



TEST METHOD

Effective: 23 April 2025
Supersedes: New

DOWM 102990-E25A

Cis- and Trans-1,3-Dichloropropene in 1,3-Dichloropropene by Gas Chromatography

1. Scope

- 1.1 This method is applicable to the determination of the following in 1,3-dichloropropene.

Analyte	Applicable Range (%, w/w)
Cis-1,3-dichloropropene	25 to 98
Trans-1,3-dichloropropene	22 to 84
Total 1,3-dichloropropene	N/A

Note: The sample may contain additives. These include up to 2.4% (w/w) epoxidized soybean oil.

- 1.2 Validation data was originally generated under Good Laboratory Practice (GLP) conditions (Section 17) and conforms with SANCO/3030/99 rev 5.

2. Principle

- 2.1 A sample of 1,3-dichloropropene is diluted in ethyl acetate containing internal standard (chlorobenzene) and analyzed by gas chromatography. The components are separated and detected with a thermal conductivity detector. Quantitation is by internal standard (chlorobenzene) based on peak area ratios.

3. Summary

- 3.1 A sample of 1,3-dichloropropene is diluted in ethyl acetate containing internal standard (chlorobenzene) and analyzed by gas chromatography. The components are separated and detected with a thermal conductivity detector. Quantitation is by internal standard based on peak area ratios.
- 3.2 This method is applicable to the determination of cis-1,3-dichloropropene, trans-1,3-dichloropropene and total 1,3-dichloropropene in 1,3-dichloropropene.
- 3.3 The low end of applicable range lies at 25 and 22% (w/w) for the cis- and trans-isomer respectively. The upper end of applicable range lies at 98 and 84% (w/w) for the cis- and trans-isomer respectively.

- 3.4 The average marginal recovery (see Note 16.2) for cis-1,3-dichloropropene was 101.1% and the average marginal recovery for trans-1,3-dichloropropene was 100.3%.
- 3.5 Replicate analyses of a sample of 1,3-dichloropropene on two separate days gave a relative standard deviation for cis-1,3-dichloropropene of 0.21% and for trans-1,3-dichloropropene of 0.17% at an average concentration of 48% (w/w) and 50% (w/w), respectively. The analysis is complete in 30.9 minutes.

4. Safety

- 4.1 Each analyst must be acquainted with the potential hazards of the equipment, reagents, products, solvents, and procedures before beginning laboratory work. SOURCES OF INFORMATION INCLUDE: OPERATION MANUALS, SAFETY DATA SHEETS, LITERATURE AND OTHER RELATED DATA. Safety information should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents must be in compliance with applicable governmental and company requirements.
- 4.2 cis/trans-1,3-dichloropropene is toxic and may be fatal if swallowed or inhaled. It is suspected of causing cancer and may cause skin and eye irritation/damage. It is a flammable liquid with a flash point of 28 °C. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.3 Ethyl acetate is a flammable liquid with a flash point of -4 °C. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.4 Chlorobenzene is harmful if inhaled and causes skin irritation. It is a flammable liquid with a flash point of 27 °C and it is toxic to aquatic life. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).

5. Interferences

- 5.1 No direct interferences have been observed in the use of this method. If results are suspect based on the analytical history of the product, the data should be confirmed by an alternate method.

Note: The presence of epoxidized soybean oil additive has been observed to cause no interference. See Figures 2 and 3 for a formulation blank and accompanying solvent bank.

6. Apparatus

- 6.1 Analytical balance: capable of weighing to 0.0001 g. Mettler-Toledo XPE304, available from Mettler-Toledo, Inc., or equivalent.
- 6.2 Gas chromatograph: Agilent model 6890, equipped with split/splitless capillary injection port, autosampler and thermal conductivity detector (TCD), available from Agilent Technologies, Inc., or equivalent.
- 6.3 Agilent J&W Scientific DB-1701, 60 m x 0.32 mm x 1 µm capillary column, available from Agilent Technologies, Inc., or equivalent.
- 6.4 Chromatography data system: OpenLab Software version 2.5, available from Agilent Technologies, Inc., or equivalent.
- 6.5 Autosampler vials: 1.5-mL with screw caps, available from VWR, or equivalent.

7. Reagents

7.1 Ethyl acetate: HPLC grade, Riedel-de Haën 33211, available from Honeywell Research Chemicals, or equivalent.

7.2 Chlorobenzene, 99.9%, available from Sigma Aldrich, or equivalent.

Note: The purity of this standard should either be provided by the supplier or determined by the analyst for use in Section 8.2.

7.3 1,3-dichloropropene reference substance, known cis- and trans-1,3-dichloropropene content, here: 99.0% (cis + trans), 53.3% cis, 45.7% trans, GLP certified, available from Customer Information Group, The Dow Chemical Company.

8. Reagent Solutions

8.1 Calibration solution:

8.1.1 Transfer (and record to the nearest 0.0001 g) 1 mL of chlorobenzene internal standard (Section 7.2) into a 1-ounce jar.

8.1.2 Add (and record to the nearest 0.0001 g) 2 mL of 1,3-dichloropropene reference standard (Section 7.3) to the jar in Section 8.1.1. Cap and mix well.

8.1.3 Add 20 mL of ethyl acetate to the jar in Section 8.1.2. Cap and mix well.

9. Analysis Conditions

Note: The parameters summarized below were used in the validation of the method. Pressures, flow rates, and integrator parameters will depend on each chromatographic system and may differ from those stated below.

Instrument:	Agilent model 6890 gas chromatograph
Injection:	
Inlet type:	Split/Splitless
Inlet temperature:	130 °C
Inlet liner:	Restek Sky 4 mm straight with glass wool, or equivalent
Injection volume:	1 µL
Split ratio:	1:38
Syringe:	5 or 10-µL (with metal plunger to avoid PTFE swelling)
Syringe wash:	Ethyl acetate
Chromatographic conditions:	
Column:	Agilent J&W Scientific DB-1701, 60 m x 0.32 mm x 1 µm capillary column
Flow:	1.9 mL/min, helium (constant flow mode)
Temperature program:	40 °C (2 min hold), to 80 °C at 5 °C/min, hold for 7.5 min, to 110 °C at 5 °C/min, hold for 1 min, to 270 °C at 25 °C/min, no hold
Detector:	Thermal conductivity detector (TCD)
Detector Temperature:	280 °C
Make-up flow:	5 mL/min, helium
Reference flow:	15 mL/min, helium
Run time:	30.9 min

- 9.1 A representative chromatogram is illustrated in Figure 1.

10. Calibration

- 10.1 Inject two 1- μ L aliquots of the calibration standard into the chromatograph and separate each according to the chromatographic conditions outlined in Section 9.
- 10.2 Calibrate the chromatography data system according to the manufacturer's operating instructions for an internal standard calibration (if manual calculations are used, proceed to the next section).
- 10.3 If manual calculations are used, calculate the relative response factors for the analyte of interest (cis-1,3-dichloropropene or trans-1,3-dichloropropene) for each injection as follows:

$$\text{RRF}_i = \frac{W_{RS} \times C_{i,RS} \times A_{IS}}{A_{i,CS} \times W_{IS}}$$

where:

- RRF_i = relative response factor for the analyte of interest, *i*
 W_{RS} = weight (g) of the 1,3-dichloropropene reference substance (Section 7.3) in the calibration solution (Section 8.1.2).
 $C_{i,RS}$ = concentration (weight fraction) of the analyte of interest, *i* in the 1,3-dichloropropene reference substance (Section 7.3)
 A_{IS} = peak area (area counts) for the internal standard chlorobenzene obtained from the analysis of the calibration standard (Section 10.1)
 $A_{i,CS}$ = peak area (area counts) of analyte obtained from the analysis of the calibration standard (Section 10.1)
 W_{IS} = weight (g) of the internal standard chlorobenzene (Section 7.2) in the calibration solution (Section 8.1.1).

11. Procedure

- 11.1 Sample solution:
 - 11.1.1 Transfer (and record to the nearest 0.0001 g) 1 mL of chlorobenzene internal standard (Section 7.2) into a 1-ounce jar.
 - 11.1.2 Add (and record to the nearest 0.0001 g) 2 mL of 1,3-dichloropropene sample to the jar in Section 11.1.1. Cap and mix well.
 - 11.1.3 Add 20 mL of ethyl acetate to the jar in Section 10.1.2. Cap and mix well.
- 11.2 Inject a 1- μ L aliquot of the sample solution (Section 10.1) into the chromatograph and separate according to the chromatographic conditions outlined in Section 9.
- 11.3 Report results to two significant figures.

12. Calculations

- 12.1 If manual calculations are used, calculate the concentration of the analyte of interest in the original sample as follows:

$$C_i = \frac{RRF_i \times A_i \times W_{IS}}{A_{IS} \times W_S} \times 100\%$$

where:

- C_i = concentration (% w/w) of the analyte of interest, i in the sample.
- RRF_i = relative response factor for the analyte of interest, i (Section 11.3).
- A_i = peak area (area counts) for the analyte of interest, i obtained from the analysis of the sample solution (Section 11.2).
- W_S = weight (g) of the sample test portion added to the sample solution (Section 11.1.2).
- W_{IS} = weight (g) of the internal standard portion added to the sample solution (Section 11.1.1).
- A_{IS} = peak area (area counts) of the internal standard obtained from the analysis of the sample solution (Section 11.2).
- 100% = conversion to percent.

- 12.2 If manual calculations are used, calculate the total concentration of 1,3-dichloropropene in the original sample as follows:

$$C_{1,3\text{-dichloropropene}} = C_{cis-1,3\text{-dichloropropene}} + C_{trans-1,3\text{-dichloropropene}}$$

where:

- $C_{1,3\text{-dichloropropene}}$ = total concentration (% w/w) of 1,3-dichloropropene in the sample.
- $C_{cis-1,3\text{-dichloropropene}}$ = concentration (% w/w) of cis-1,3-dichloropropene in the sample.
- $C_{trans-1,3\text{-dichloropropene}}$ = concentration (% w/w) of trans-1,3-dichloropropene in the sample.

13. Precision

- 13.1 Precision data determined from multiple analyses [$n = 10$] of a single sample of 1,3-dichloropropene are given below. The analyses were performed over a 2-day period.
- 13.2 The Horwitz ratio [H_r] was determined, where $H_r = RSD/RSD_r = RSD/(0.67*2^{(1-0.5*\log c_{mf})})$, where c_{mf} is the average concentration in mass fraction, RSD is the relative standard deviation, and RSD_r is the RSD under reproducibility conditions. A Horwitz ratio of $H_r \leq 1$ is acceptable. The values are shown below.
- 13.3 At the 95% confidence level, individual measurements on similar samples may vary from the long-term average by the values shown below [$\pm t_{(n-1)} \times s$; where $t_{(n-1)}$ = t-value at $n-1$ degrees of freedom, and s = standard deviation of the validation data].
- 13.4 This assumes a normal distribution of results. The validity of this assumption has been verified using the Shapiro-Wilk test for normality. The test confirmed that the results could originate from normal distributions.
- 13.5 Equal variability between locations is assumed.

Analyte	n	t _(n-1)	Average	Relative Standard Deviation	At the 95% confidence level, individual measurements may vary from the long-term average by:	RSD _r	H _r
V			(%, w/w)	(%)	(± %)	(%)	
cis-1,3-dichloropropene	10	2.26	48	0.21	0.5	1.5	0.14
trans-1,3-dichloropropene	10	2.26	50	0.17	0.4	1.5	0.11
total 1,3-dichloropropene	10	2.26	98	0.16	0.4	1.3	0.12

14. Accuracy (Note 16.2)

- 14.1 Recoveries from the analysis of two spiked samples based on the calculated concentration of the analyte(s) in the spiked samples are given below:

Analyte	Concentration Added (%, w/w)	Average Marginal Recovery (%)	Range of Recoveries (%)
cis-1,3-dichloropropene	45	101.1	101.1-102.8
trans-1,3-dichloropropene	37	100.3	100.3-100.9

15. Linearity

- 15.1 Method response was found to be linear over the concentration ranges given below:

Analyte	Linear Concentration Range in Sample Solution (mg/mL)	Linear Concentration Range in Sample (%, w/w)
cis-1,3-dichloropropene	27 - 100	25 - 98
trans-1,3-dichloropropene	23 - 89	22 - 84
internal standard chlorobenzene	22 - 91	N/A

16. Notes

- 16.1 Analytical method performance can be affected by minor differences in instrumentation, reagents, and laboratory technique. Consequently, the method should be qualified in the performing laboratory to confirm its performance and suitability. In addition, analytical instruments should be calibrated at appropriate frequencies.
- 16.2 Marginal recovery is based on added analyte only.

17. Good Laboratory Practice

- 17.1 Apart from the chromatograms in Figure 2 and Figure 3, as well as the recovery study, all phases of the validation study were conducted according to the following Good Laboratory Practice Standard:

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

- 17.2 The accuracy study was conducted by a test facility certified to comply with the principles of Good Laboratory Practice by the Italian ministry of health in accordance with article 4 of Legislative Decree nr. 50 of March 2nd, 2007 and article 3(15) of Italian Ministry Decree of January 13th, 2016. (Date of issuance: July 12th, 2024).
- 17.3 Recording of the formulation blank chromatogram (Figure 2) and an accompanying solvent blank (Figure 3) was recorded by Dow internally and did not comply with GLP criteria.

18. References

- 18.1 SANCO (2019) *Technical Active Substance and Plant protection products: Guidance for generating and reporting methods of analysis in support of pre- and post-registration data requirements for Annex (Section 4) of Regulation (EU) No 283/2013 and Annex (Section 5) of Regulation (EU) No 284/2013*, SANCO/3030/99 rev.5, European Commission, (22-MAR-2019).

Figure 1. Representative chromatograms obtained using the conditions outlined in Section 9 of this method.

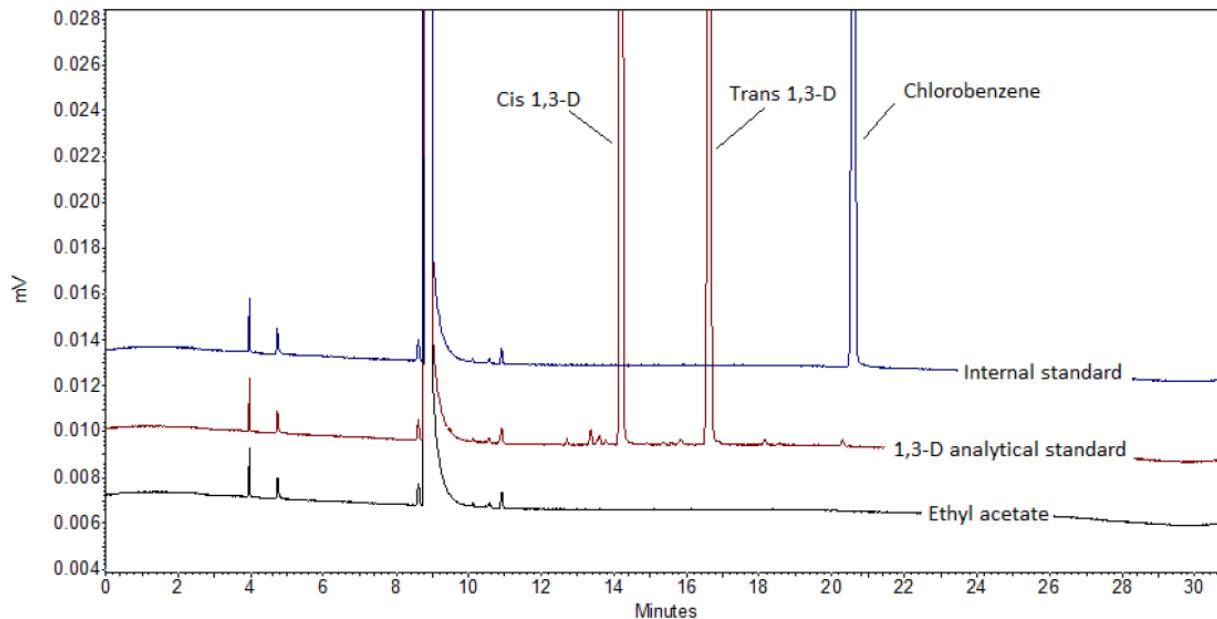


Figure 2. Representative chromatogram of a formulation blank obtained using the conditions outlined in Section 9 of this method. This chromatogram was **not** recorded under GLP-conditions.

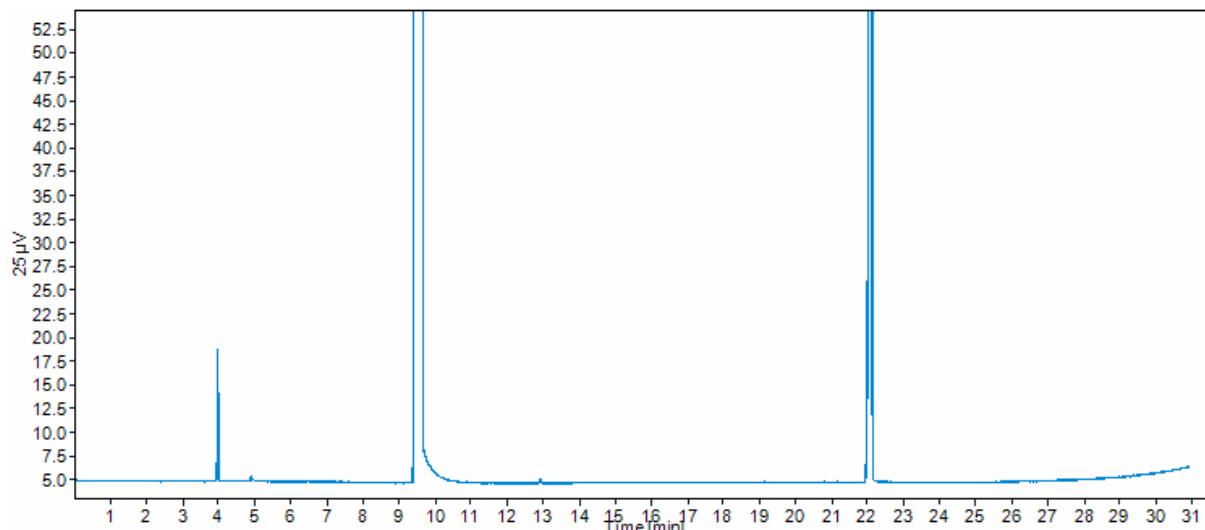


Figure 3. Representative chromatogram of a solvent and internal standard blank obtained using the conditions outlined in Section 9 of this method. This chromatogram was **not** recorded under GLP-conditions.

