



Standard Practice for Analysis of Halogenated Organic Solvents and Their Admixtures by Gas Chromatography¹

This standard is issued under the fixed designation D 6806; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the determination of impurities, stabilizers and assay of halogenated organic solvents and their admixtures by gas chromatography.

1.2 It is not the intent of this practice to provide a specific method of gas chromatography. The intent of this practice is to define what is required for a user to demonstrate that a method to be used is valid. The reason for this approach, as opposed to stating a method, is that gas chromatography is such a dynamic field that methods are often obsolete by the time they are validated. The use of this practice allows the user to use most effective technology and demonstrate that the method in use complies with a standard practice and is valid for the analysis of halogenated organic solvents and their admixtures.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

E 180 Practice for Determining the Precision and Bias of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals²

3. Terminology

3.1 Purity and assay are used interchangeably in this standard.

3.1.1 Purity or assay are defined as $100 - \text{sum}(\text{impurities} + \text{stabilizer})$ when impurities and stabilizers are expressed in %;

3.1.2 Or $100 - [\text{sum}(\text{impurities} + \text{stabilizer})/10\ 000]$ when impurities are expressed in ppm.

3.2 Accuracy is defined per A2.2.1 of Practice E 180 or the agreement between an experimentally determined value and the accepted reference value.

3.3 Precision is defined per A2.1.7 of Practice E 180 or the degree of agreement of repeated measurements of the same

property. It is generally expressed in standard deviations or percent relative standard deviation $(s/X) \cdot 100$, also known as coefficient of variation.

4. Summary of Practice

4.1 This practice will define the requirements for a gas chromatographic (GC) method to be valid for the determination of impurities, stabilizers and assay of halogenated organic solvents and their admixtures.

5. Method Requirements

5.1 The GC method must give adequate separation of the impurities and stabilizers common to the product in question so that the instrument response (area counts, milivolts, etc.) to the individual impurities or stabilizers can be measured with adequate precision and accuracy as defined in Section 6. Process knowledge from the supplier or manufacturer of the product is a resource of information as to what those impurities and stabilizers are. GC-Mass Spectrometry (GC-MS) is another resource to initially determine what components are present to be measured. See Table 1 for a list of possible impurities and stabilizers for each product.

5.2 Non polar capillary columns of about 0.32 mm by 30 m generally work well. Table 2 provides a list of columns that may prove suitable for the analysis of the halogenated organic products.

5.3 *Instrument Conditions*—The following GC conditions are often appropriate for the analysis of halogenated organic products and their admixtures though actual conditions should be optimized for the analysis being performed.

5.4 The separation is determined to be adequate by preparing standards of known amounts of the impurities and stabilizers in concentrations near enough to the expected concentrations in the sample for the instrument response to be linear over the concentration range of interest. Repeated injections (minimum of three) of this standard are made and the accuracy and precision of the method for the individual impurities and stabilizers are determined.

5.5 Response to components must not be out of range of the detector and should be sufficiently Gaussian (symmetrical) to allow adequate measurement as defined by Section 6. Out of range response can be corrected by changing the range of the instrument or changing sample size.

¹ This practice is under the jurisdiction of ASTM Committee D26 on Halogenated Organic Solvents and Fire Extinguishing Agents and is the direct responsibility of Subcommittee D26.04 on Test Methods.

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² *Annual Book of ASTM Standards*, Vol 15.05.

TABLE 1 Impurities and Stabilizer

Product	Possible Impurities and Stabilizers	
Methylene Chloride	Methyl Chloride	
	Vinyl Chloride	
	Ethyl Chloride	
	Vinylidene Chloride	
	Trans 1,2-Dichloroethylene	
	Cis 1,2-Dichloroethylene	
	Chloroform	
	Carbon Tetrachloride	
	2-Methyl-2-Butene	
	Cyclohexane	
	Cyclohexene	
	Propylene Oxide	
	Perchloroethylene	Trichloroethylene
		Carbon Tetrachloride
1,1,2-Trichloroethane		
1,1,2,2-tetrachloroethane		
1,1,1,2-tetrachloroethane		
Penta Chloroethane		
Hexachloroethane		
N-Methyl Morpholine		
Para Tertiary Amyl Phenol		
Cyclohexene Oxide		
BHT		
N-Methyl Pyrrole		
Ethoxy Propionitrile		
Trichloroethylene		Cis and trans 1,2-dichloroethylene
	1,1,2-trichloroethane	
	Carbon tetrachloride	
	1,1,2,2-tetrachloroethane	
	1,1,1,2-tetrachloroethane	
	Ethylene Dichloride	
	Propylene Dichloride	
	Diisopropyl Amine	
	Butylene Oxide	
	Thymol	
	N-Methyl Pyrrole	
	Ethyl Acetate	
	Diisobutylene	

TABLE 2 Suggested GC Columns

DB 624
DB 5
DB 1701

TABLE 3 Instrument Conditions

Detector	Flame ionization detector or other detector of sufficient sensitivity to accurately measure components of interest
Injector Temperature	200°C
Detector Temperature	200°C
Oven Temperature for Isothermal	80°C
Programmed Oven Temperature	50 to 200°C
Carrier Gas	Helium or hydrogen
Carrier Gas Flow Rate	1 to 3 mL/min
Sample Size	0.5 µ to 1.0 µ
Split Ratio	50:1

5.6 Purity or assay of unblended halogenated organic solvents will be determined by determining the amounts of the individual impurities and stabilizers and subtracting the total of those impurities and stabilizers from 100 %. Purity or assay will, unless otherwise stated, be determined by subtracting from 100, the sum of impurities (as determined by gas

chromatography) and stabilizers only. The values for water, acidity, non-volatile matter and other such components will not be subtracted from 100 % to determine the purity or assay of the material in question unless the specifications call for these items to be included in the total to be subtracted from 100.

5.7 Area percent is generally not suitable for halogenated organic products as the sensitivity to a flame ionization detector varies greatly between components, particularly stabilizers which do not contain chlorine. Calibration of the instrument should be done using a standard containing the components of interest in concentrations similar to that expected in the sample being analyzed.

5.8 Precision for the assay is determined by performing statistical analysis of the purity or assay of individual injections which is determined by 100 % – sum(stabilizers + impurities). The units for assay or purity will be weight percent unless otherwise specified.

6. Precision and Bias ³

6.1 Adequate precision and bias is defined by the needs of the user of the method.

6.2 As a general guideline, the following table shows precision of a good gas chromatographic method. These values were determined experimentally in a round robin between different laboratories in different companies. Automatic injectors were in common use in all participating laboratories and were used in the round robin.

TABLE 4 Expected Precision

Concentration	% Relative Standard Deviation
1 to 25 ppm	12
25 to 100 ppm	2
100 to 10 000	1
1 to 25 %	0.8
25 to 75 %	0.5
75 to 100 % Direct Measurement	0.5
By Difference	0.1

6.3 The average and standard deviation of recovery (average of 3 or 4 results) has been determined to be 100.29 ± 8.02 % with 99.7 % falling between 76 and 124 %. Eighty five percent were found to fall between 95 and 105 % recovery.

6.4 The lower detection limit can be assumed to be three times the noise level of the chromatogram. The lower quantification limit can be assumed to be ten times the noise level. The noise level is determined by starting a run without an injection and allowing the run to go to completion through the normal temperature program and time. Take an average of all of the area counts seen in three such blank runs. This average area count will be the background noise for the method.

7. Keywords

7.1 accuracy; gas chromatography; halogenated organic solvent; precision

³ A research report is available from ASTM Headquarters. Request RR:D26-1018.



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