



TEST METHOD

Effective: 22 April 2025
Supersedes: New

DOWM 102989-E25A

Impurities 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)
2-chloro-2-methylpentane	0.077 to 1.8
2-chloro-4-methylpentane	0.074 to 1.6
2-chloro-2,3-dimethylbutane	0.028 to 3.4
3-chloro-2-methylpentane	0.021 to 0.83
1,3-dichloropropane	0.040 to 2.3
1,2,2-trichloropropane	0.041 to 2.5
cis-1,3,3-trichloropropene	0.079 to 2.4
trans-1,3,3-trichloropropene	0.042 to 1.3

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 GLP conditions (see Section 17. Good Laboratory Practice) and conforms with SANCO/3030/99 rev 5.

2. Principle

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

3. Summary

- 3.1 A sample of 1,3-dichloropropene technical grade is diluted in ethyl acetate and analyzed by gas chromatography. The components are separated and detected with a thermal conductivity detector. Quantitation is by external standard based on peak area.
- 3.2 This method is applicable to the determination of 2-chloro-2-methylpentane, 2-chloro-4-methylpentane, 2-chloro-2,3-dimethylbutane, 3-chloro-2-methylpentane, 1,3-dichloropropane, 1,2,2-trichloropropane, cis-1,3,3-trichloropropene, and trans-1,3,3-trichloropropene in 1,3-dichloropropene over the ranges shown in Section 1.1.

- 3.3 The low end of applicable ranges lies between 0.021 and 0.079% (w/w) depending on the analyte. The upper end of applicable ranges lies between 0.573 and 3.41% (w/w) depending on the analyte.
- 3.4 The average recoveries range between 101.2 and 109.8% depending on the analyte with relative standard deviations of 8.3 to 12.9%.
- 3.5 Replicate analyses of either of two samples for each analyte on two separate days gave relative standard deviations of 1.1 to 6.8%. 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 1,3-dichloropropene technical grade 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. It may cause serious eye irritation, drowsiness or dizziness. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.4 2-chloro-2-methylpentane is a toxic and flammable liquid with a flash point of 17.2 °C. It may cause skin, serious eye, and respiratory irritation. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.5 2-chloro-4-methylpentane is a toxic and flammable liquid with a flash point of 20.8 °C. It may cause skin and eye irritation. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.6 2-chloro-2,3-dimethylbutane is a toxic and flammable liquid with a flash point of 14.9 °C. It may cause skin, serious eye, and respiratory irritation. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.7 3-chloro-2-methylpentane is a toxic and flammable liquid with a flash point of 20.8 °C. It may cause serious eye irritation. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.8 1,3-dichloropropane is a toxic and flammable liquid with a flash point of 36 °C. It may cause skin, serious eye, and respiratory irritation. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.9 1,2,2-trichloropropane is a toxic and flammable liquid with a flash point of 44.1 °C. It may cause skin, serious eye, and respiratory irritation. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).
- 4.10 cis-1,3,3-trichloropropene is a toxic and flammable liquid with a flash point of 18.7 °C. It may cause skin, serious eye, and respiratory irritation. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).

- 4.11 trans-1,3,3-trichloropropene is a toxic and flammable liquid with a flash point of 18.7 °C. It may cause skin, serious eye, and respiratory irritation. 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 4 and 5 for a formulation blank and accompanying solvent blank.

6. Apparatus

- 6.1 Analytical balance: capable of weighing to 0.0001 g, Mettler model AE200, 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 Capillary column: 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.
- 6.6 Volumetric flasks: 10-mL, available from VWR, or equivalent.

7. Reagents

- 7.1 Ethyl acetate: HPLC grade, Riedel-de Haën 33211, available from Honeywell Research Chemicals, or equivalent.
- Note: The analyst should run a blank measurement of the ethyl acetate to confirm its impurities do not cause interferences with the analyte.*
- 7.2 2-chloro-2-methylpentane standard, 100%, available from Customer Information Group, The Dow Chemical Company.
- 7.3 2-chloro-4-methylpentane standard, 75%, available from Customer Information Group, The Dow Chemical Company.
- 7.4 2-chloro-2,3-dimethylbutane standard, 100%, available from Customer Information Group, The Dow Chemical Company.
- 7.5 Mixture of 3-chloro-2-methylpentane standard (23%), and 2-chloro-2-methylpentane (76%), available from Customer Information Group, The Dow Chemical Company.
- 7.6 1,3-dichloropropane standard, 99.5%, available from Customer Information Group, The Dow Chemical Company.

- 7.7 1,2,2-trichloropropane standard, 96%, available from Customer Information Group, The Dow Chemical Company.
- 7.8 cis-1,3,3-trichloropropene, 96%, available from Customer Information Group, The Dow Chemical Company.
- 7.9 trans-1,3,3-trichloropropene standard, 95%, available from Customer Information Group, The Dow Chemical Company.

Note: Ideally the purity of these standards should be determined by analysis under GLP.

8. Reagent Solutions

8.1 Calibration stock solution:

8.1.1 Weigh (and record to the nearest 0.1 mg) 150 ± 50 mg of each analyte (Sections 7.2 to 7.9) into a 10-mL volumetric flask.

8.1.2 Dilute the flask in Section 8.1.1 to volume with ethyl acetate (Section 7.1). Cap and mix well.

8.2 Calibration standard:

8.2.1 Transfer 1 mL of the solution in Section 8.1.2 to a 10-mL volumetric flask.

8.2.2 Dilute the flask in Section 8.2.1 to volume with ethyl acetate (Section 7.1). Cap and mix well.

8.3 Determine the concentration of (analyte) in the calibration standard as follows:

$$C_{\text{analyte,CS}} = \frac{W_{\text{analyte,CSS}} \times P_{\text{analyte,standard}}}{V_{\text{CCS}}} \times \frac{1}{10}$$

where:

$C_{\text{analyte,CS}}$	=	concentration (mg/mL) of (analyte) in the calibration standard
$W_{\text{analyte,CSS}}$	=	weight (mg) of (analyte) in the calibration stock solution (Section 8.1.1)
$P_{\text{analyte,standard}}$	=	purity of (analyte) in the original standards (Sections 7.2 to 7.9)
V_{CCS}	=	volume (mL) of the calibration stock solution (Section 8.1)
1/10	=	dilution factor (1 mL/10 mL) for the calibration standard preparation (Section 8.2)

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:	150 °C
Injection volume:	2 µL
Split ratio:	1:38
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 an aliquot of the calibration standard into the chromatograph and separate 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 external standard calibration (if manual calculations are used, proceed to the next section).
- 10.3 If manual calculations are used, calculate the response factor for (analyte) as follows:

$$RF_{\text{analyte}} = \frac{C_{\text{analyte,CS}}}{A_{\text{analyte,CS}}}$$

where:

- | | | |
|-------------------------|---|---|
| RF_{analyte} | = | response factor (mg/mL / area counts) for (analyte) |
| $C_{\text{analyte,CS}}$ | = | concentration (mg/mL) of (analyte) in the calibration standard (Section 8.3) |
| $A_{\text{analyte,CS}}$ | = | peak area (area counts) for (analyte) obtained from the analysis of the calibration standard (Section 10.1) |

11. Procedure

Note: The instructions given below are specific for Agilent Models. Use of a different instrument may require modification of these instructions.

- 11.1 Sample solution:
 - 11.1.1 Weigh (and record to the nearest 0.1 mg) 4.0 mL of the sample into a 10-mL volumetric flask.
 - 11.1.2 Dilute the flask in Section 11.1.1 to volume with ethyl acetate (Section 7.1). Cap and mix well.
- 11.2 Inject an aliquot of the sample solution (Section 11.1) into the chromatograph and separate according to the chromatographic conditions outlined in Section 9.

12. Calculations

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

$$C_{\text{analyte}} = \frac{RF_{\text{analyte}} \times A_{\text{analyte}} \times V_{\text{SS}}}{W_{\text{S}}} \times 100\%$$

where:

- C_{analyte} = concentration (% w/w) of (analyte) in the sample
 RF_{analyte} = response factor (mg/mL / area counts) for (analyte) (Section 10.3)
 A_{analyte} = peak area (area counts) for (analyte) obtained from the analysis of the sample solution (Section 11.2)
 W_s = weight (mg) of the sample test portion added to the sample solution (Section 11.1.1)
 V_{ss} = volume (mL) of the sample solution (Section 11.1.1)
 100% = conversion to percent

12.2 Report results to two significant figures.

13. Precision

13.1 Precision has been determined by analysis of either of two samples of 1,3-dichloropropene. For each sample 11 aliquots were prepared and analyzed over a two-day period. Data are given below.

13.2 The Horwitz ratio [H_r] was determined, where $H_r = RSD/RSD_r = RSD/(0.67 \cdot 2^{(1-0.5 \cdot \log c_{mf})})$, where c_{mf} is the average concentration in mass fraction. 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 [$\pm t_{(n-1)} \times RSD$; where $t_{(n-1)} = t$ -value at (n-1) degrees of freedom].

13.4 This assumes a normal distribution of results. The validity of this assumption has been verified for 3-chloro-2-methylpentane, 1,3-dichloropropane, and trans-1,3,3-trichloropropene using the Shapiro-Wilk test for normality. The test confirmed that these results could originate from normal distributions. For other analytes, the exact nature of the distribution is unknown. Based on Chebychev's Inequality Theorem, 4.47 was used as an estimate for the t-value at the 95% confidence level (Reference 18.2)

13.5 Equal variability between locations is assumed.

Sample	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
				(%, w/w)	(%)	(\pm %)	(%)	
1	2-chloro-2-methylpentane	11	4.47	0.37	1.5	3.3	3.1	0.48
1	2-chloro-4-methylpentane	11	4.47	0.15	2.0	4.5	3.6	0.56
1	2-chloro-2,3-dimethylbutane	11	4.47	0.13	3.4	7.6	3.6	0.93
1	3-chloro-2-methylpentane	11	2.23	0.089	3.0	6.7	3.9	0.78
2	1,3-dichloropropane	11	2.23	0.084	3.9	8.7	3.9	1.0
2	1,2,2-trichloropropane	11	4.47	0.15	2.0	4.5	3.6	0.56
2	cis-1,3,3-trichloropropene	11	4.47	0.26	1.1	2.5	3.3	0.34
2	trans-1,3,3-trichloropropene	11	2.23	0.049	6.8	15	4.2	1.6

Note: A Horwitz ratio above 1 for trans-1,3,3-trichloropropene is deemed acceptable as the LOQ study performed by a different lab (Section 16) finds an acceptable Horwitz ratio (Section 16) and the concentration is close to the LOQ.

14. Accuracy

- 14.1 Recoveries from the analysis of up to n = 16 synthetic mixtures based on the calculated concentration of the analyte(s) in the synthetic mixtures are given below:

Analyte	n	Concentration Range	Average Recovery	Range of Recoveries	Standard Deviation of Recoveries
		(%, w/w)	(%)	(%)	(%)
2-chloro-2-methylpentane	3	0.050 - 1.8	104.3	94.6 - 112.2	8.9
2-chloro-4-methylpentane	5	0.020 - 1.6	103.5	94.0 - 125.8	13.1
2-chloro-2,3-dimethylbutane	16	0.028 - 3.6	105.0	78.4 - 118.2	9.7
3-chloro-2-methylpentane	4	0.015 - 1.4	105.9	96.4 - 125.8	13.8
1,3-dichloropropane	14	0.040 - 3.8	101.2	91.0 - 120.5	8.3
1,2,2-trichloropropane	11	0.041 - 4.1	102.4	92.8 - 118.9	9.5
cis-1,3,3-trichloropropene	11	0.042 - 2.4	107.3	97.7 - 126.5	9.8
trans-1,3,3-trichloropropene	14	0.042 - 3.2	109.8	96.5 - 136.6	12.9

15. Linearity

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

Analyte	Linear Concentration Range in Sample Solution	Linear Concentration Range in Sample
	(mg/mL)	(%, w/w)
2-chloro-2-methylpentane	0.16 - 13	0.034 - 2.7
2-chloro-4-methylpentane	0.092 - 12	0.019 - 2.5
2-chloro-2,3-dimethylbutane	0.13 - 16	0.027 - 3.4
3-chloro-2-methylpentane	0.099 - 4.0	0.021 - 0.83
1,3-dichloropropane	0.17 - 11	0.036 - 2.3
1,2,2-trichloropropane	0.19 - 12	0.039 - 2.5
cis-1,3,3-trichloropropene	0.38 - 12	0.079 - 2.5
trans-1,3,3-trichloropropene	0.19 - 6.1	0.040 - 1.3

16. Limit of Quantitation

- 16.1 The limit of quantitation (LOQ) was determined by standard addition with acceptable recovery and precision. A low concentration sample fortified with a low amount of analyte(s) was analyzed over 5 injections.

Analyte	Fortification and LOQ Level	Mean Recovery	RSD	RSD _r	H _r
	(%, w/w)	(%)	(%)	(%)	
2-chloro-2-methylpentane	0.077	107.0	3.7	3.9	0.94
2-chloro-4-methylpentane	0.074	92.0	3.5	4.0	0.88
2-chloro-2,3-dimethylbutane	0.016	101.6	3.1	5.0	0.61
3-chloro-2-methylpentane	0.013	93.2	4.4	5.1	0.87
1,3-dichloropropane	0.018	91.3	4.9	4.9	0.99
1,2,2-trichloropropane	0.016	100.4	3.1	5.0	0.62
cis-1,3,3-trichloropropene	0.008	95.1	4.8	5.6	0.87
trans-1,3,3-trichloropropene	0.020	100.6	4.7	4.8	0.97

17. Good Laboratory Practice

- 17.1 Apart from the presented chromatograms and the LOQ 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 Recording of chromatograms (Figures 1 to 3) was done in a test facility inspected by the UK Good Laboratory Practice Monitoring Authority to be in compliance with the OECD Principles of Good Laboratory Practice. (Date of inspection: March 22nd, 2023)
- 17.3 The LOQ 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).
- 17.4 Recording of the formulation blank chromatogram (Figure 4) and an accompanying solvent blank (Figure 5) for illustration was recorded by Dow internally and did not comply with GLP criteria.

18. References

- 18.1 “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).
- 18.2 Bain, L. J.; Engelhardt, M. *Introduction to Probability and Mathematical Statistics*, 2nd Edition, Duxbury Press, Boston, 1992, p. 76.

Figure 1. A representative chromatogram of a 1,3-dichloropropene sample obtained using the conditions outlined in Section 9 of this method.

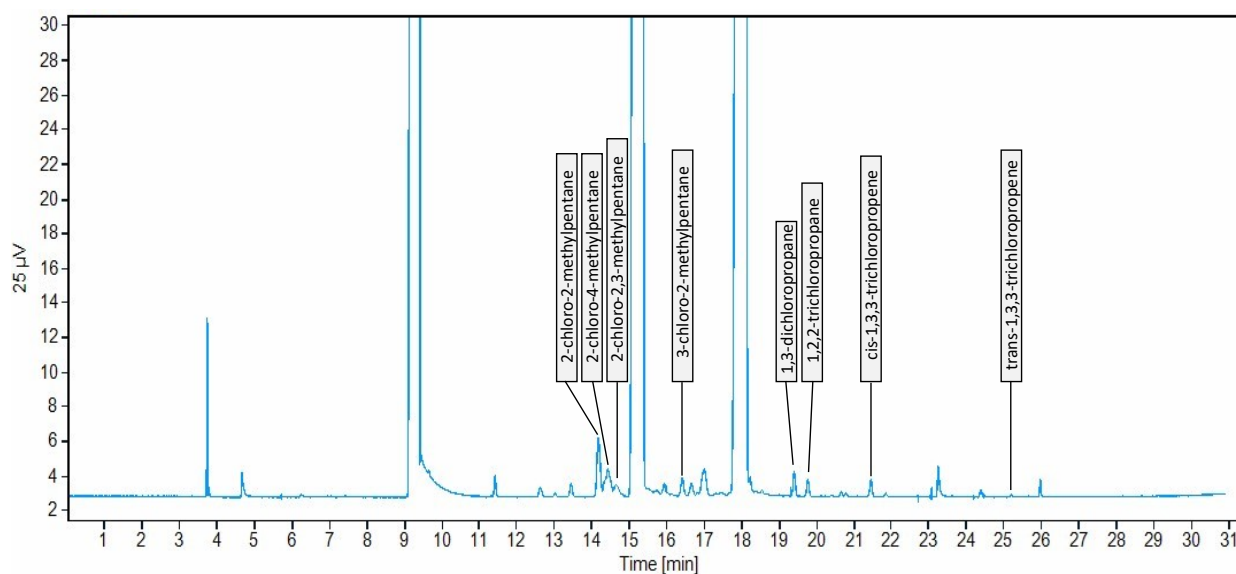


Figure 2. A representative chromatogram of a calibration solution (Section 8) obtained using the conditions outlined in Section 9 of this method.

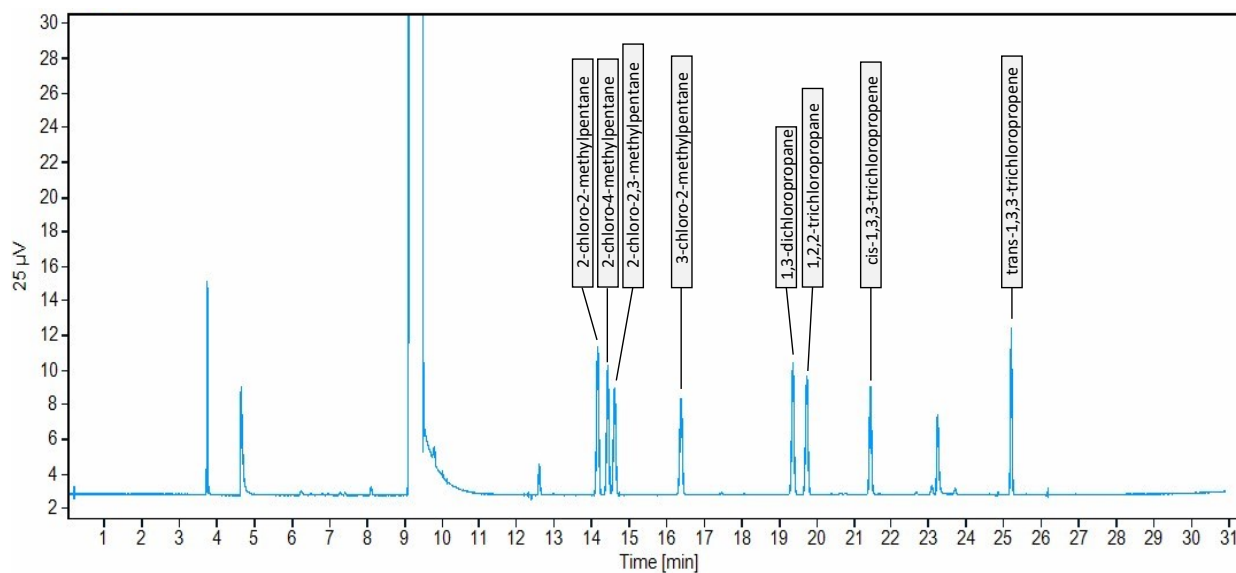


Figure 3. A representative chromatogram of a solvent blank obtained using the conditions outlined in Section 9 of this method.

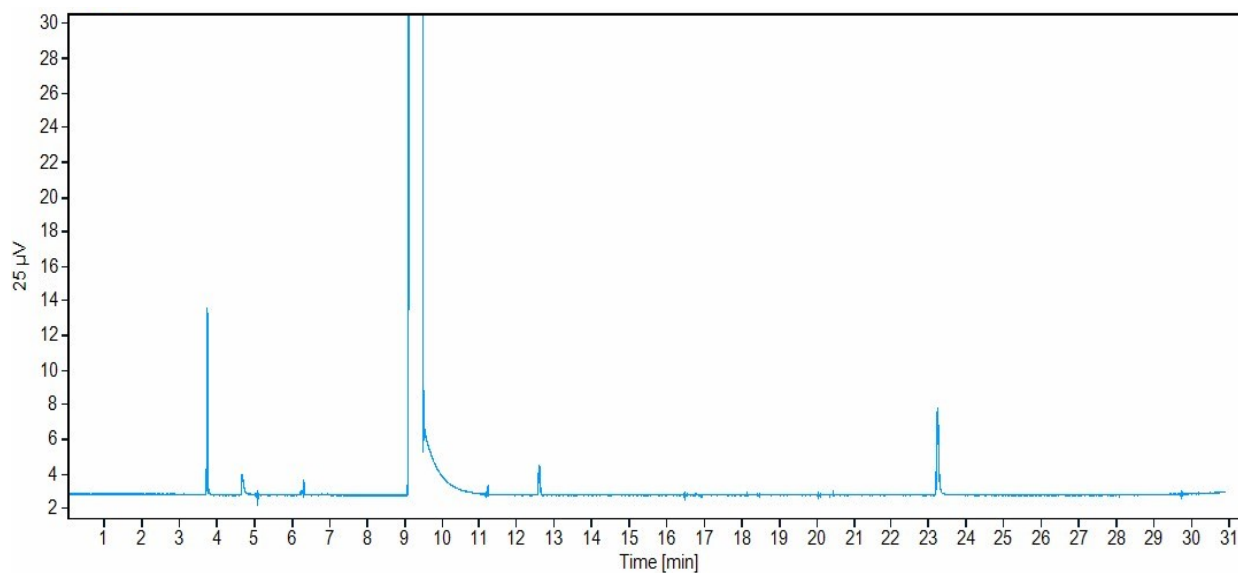


Figure 4. A representative chromatogram of a formulation blank obtained using the conditions outlined in Section 9 of this method. This chromatogram was **not** recorded under GLP-conditions.

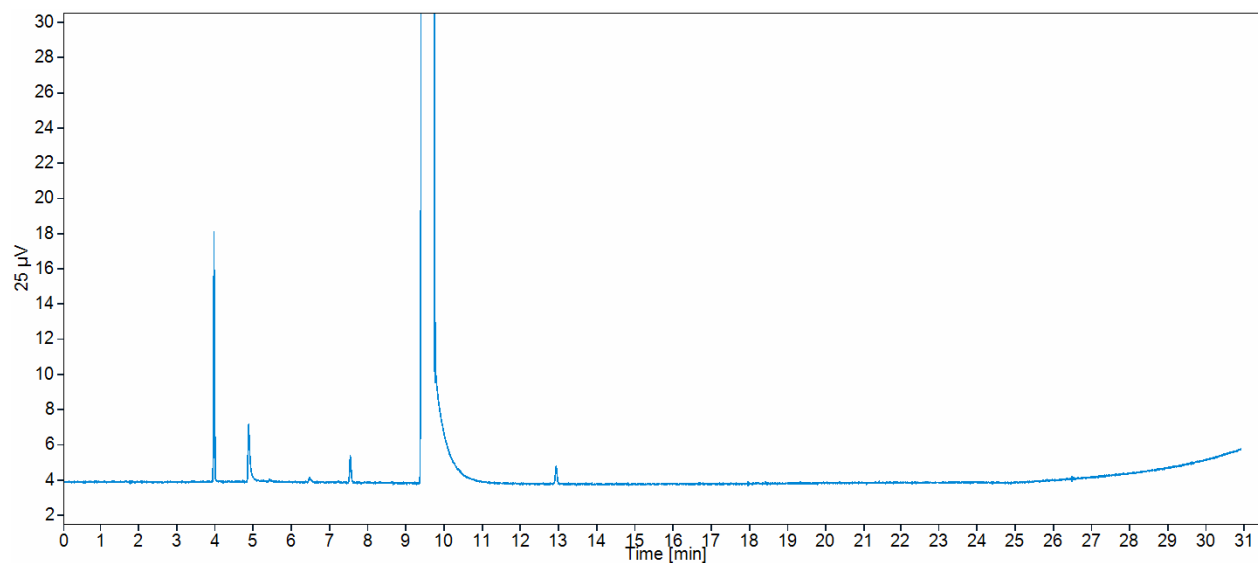


Figure 5. A representative chromatogram of a solvent blank obtained on the same GC system as used in Figure 4 using the conditions outlined in Section 9 of this method. This chromatogram was **not** recorded under GLP-conditions.

