TEST METHOD

1,2-Dichloropropane in 1,3-Dichloropropene by Gas Chromatography

1. Scope

1.1   This method is applicable to the determination of 1,2-dichloropropane in 1,3-dichloropropene over the range of 0.0040 to 0.0164% (w/w).

Note: The sample may contain up to 2.4% (w/w) epoxidized soybean oil as an additive, which does not interfere with the analysis (Section 5.1).

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 is diluted in ethyl acetate and analyzed by gas chromatography. The components are separated and detected with a flame ionization detector. Quantitation is by external standard based on peak area.

3. Summary

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

3.2   This method is applicable to the determination of 1,2-dichloropropane in 1,3-dichloropropene over the range of 0.0040 to 0.0164% (w/w).

3.3   The average marginal recovery for 1,2-dichloropropane in 1,3-dichloropropene was 104.9%, with a relative standard deviation of 4.6%. Detector response was shown to be linear for 1,2-dichloropropane over a range of 0.0032 % (w/w) to 0.0164 % (w/w).

3.4   Replicate analyses of two samples of 1,3-dichloropropene on two separate days gave a relative standard deviation of 2.05% and 1.15% at an average concentration of 0.0081% (w/w) and 0.0144% (w/w) respectively. The analysis is complete in 66.3 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 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   1,2-dichloropropane is toxic if inhaled. It is presumed to causing cancer. It is a flammable liquid with a flash point of 15 °C. Refer to the current SDS for the most up-to-date safety guidelines (Section 4.1).

4.4   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).

4.5   Hydrogen is a highly flammable gas, with an almost invisible flame. It has a very low ignition energy (0.019 mJ) and a very broad flammability range (4-75% in air). Design and install all hydrogen delivery systems in accordance with site safety and loss prevention practices. Hydrogen generators which operate at low pressure and flow rate are highly recommended to mitigate safety concerns inherent with hydrogen cylinders. Hydrogen cylinders should be stored outdoors in an electrically classified area for the safety of lab and emergency services personnel. Mitigate overpressure scenarios due to a failing pressure regulator by means of a pressure relief device and proper vent. Install flow restrictors or automatic flow shut-off valves to minimize or stop flow in case of a significant leak. Install redundant isolation valves both near the equipment and outside the laboratory. Leak prevention , especially indoors, is important. Minimize potential leak points in hydrogen delivery systems, including connectors or valves. Welded connections are recommended over couplings. If couplings are used, they must be located in ventilated areas. Do not use connectors in drop ceilings or walls. Cap all open line terminations. Leak check all connections prior to use.

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 5 and 6 for a formulation blank and an accompanying solvent blank.

Note: The peak shown to elute before 1,2-dichloropane does not interfere with the analyte and was identified to be ethyl propionate, which is a common impurity of the ethyl acetate solvent used in this method.

6.   Apparatus

6.1   Analytical balance: capable of weighing to 0.1 mg, Mettler model AE260, available from Mettler-Toledo, Inc., or equivalent.

6.2   Gas chromatograph: equipped with split/splitless capillary injection port, autosampler and flame ionization detector (FID), model 6890, 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 3.4, available form Agilent Technologies, Inc., or equivalent.

6.5   Autosampler vials: 1.5 mL with screw caps, available from VWR, or equivalent.

6.6   Volumetric flasks: 20-mL and 50-mL, available from VWR, or equivalent.

7.   Reagents

7.1   1,2-dichloropropane reference standard, AGR277102, 99%, available from Customer Information Group, The Dow Chemical Company.

Note: The purity of this standard should either be provided by the supplier or determined by the analyst for use in Section 8.1.

7.2   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.

8.   Reagent Solutions

8.1   Calibration stock solution:

8.1.1   Weigh (and record to the nearest 0.1 mg) 50 mg of 1,2-dichloropropane (Section 7.1) into a 50-mL volumetric flask.

8.1.2   Add ethyl acetate (Section 7.2) to the mark of the volumetric flask in 8.1.1. Cap and mix well.

8.2   Calibration standard:

8.2.1   Transfer 1.0 mL of the 1,2-dichloropropane stock solution in Section 8.1 to a 20-mL volumetric flask.

8.2.2   Add ethyl acetate (Section 7.2) to the mark of the volumetric flask in 8.2.1. 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 6890
Detector: flame ionization
Injector: capillary, split (60:1)
Column: J&W Scientific DB-1701, 60 m x 0.32 mm x 1 μm
Temperatures:
    Oven: 50 °C, hold for 20 min
                                      0.5 °C/min to 70 °C, hold for 0 min
                                      30 °C/min to 260 °C, hold for 0 min
    Injection port: 180 °C
    Detector: 260 °C
Flows:
    Carrier gas: helium, 2.2 mL/min, constant flow
    Air: 360 mL/min
    Hydrogen: 30 mL/min
    Make-up: 30 mL/min, helium
    Split: automatically (132 mL/min)
Chromatography data system: OpenLab 3.4
Injection volume: 2 μL
Run Time: 66.3 min

9.1   Representative chromatograms are illustrated in Figure 1, Figure 2, Figure 3, and Figure 4.

10.   Calibration

10.1   Inject a 2-μL aliquot of the calibration standard into the chromatograph and separate according to the chromatographic conditions outlined in Section 9. Repeat the process for a second chromatogram. A representative chromatogram is illustrated in Figure 3.

10.2   Calibrate the chromatography data system according to the manufacturer's operating instructions for an external standard calibration using both chromatograms (if manual calculations are used, proceed to the next section).

10.3   If manual calculations are used, calculate a response factor for 1,2-dichloropropane for both chromatograms with the formula below. Use the average of both response factors as outcome of the calibration.

$$RF_{1,2\text{-dichloropropane}} = \frac{W_{1,2\text{-dichloropropane,RS}} \times P}{A_{1,2\text{-dichloropropane,CS}} \times 50 \text{ mL}} \times \frac{1}{20}$$

where:

$RF_{1,2\text{-dichloropropane}}$	=	response factor [mg/(mL × area counts)] for 1,2-dichloropropane
$W_{1,2\text{-dichloropropane,RS}}$	=	weight (mg) of 1,2-dichloropropane reference standard in the calibration stock solution (Section 8.1.1)
$A_{1,2\text{-dichloropropane,CS}}$	=	peak area (area counts) for 1,2-dichloropropane obtained from the analysis of the calibration standard (Section 10.1).
P	=	purity of the reference standard, expressed as mass fraction.
50 mL	=	volume of the calibration stock solution (Section 8.1).
1/20	=	dilution factor (1 mL/20 mL) for the calibration standard preparation (Section 8.2)

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) 2.0 mL of the sample into an appropriate container using a volumetric pipette.

11.1.2   Dilute the flask in Section 11.1.1 by addition of 3.0-mL ethyl acetate (Section 7.2) using a volumetric pipette. 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.

11.3   Report results to the nearest 0.0001% (w/w).

12.   Calculations

12.1   If manual calculations are used, calculate the concentration of 1,2-dichloropropane in the original sample as follows:

$$C_{1,2\text{-dichloropropane}} = \frac{RF_{1,2\text{-dichloropropane}} \times A_{1,2\text{-dichloropropane}} \times V_{SS}}{W_S} \times 100\%$$

where:

$C_{1,2\text{-dichloropropane}}$ = concentration (%, w/w) of 1,2-dichloropropane in the sample

$RF_{1,2\text{-dichloropropane}}$ = response factor [mg/(mL x area counts)] for 1,2-dichloropropane (Section 10.3)

$A_{1,2\text{-dichloropropane}}$ = peak area (area counts) for 1,2-dichloropropane 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)

100% = conversion to percent

13.   Precision

13.1   Precision data was determined by analysis of two samples of 1,3-dichloropropene. For each sample 10 sample solutions were prepared and analyzed over a two-day period. Results are given below.

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})), and 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 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.

Sample	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)	(%)	(±%)	(%)	
1	10	2.26	0.0081	2.05	4.64	5.54	0.4
2	10	2.26	0.0144	1.15	2.59	5.08	0.2

14. Accuracy

14.1 Marginal recoveries from the analysis of 12 spiked samples based on the calculated concentration of the 1,2-dichloropropane in the spiked samples are given below:

Analyte	Spiked Concentration Range	Average Recovery	Range of Recoveries	Standard Deviation of Recoveries
	(%, w/w)	(%)	(%)	(%)
1,2-dichloropropane	0.0016 - 0.0142	104.9	94.1 - 110.1	4.6

Note: The initial concentration of 1,2-dichloropropane was 0.0023 to 0.0024% (w/w) depending on which 1,3-dichloropropene sample was used. The range of the total 1,2-dichloropropane concentrations is 0.0040 to 0.0165 % (w/w).

15. Linearity

15.1 Method response was found to be linear over the range of 0.0032 to 0.0164% (w/w) 1,2-dichloropropane.

16. Limit of Quantitation

16.1 The limit of detection (LOQ) of 1,2-dichloropropane in 1,3-dichloropropene was determined to be 0.0020% (w/w) by standard addition with acceptable recovery and precision. A low concentration sample with a fortified amount of 0.0020% (w/w) of 1,2-dichloropropane was analyzed over 5 injections.

Sample	Fortification	Mean recovery	RSD	RSD_r	H_r
	(%, w/w)	(%)	(%)	(%)	
1,3-dichloropropene	0.0020	95.7	1.9	6.8	0.28

Note: This data fulfills the LOQ criteria of SANCO/3030/99 rev.5.

Note: The limit of detection (LOD) was not explicitly determined since it is not required or defined by SANCO/3030/99 rev.5. However, based on precision sample 1, LOD ,defined as three times the standard deviation of a low concentration sample, can be estimated to be 0.0005% (w/w).

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 4) 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 5) and an accompanying solvent blank (Figure 6) 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).

Figure 1.   A representative chromatogram of a 1,3-dichloropropene sample obtained under GLP-conditions using the conditions outlined in Section 9 of this method.
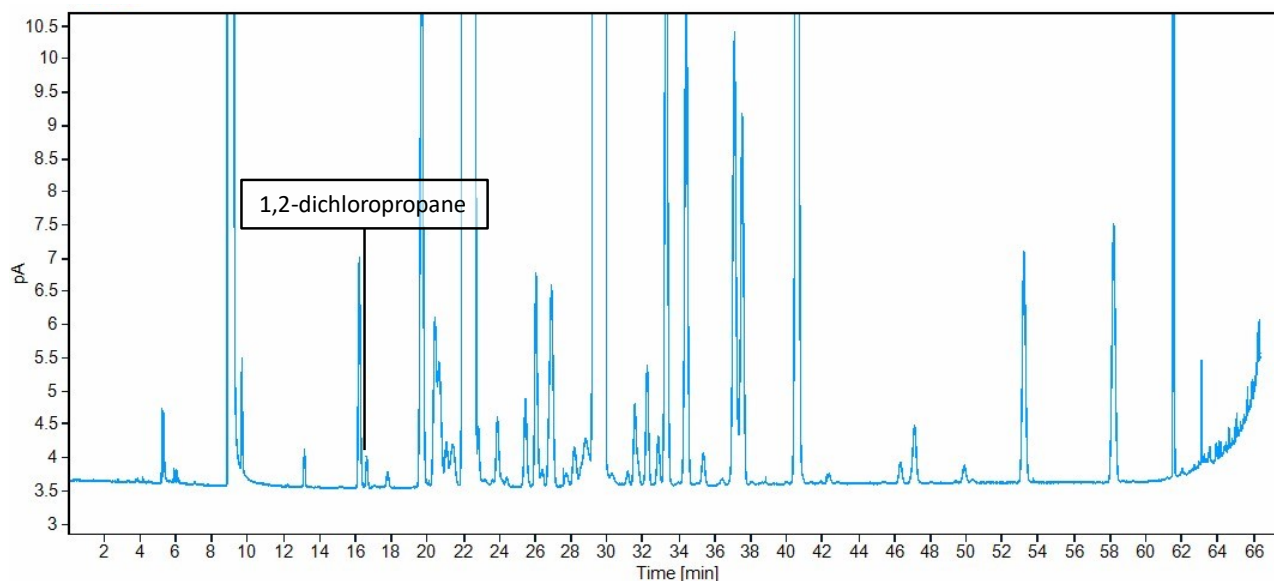
Figure 2.   An enlarged section of the representative chromatogram in Figure 1. showing the 1,2-dichloropropane peak in more detail.
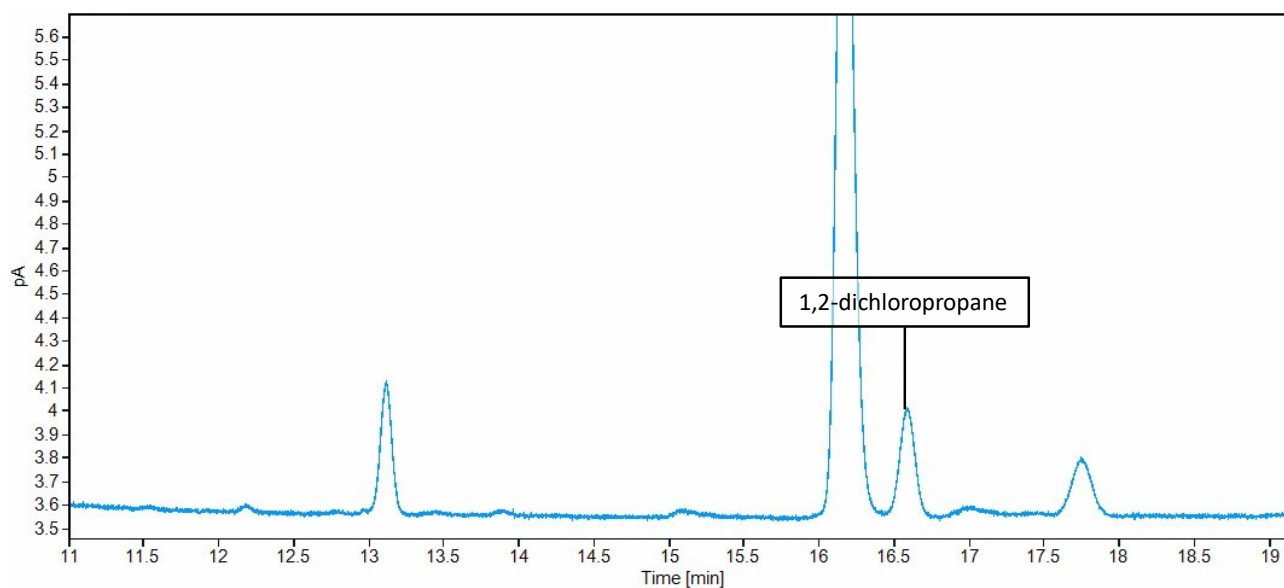
Figure 3.   A representative chromatogram of a calibration solution obtained under GLP-conditions using the conditions outlined in Section 9 of this method.
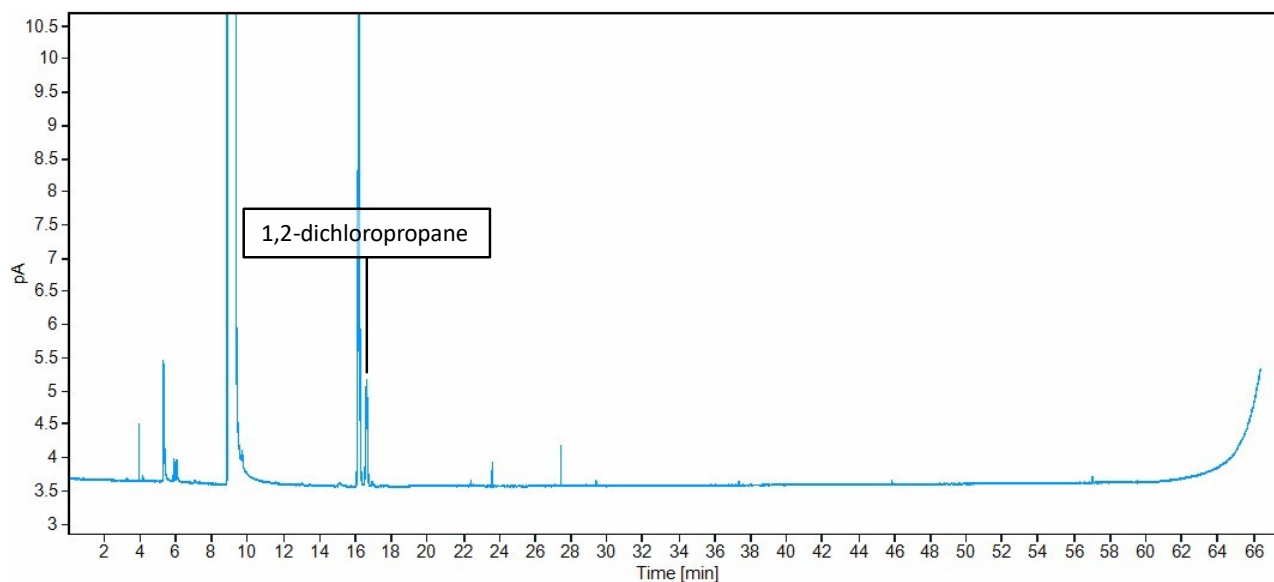

Figure 4.   A representative chromatogram of a solvent blank obtained on the same GC system as used in Figures 1 to 3 under GLP-conditions using the conditions outlined in Section 9 of this method.
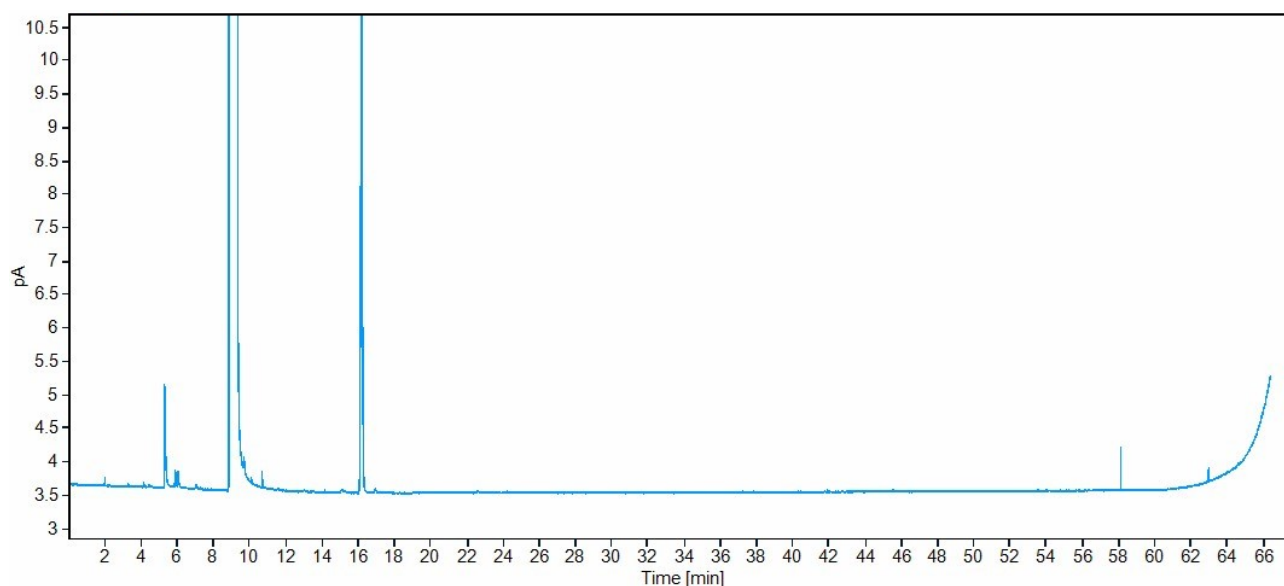
Figure 5.   A representative chromatogram of a formulation blank obtained using the conditions outlined in Section 9 of this method. This chromatogram was **not** recorded under GLP-conditions.
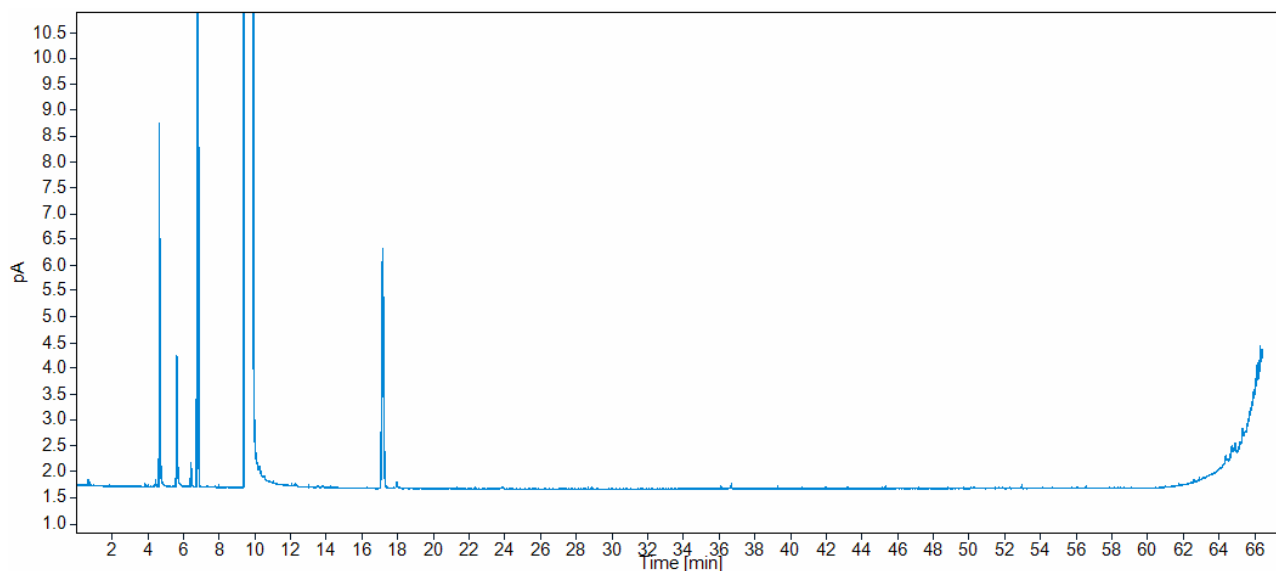

Figure 6.   A representative chromatogram of a solvent blank obtained on the same GC system as used in Figure 5 using the conditions outlined in Section 9 of this method. This chromatogram was **not** recorded under GLP-conditions