TCE)}$ = Area of 1,1,2-trichloroethane peak obtained during analysis of the calibration solution

The following is an example calculation for 1,1,2-trichloroethane in Standard 201401677-5A calibration solution (\\elntrd12\EZChrom\Projects\202gc102\DAS-AM\DAS-AM-G-14-50\Precision\Precision day 1\002-Standard 201401677-5A.dat:

$$\text{Rf}_{(TCE)} = \frac{0.962 \text{ mg/mL}}{23489} = 4.09553\text{e} - 5$$

where:

$\text{Rf}_{(TCE)}$ = Response factor for 1,1,2-trichloroethane
$\text{Concentration}_{(TCE)}$ = 0.962 mg/mL
$\text{A}_{(TCE)}$ = 23489

The response factors from all standard injections during a run sequence were averaged to calculate $\text{RF}_{(avg)}$. The $\text{RF}_{(avg)}$ for 1,1,2-trichloroethane in run sequence \\elntrd12\ezchrom\Projects\202gc102\DAS-AM\DAS-AM-G-14-50\Precision\Precision day 1\Precision day 1.seq was 4.11089e-5.

3. Calculation of the weight % of 1,1,2-trichloroethane in the sample:

$$Wt\%_{(TCE)} = \frac{A_{(TCE)} \text{ x } RF_{avg\ (TCE)}}{Wt_{sample}} \text{x DF x } 100$$

where:

$Wt\%_{(TCE)}$	= Weight % of 1,1,2-trichloroethane in the sample
$A_{(TCE)}$	= Area of 1,1,2-trichloroethane obtained during analysis of the sample solution
$RF_{avg\ (TCE)}$	= Average response factor for 1,1,2-trichloroethane
Wt_{sample}	= Weight of sample in sample solution, mg
Dilution factor (DF)	= Dilution factor (5 mL for samples prepared as described in the method)

The following is an example calculation for 1,1,2-trichloroethane in sample solution Precision day 1-1 (\\elntrd12\EZChrom\Projects\202gc102\DAS-AM\DAS-AM-G-14-50\Precision\Precision day 1\006-Precision day 1-1.dat)

$$Wt\%_{(TCE)} = \frac{4562 \text{ x } 4.11089e-5}{2432.5} \text{ x } 5 \text{ x } 100 = 0.0385\%$$

where:

$Wt\%_{(TCE)}$	= Weight % of 1,1,2-trichloroethane in the sample
$A_{(TCE)}$	= Peak area for 1,1,2-trichloroethane in the sample solution (4562)
$RF_{avg\ (TCE)}$	= Average response factor for 1,1,2-trichloroethane (4.11089e-5)
Wt_{sample}	= 2432.5 mg
Dilution factor	= 5 mL

4. Statistical Methods

The statistical methods used in this study were means, standard deviations, relative standard deviations, Grubbs test for outliers, Horwitz equation for acceptable repeatability, linear regression, and t-test.

$$\text{Average (arithmetic mean)} = \frac{\text{sum of all numbers ("x")}}{n}$$

$$\text{Standard deviation} = \sqrt{\frac{\sum (x - \bar{x})^2}{(n-1)}}$$

$$\text{relative standard deviation} = \frac{\text{standard deviation}}{\text{average}} \text{ x } 100$$

$$\text{Horwitz } RSD_R = 2^{(1-0.5\log C)}$$

where C = concentration of the analyte in the sample as a decimal fraction

$$\text{Horwitz } RSD_r = RSD_R \times 0.67$$

Linear regression: $y = mx + b$
Where m = the slope of the line and b = the intercept

5. Spreadsheet and Data System Calculations

Calculation of response factors and weight percent values were performed with a chromatography data system. Calculation of regression analysis and remaining calculations were performed with an Excel spreadsheet. Calculations by hand using the data provided in the examples and tables may have slight differences due to rounding and significant figures used by the EZ Chrom Elite chromatography data system or an Excel spreadsheet.

IV. RESULTS AND DISCUSSION

A. Precision

The precision of the method was evaluated by preparing and analyzing five aliquots of 1,3-dichloropropene TGAI on each of two days. Fresh standard solutions were prepared for each group of samples. The average concentration and relative standard deviation (RSD) of the combined results from days 1 and 2 were calculated. Results are summarized in Table I.

The acceptability of the RSD was assessed by the Horwitz equation. Since the experimental RSD was less than the Horwitz RSD_r for 1,1,2-trichloroethane, the precision of the method was acceptable. A typical chromatogram of a calibration solution and a sample solution are shown in Figures 1 and 2, respectively.

System precision was determined by analyzing a prepared 1,1,2-trichloroethane TGAI sample six times. Results are summarized in Table II.

B. Recovery

The recovery (accuracy) of the method was evaluated by analysis of a series of samples prepared by fortifying the test system with 1,1,2-trichloroethane as described in Section III.D.5 and in Table III. The applicable validation concentration ranges are provided in Table IV.

Recovery data are summarized in Table V. Recovery results were found to be acceptable based on SANCO guidelines (SANCO/3030/99 rev.4).

C. Linearity

Linearity of detector response was evaluated using the recovery samples. The relationship between peak area and concentration was linear for 1,1,2-trichloroethane. Results are summarized in Figure 3.

D. Stability

Stability was determined by analyzing the day one method precision samples and standards three days after the initial analysis. Fresh standard solutions were prepared for the reanalysis. The t-test was used to compare the results and indicated that concentrations for 1,1,2-trichloroethane in stored sample solutions were statistically equivalent to the original results. Therefore, the sample solutions are considered to be stable at lab ambient conditions for at least three days. Results are summarized in Table VI.

The average recovery for stored standard solutions was 101%, which indicated that standard solutions are stable for at least 3 days when stored at lab ambient conditions. Results are shown in Table VII.

E. Interferences

No interferences for 1,1,2-trichloroethane were observed from the EMD ethyl acetate solvent blank, the test substances or the 1,3-dichloropropene test system in the analytical method.

Several of the impurity standards contained small amounts of other test substances. The amount of interference will depend on the purity of the reference standards. If the purity of the test substances decreases, or a test substance of lower purity is obtained, the test substance should be re-evaluated to determine its suitability for use in a combined standard solution or the test substance should be prepared separately.

A high purity ethyl acetate (such as EMD min 99.9%) must be used for the preparation and analysis of 1.3-dichloropropene TGAI samples according to this method. Alternative suppliers and purities of ethyl acetate should be evaluated prior to use.

Example chromatograms are shown in Figures 4-6.

F. LOD/LOQ

The Recovery 1A sample was used for determination of LOQ. For the analytical evaluation of LOQ, the precision of the replicate analyses was evaluated against the expected relative standard deviation calculated by the Horwitz equation and found to be acceptable at the prepared level for 1,1,2-trichloroethane. For 1,1,2-trichloroethane, the recovery was found to be within the acceptable range (75 to 125%). The results for the evaluation of LOQ and LOD are presented in Tables VIII and IX.

V. CONCLUSIONS

This method is applicable to the determination of 1,1,2-trichloroethane in 1,3-dichloropropene TGAI over the range of 0.0108 to 1.05%.

The recovery, linearity, and precision data have shown this method to be acceptable for the determination of 1,1,2-trichloroethane in 1,3-dichloropropene.

If the method is used with another set of equipment, it is suggested that method precision, linearity, and method limits be re-determined.

This report accurately reflects what was done during the course of the study and includes all amendments and/or deviations to the protocol.

This report satisfies the data requirement for U.S. EPA OPPTS Guideline 830.1800, Enforcement Analytical Method.

The statistical methods used were means, standard deviations, relative standard deviations, Horwitz equation, regression analysis, t-test, and Grubbs test for outliers. The databook(s), raw data and the original copy of the final report for this study will be stored in the Dow AgroSciences LLC test facility archives at 9330 Zionsville Road, Indianapolis, Indiana.

VI. TABLES

Table I. Method Precision Data for 1,1,2-trichloroethane in 1,3-dichloropropene TGAI

Date	Sample Id	Wt% 1,1,2-trichloroethane
3-March-2015	Precision day 1-1	0.0385
	Precision day 1-2	0.0385
	Precision day 1-3	0.0353
	Precision day 1-4	0.0358
	Precision day 1-5	0.0378
6-March-2015	Precision day 2-1	0.0367
	Precision day 2-1	0.0370
	Precision day 2-3	0.0366
	Precision day 2-4	0.0384
	Precision day 2-5	0.0356
Overall Average		0.037
Std. Dev.		0.0012
Overall RSD		3.3
Horwitz RSD_R		6.6
Horwitz RSDr		4.4
Acceptable (Overall RSD<Horwitz RSDr)		Acceptable

Table II. System Precision Data for 1,1,2-trichloroethane in 1,3-dichloropropene TGAI

Sample Id	Wt% 1,1,2-trichloroethane
Precision day 1-1 injection 1	0.0355
Precision day 1-1 injection 2	0.0371
Precision day 1-1 injection 3	0.0350
Precision day 1-1 injection 4	0.0349
Precision day 1-1 injection 5	0.0367
Precision day 1-1 injection 6	0.0351
Average	0.036
Std. Dev.	0.0011
RSD	2.9

Table III. Preparation of Recovery Samples for 1,1,2-trichloroethane in 1,3-dichloropropene TGAI

Sample	Stock concentration, mg/mL	Volume stock added, mL	Weight 1,1,2-TCE mg[1]	Weight 1,3-dichloropropene TGAI, mg	Total weight, mg[2]	Wt% 1,1,2-TCE added[3]
Recovery 0A	NA	NA	NA	2435.1	2435.1	0
Recovery 1A	2.64	0.1	0.264	2435.8	2436.1	0.0108
Recovery 2A	2.64	0.25	0.660	2437.1	2437.8	0.0270
Recovery 3A	2.64	0.5	1.32	2432.2	2433.5	0.0541
Recovery 4A	2.64	1	2.64	2432.6	2435.2	0.108
Recovery 5A	2.64	2	5.28	2430.0	2435.3	0.216
Recovery 6A	26.0	0.5	13.0	2435.7	2448.7	0.530
Recovery 7A	26.0	0.7	18.2	2435.6	2435.8	0.740
Recovery 8A	26.0	1	26.0	2434.5	2460.5	1.05

[1]The weight of 1,1,2-TCE added = Stock concentration, mg/mL x volume of stock added, mL
Note: weight of 1,1,2-TCE is not corrected for purity (99.9%)

[2]The total sample weight is the sum of weights from 1,1,2-trichloroethane and 1,3-dichloropropene TGAI.

[3]The weight% of 1,1,2-TCE added $= \frac{\text{Weight 1,1,2-TCE, mg x 0.999}}{\text{Total weight, mg}} \text{ x } 100$

Table IV. Concentrations of 1,1,2-trichloroethane in Recovery Samples

Sample	Weight 1,1,2-TCE added, mg*	Purity corrected weight, mg	Concentration 1,1,2-TCE, mg/mL**
Recovery 0A	NA	NA	NA
Recovery 1A	0.264	0.264	0.0527
Recovery 2A	0.660	0.659	0.132
Recovery 3A	1.32	1.32	0.264
Recovery 4A	2.64	2.64	0.527
Recovery 5A	5.28	5.27	1.05
Recovery 6A	13.0	13.0	2.59
Recovery 7A	18.2	18.2	3.63
Recovery 8A	26.0	25.9	5.19

*See Table V for preparation of the recovery samples.

**The concentration of 1,1,2-trichloroethane in the recovery solutions was calculated as follows:

$$\text{Concentration(TCE)} = \frac{Wt_{(TCE)} \times P_{(TCE)}/100}{V}$$

where:

$Concentration_{(TCE)}$ = Concentration of 1,1,2-trichloroethane in the sample solution, mg/mL
$Wt_{(TCE)}$ = Weight of the 1,1,2-trichloroethane reference substance added to the recovery sample, mg
$P_{(TCE)}$ = Purity of the 1,1,2-trichloroethane reference substance
V = Volume of solution (5 mL)

Table V. Recovery Data for 1,1,2-trichloroethane

Sample ID	Rep	Theoretical Weight %	Peak Area	Weight % Found	% Recovery	Average % Recovery
Recovery 0A	1	0	ND	NA	NA	NA
Recovery 0A	2	0	ND	NA	NA	
Recovery 1A*	1	0.0108	1383	0.0129	120	119
Recovery 1A*	2	0.0108	1363	0.0127	118	
Recovery 2A	1	0.0270	3025	0.0282	105	107
Recovery 2A	2	0.0270	3141	0.0293	109	
Recovery 3A	1	0.0540	5983	0.0560	103	104
Recovery 3A	2	0.0540	6044	0.0565	104	
Recovery 4A	1	0.108	11988	0.112	104	104
Recovery 4A	2	0.108	12035	0.112	104	
Recovery 5A	1	0.216	23498	0.220	102	102
Recovery 5A	2	0.216	23561	0.220	102	
Recovery 6A	1	0.530	58088	0.540	102	101
Recovery 6A	2	0.530	57649	0.536	101	
Recovery 7A	1	0.740	80265	0.744	101	101
Recovery 7A	2	0.740	80333	0.745	101	
Recovery 8A	1	1.05	116654	1.08	103	103
Recovery 8A	2	1.05	116552	1.08	103	
					Average	105
					Std.Dev.	5.9
					RSD	5.6

*Recovery 1A sample was also used to evaluate LOQ

Table VI. Stability Data for 1,1,2-trichloroethane in 1,3-dichloropropene TGAI

Sample Id	Wt % 1,1,2-trichloroethane	
	3-March-2015	6-March-2015
Precision day 1-1	0.0385	0.0385
Precision day 1-2	0.0385	0.0354
Precision day 1-3	0.0353	0.0334
Precision day 1-4	0.0358	0.0380
Precision day 1-5	0.0378	0.0360
Average	0.037	0.036
Standard Deviation (SD)	0.0015	0.0021
SD^2	0.0000023	0.0000043
Number of samples (n)	5	5
Degrees of freedom	8	
t Critical two-tail (95%)	2.31	
t Stat	0.80	
Statistical outcome (Acceptable if |tStat| ≤ tcritical)	Acceptable	

Table VII. Standard Stability Data for 1,1,2-trichloroethane

Standard ID	Standard Concentration as prepared, mg/mL	Standard Concentration after 3 days at lab ambient temperature, mg/mL*	% Recovery
201401677-5A	0.962	0.968	101
201401677-5A	0.962	0.966	100
201401677-5B	1.01	1.03	102
201401677-5B	1.01	1.03	102
Average recovery			101

*Analyzed as unknown using freshly prepared standard solutions

Table VIII. Limit of Quantitation for 1,l,2-trichloroethane

Sample ID	Height	Wt% found	% Recovery
Recovery 1A - Rep 1*	***328****	***0.014****	***127****
Recovery 1A - Rep 2	305	0.012	111
Recovery 1A - Rep 3	296	0.011	106
Recovery 1A - Rep 4	304	0.012	114
Recovery 1A - Rep 5	296	0.012	107
Recovery 1A - Rep 6	317	0.012	111
Overall Average	304	0.012	110
Standard Dev	--	0.00035	--
Overall RSD	--	2.9	--
Horwitz RSD_R	--	7.8	--
Horwitz RSDr	--	5.2	--
Acceptable (Overall RSD<Horwitz RSDr)	--	Yes	--
Signal / Noise (2H/h; h = 62)	10	--	--

*Discarded as an outlier using the Grubbs test (95% confidence level)

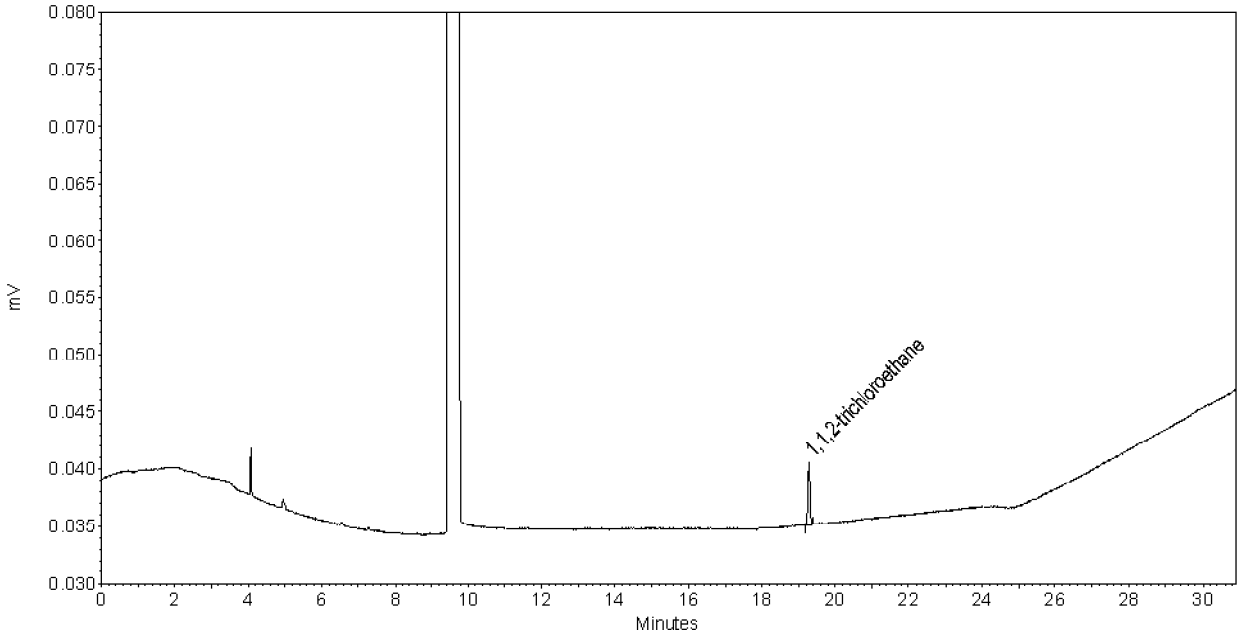
Overall Recovery = Measured wt.% / Theoretical wt.% × 100
Theoretical Wt% = 0.0108

Table IX. Limit of Detection for 1,1,2-trichloroethane

Sample ID	Height	Wt% found
LOD 1A - Rep 1	151	0.0055
LOD 1A - Rep 2	150	0.0051
LOD 1A - Rep 3	168	0.0065
LOD 1A - Rep 4	159	0.0070
LOD 1A - Rep 5	153	0.0061
LOD 1A - Rep 6	153	0.0054
Overall Average	156	0.006
Signal / Noise (2H/h; h = 62)	5	

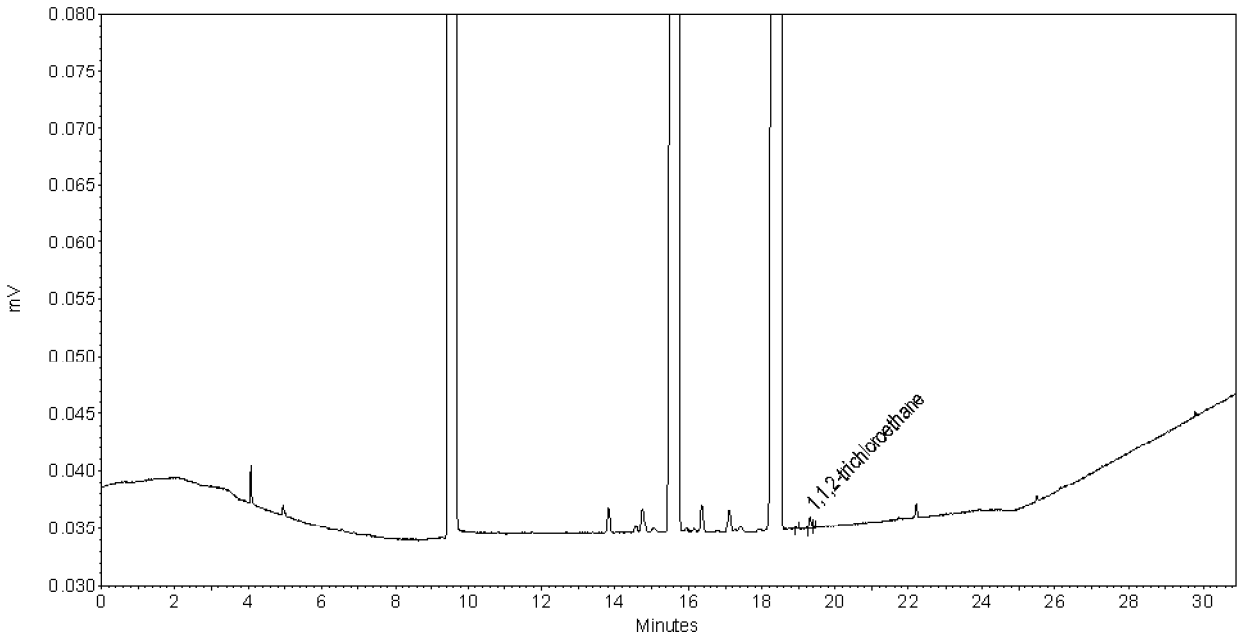
VII. FIGURES

Figure 1. Representative Chromatogram of the 1,1,2-trichloroethane Standard Solution



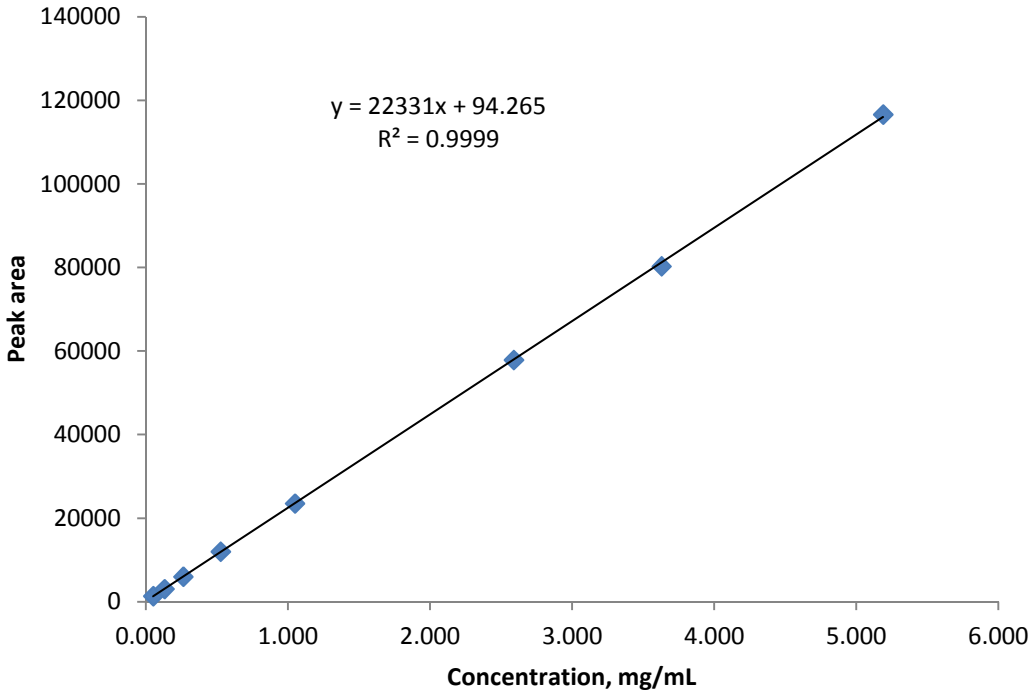
Data file: \\elntrd12\EZChrom\Projects\202gc102\DAS-AM\DAS-AM-G-14-50\Precision\Precision day 1\002-Standard 201401677-5A.dat

Figure 2. Representative Chromatogram of a 1,3-dichloropropene TGAI Solution



Data file: \\elntrd12\EZChrom\Projects\202gc102\DAS-AM\DAS-AM-G-14-50\Precision\Precision day 1\006-Precision day 1-1.dat

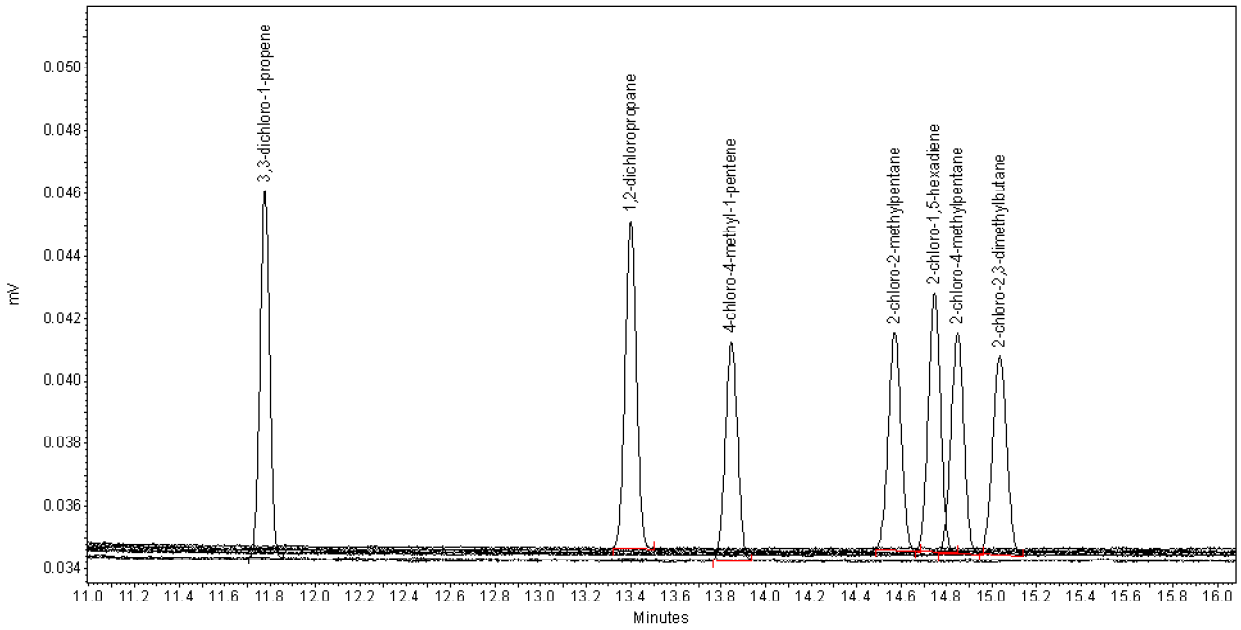
Figure 3. Linearity of 1,1,2-trichloroethane



Sample ID	Weight %[1]	Peak Area[2]	Concentration (mg/mL)[3]
Recovery 1A	0.0108	1373	0.0527
Recovery 2A	0.0270	3083	0.132
Recovery 3A	0.0541	6014	0.264
Recovery 4A	0.108	12012	0.527
Recovery 5A	0.216	23530	1.05
Recovery 6A	0.530	57869	2.59
Recovery 7A	0.740	80299	3.63
Recovery 8A	1.05	116603	5.19

1. Weight % is amount added in recovery samples
2. Area is the average of two injections
3. Concentration, mg/mL = mg 1,1,2-TCE in recovery sample/5 mL

Figure 4. Chromatograms of Impurities from Interferences Evaluation (Region 1, 11 to 16 min)

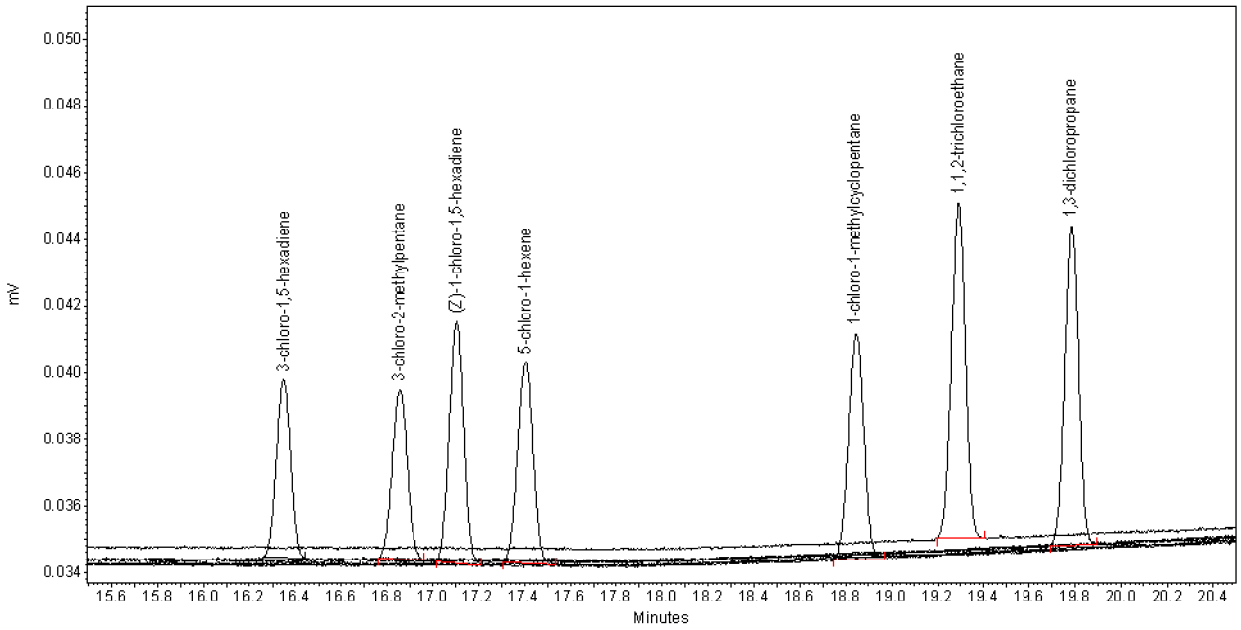


Data path: \\elntrd12\EZChrom\Projects\202gc102\DAS-AM\DAS-AM-G-14-50\Interferences\

Sample	Filename
TSN030579-0001 3,3-dichloro-1-propene (M)	016-TSN030579-0001.dat
AGR277102 1,2-dichloropropane (A)	004_AGR277102.dat
TSN303759 4-chloro-4-methyl-1-pentene (N)	019-TSN303759.dat
AGR238091 2-chloro-2-methylpentane (B)	005-AGR238091.dat
TSN030278-0001 2-chloro-1,5-hexadiene (C)	006-TSN030278-0001.dat
TSN106505 2-chloro-4-methylpentane (D)	007-TSN106505.dat
TSN028018-0001 2-chloro-2,3-dimethylbutane (E)	008-TSN028018-0001.dat

* 2-chloro-1,5-hexadiene (Impurity C) is analyzed in DAS-AM-05-10 due to incomplete resolution from impurity D using the chromatography conditions in this method.

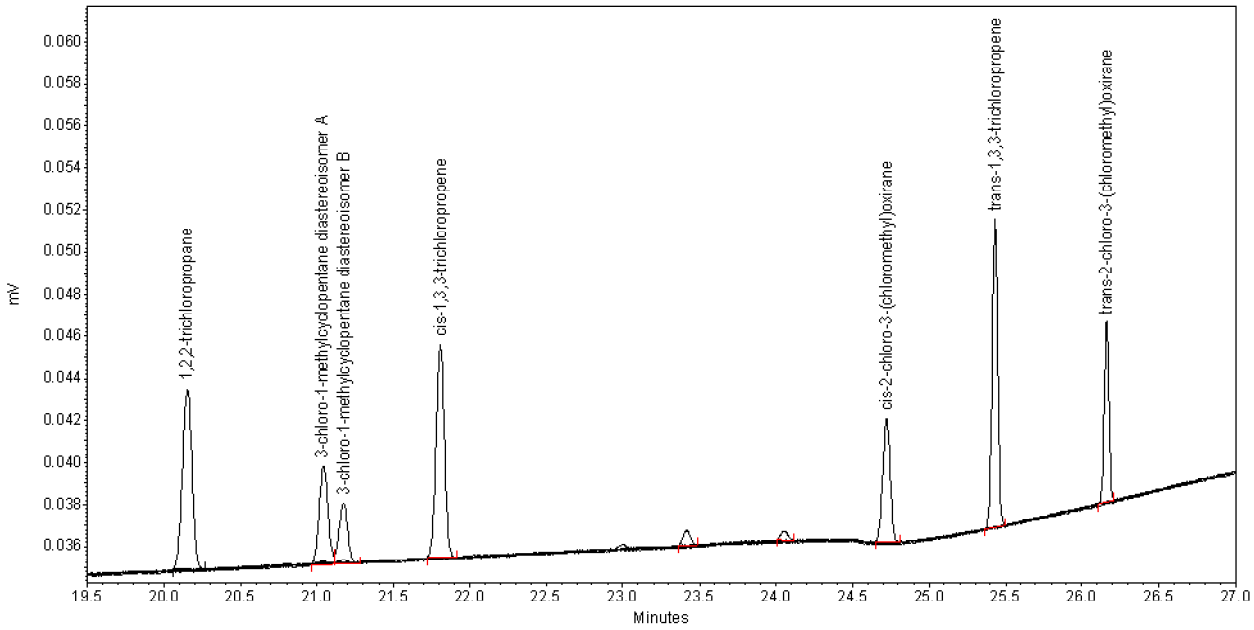
Figure 5. Chromatograms of Impurities from Interferences Evaluation (Region 2, 15.5 to 20.5 min)



Data path: \\elntrd12\EZChrom\Projects\202gc102\DAS-AM\DAS-AM-G-14-50\Interferences\

Sample	Filename
TSN303599 3-chloro-1,5-hexadiene (F)	009-TSN303599.dat
TSN303946 3-chloro-2-methylpentane (G)	010-TSN303946.dat
TSN304464 1-chloro-1,5-hexadiene (P)	018-TSN304464.dat
TSN106329 5-chloro-1-hexene (O)	017-TSN106329.dat
TSN303032 1-chloro-1-methylcyclopentane (R)	020-TSN303032.dat
AGR238090 1,3-dichloropropane (H)	011-AGR238090.dat
Aldrich lot 28896MMV 1,1,2-trichloroethane	003-Aldrich lot 28896MMV.dat

Figure 6. Chromatograms of Impurities from Interferences Evaluation (Region 3, 19.5 to 27 min)



Data path: \\elntrd12\EZChrom\Projects\202gc102\DAS-AM\DAS-AM-G-14-50\Interferences\

Sample	Filename
TSN301451 1,2,2-trichloropropane (I)	012-TSN301451.dat
TSN303341 3-chloro-1-methylcyclopentane (Q)	002-TSN303341.dat*
AGR238088 Cis-1,3,3-trichloropropene (J)	013-AGR238088.dat
TSN307901 Cis/Trans-2-chloro-3-(chloromethyl)oxirane (K)	014-TSN307091.dat
AGR238086 Trans-1,3,3-trichloropropene (L)	015-AGR238086.dat

*All interference samples were run under sequence “Interference evaluation.seq” except for sample TSN303341, which was analyzed under sequence “Interference evaluation-3.seq”. Initial analysis resulted in a significantly longer than expected retention time for the ethyl acetate solvent peak.

APPENDIX I. ANALYTICAL METHOD SUMMARY

Analytical Method Summary – Analytical Method and Validation for the Determination of Impurities in 1,3-Dichloropropene Technical Grade Material – Method NA-AM-98-081.00 Extension

1. Preparation of calibration solutions

   Prepare a solution of the 1,1,2-trichloroethane reference substance in duplicate by accurately weighing approximately 50 mg into a 50-mL volumetric flask (record weight to the nearest 0.1 mg). Dilute to the mark with ethyl acetate and mix well.

2. Preparation of sample solutions

   Using a volumetric pipet, add 2 mL of 1,3-dichloropropene into a 5 mL volumetric flask (record weight to the nearest 0.1 mg) and dilute to volume with ethyl acetate. Mix well.

3. Instrumentation and Conditions:

   GC analysis conditions:

Column:	DB-1701 60 m x 0.32 mm x 1µm	
Inlet temperature:	150°C	
Split ratio:	38:1	
Injection volume:	2 µL	
Column flow:	Constant flow at 1.9 mL/min Helium	
Column temperature:	40°C hold for 2 minutes, 5°C/minute to 80°C, hold for 7.5 minutes 5°C/minute to 110°C, hold for 1 minutes 25°C/minute to 270°C, hold for 0 minutes	
Detector:	Thermal conductivity (TCD)	
Detector temperature:	280°C	
Detector flow rate:	Reference Flow (Helium): 15 mL/min Make-up (Helium): 5 mL/min	
Run Time:	30.9 minutes	
Integrator:	Agilent EZChrom	
Retention Time:	1,1,2-trichloroethane	~ 19.3 min

   Approximate time to prepare and analyze sample: 4 hours

4. Calculations:

   Calculation of response factors and weight percent values can be performed with a computing integrator/data system or with a spreadsheet.

a. Calculation of the concentration of 1,1,2-trichloroethane in the calibration solutions:

$$Concentration_{(TCE)} = Wt_{(TCE)} \times Purity_{(TCE)}/DF$$

where:

$Concentration_{(TCE)}$ = Concentration of 1,1,2-trichloroethane in the calibration standard solution, mg/mL

$Wt_{(TCE)}$ = Weight of the 1,1,2-trichloroethane reference substance added to the calibration solution, mg

$Purity_{(TCE)}$ = Purity of the 1,1,2-trichloroethane reference substance, expressed as a decimal

DF = Dilution factor (50 mL)

b. Calculation of the response factor for 1,1,2-TCE in the calibration solutions:

$$RF_{(TCE)} = \frac{Conc_{(TCE)}}{A_{(TCE)}}$$

where:

$Rf_{(TCE)}$ = Response factor for 1,1,2-trichloroethane

$Conc_{(TCE)}$ = Concentration of 1,1,2-trichloroethane in standard solution, mg/mL

$A_{(TCE)}$ = Area of 1,1,2-trichloroethane obtained during analysis of the calibration solution

c. Calculation of the weight % of 1,1,2-TCE in the sample:

$$Wt\%_{(TCE)} = \frac{A_{(TCE)} \times RF_{(avg\ TCE)}}{Wt_{sample}} \times DF \times 100$$

where:

$Wt\%_{(TCE)}$ = Weight % of 1,1,2-trichloroethane in the sample

$A_{(TCE)}$ = Area of 1,1,2-trichloroethane obtained during analysis of the sample solution

$RF_{(avg\ TCE)}$ = Average response factor for 1,1,2-trichloroethane

Wt_{sample} = Weight of sample in sample solution, mg

DF = Dilution factor for samples (5 mL)

Example chromatograms are attached.

Additional details are provided in the body of the report.

Figure 1. Representative Chromatogram of a Calibration Solution

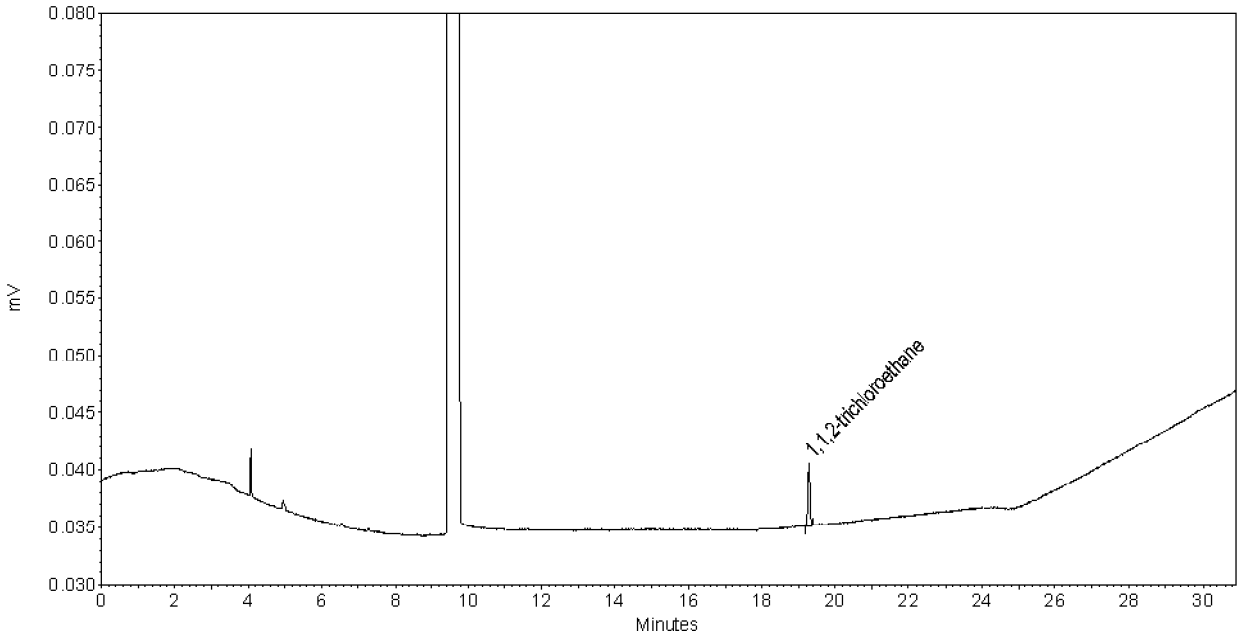


Figure 2. Representative Chromatogram of a Sample Solution of 1,3-dichloropropene TGAI