



# e1 Methanol Handbook

August 2013

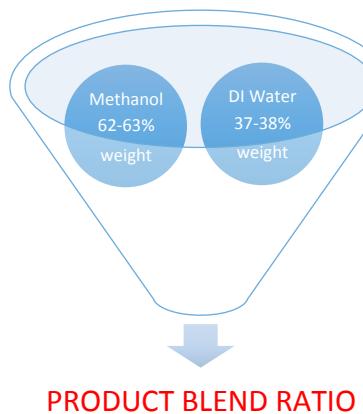
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# 1. e1 Methanol Blend Description - Summary

**DISCLAIMERS:** 1) Methanol is classified by the International Code Council (ICC) and the National Fire Protection Agency (NFPA) under the Uniform Fire Code as a “1B Flammable Liquid”. Guidelines for handling 1B flammable liquids are provided by codes and standards published by ICC, NFPA, and the International Fire Code. 2) Improper fuel blending or fuel inputs that do not meet the purity requirements in this specification may cause product malfunction and void the e1 Warranty for Hydrogen Generators. CAUTION- Before handling, transporting or storing methanol, refer to the Material Safety Sheet and Methanol Safe Handling FAQ's contained in this handbook, or contact the Methanol Institute at [www.methanol.org](http://www.methanol.org)

**PRODUCT DESCRIPTION:** The fuel blend for e1 reformers is a hydrogen rich mixture of methanol & purified water. **e1 specifies IMPCA grade methanol and water purified to ASTM Type III grade.** This blend description summary sheet provides; 1) fuel sourcing; 2) product blend ratio; 3) methanol/water purity standards; 4) storage guidelines; 5) transportation and handling guidelines.



1. Fuel Sourcing. IMPCA grade methanol is available worldwide, and regionally through petroleum or chemical distributors. These regional resellers may have “drumming” capabilities, that is, the ability to blend methanol and pure water at their fuel depot. The fuel may be blended onsite according to the following specifications, or purchased pre-blended from chemical or fuel distributors. Brenntag Corporation offers the fuel blend in several container sizes under the brand name of HydroPlus. Brenntag part #'s are listed below.
2. Product Blend Ratio. Mixed by weight, not volume. Methanol content: 62-63%; Distilled or De-Ionized water meeting a minimum of ASTM Type III standards: 37-38%. Methanol and water volume vary according to temperature, so it is important to measure blend by weight. The following calculation is based on ambient temperature at 20C. Note: container should be pre-weighed, then its weight factored out of blend equation.

Example A: 55 gallon drum mixed by weight at 62.5% methanol/37.5% DI water:  
35.4 gallons methanol @ 6.63 lbs/gal = 235 lbs methanol (.625 weight)  
17 gallons DI water @ 8.35 lbs/gal = 142 lbs DI water (.375 weight)  
377 lb batch weight (excluding drum) makes about 52.4 gallons at 20C

BRENNTAG: #812546 (HydroPlus) 55 gallon drum

Example B: 5 gallon tank mixed by weight, same mix ratio:  
3.3 gallons methanol @ 6.63 lbs/gal = 22 lbs methanol (.625 weight)

1.5 gallons DI water @ 8.35 lbs/gal = 13 lbs DI water (.375 weight)  
35 lb batch weight (excluding container) makes about 4.8 gallons at 20C

BRENNETAG: #919514 (HydroPlus) 5 gallon container

3. Water must be distilled or de-Ionized and meet ASTM Type III purity standards or higher. Water may be sourced already purified, or purified at the distribution location using a water purification vessel supplied by a water purification reseller. WATER PURITY STANDARD: (ASTM Type III Refer to [www.astm.org](http://www.astm.org) category D1193-06 Regeant Water for additional information.

Type III grade of reagent water shall be prepared by distillation, ion exchange, continuous electrodeionization reverse osmosis, or a combination thereof, followed by polishing with a 0.45-um membrane filter.

Electrical conductivity, max, uS/cm at @ 25C	4.0
Electrical resistivity, min, Mcm @ 25 C	0.25
pH @ 25 C	A
Total organic carbon (TOC), max ug/L	200
Sodium, max, ug/L	10
Chlorides, max, ug/L	10
Total silica, max, ug/L	500

WATER SOURCING/NORTH AMERICA- Local water purification companies provide purification vessels capable of cleaning water to ASTM Type III standards. USA: [www.culligan.com](http://www.culligan.com) "Find Your Dealer", or [www.purewatersolutions.com](http://www.purewatersolutions.com), [www.parish-supply.com](http://www.parish-supply.com) Canada: [www.cwwltd.com](http://www.cwwltd.com). Internet Search "water purification".

4. Storage Guidelines. Methanol blended with water is considered a flammable material, and can be corrosive to some non-ferrous alloys, and react with certain plastics and composites. Recommended storage vessels include 55-gallon plastic drums, or plastic-lined steel drums or containers, or plastic or 304 stainless steel totes. For additional detail, refer to Methanol Safe Handling FAQ's and Technical Bulletins available at [www.methanol.org](http://www.methanol.org) and by codes and standards published by ICC, NFPA, and the International Fire Code.
5. Transportation and Handling Guidelines. Methanol is classified by the International Code Council (ICC) and the National Fire Protection Agency (NFPA) under the Uniform Fire Code as a "1B Flammable Liquid". For specific transportation standards, reference the Department of Transportation, International Maritime Organization, International Air Transport Association, and the Intergovernmental Organization for International Carriage by Rail.

# 2. Methanol Fuel Testing

**WARNING: Failure to use qualified fuel in Element 1 hydrogen generators may lead to premature failure of the system and void the product Warranty. e1 specifies IMPCA grade methanol and water purified to ASTM Type III grade.**

Methanol/water fuel quality is critical to the correct and reliable operation of the H-series hydrogen generator, care should be taken to ensure that fuel is quality checked when either purchasing pre-blended fuel or mixing it on-site.

Once fuel quality has been demonstrated, periodic checks to ensure quality is maintained will help the hydrogen generator reliably make optimum quantity and quality hydrogen for many hours.

There are five tests recommended by Element 1:

## **Appearance Test**

1. Check that the methanol/water fuel blend has been shipped or stored in the approved storage container materials (see “Methanol and Water Feedstock Blend” document, section 4 (a), “Storage Guidelines” under the Element 1 website Resources). Deionized water is extremely corrosive to many metals and rust or metal oxides will contaminate the fuel.
2. Pour a sample of the methanol/water fuel into a previously cleaned, clear 250 ml graduated cylinder approved for methanol contact.
3. Hold the graduated cylinder up to a bright light (sun, flashlight, etc) and look for any suspended particles.
4. Reject the fuel if any particles are detected in the fuel. Particles can cause the fuel pump to fail, clog the reactor and cause pre-mature failure of the hydrogen generator.

## **Conductivity Test**

1. Rinse the conductivity detector contacts with distilled or deionized water.
2. Insert the detector contacts into the fuel and measure the conductivity of the sample from the meter.
3. Fuel conductivity should not be higher than  $10\mu\text{S}$ . Conductivity levels higher than this is reason for fuel rejection, as fuel contamination from salts or minerals is indicated.

## **Weight Percent Methanol Test**

1. In a clear 250 ml graduated cylinder, pour in enough fuel sample to float the 0.800 to 0.910 range hydrometer (roughly 175 mls).
2. Spin the hydrometer to dislodge any bubbles that are sticking to the hydrometer. Bubbles will cause the hydrometer to float too high and create an inaccurate density reading.
3. Insert the digital thermometer into the graduated cylinder and read the temperature.
4. Read the specific gravity on the linear scale. Using the “Weight Percent Methanol in mixture of Methanol/Water” graph, below, determine the weight percent methanol by using the fuel temperature and density.

**Weight Percent Methanol in mixture of Methanol/Water**

Temp (Celsius)	Light Weight %		Optimum Weight % Methanol		Unsafe Weight % Methanol		
	60	61	62	63	64	65	66
0	0.910	0.908	0.906	0.904	0.901	0.899	0.897
2	0.909	0.907	0.904	0.902	0.900	0.898	0.896
4	0.907	0.905	0.903	0.901	0.899	0.896	0.894
6	0.906	0.904	0.901	0.899	0.897	0.895	0.893
8	0.904	0.902	0.900	0.898	0.896	0.893	0.891
10	0.903	0.901	0.898	0.896	0.894	0.892	0.889
12	0.901	0.899	0.897	0.895	0.893	0.890	0.888
14	0.900	0.898	0.895	0.893	0.891	0.889	0.886
16	0.898	0.896	0.894	0.892	0.890	0.887	0.885
18	0.897	0.895	0.893	0.890	0.888	0.886	0.883
20	0.895	0.893	0.891	0.889	0.887	0.884	0.882
22	0.894	0.892	0.89	0.887	0.885	0.883	0.880
24	0.892	0.890	0.888	0.886	0.884	0.881	0.879
26	0.891	0.889	0.887	0.884	0.882	0.880	0.877
28	0.889	0.887	0.885	0.883	0.881	0.878	0.876
30	0.888	0.886	0.884	0.881	0.879	0.877	0.874

As an example, if the fuel temperature is 28C, and the density of the fuel measured 0.884, the weight percent methanol of the fuel would be 62.5%, in the optimum weight percent range of 62 – 63 weight percent methanol. If the fuel tested at 64 or greater weight percent methanol (Unsafe Weight % Methanol), DO NOT RUN THE FUEL! High weight percent methanol will clog the reformer and cause premature failure. If the weight percent methanol is less than 62 (Light Weight %), the fuel will still work (down to 59 weight percent methanol) but will deliver lower amounts of hydrogen.

### Miscibility Test

1. Dilute one volume of mixed fuel with two volumes of DI or distilled water in a clear container
2. Check for any cloudiness or turbidity. If the sample is not clear, reject the fuel. Cloudiness or turbidity when mixed with excess water indicates some type of hydrocarbon contamination that could harm the reformer.

### Silica Test

1. Follow the instructions on the silica test kit to test the fuel for silica. High silica content will eventually clog the hydrogen generator. Light yellow to slightly green test results are okay, while dark green to blue results mean the fuel should not be used.

### 3. IMPCA Methanol Reference Specifications



**IMPCA**  
INTERNATIONAL METHANOL PRODUCERS & CONSUMERS ASSOCIATION

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## **IMPCA METHANOL REFERENCE SPECIFICATIONS**

*a.i.s.b.l. International Methanol Producers & Consumers Association i.v.z.w.*  
Avenue de Tervueren 270 Tervurenlaan - 1150 Brussels - Belgium  
Phone: + 32 (0)2 741 86 83 - Fax: + 32 (0)2 741 86 84 - e-mail: [info@impca.be](mailto:info@impca.be) - [www.impca.be](http://www.impca.be) - VAT: BE 434 211 194

## IMPCA REFERENCE SPECIFICATIONS

ITEM	LIMIT	METHOD
Appearance	Clear and free of suspended matter	IMPCA 003-98
Purity % WT on dry basis	Min 99.85	IMPCA 001-02
Acetone mg/kg	Max 30	IMPCA 001-02
Colour PT-CO	Max. 5	ASTM D1209-05
Water % W/W	Max. 0.1	ASTM E1064-05
Distillation Range at 760 mm Hg	Max. 1.0 °C to include $64.6^\circ \pm 0.1^\circ$	ASTM D1078-05
Specific Gravity 20°/20°	0.791-0.793	ASTM D4052-09
Potassium Permanganate Time test at 15 °C, minutes	minimum 60	ASTM D1363-06
Ethanol mg/kg	max 50	IMPCA 001-02
Chloride as Cl⁻ mg/kg	max 0.5	IMPCA 002-98
Sulphur mg/kg	max 0.5	ASTM D 3961-98 or ASTM D 5453-09
Hydrocarbons	pass test	ASTM D 1722-09
Carbonisable Substances (Sulfuric Acid Wash Test)		
Pt-Co Scale	max 30	ASTM E 346-08
Acidity as Acetic acid mg/kg	max 30	ASTM D 1613-06
Total Iron mg/kg	max 0.1	ASTM E 394-09
Non Volatile Matter mg/1000 ml	max 8	ASTM D 1353-09
TMA	optional (see notes for recommended methods)	
Aromatics	optional (see notes for recommended methods)	

**Note :**

In case some specific consumers or producers wish to have more specific information on **TMA** (which can be considered as an impurity generating bad smell) and/or **Aromatics** (in case the previous cargos have been Aromatics).

IMPCA recommends to use the following methods :

TMA	TMA test	ASTM E 346-08
Aromatics	UV test	IMPCA 004-08

**1. Scope**

This method describes a procedure for the determination of the purity and impurities (e.g. acetone, ethanol) of Methanol.

**2. Warning**

See Material Safety Data Sheet of Methanol.

**3. Method summary**

Internal standard is added to the sample and subsequently the major impurities are identified and quantified by GC/FID. The purity on dry basis is calculated.

**4. Apparatus**

- 4.1 Gaschromatograph with FID detector (Agilent 6890, Split/Splitless Injector / FID-Detector or equivalent).
- 4.2 GLC column (DB 1 - 60 m x 0.32 mm ID and 5.0 µm film thickness) or equivalent.
- 4.3 Volumetric flask 100 ml.
- 4.4 Micropipette of 10 µl.

**5. Chemicals**

- 5.1 sec-Butanol (= 2-Butanol).
- 5.2 Ethanol.
- 5.3 iso-Propanol (= 2-Propanol).
- 5.4 iso-Butanol (= 2-Methyl-1-Propanol).
- 5.5 Acetone.
- 5.6 Methylacetate.
- 5.7 Quality control sample.

**6. Procedure**

- 6.1 Prepare the gaschromatograph as described in the manual and use the correct settings  
Injection temperature : 275 °C.

Detection temperature : 275 °C.

Oven temperature profile:

start 5 min. @ 50 °C ;  
rise 1 @ 5 °C/min until 100 °C ; hold 0 min ;  
rise 2 @ 10 °C/min until 250 °C ;  
final hold 4 min.

Carrier gas : Helium, 100kPa

Split : 50 ml/min.

Column pressure : approx. 100 kpa.

Injection volume : 1 µl.

- 6.2 When the method is newly set-up or not used for a long period, determine the response factors for all relevant impurities for 2 concentration levels (e.g. 5 mg/kg and 100 mg/kg).

- The difference between the response factors determined at both levels should not exceed 5%. The average response factors are used for the quantification of the individual impurities.
- 6.3 Run a GLC scan of the Quality control sample (5.7).
  - 6.4 When the quality of the determination is within the predetermined criteria, the response factors are still valid. In all other cases new response factors may have to be determined prior to the reanalysis of the quality control sample. When the quality control sample still is not within the predetermined criteria, a new control sample will have to be prepared and checked
  - 6.5 Run a GLC scan of the sample under the same GLC conditions.
  - 6.6 Transfer approx. 80 ml of sample to a 100 ml volumetric flask.
  - 6.7 Add 10 µl of sec-Butanol (5.1) as internal standard and fill up to the mark with sample and homogenise.
  - 6.8 Run a GLC scan of this mixture under the same GLC conditions.

## 7. Calculation

Calculate the concents of the impurities ethanol, iso-propanol, iso-butanol, acetone and methylacetate in mg/kg by the internal standard method as follows :

$$\text{component } X, \text{mg/kg} = \frac{\text{Area (component in mixture)}}{\text{Area (istd in mixture)}} \times RF \times \text{conc.(istd in mixture)}$$

where :

*RF* = response factor for the component relative to sec-Butanol  
*conc.(istd in mixture)* = concentration of sec-Butanol in mg/kg.

When already some sec-Butanol is present in the original sample, a correction in the internal standard concentration has to be made.

Calculate the purity on dry basis in %M/M as follows :

$$\text{purity on dry basis, \% M / M} = 100\% - \frac{\text{sum of all impurities in mg/kg}}{10,000}$$

Note that one should not subtract the water content.

## 8. Report

The ethanol content should be reported in mg/kg and rounded to the nearest whole mg/kg.  
 The lower limit of the determination of the ethanol content is 5 mg/kg and of the other impurities 10 mg/kg.

The purity on dry basis should be reported in %M/M and rounded to 0.01 %M/M.

## 9. Precision

The precision of this determination is yet unknown.

**1. Scope**

This method describes a procedure for the determination of *anorganic* chloride in methanol in the range of 0.25 mg/kg to 10 mg/kg.

**2. Warning**

*See Material Safety Data Sheets of Methanol, Glacial Acetic Acid and Silver Nitrate.*

**3. Method summary**

A weight amount of sample is dissolved in a known volume of titration solvent containing already some chloride. The mixture is potentiometrically titrated with standard alcoholic silver nitrate.

*The determination is carried out in duplicate. Quality criteria for the blank determination, the difference of the duplicate analysis results and the QC sample have to be met.*

**4. Apparatus**

- 4.1 Titroprocessor - Metrohm, model 670, equipped with a combi Ag/AgCl electrode or equivalent instrument.
- 4.2 Volumetric flask 1000 ml.
- 4.3 Pipettes of 10 ml and 100 ml.
- 4.4 PTFE coated stirring bar.

**5. Chemicals****5.1 Titration Solvent :**

Mix 850 ml acetone, 150 ml glacial acetic acid and 10 ml of 1 mmol/l hydrochloric acid.  
Note : Ensure that sufficient titration solvent is prepared to test each series of samples and blanks.

**5.2 Silver nitrate stock solution :**

Standard solution, 0.1 N in water. Prepare, store and standardize according to ASTM E200.

**5.3 Alcoholic silver nitrate solution :**

Standard solution, 0.001 N in isopropanol. Pipette 10.00 ml of standard 0.1 N silver nitrate (5.2) into a 1000 ml volumetric flask, make up to the mark with isopropanol and homogenize.

**5.4 Quality control sample with a chloride concentration of 0.3 - 1.0 mg/l.****6. Procedure**

- 6.1 Perform the analysis in duplicate.
- 6.2 Prepare the titroprocessor and electrodes as described in the manual.
- 6.3 Weigh 50 g sample to the nearest 0.1 g (= m gram) into the titration vessel. Pipette 100 ml of titration solvent (5.1) into the titration vessel and add a PTFE coated stirring bar.
- 6.4 Place the titration vessel on the magnetic stirrer of the titroprocessor and immerse the electrode in the sample solution. Immerse the tip of the burette below the surface of the liquid and adjust the magnetic stirrer to produce vigorous stirring without splattering. Ensure that the sample is completely dissolved.

- 6.5 Titrate the sample with 0.001 N alcoholic silver nitrate (5.3) according to the manual of the titroprocessor.
- 6.6 For each series of sample determinations, carry out 2 blank determinations, following the procedure described in 6.3 - 6.5, but omitting the sample. The blank titration *volumes* should not differ by more than 0.02 ml.
- 6.7 *For each series of sample determinations, determine the chloride content of a QC sample (5.4), following the procedure described in 6.3 - 6.5. The results of the QC sample must be 0.8 - 1.2 times the theoretical value.*

## 7. Calculation

Calculate the chloride content in mg/kg for each single determination as follows :

$$\text{chloride, mg/kg} = \frac{(V_1 - V_2) \times C \times 35.5 \times 1000}{m \times 100}$$

where :

- $V_1$  = volume in ml of alcoholic silver nitrate (5.3) used for sample titration.  
 $V_2$  = average volumes in ml of alcoholic silver nitrate (5.3) used for the two blank titrations  
 $C$  = riter of the standardised aqueous silver nitrate solution (5.2).  
 $m$  = sample weight in g.

*The average of the two duplicate determinations is calculated as final result.*

## 8. Report

The chloride content should be reported in mg/kg and rounded to the nearest 0.1 mg/kg. The lower limit of this determination is 0.25 mg/kg.

## 9. Precision

The difference between successive test results, obtained by the same operator using the same apparatus on identical test material, exceeds 0.03 mg/kg only in 1 case in 20. *Differences greater than this should be considered suspect.*

*The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, exceeds 0.3 mg/kg only 1 case in 20. Differences greater than this should be considered suspect.*

**1. Scope**

This method is for the uniform description of the appearance of methanol by visual inspection.

**2. Warning**

See Material Safety Data Sheets of Methanol.

**3. Method summary**

A sample, in a clean, clear and colourless glass bottle is inspected for the presence of visual contamination.

**4. Apparatus**

4.1 A clean 500 ml or 1 l clear and colourless glass bottle.

**5. Chemicals**

None.

**6. Procedure**

6.1 All samples should be drawn in 500 ml or 1 l clear glass bottles.

6.2 Swirl the sample (do not shake to avoid introduction of air bubbles) and examine through the side of the bottle (not from top to bottom) for the presence of contamination by suspension, sediments, oil, surface contamination and turbidity.

**7. Calculation**

None.

**8. Report**

The liquid should be clear and free from suspended matter.

Report one of the following options :

\*) Clear and free from suspended matter.

\*) Clear and particles (type and estimated amount); types may be rust, floating particles, black particles, fibres, etc.

\*) Hazy

**9. Precision**

The result of this test is not numerical, so precision limits are not applicable.

**1. Scope**

This method describes a procedure for the determination of the transmittance of methanol at wavelengths in the region 220 to 350 nm. The results provide a measure of impurities in a sample with respect to ultraviolet absorbing compounds like aromatics. The lower limit of determination is 1-10 mg/kg, depending on the impurity present and the UV spectrophotometer used.

**2. Warning**

See Material Safety Data Sheets of Methanol, Benzene, Toluene, Phenol and Styrene.

**3. Method summary**

This method describes a procedure for the determination of ultraviolet absorbing contaminations in methanol by using a double beam UV spectrophotometer in the range of 190 - 350 nm and demineralised water as reference.

When no UV absorbing contaminants are present the UV-curve will be smooth. When one or more aromatic compounds are present, one or more peaks are observed in the range 190 - 350 nm.

**4. Apparatus**

- 4.1 Ultraviolet Spectrophotometer, double beam, suitable for measurement at wavelengths in the region 190 to 350 nm, having a spectral bandwidth of 2.0 nm or less at 220 nm, wavelength accuracy  $\pm 0.5$  nm or less at 220 nm, wavelength repeatability 0.3 nm or less at 220 nm and a photometric accuracy of  $\pm 0.5\%$  T or less, in the transmittance region above 50 % T. Stray light shall be less than 0.1 % at 220 nm.  
The apparatus should be sensitive enough to detect the concentrations of aromatic compounds as given in appendix 2.
- 4.2 Matched quartz cuvettes with pathlengths of 50 mm  $\pm 0.1$  mm.

**5. Reagents and Materials**

- 5.1 Demineralised water
- 5.2 Reference sample of high purity methanol (aromatic contaminants < 1 mg/kg)
- 5.3 Pure aromatic compounds (e.g. benzene, toluene, styrene, phenol, ethylbenzene, cumene, xylenes)
- 5.4 Holmium Oxide Wavelength Calibration Filter (the standard reference material SRM 2034, available from NIST is suitable)
- 5.5 Standard Absorbance Solution - Prepare freshly a solution of 10.0 mg/kg toluene in the highest available quality Methanol (Also the standard reference material SRM 2031, available from NIST is suitable. In addition, SRM 935a may be used)

**6. Calibration / Quality Control**

- 6.1 Check the wavelength calibration with the Holmium oxide filter [5.4].
- 6.2 Check the photometric accuracy with a suitable standard solution [5.5] using procedure [7].
- 6.3 Record the measured absorbances of the standard solution [5.5] on control charts. Measure the standard solution each time a test sample(s) is tested, using the same calibration

procedure as applied for the sample. If the measured value exceeds the action limit of the control chart, take appropriate action before proceeding with sample tests.

**7. Measurement Procedure**

- 7.1 Adjust the spectrophotometer to the optimum instrument settings, selecting the slit width to give a spectral bandwidth of 2.0 nm or less. A spectral bandwidth of 2.0 nm is preferred as lower bandwidths increase the noise level of the spectral data.
- 7.2 Fill two 50-mm matched cuvettes [4.2] with water [5.1]. Make sure the cell windows are clear and the water is free of bubbles. Place the cuvettes in the cell compartment of the spectrophotometer, noting the direction of the cells inside the cell holder, and measure the absorbances at 220, 250, 268.5, and 300 nm. With properly matched cuvettes, the maximum absorbance should be less than 0.01 absorbance units.
- 7.3 Rinse the sample cuvette with sample. Fill the cuvette with sample. Avoid producing bubbles in the sample.
- 7.4 Place the cuvette in the spectrophotometer. Adjust the Y-scale (absorption) so that Y-max equals 0.4 absorbance units; scan the range 190 nm to 350 nm and measure the absorbances at 220, 250, 268.5 and 300 nm.
- 7.5 Compare the recorded scan with the reference methanol scans.
- 7.6 When the scan is smooth and closely resembling the scan of the blank methanol (appendix 1), the tested methanol is free of aromatic compounds and 'pass' can be reported. The curve obtained should contain no clearly defined peaks or shoulders.
- 7.7 When the scan is **not** smooth and/or **not** closely resembling the scan of the blank methanol (appendix 1), but more like one of the scans in appendix 2, the tested methanol is containing some aromatic compound(s) and 'fail' must be reported.

**8. Calculation**

Not applicable as the absorbances are used without further calculation and the result of the UV-scan is merely qualitative.

**9. Report**

Report the measures absorbances rounded as X.XXX at 220, 250, 268.5, and 300 nm.  
The result of the UV-scan is qualitative and must be reported as pass or fail only. When a test sample is found positive and 'fail' is reported, the result must be confirmed by independent GLC-analysis.

**10. Precision**

The reproducibility estimate of this determination is based on the results of study iis06C07. In this interlaboratory study three samples with different toluene concentrations (0, 10 and 50 mg/kg) were tested by 11 different laboratories, see below table.

Wavelength	Absorbance range	Standard deviation	Degrees of freedom	95% limit
nm	abs	%		%
220	1.4 – 2.0	10.3	10	28.7
250	0.41 - 0.64	3.6	10	10.1
268.5	0.11 – 0.44	9.7	10	27.1
300	0 – 0.01	53.5	10	150

# 4. Water Purity Specifications – ASTM Type III

**WARNING: Failure to use qualified fuel in Element 1 hydrogen generators may lead to premature failure of the system and void the product Warranty.**

Water must be distilled or de-ionized and meet ASTM Type III purity standards or higher. Water may be sourced already purified, or purified at the distribution location using a water purification vessel supplied by a water purification reseller. WATER PURITY STANDARD: (ASTM Type III Refer to [www.astm.org](http://www.astm.org) category D1193-06 Regeant Water for additional information.

Type III grade of reagent water shall be prepared by distillation, ion exchange, continuous electrodeionization reverse osmosis, or a combination thereof, followed by polishing with a 0.45-um membrane filter.

Electrical conductivity, max, uS/cm at @ 25C	4.0
Electrical resistivity, min, Mcm @ 25 C	0.25
pH @ 25 C	A
Total organic carbon (TOC), max ug/L	200
Sodium, max, ug/L	10
Chlorides, max, ug/L	10
Total silica, max, ug/L	500

WATER SOURCING/NORTH AMERICA- Local water purification companies provide purification vessels capable of cleaning water to ASTM Type III standards.

USA: [www.culligan.com](http://www.culligan.com) “Find Your Dealer”, or [www.purewatersolutions.com](http://www.purewatersolutions.com), [www.parish-supply.com](http://www.parish-supply.com)

Canada: [www.cwwltd.com](http://www.cwwltd.com).

Internet Search “water purification”.

Frequently Asked Questions About Methanol Safe Handling

1. When is a dilute solution of methanol considered "hazardous" for purposes of disposal?

Used or waste methanol is considered a hazardous waste in the United States. Waste methanol in concentrations equal to or greater than 24% by weight meets the US Environmental Protection Agency's definition of an ignitable hazardous waste. Product grade methanol, when disposed, is a listed hazardous waste. Waste methanol, or water contaminated with methanol, is considered a hazardous waste and must never be discharged directly into sewers or surface waters. It may only be disposed of at a licensed facility permitted to handle hazardous waste. Contaminated product, soil, or water with methanol must be moved only by registered transporters in approved, properly labeled containers. The recommended disposal method for methanol is incineration for heating value recovery. Concentrated liquid methanol can be used as secondary fuel in systems compatible with water-soluble waste. Waste methanol is also amenable to reclaiming by filtration and distillation. For more information on methanol waste treatment and disposal consult Chapter 8.6 of the Methanol Institute's Methanol Safe Handling Manual.

2. What kinds of drums are recommended for methanol storage, only steel or are some plastics acceptable?

There are no standard or universal answers for questions regarding materials selection for methanol storage. The following information is provided as general guidance only. Mild steel is usually selected as the construction material for methanol storage containers. If moisture and trace amounts of inorganic salts are expected to exist within the container from time to time, then one should consider upgrading from carbon steel to 316 L stainless steel, or even a titanium or molybdenum stabilized grade of 316 L stainless steel. Many resins, nylons, and rubbers, such as neoprene, nitrile (Buna-N), and ethylene propylene (EPDM), are suitable for methanol service, though some are more appropriate in flowing applications and others for static service. One important consideration is that plastic storage containers are more susceptible to physical damage than metal ones (e.g., if dropped or hit by a forklift). Pure anhydrous methanol is mildly corrosive to lead and aluminum alloys, and more so to magnesium, and platinum. Methanol-water solutions can be corrosive to some non-ferrous alloys depending on application and environmental circumstances, including copper alloy, galvanized steel, and aluminum alloy components, and some plastics and composites. For more information on methanol storage consult Chapter 3.2 of the Methanol Institute's Methanol Safe Handling Manual.

3. How much methanol can be stored at a residence for the purpose of home biodiesel fuel production?

Requirements vary substantially by local jurisdiction depending on the Fire Marshall and the building code. According to the International Fire Code, the maximum aggregate quantity of Class IB flammable liquids, such as methanol, in use and storage in a building may not exceed 120 gallons, provided requirements for explosion-proof electrical service, ventilation systems, flammable storage cabinets, fire protection, spill containment, segregation of incompatible corrosive and flammable materials, and issuance of a hazardous materials permit are met. In addition, special restrictions apply to residential buildings, including maximum amount in use of 10 gallons, prohibition against flammable storage in basements, limits on stacking heights, and set back distances for outdoor storage. These restrictions make the typical single family dwelling or apartment unsuitable for biodiesel fuel production. For these reasons, the handling and storage of methanol for home biodiesel production is not recommended, unless substantial and costly safety measures are implemented. For more information on precautions regarding

biodiesel fuel production consult Chapter 2.3.3 of the Methanol Institute's Methanol Safe Handling Manual.

**4. What types of extinguishers should be used to put out small methanol fires?**

Small methanol fires can be extinguished with portable, dry chemical extinguishers and/or water spray provided the volume of water is at least four times the volume of the methanol pool. However, this is only advisable if there is a way to contain the water, otherwise the methanol fire can spread. Methanol flame is low temperature and non-luminous, therefore, when methanol catches fire, it burns with a clear blue flame that is very difficult to see in bright sun light. Methanol may be on fire and you may not be able to discern the hazard of a fire by looking for a flame. Methanol vapor can be ignited throughout a wide range of concentrations in air. Large methanol pool fires are best extinguished with Alcohol Resistant Aqueous Film Forming Foam (AR-AFFF) with 6% foam-water proportioning equipment. For more information on methanol fire safety consult Chapter 6 of the Methanol Institute's Methanol Safe Handling Manual.

**5. How do you clean up small methanol spills?**

Small spills should be controlled with sand, earth, or other non-combustible absorbent material, and the area then flushed with water. Larger spills should be diluted with water and contained with sand or other barrier material for later collection and disposal. Spills onto paved or bare ground should be contained by surrounding the liquid with mechanical or chemical barriers, such as sand, vermiculite, zeolite, or absorbent dikes. For small spills, the spill surface should be covered with the absorbent materials or activated carbon to capture the pooled methanol. After use, the contaminated sorbent materials or soil containing methanol should be removed and packed for recovery, recycling, or disposal as hazardous waste. Methanol spills should be kept from flowing into confined spaces, such as sumps, manholes, and utility tunnels, where vapors may be released and accumulate, potentially reaching flammable concentrations. These spaces should be checked for explosive atmospheres prior to re-occupancy. Only properly trained and equipped employees should be allowed to participate in methanol spill control and cleanup operations. For more information on methanol emergency response consult Chapter 7 of the Methanol Institute's Methanol Safe Handling Manual.

**6. How long is the storage stability of methanol?**

Methanol is a stable material when stored in an appropriate container and suitable environmental conditions. It is mildly corrosive to lead alloys. As it is 100% miscible in water, the presence of moisture or trace amounts of inorganic salts can result corrosion of the metal container. Hazardous polymerization will not occur under normal storage conditions. Properly protected from contamination, methanol shelf life is indefinite. For more information on methanol chemical and physical properties consult Appendix B of the Methanol Institute's Methanol Safe Handling Manual.

**7. When responding to a highway/rail accidents involving methanol spills, what is the recommended evacuation distance?**

Response actions relating to rail tankers apply equally for tankers attached to tractor haul trucks and to tank trailers towed by tractor haul trucks. In the event of a rail car derailment or tanker truck roll over, first responders should treat methanol as highly flammable and highly toxic. The 2008 edition of the *Emergency Response Guidebook* (ERG2008) recommends an immediate isolation distance of 150 feet (50 meters) in all directions. In the event of accidental release as a result of the accident or some other circumstance that compromises containment, ERG2008 recommends that responders isolate and consider evacuating in all directions from the release to a radial distance of one half mile (800 meters). Ignition sources must be eliminated to a distance of at least one half mile (800 meters). So-called "running fires" may be expected with large volume releases as the ignited material flows out of the tanker. Running fires are particularly hazardous if allowed to flow into sewers and drains. Flashback can be expected. For

more information on methanol spill response and fire safety consult Chapters 6 and 7 of the Methanol Institute's Methanol Safe Handling Manual.

**8. For employees unloading methanol, what PPE is required? Do they need to wear fire resistant clothing?**

Exposure to methanol can occur via inhalation, skin or eye absorption, or ingestion. The level of risk of exposure to methanol will dictate the appropriate level of personal protective equipment required. At a minimum, safety glasses with side shields or chemical safety goggles and task appropriate gloves are recommended. For routine unloading of methanol where splashing or skin absorption is not anticipated, natural fiber clothing (cotton) is adequate. Avoid wearing synthetic fiber clothing when there is a risk of fire from handling methanol. A chemical resistant apron, butyl or nitrile rubber gloves, and rubber boots, and a full face-shield worn over goggles for additional protection, (but not as a substitute for goggles), may be needed where there is a risk of splashing, such as in coupling and uncoupling hoses or lines. Chemical-resistant clothing/materials should be worn if repeated or prolonged skin contact with methanol is expected. Respiratory protection should be selected based on hazards present and the likelihood of potential exposure. Air purifying respirators with organic vapor (OVA) cartridges are not appropriate protection against methanol vapors due to the very short service life of the OVA cartridge before it becomes saturated, and there are no means of knowing when the vapors break through and the cartridge is no longer offering protection. The use of a supplied air respirator with a full face piece operated in a pressure-demand or other positive-pressure mode is the recommended respiratory protection. Personal protection equipment for the responders should, at a minimum, include chemical splash goggles and face shield, butyl or nitrile gloves, rubber boots, chemical resistance coveralls, and provision for supplied fresh breathing air, such as full face, positive pressure SCBA. Fire resistant clothing is only necessary when fighting a fire. For more information on methanol personal protective equipment consult Chapter 4.2.2 of the Methanol Institute's Methanol Safe Handling Manual.

**9. When are grounding and bonding needed for methanol transfer operations?**

Grounding is designed to create a path of least resistance for any generated electrical charge between a conductive object and the earth. Bonding is a measure intended to dissipate static electricity generated during fluid transfer through a conductive or nonconductive material by making a connection between a grounded object and an ungrounded object. Grounding and bonding are especially important in protecting methanol blends from accidental ignition resulting from static discharge when transferring fluids from one container or tank to another. While pure methanol itself is not a static accumulator, it is appropriate to use bonding or grounding for containers, piping, and drums. An electrical potential difference (PD) can exist between two containers or pipes and bonding neutralizes the PD, reducing the likelihood of a static discharge. Tanks, storage vessels, and drums should be grounded with copper straps or cables equipped with carbide-tipped clamps to ensure a strong electrical contact through nonconductive surface coatings, such as paint. When dispensing methanol from a grounded metal container, it and the associated fill equipment, including dip pipes, conductive hose, and pump, as well as the receiving container should be bonded together. Dip-tube-filling should be used in tanks or vessels to protect against ignition from static electricity generated as a result of liquid falling through air. Extend the pipe to within one inch (25 mm) of the bottom of the receiving container. Start pouring slowly until the container is filled to a level equivalent to two pipe diameters up the side of the fill pipe. Some plastic-lined metal containers should be treated as non-conductive. Plastic containers cannot be grounded and should not be used for Class I Flammable liquids, such as methanol, without expert review. If a plastic container must be used, follow the same procedure as for metal containers. Ensure procedures are in place to ground, and periodically verify grounding. For more information on methanol bonding and grounding consult Chapter 3.2.5 of the Methanol Institute's Methanol Safe Handling Manual.

METHANOL SAFE HANDLING FREQUENTLY ASKED QUESTIONS

- 10. What precautions are needed when welding or torch cutting tanks or containers that were used to store methanol?**

Methanol is extremely flammable and releases vapors at or below ambient temperatures. It has the potential to catch fire when hot work such as, welding, brazing, soldering, cutting, heat treating, grinding, and using power-actuated tools, is performed near methanol sources. When mixed with air, methanol can burn in the open. Methanol spills may travel short distances (yards or meters) along the ground before reaching a point of ignition and flashing back. The hazards associated with hot work can be reduced by implementing an effective hot work program that includes prior work authorization, safe welding practices, and a fire watch. For more information on performing hot work safely consult Chapter 4.3.2 of the Methanol Institute's Methanol Safe Handling Manual.

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**SECTION 1 – CHEMICAL PRODUCT AND COMPANY IDENTIFICATION**

**MSDS Name:** Methanol

**MSDS Preparation Date:** 06/19/2009

**Synonyms or Generic ID for Methanol:** Carbinol; Methyl alcohol; Methyl hydroxide; Monohydroxymethane; Wood alcohol; Wood naptha; Wood spirits; Columbian spirits; Methanol.

**Chemical Family:** Methanol Family

**Formula:** CH<sub>3</sub>OH

**Molecular Weight:** N/A

**PIN (UN#/ NA#):** UN1230

**Company Identification:**

Microbial ID.  
125 Sandy Drive  
Newark, DE 19713

**For Information, call:** (800)276-8068, (302)737-4297

**For Domestic CHEMTREC assistance, call:** 800-424-9300

**For International CHEMTREC assistance, call:** 703-527-3887

**SECTION 2 – COMPOSITION, INFORMATION ON INGREDIENTS**

67-56-1	Methanol	<99%	200-659-6	Irritant, Flammable
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**NFPA Rating:** (estimated) Health: 1; Flammability: 3; Instability: 0

State: Liquid	Appearance: colorless	Odor: Alcohol-like, weak odor
Boiling Point: 64.7°C@760mmHg	pH: Not available	Specific Gravity: 7910g/cm3@20°C
Vapor Pressure (mm Hg): 128mmHg @20°C		Vapor Density (AIR=1): 1.11
Flash Point: 12°C		Solubility in Water: miscible

**SECTION 3 – HAZARDS IDENTIFICATION**

**Appearance:** Colorless liquid, Flash Point: 12°C, 53.6°F.

**Danger! Poison!** May be fatal or cause blindness if swallowed. Vapor harmful. **Flammable liquid and vapor.** Harmful if swallowed, inhaled, or absorbed through the skin. Causes eye, skin, and respiratory tract irritation. May cause central nervous system depression. Cannot be made non-poisonous.

**Target Organs:** Eyes, nervous system, optic nerve.

**Potential Health Effects**

**Eye:** May cause painful sensitization to light. Methanol is a mild to moderate eye irritant. Inhalation, ingestion or skin absorption of methanol can cause significant disturbance in vision, including blindness.

**Skin:** Causes moderate skin irritation. May be absorbed through the skin in harmful amounts. Prolonged and or repeated contact may cause defatting of skin and dermatitis. Methanol can be absorbed through the skin, producing systemic effects that include visual disturbances.

**Ingestion:** May be fatal or cause blindness if swallowed. Aspiration hazard. Cannot be made non-poisonous. May cause gastrointestinal irritation with nausea, vomiting and diarrhea. May cause systematic toxicity with acidosis. May cause central nervous system depression, characterized by excitement, followed by headache, dizziness, drowsiness, and nausea. Advanced stages may cause collapse, unconsciousness, coma, and possible death due to failed respiratory failure. May cause cardiopulmonary system effects.

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**Inhalation:** Methanol is toxic and can very readily form extremely high vapor concentrations at room temperature. Inhalation is the most common route of occupational exposure. At first, methanol causes CNS depression with nausea, headache, vomiting, dizziness and incoordination. A time period with no obvious symptoms follows (typically 8-24 hrs). This latent period is followed by metabolic acidosis and severe visual effects which may include reduced reactivity and/or increased sensitivity to light, blurred, double and/or snowy vision, and blindness. Depending on the severity of exposure and the promptness of treatment, survivors may recover completely or may have permanent blindness, vision disturbances and/or nervous system effects.

**Chronic:** Prolonged or repeated skin contact may cause dermatitis. Chronic exposure may cause effects similar to those of acute exposure. Methanol is only very slowly eliminated from the body. Because of this slow elimination, methanol should be regarded as a cumulative poison. Though a single exposure may cause no effect, daily exposures may result in the accumulation of a harmful amount. Methanol has produced fetotoxicity in rats and teratogenicity in mice exposed by inhalation to high concentrations that did not produce significant maternal toxicity.

#### **SECTION 4 – FIRST AID MEASURES**

**Eyes:** In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical aid.

**Skin:** In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical aid immediately. Wash clothing before reuse.

**Ingestion:** Potential for aspiration if swallowed. Get medical aid immediately. Do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If vomiting occurs naturally, have victim lean forward.

**Inhalation:** If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical aid.

**Notes to Physician:** Effects may be delayed.

**Antidote:** Ethanol may inhibit methanol metabolism.

#### **SECTION 5 – FIRE FIGHTING MEASURES**

**General Information:** Ethanol may inhibit methanol metabolism. As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and full protective gear. During a fire, irritating and highly toxic gases may be generated by thermal decomposition or combustion. Use water spray to keep fire-exposed containers cool. Water may be ineffective. Material is lighter than water and a fire may be spread by the use of water. Vapors are heavier than air and may travel to a source of ignition and flash back. Vapors can spread along the ground and collect in low or confined areas.

**Extinguishing Media:** For small fires, use dry chemical, carbon dioxide, water spray or alcohol-resistant foam. Water may be ineffective. For large fires, use water spray, fog or alcohol-resistant foam. Do NOT use straight streams of water.

**Flash Point:** 12 deg C ( 53.60 deg F)

**Autoignition Temperature:** 455 deg C ( 851.00 deg F)

**Explosion Limits, Lower:** 6.0 vol %

**Upper:** 31.00 vol %

**NFPA Rating:** (estimated) Health: 1; Flammability: 3; Instability: 0

#### **SECTION 6 – ACCIDENTAL RELEASE MEASURES**

**General Information:** Use proper personal protective equipment as indicated in Section 8.

**Spills/Leaks:** Use water spray to disperse the gas/vapor. Remove all sources of ignition. Absorb spill using an absorbent, non-combustible material such as earth, sand, or vermiculite. Do not use combustible materials such as sawdust. Use a spark-proof tool. Provide ventilation. A vapor suppressing foam may be used to reduce vapors. Water spray may reduce vapor but may not prevent ignition in closed spaces.

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**SECTION 7-HANDLING AND STORAGE**

**Handling:** Wash thoroughly after handling. Remove contaminated clothing and wash before reuse. Ground and bond containers when transferring material. Use spark-proof tools and explosion proof equipment.

Avoid contact with eyes, skin, and clothing. Empty containers retain product residue, (liquid and/or vapor), and can be dangerous. Keep container tightly closed. Do not ingest or inhale. Do not pressurize, cut, weld, braze, solder, drill, grind, or expose empty containers to heat, sparks or open flames. Use only with adequate ventilation. Keep away from heat, sparks and flame. Avoid use in confined spaces.

**Storage:** Keep away from heat, sparks, and flame. Keep away from sources of ignition. Store in a cool, dry, well-ventilated area away from incompatible substances. Flammables-area. Keep containers tightly closed.

**SECTION 8 – EXPOSURE CONTROL/ PERSONAL PROTECTION**

**Engineering Controls:** Use explosion-proof ventilation equipment. Facilities storing or utilizing this material should be equipped with an eyewash facility and a safety shower. Use adequate general or local exhaust ventilation to keep airborne concentrations below the permissible exposure limits.

Chemical Name	ACGIH	NIOSH	OSHA – Final PELs
Methanol	200 ppm TWA; 250 ppm STEL; Skin - potential significant contribution to overall exposure by the cutaneous route	200 ppm TWA; 260 mg/m <sup>3</sup> TWA 6000 ppm IDLH	200 ppm TWA; 260 mg/m <sup>3</sup> TWA

**OSHA Vacated PELs:** Methanol: 200 ppm TWA; 260 mg/m<sup>3</sup> TWA

**Personal Protective Equipment**

**Eyes:** Wear chemical splash goggles.

**Skin:** Wear butyl rubber gloves, apron, and/or clothing.

**Clothing:** Wear appropriate protective clothing to prevent skin exposure.

**Respirators:** Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

**SECTION 9 – PHYSICAL AND CHEMICAL PROPERTIES**

**Physical State:** Clear liquid

**Appearance:** clear, colorless - APHA: 10 max

**Odor:** alcohol-like - weak odor

**pH:** Not available.

**Vapor Pressure:** 128 mm Hg @ 20 deg C

**Vapor Density:** 1.11 (Air=1)

**Evaporation Rate:** 5.2 (Ether=1)

**Viscosity:** 0.55 cP 20 deg C

**Boiling Point:** 64.7 deg C @ 760 mmHg

**Freezing/Melting Point:** -98 deg C

**Decomposition Temperature:** Not available.

**Solubility:** miscible

**Specific Gravity/Density:** .7910 g/cm<sup>3</sup> @ 20°C

**Molecular Formula:** CH<sub>4</sub>O

**Molecular Weight:** 32.04

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**SECTION 10 – STABILITY AND REACTIVITY**

**Chemical Stability:** Stable under normal temperatures and pressures.

**Conditions to Avoid:** High temperatures, ignition sources, confined spaces.

**Incompatibilities with Other Materials:** Oxidizing agents, reducing agents, acids, alkali metals, potassium, sodium, metals as powders (e.g. hafnium, raney nickel), acid anhydrides, acid chlorides, powdered aluminum, powdered magnesium.

**Hazardous Decomposition Products:** Carbon monoxide, irritating and toxic fumes and gases, carbon dioxide, formaldehyde.

**Hazardous Polymerization:** Will not occur.

**SECTION 11 – TOXICOLOGICAL INFORMATION**

**RTECS#:**

CAS# 67-56-1: PC1400000

**LD50/LC50:**

CAS# 67-56-1:

Draize test, rabbit, eye: 40 mg Moderate;  
Draize test, rabbit, eye: 100 mg/24H Moderate;  
Draize test, rabbit, skin: 20 mg/24H Moderate;  
Inhalation, rabbit: LC50 = 81000 mg/m<sup>3</sup>/14H;  
Inhalation, rat: LC50 = 64000 ppm/4H;  
Oral, mouse: LD50 = 7300 mg/kg;  
Oral, rabbit: LD50 = 14200 mg/kg;  
Oral, rat: LD50 = 5600 mg/kg;  
Skin, rabbit: LD50 = 15800 mg/kg;

Human LD<sub>50</sub> Oral: 143 mg/kg; Human LD<sub>50</sub> Oral: 428 mg/kg; Human TC<sub>50</sub> Inhalation: 300 ppm caused visual field changes & headache; Monkey LD<sub>50</sub> Skin: 393 mg/kg. Methanol is significantly less toxic to most experimental animals than humans, because most animal species metabolize methanol differently. Non-primate species do not ordinarily show symptoms of metabolic acidosis or the visual effects which have been observed in primates and humans.

**Carcinogenicity:**

CAS# 67-56-1: Not listed by ACGIH, IARC, NTP, or CA Prop 65.

**Epidemiology:** No information found

**Teratogenicity:** There is no human information available. Methanol is considered to be a potential developmental hazard based on animal data. In animal experiments, methanol has caused fetotoxic or teratogenic effects without maternal toxicity.

**Reproductive Effects:** See actual entry in RTECS for complete information.

**Mutagenicity:** See actual entry in RTECS for complete information.

**Neurotoxicity:** ACGIH cites neuropathy, vision and CNS under TLV basis.

**SECTION 12 – ECOLOGICAL INFORMATION**

**Ecotoxicity:** Fish: Fathead Minnow: 29.4 g/L; 96 Hr; LC50 (unspecified)Fish: Goldfish: 250 ppm; 11 Hr; resulted in deathFish: Rainbow trout: 8000 mg/L; 48 Hr; LC50 (unspecified)Fish: Rainbow trout: LC50 = 13-68 mg/L; 96 Hr.; 12 degrees CFish: Fathead Minnow: LC50 = 29400 mg/L; 96 Hr.; 25 degrees C, pH 7.63Fish: Rainbow trout: LC50 = 8000 mg/L; 48 Hr.; UnspecifiedBacteria: Phytobacterium phosphoreum: EC50 = 51,000-320,000 mg/L; 30 minutes; Microtox test No data available.

**Environmental:** Dangerous to aquatic life in high concentrations. Aquatic toxicity rating: TLm 96>1000 ppm. May be dangerous if it enters water intakes. Methyl alcohol is expected to biodegrade in soil and water very rapidly. This product will show high soil mobility and will be degraded from the ambient atmosphere by the reaction with photochemically produced hydroxyl radicals with an estimated half-life of 17.8 days. Bioconcentration factor for fish (golden ide) < 10. Based on a log K<sub>ow</sub> of -0.77, the BCF value for methanol can be estimated to be 0.2.

**Physical:** No information available.

**Other:** No information available.

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**SECTION 13 – DISPOSAL CONSIDERATIONS**

Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. US EPA guidelines for the classification determination are listed in 40 CFR Parts 261.3. Additionally, waste generators must consult state and local hazardous waste regulations to ensure complete and accurate classification.

**RCRA P-Series:** None listed.

**RCRA U-Series:**

CAS# 67-56-1: waste number U154 (Ignitable waste).

**SECTION 14 – TRANSPORT INFORMATION**

	<b>US DOT</b>	<b>CANADA TDG</b>
<b>Shipping Name:</b>	Methanol	Methanol
<b>Hazard Class:</b>	3	3
<b>UN Number:</b>	UN1230	UN1230
<b>Packing Group:</b>	II	II
<b>Additional Information</b>		Flash Point 12°C

**SECTION 15 – REGULATORY INFORMATION**

**US FEDERAL**

**TSCA**

CAS# 67-56-1 is listed on the TSCA inventory.

**Health & Safety Reporting List**

None of the chemicals are on the Health & Safety Reporting List.

**Chemical Test Rules**

None of the chemicals in this product are under a Chemical Test Rule.

**Section 12b**

None of the chemicals are listed under TSCA Section 12b.

**TSCA Significant New Use Rule**

None of the chemicals in this material have a SNUR under TSCA.

**CERCLA Hazardous Substances and corresponding RQs**

CAS# 67-56-1: 5000 lb final RQ; 2270 kg final RQ

**SARA Section 302 Extremely Hazardous Substances**

None of the chemicals in this product have a TPQ.

**SARA Codes**

CAS # 67-56-1: immediate, fire.

**Section 313**

This material contains Methanol (CAS# 67-56-1, > 99%), which is subject to the reporting requirements of Section 313 of SARA Title III and 40 CFR Part 373.

**Clean Air Act:**

CAS# 67-56-1 is listed as a hazardous air pollutant (HAP).

This material does not contain any Class 1 Ozone depleters.

This material does not contain any Class 2 Ozone depleters.

**Clean Water Act:**

None of the chemicals in this product are listed as Hazardous Substances under the CWA.

None of the chemicals in this product are listed as Priority Pollutants under the CWA.

None of the chemicals in this product are listed as Toxic Pollutants under the CWA.

**OSHA:**

None of the chemicals in this product are considered highly hazardous by OSHA.

**STATE**

CAS# 67-56-1 can be found on the following state right to know lists: California, New Jersey, Pennsylvania, Minnesota, Massachusetts.

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**California Prop 65**

California No Significant Risk Level: None of the chemicals in this product are listed.

**European/International Regulations**

**European Labeling in Accordance with EC Directives**

**Hazard Symbols:**

T F

**Risk Phrases:**

R 11 Highly flammable.

R 23/24/25 Toxic by inhalation, in contact with skin and if swallowed.

R 39/23/24/25 Toxic : danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.

**Safety Phrases:**

S 16 Keep away from sources of ignition - No smoking.

S 36/37 Wear suitable protective clothing and gloves.

S 45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

S 7 Keep container tightly closed.

**WGK (Water Danger/Protection)**

CAS# 67-56-1: 1

**Canada - DSL/NDSL**

CAS# 67-56-1 is listed on Canada's DSL List.

**Canada - WHMIS**

This product has a WHMIS classification of B2, D1B, D2B.

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations and the MSDS contains all of the information required by those regulations.

**Canadian Ingredient Disclosure List**

CAS# 67-56-1 is listed on the Canadian Ingredient Disclosure List.

**SECTION 16 – Other Information**

This Material Safety Data Sheet has been prepared in accordance with 29 CFR 1910.1200 and contains information believed to be accurate and complete at the date of preparation. The statements contained herein are offered for informational purposes only and are based upon technical data. MIDI Inc. believes them to be accurate but does not purport to be all-inclusive. The above-stated product is intended for use only by persons having the necessary technical skills and facilities for handling the product at their discretion and risk. Since conditions and manner of use are outside our control, we (MIDI Inc.) make no warranty of merchantability or any such warranty, express or implied with respect to information and we assume no liability resulting from the above product or its use. Users should make their own investigations to determine suitability of information and product for their particular purposes.

## Atmospheric Above Ground Tank Storage of Methanol

### *Introduction*

Guidelines for designing, fabricating, constructing, repairing, and safeguarding above-ground methanol storage tanks is essentially the same as that for liquid transportation fuels such as ethanol and gasoline, and flammable liquid feed stocks such as benzene, acetone, and toluene. However, physical and chemical properties of methanol are unique to methanol and are not the same as those of other bulk-stored flammable liquids. Some considerations of tank storage are unique to methanol.

One important consideration is flammability range. Because the upper flammability limit of methanol is 36 percent by volume (vol%) compared to that of gasoline which is 6-7 vol%, methanol vapor can ignite and burn inside tank vapor space.

Corrosion is another consideration. Methanol is a conductive polar solvent; gasoline is a non-conductive, non-polar solvent. Galvanic and dissimilar metal corrosion in methanol service may be high if incompatible materials are placed in electrical contact with one another. Cathodic protection, and regulator inspection of methanol storage tanks and trim hardware is vitally important to avoid corrosion failure.

Principal considerations of tank storage of methanol are siting, liquid and vapor containment, electrical grounding, cathodic protection, protection from stray currents, in-tank vapor control, vapor space fire suppression, and management of inhalation, ingestion, and dermal contact.

Methanol Institute recommends that users familiarize themselves with relevant codes and standards, and devise and implement a disciplined layers of protection program to prevent spills, accidental release, overpressure, ignition, and fire suppression. It is essential that fire detection, alarm, response, and suppression be rapid and effective.

Guidance for design, fabrication, construction, and tank safety are available in American Petroleum Institute (API) publications:

- API Standard 620, *Design and Construction of Large, Welded, Low-Pressure Storage Tanks*
- API Standard 653, *Tank Inspection, Repair, Alteration, and Reconstruction*.

Provisions for siting, electrical grounding, berthing, and safeguarding above ground storage tanks containing flammable liquids are given by the International Code Council (ICC) and the National Fire Protection Agency (NFPA). Guidelines are available in:

- NFPA 1 *Uniform Fire Code*
- NFPA 30, *Flammable and Combustible Liquids Code*.

Considerations not addressed in the above-sited references are specific to methanol storage, namely,

- Materials selection
- Purity protection
- Fire prevention, suppression and spill containment.

### ***Tank Materials of Construction & Trim Materials Compatibility***

Methanol is classified by the International Code Council and the National Fire Protection Agency as a class IB flammable liquid. Other IB liquids are ethanol, hydrocarbon fuels such as gasoline and

kerosene, and reactants such as benzene, acetone, and toluene. No. 1 diesel, No. 2 diesel, and biodiesel are classified as combustible motor fuels, and are also handled and stored in above ground atmospheric storage tanks.

Methanol gasoline fuel blends are subject to phase separation in the presence of water. Methanol and water, two polar compounds, form a mixture which separates from gasoline, a non-polar mixture of C<sub>4</sub> thru C<sub>12</sub> hydrocarbons. Methanol boils at 149 °F; gasoline boils over a range of temperatures extending from < 140 to 390 °F.

Methanol tanks can be constructed of either carbon steel or 300 series austenitic stainless steel. Carbon steel has the advantage of lower capital cost, but the disadvantage of higher life cycle cost due to increased maintenance and costs associated with corrosion protection. Because methanol is a polar solvent, galvanic corrosion is more prevalent with methanol than with other commonly-used motor fuels.

Because of its very high affinity to form mixtures with water, methanol is hygroscopic and extracts moisture from ambient air that enters tank vapor space during normal liquid level cycling. In the presence of neat or technical grade methanol, the small amount of water added by desiccation of atmospheric air does not substantially increase the rate of general corrosion. Never-the-less, because of the relatively high conductivity of liquid methanol, corrosion induced failures of carbon steel tanks have been reported. Efforts to coat interior tank surfaces with epoxy resin have met with limited success. Typical coating life is less than seven years, and the coatings tend to form an electrically non-conductive barrier between the methanol and the tank, thereby complicating bonding and grounding. Recent reports indicate progress is being made in developing more suitable electrically conductive spray-on tank liner coatings.

Galvanic corrosion of dissimilar trim materials may be accelerated in methanol service, particularly trim materials of aluminum, lead, magnesium, copper, zinc and platinum alloys. An example of this resulted in a methanol tank fire when the aluminum alloy flame arrester corroded to the point of being non-functional. "The Chemical Safety Board concluded that the flame arrester did not prevent the fire outside the tank from igniting the tank contents. Routine inspections would have detected the corrosion in the flame arrester that occurred over 12 years. The use of an aluminum flame arrester in methanol service coupled with the lack of inspection and maintenance allowed the flame arrester to corrode to the point that it no longer functioned."

Galvanized steel is not suitable for methanol service.

If the methanol-water mixture forms within a gasoline-methanol blend and separates from the gasoline as a separate phase, then localized corrosion may be accelerated. If the water phase accumulates chloride salts due to proximity to a coastal environment, then under-deposit corrosion, localized pitting corrosion, and crevice corrosion may be accelerated. In extreme cases, stress corrosion cracking (SCC) of high carbon, non-molybdenum stabilized austenitic stainless steel weld heat- affected zones may result due to localized exposure to water containing high concentrations of chlorides.

Methanol is one of the few specialized environments, which may cause SCC in titanium alloys. SCC failures have occurred in dry methanol, methanol/acid and methanol/halide mixtures. Water is an effective inhibitor and will maintain the passivity of titanium alloys in some environments.

Titanium Alloy Grade	%water- Intermittent exposure <sup>1</sup>	% water - Sustained exposure
1,2,7,11,16,17	1.5	2.0
9, 12	2.0	2.0
28	2.5	3.0
5,23	3.0	3.0
19, 29, 6-2-4-6	5.0	10.0

Where-as, SCC has been observed in ethanol tanks, this phenomenon has not been reported for methanol service. Never-the-less, good practice for analysis of failed components should include consideration of phenomena observed in ethanol service.

Plastics are generally not recommended for storage purposes due to long-term deterioration of plasticizers, loss of mechanical integrity, and risk of methanol contamination. Many resins, nylons and rubbers, particularly nitrile (Buna-N), ethylene-propylene, Teflon and neoprene are used satisfactorily as components of equipment in methanol service.

#### ***Methanol Purity Protection***

Carbon steel is more likely to corrode and cause methanol contamination than stainless steel, particularly in the presence of moist air and/or water in coastal environments. This can be mitigated by padding tank free-board space with dry inert gas such as nitrogen.

Stainless steel has higher capital cost than carbon steel, but offers the advantage of lower life cycle maintenance cost, and reduced likelihood of methanol contamination. Three-hundred series stainless steel alloys are recommended. Alloy selection and welding procedures should avoid sensitization of weld heat-affected zones. The American Welding Society (AWS) and the American Society of Metals (ASM) offer guidelines for preventing heat-affected zone sensitization.

The National Association of Corrosion Engineers (NACE) offers guidance for cathodic protection of above ground storage tanks.

Methanol absorbs moisture from air. If tank liquid level cycles through large volumes on frequent intervals, then moisture-laden ambient air may be pulled into the tank. This may be particularly harmful in a coastal environment where moisture laden air carries dissolved chloride salts. If the facility is in a region that has characteristically high relative humidity, then methanol will dry the air in the vapor space of the tank and thereby self-contaminate the contained methanol.

If purity is an important consideration, then inert gas padding and stainless steel tanks may be economically justified as product quality and risk reduction measures. Be certain to pay equal attention to selecting compatible trim materials.

Water absorption can be eliminated by padding tank vapor space with an inert gas such as argon or nitrogen, or by padding the vapor space with dry natural gas. If natural gas is used, then measures to eliminate ignition must be thorough, consistent, and rigorously enforced. Methane is a lighter-than-air gas and is expected to float up and away from the tank vent when expelled. Never-the-less, precaution should be taken to avoid accidental ignition of expelled methane by controlling potential ignition sources

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<sup>1</sup> Intermittent exposure is short term non-continuous contact; sustained exposure is long term continuous contact.

near and above the tank. Hot work above unpadded and methane-padded methanol tanks must be managed and controlled.

Inert gas padding reduces the need for controlling ignition sources, providing methanol vapor and/or condensed vapors do not leave the tank by way of a gravity drain that discharges alongside the tank. Inert padding protects against contamination, accidental ignition, and exposure to airborne toxic vapor.

Incidentally, tank vapor space inerting may be required in order to obtain a variance regarding setback distances. Refer to International Fire Code (IFC) -2000 Sections 911.1 and 3404.2.9.5.1 for guidelines regarding variances in setback distance.

#### ***Fire Prevention***

The U.S. Department of Transportation (DOT) classifies methanol as a "Primary Class" 3.2 flammable liquid and a "Secondary Class" 6.1 toxic substance. Protective safeguards should be developed for both hazards which may be present near tanks and within spill impoundment areas. This includes protection of workers during normal operation and maintenance, and safeguarding fire fighters and first responders during accidental releases.

The International Code Council (ICC) and the National Fire Protection Association (NFPA) designate methanol as a Class IB *flammable liquid*. Class IB liquids are characterized by flash points below 73 °F and boiling points at or above 100 °F. Gasoline is another example of a commonly-used Class IB liquid, but with important differences due to the polarity of methanol, and the non-polarity of gasoline.

Practically speaking, the vapor pressure of Class IB liquids under commonly-expected conditions of outside tank storage is high during warm portions of the year. The vapor phase is the most hazardous physical state of methanol; airborne methanol vapors are mobile, and are readily ignited and readily enter the body by way of the lungs. Hazard management is especially important when the temperature of the liquid phase rises above flash point temperature. The fact that flash point temperature of methanol is low indicates substantial amounts of vapor are present immediately above the liquid surface and within the vapor space of the tank. Liquids with vapor pressure greater than 10 mm Hg are considered flammability-explosion hazards. The vapor pressure of methanol is several times this value at commonly encountered ambient storage temperatures. Ignition may occur both within and outside the tank, and may be accompanied by tank liquid contents roll-over due to external heating and subsequent Boiling Liquid Expanding Vapor Explosion (BLEVE).

Depending on liquid temperature, vapor may be capable of supporting combustion if the vapor-air composition is within the flammable range, and if vapors are exposed to a sufficiently energetic ignition source. The flammable range of methanol is much broader (6 vol% to 36 vol %) than that of gasoline (1.4 v% to 7 v%). Ignition energy of methanol is 0.14 millijoules (mJ) compared to that of gasoline at 0.20 mJ. These values are essentially the same as those for most motor fuels, and therefore not a major factor in assessing ease of ignition. Flash point temperature, vapor pressure (or Reid vapor pressure), upper and lower flammability limits, autoignition temperature, and heat of combustion are more important parameters when assessing the relative ease of ignition and hazard severity of methanol and gasoline.

Methanol fires are more likely to occur than gasoline fires within tank freeboard space when liquid temperature is near or above the methanol flash point temperature (52 °F). The vapor pressure of methanol is 90 mm Hg at 68 °F and that of gasoline is 190 mm Hg at 68 °F. The volumetric concentration of gasoline vapor is much higher at a given temperature than that of methanol. This may cause vapor concentration of gasoline to exceed the 7 v% upper flammable limit, but not the concentration of 36 v% of the upper flammability limit of methanol. Safeguards for gasoline tank fires are not necessarily sufficient to prevent methanol tank fires.

During tank filling, methanol vapor is displaced through tank vents to atmosphere thereby creating potential flammability and toxicity hazards in the ambient air which surrounds the tank. These hazards can be controlled using either of two strategies:

- Eliminating ignition sources and recognizing toxicity hazards in the proximity of the tank by classifying the area surrounding the tank as a hazardous location.
- Excluding air from tank vapor space by inerting or gas blanketing.

Tank storage of methanol requires strict and rigorously-enforced provisions to prevent over filling and tank overflow. Tank maximum allowable working volume must always allow additional volume for liquid expansion. The volumetric coefficient of thermal expansion for methanol (0.00066 / °F) is greater than that of gasoline (0.00056 / °F). A general rule of thumb is to allow 20% of tank working volume for liquid expansion.

Guidelines for sizing the volume of a methanol tank containment dike are not the same as for fuels such as gasoline and diesel. Spill containment must allow extra capacity for the substantial volume of fire water (greater than 5 parts water to 1 part methanol) necessary to dilute methanol to a non-flammable concentration. This consideration is discussed in detail under the heading of "Spill Containment."

Provisions for controlling potential ignition sources near methanol liquid storage tanks are more or less the same as those for gasoline. The lower flammable limit of gasoline vapor is 1.4 v% compared to 7 v% for methanol. The relative density of gasoline vapor is 3 to 4, compared to that of methanol which is 1.1. Gasoline vapor will travel further along the ground without being diluted below the lower flammability limit and will ignite at much lower concentration than methanol vapor. Generally speaking, the hazard zone for ignition of methanol vapor is less restrictive than that of gasoline. The perimeter of hazard zones for methanol must consider both the toxicity and the flammability of methanol. Refer to the following for information on classifying, designating, and safeguarding hazardous locations:

- A.W. Cox, F.P. Lees, and M.L. Ang: *Classification of Hazardous Locations*, Published by Institution of Chemical Engineers, Davis Building, 165-171 Railway Terrace, Rugby, Warwickshire, CV21 3HQ, England, © 1990, ISBN 0 85295 258 9
- NFPA 70E, *Standard for Electrical Safety Requirements for Employee Work Places*.
- NFPA 70, *National Electrical Code*.

The United States Occupational Safety and Health Administration (OSHA) among others, provides guidance for permitting, testing, entering, and safeguarding employees during performance of hot work within hazardous locations and confined spaces. The applicable sections of Title 29 of the Code of Federal Regulations (CFR) are:

- 29CFR1910.106, *Flammable and Combustible Liquids*
- 29CFR1910.146, *Confined Space Entry*
- 29CFR1910.252, *Fire Protection and Prevention*
- 29CFR1910.253, *Oxygen Fuel Gas Welding and Cutting*
- 29CFR1910.254, *Arch Welding and Cutting*
- 29CFR1910.255, *Resistance Welding*
- 29CFR1917.152, *Marine Terminals Welding, Cutting, and Hot Work*
- 29CFR1910.301, *Electrical Safety*

Other applicable references include:

- API Publication 2201, *Procedures for Welding or Hot Tapping on Equipment Containing Flammables*
- NFPA 51-B, *Fire Prevention During Welding, Cutting, and Other Hot Work*
- Association of Energy Services Companies (AESCo) *Hot Work*

- American National Standards Institute (ANSI) Z49.1-67, *Safety in Welding and Cutting*
- American Welding Society (AWS) Z49.1-88, *Safety in Welding and Cutting and Applied Processes*.

### ***Fire Suppression***

Fire suppression may use any of several media:

- alcohol resistant fire-fighting, fire-extinguishing foam (AR-AFFF)
- dry chemical extinguishers (for small fires)
- CO<sub>2</sub>
- Water mist spray.

Guidelines for foam extinguishing systems with optimum application rates are provided in NFPA 11.

Fixed fire monitors may be used to cool tank walls and to extinguish flames provided at least five parts water is added for every one part of methanol: i.e., methanol concentration is diluted to less than 15%. Water-methanol solutions are flammable to compositions of about ≈ 80 v% water.

Some facilities equip methanol tanks with an internal foam delivery system combined with an internal floating roof. Care must be taken to coat the internal floating roof if it is constructed of aluminum or aluminum/magnesium alloy. Methanol is mildly corrosive to aluminum-magnesium, aluminum-copper, and copper-zinc alloys.

### ***Tank Spill Containment***

General guidance for liquid hydrocarbon (gasoline, kerosene, and diesel) spill containment is to size the containment volume to at least 110% of the working volume of the largest tank within a tank battery. This volume accommodates a worst case, full tank breech when precipitated moisture is present within the containment without overflowing containment dikes. Guidelines for spill containment are provided in NFPA 1, NFPA 30, and federal regulations for spill prevention: 40CFR110 and 112.

Because methanol is highly soluble in water, and because flammability of water-methanol solutions is persistent to high proportions of water, it is suggested that the containment volume for methanol tank spills be enlarged accordingly if water is to be used as an extinguishing medium. The additional containment volume must be sufficient to allow responders to use water as a suppressant without overflowing the tank impoundment dike. If alcohol resistant foam is used, then less volume is required for spill containment. Provisions must insure that a sufficient amount of AR-AFFF suppressant is onsite and available to extinguish worst case fire scenarios.

## Methanol Drum Transport, Handling, and Storage

### *Introduction*

Totes, drums (55 gallon), and cans (5 gallon, and 1 gallon) are used to transport, store, and dispense methanol in a wide variety of circumstances by low volume users. Non-bulk transport and storage of hazardous material are regulated activities in the U.S. and some other countries. Failure to adhere to applicable regulations may be punishable by fines and imprisonment. Requirements are specific to the country and the circumstances; however requirements will generally consist of the following; shipping papers, container labeling, transport vehicle placarding, driver training and licensing, and availability of emergency response equipment. If you are not a designated hazardous materials carrier, then it may be against the law to transport methanol in totes, drums, and cans.

Do not transport methanol in your personal vehicle. Do not store methanol totes, drums, or cans indoors or in your home. Storage requires precautions for flammable loading, fire-safe storage, ventilation, spill containment, spill cleanup, and fire suppression.

Never use mouth suction to siphon-transfer methanol. Methanol liquid and vapor are toxic to humans. Exposure is cumulative and may result in harm if vapor or liquid are inhaled, ingested, or contacted with skin for extended periods of time.

Methanol (CAS: 67-56-1, NIOSH: PC-1400000, DOT: 1230, UN-1230, NA-1230) is classified by the International Code Council (ICC) and the National Fire Protection Agency (NFPA) under the *Uniform Fire Code* as a “IB Flammable Liquid” and by the United Nations as a “1993 Class 3 Flammable Liquid.” NFPA and Department of Transportation (DOT) rank Flammability as a 3 primary hazard, and toxicity, as a 6.1 ranked secondary hazard. Guidelines for handling IB flammable liquids are provided by codes and standards published by ICC, NFPA, and the International Fire Code.

ICC and NFPA guidelines are recommended as ‘best practices,’ but are not mandatory unless deemed so by national, or local authority. Within the United States, local authority generally rests with the local Fire Marshal. Mandatory regulations have been developed within the United States by the Occupational Safety and Health Administration (OSHA), an agency of the federal government. Specific safe handling practices are given under three separate regulations for various industries, circumstances, and work environments:

- General Industry: 29 Code of Federal Regulations (CFR) 1910.106
- Construction Industry: 29 CFR 1926.152
- Shipyard Industry: 29 CFR 1915.36).

Guidelines for international transportation of flammable liquids are available from the following bodies:

- International Maritime Organization, *International Maritime Dangerous Goods (IMDG) Code* (volumes, 1, 2, and Supplement)
- International Air Transport Association (IATA), *Dangerous Goods Regulations*
- Intergovernmental Organization for International Carriage by Rail, *Regulations concerning the International Carriage of Dangerous Goods by Rail*.

Transportation within the United States is governed by the Department of Transportation (DOT), an agency of the federal government. DOT regulations are available in 49CFR which can be accessed on the internet or purchased in book format at a nominal cost over the internet.

Drums, totes, and cans are transported, stored, and handled by the vast majority of methanol users. This discussion focuses on 5-gallon and 55-gallon quantities packaged in metal containers.

Plastic containers are not recommended for long-time storage or shipment of methanol because the solvent properties of methanol may degrade the plastic, causing the containers to lose structural integrity.

#### ***Storage of Methanol-Containing Totes, Drums, and Cans***

Guidance for safe storage of methanol is provided by ICC, NFPA, and the International Fire Code. ICC and NFPA guidelines are available in:

- NFPA 1, *Uniform Fire Code*.
- NFPA 30, *Flammable and Combustible Liquids Code*.

Methanol storage areas should be curbed with a compatible material such as concrete, ventilated to prevent accumulation of vapors, and drained to a safe location which is remote from the storage area. Storage areas should be equipped with vapor, and heat detector/alarms. Because methanol burns with a transparent, non-luminous blue flame, combustion will likely not be detected by standard smoke detectors, and luminous-type flame detectors. Carbon monoxide and carbon dioxide detectors may serve in place of smoke detectors and luminous flame detectors. First responders use infra-red detection methods to determine if combustion is occurring. It is recommended that this type of detector be installed and alarmed to monitor methanol tote, drum, and can storage areas. Detection should be redundant with detectors positioned at right angles to one another.

If more than several drums are stored, then consideration should be given to automatic fire suppression using either fine water mist spray, or alcohol resistant fire-fighting foam (AR-FFF). Storage of multiple containers is subject to limitations on stacking height, and container density loading. Refer to the listed codes to obtain guidance, which is specific to your circumstance.

Tote and drum containers must be stored outside, not within a structure, unless placed in a liquid storage room or warehouse meeting the requirements for flammable liquids storage buildings. Five-gallon and 1-gallon containers may be stored within a building provided they are contained in a fire-safe cabinet which is grounded, and vented to an outside safe location which includes an explosion suppression devise.

#### ***Shipment of Totes, Drums, 5-Gallon Cans, and 1-Gallon Containers***

Guidance for shipment of methanol via the U.S. Postal Service is contained in United States Postal Service Publication 52, 343 *Flammable and Combustible Liquids (Hazard Class 3)*.

Transportation of drum quantities (8 to 119 gallon quantities of methanol) is regulated by multiple agencies and organizations. The regulatory authority depends on:

- Method of transport (truck, rail, air, or sea-going vessel).
- Capacity of individual containers, the number of containers which comprise a single shipment.
- Whether shipment is domestic within U.S.-controlled territory or outside of U.S. controlled territory.

Shipping oversight is the responsibility of the following regulatory bodies:

- Within the United States, the U.S. Department of Transportation (DOT), *Hazardous Material Regulations 49 CFR 100-199* and *Emergency Response Guide Book*
- United Nations Location Codes (UN/LOCODES), *UN Recommendations on Transport of Dangerous Goods* (i.e., the so-called *UN-Orange Book*)
- International Maritime Organization (IMO), *International Maritime Dangerous Goods Code (IMDG)*, Volumes 1 and 2, plus a supplement
- International Civil Aviation Organization (ICAO): *Technical Instructions for the Safe Transport of Dangerous Goods by Air*
- International Air Transportation Association (IATA), *Dangerous Goods Regulations (DGR) 3.3.*

Road, rail, airborne, and water transport of hazardous materials is controlled by DOT for goods shipped within the United States. Regulatory revisions are made almost continuously; verify that you are using current versions of the regulations.

DOT restricts aircraft transportation of Class 3 flammables (e.g., methanol) to a maximum of 1 liter on passenger aircraft and 60 liters on cargo aircraft, irrespective of the shipping company: Fed-X, UPS, etc. Drum quantities are not considered to be air transportable. Refer to 49CFR172.101, "Hazardous Materials Table" for specific information regarding shipment of methanol. Refer to 49CFR173.202 for non-bulk packaging requirements on passenger and cargo aircraft.

#### ***Container Specifications for Transporting and Storing Methanol***

Class IB Flammable Liquids are equivalent to DOT-designated PG II Flammable Liquids. Non-bulk volumes of PG II Flammable Liquids between 8 and 119 gallons are required to be packaged in DOT performance-oriented packaging identified using the United Nations identification system. Specifications for drums are established and published by Oak Ridge National Laboratory. A copy of these specifications can be obtained by contacting Oak Ridge National Laboratory, Packaging Operations Manager, Bldg. 7001, MS 6288 P.O. Box 2008, 1 Bethel Valley Road Oak Ridge, Tennessee 37831-6288. Totes, drums, and cans are available which just meet, and which exceed published specifications. Those which exceed specifications offer the potential cost-benefit of testing and re-using the containers.

Standards for DOT designated packaging requirements for drum drop, stacking, and vibration testing are as follows:

- Drop
  - American Society of Testing and Materials (ASTM) D-5276, *Standard Test Method for Drop Test of Loaded Containers by Free Fall*
  - International Organization for Standardization (ISO) 2248, *Packaging – Complete, Filled Transport Packages – Vertical Impact Test By Dropping*
- Stacking
  - ASTM D-4577, *Standard Test Method for Compression Resistance of a Container Under Constant Load*
  - ISO 2234, *Packaging – Complete, Filled Transport Packages – Stacking Tests using Static Load*
- Vibration
  - ASTM D-999, *Standard Test Method for Vibration Testing of Shipping Containers*
  - ISO 2247, *Packaging – Complete, Filled transport Packages – Vibration Test at Fixed Low Frequency*

Packaging may be re-used provided it is cleaned, refurbished, re-tested, and found to be compliant.

#### ***Shipping Regulations***

Shipping requirements for hazardous materials are rigorous and complex. Failure to comply with DOT regulations can result in civil penalties consisting of monetary fines of \$50,000 per occurrence and criminal penalties of 5-years' imprisonment.

If you are not comfortable interpreting regulations for identifying, labeling, packaging, and shipping hazardous materials, then consider obtaining professional guidance from a qualified professional who is knowledgeable about your specific circumstances.

It is unsafe to transport drum or even 5-gallon cans of methanol in the trunk of a car, even if the trunk remains open. Transportation of methanol requires special hazard and incident response training. Transporting vehicles must be placarded, and drivers must have government required papers authorizing transport.

#### ***Controlling Static Accumulation and Spark Discharge***

Liquids which have conductivity less than 50 picosiemens per meter are charge accumulators; that is, these liquids tend to accumulate static charge as a result of fluid handling in un-bonded and un-grounded fuel containment systems. Liquids which have electrical conductivity greater than 50 picosiemens per meter are not considered to be charge accumulators. The conductivity of gasoline is less than 500 picosiemens; the conductivity of methanol is substantially greater than 50 picosiemens.

Methanol is a polar material; gasoline, and most other common transportation fuels are non-polar materials. The flash temperature, ignition energy, and lower flammability limit of methanol compared to gasoline cause methanol to be less easily ignited than gasoline in many commonly-encountered circumstances. This is also true for ignition resulting from accumulation and subsequent discharge of static electricity. Charge accumulation and discharge is less likely for methanol than for gasoline, Jet, kerosene, low sulfur diesel, and other low sulfur distillates. Electrical conductivity of gasoline is 25 picosiemens per meter, which is typical for petroleum derived distillate fuels. Gasoline accumulates static electricity.

By comparison, the electrical conductivity of methanol is  $7 \times 10^6$  picosiemens per meter, and that of good quality drinking water (also a polar compound) is  $5 \times 10^8$  picosiemens per meter. Neither methanol nor water are charge accumulators. However, methanol may accumulate static charge under abnormal circumstances. Always make provisions to bond and ground methanol containers with electrical resistance less than 10 ohms ( $R_{\text{bond or ground}} \leq 10 \text{ ohms}$ ). Neat (pure) methanol does not normally have a high risk of charge accumulation, static discharge, and static spark ignition. Possible exceptions to this occur when large transient ground currents are present due to lightning strikes, nearby high voltage power lines, and other sources of ground current.

As a matter of good practice, bonding, grounding and turbulence quelling, and liquid stilling during handling procedures should be followed in the event the methanol is a blended fuel, or is contaminated with hydrocarbon and therefore has an unexpectedly low electrical conductivity. Methanol burns with a non-luminous flame which may be difficult to detect during daytime hours, and methanol vapor has a very wide flammability range (7 v% to 36 v%).

***Drum Handling and Liquid Transfer***

The difficulty of drum handling increases proportionally to the size and weight of the drum. Five gallon cans are relatively easy to handle without mechanical assistance, provided the cans are moved and handled one-at-a-time.

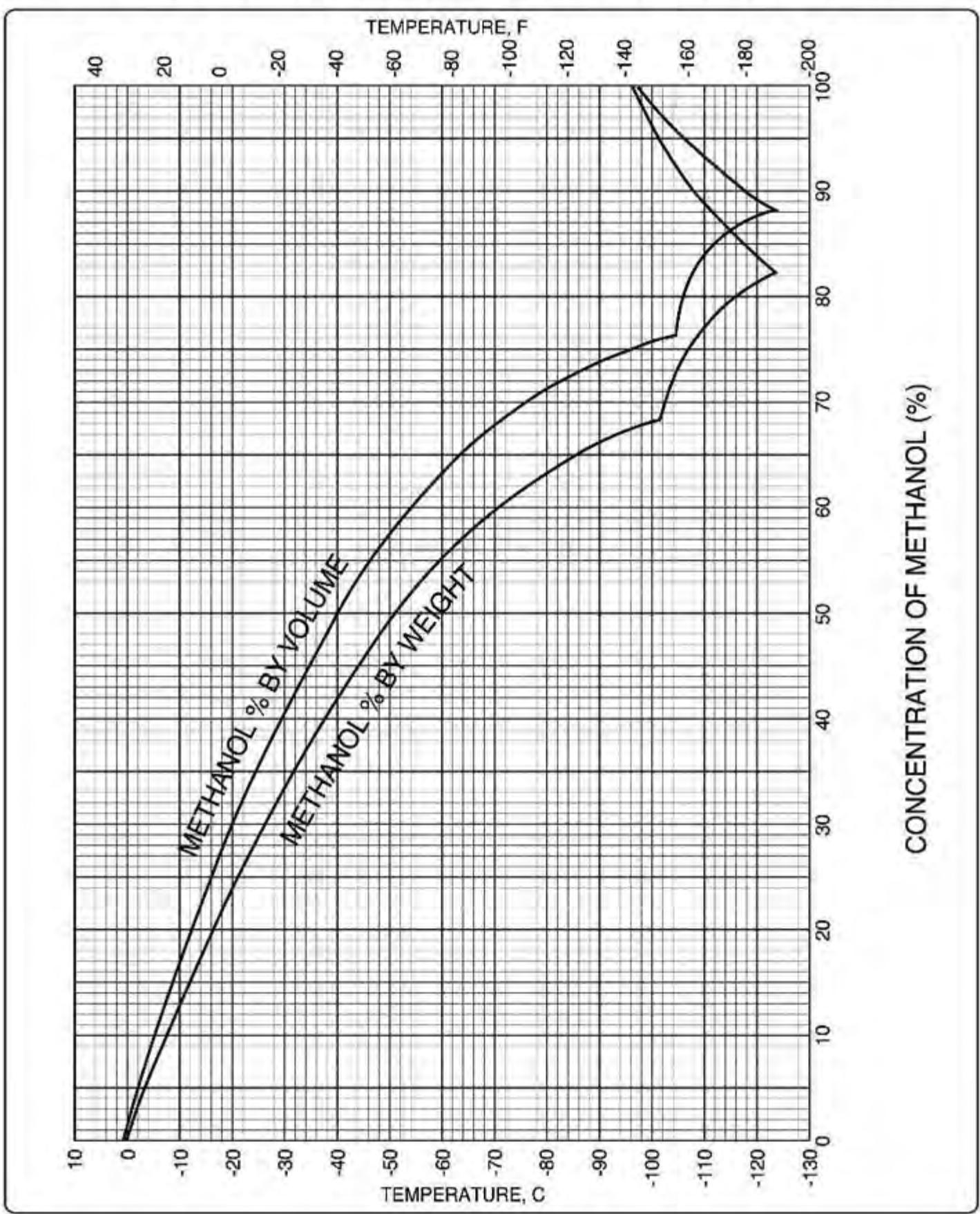
Fifty-five gallon drums contain less than 55 gallons of liquid in order to allow space for fluid volume expansion. A 55 gallon drum filled to 80% capacity with methanol weighs approximately 300 lbs. In order to move a full drum, it is necessary to use a mechanical means such as a barrel hoist or fork lift. If no mechanical means is available, then individual drums can be moved by tipping the drum on its side, and rolling it to a designated curbed storage area.

If it is necessary to remove a measured quantity of methanol from the drum without using mechanical means such as low pressure inerting, or a siphon, then it is possible to lay the drum on its side, and roll the drum into a slanted position with some form of a prop such as a short section of board under the bunged end of the drum. Position the drum with the small bung in a 12 o'clock position, and verify that the drum is chocked in a stable position. The drum and the receiving container must be bonded and grounded.

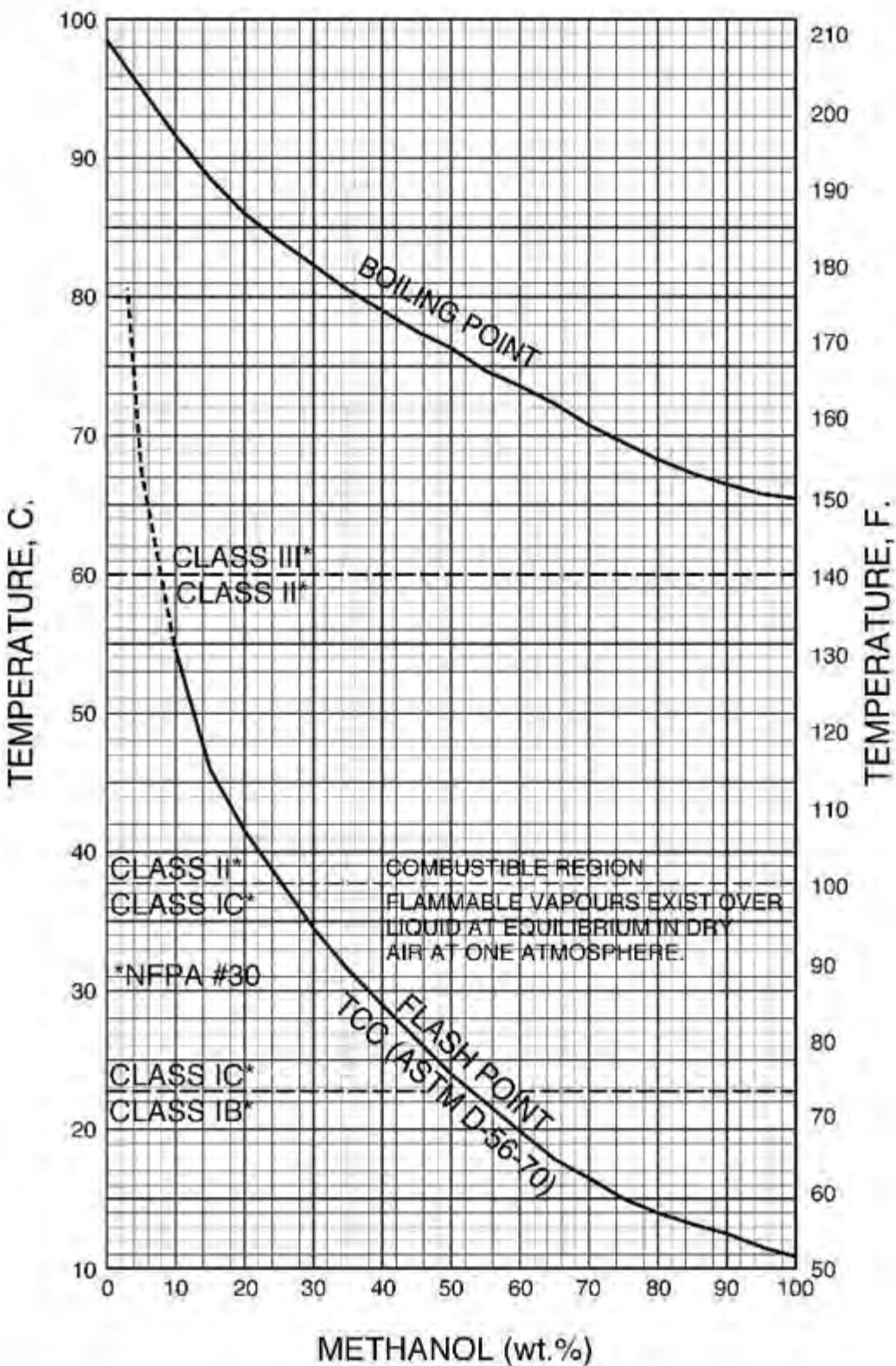
In the 12 o'clock position, the small bung is now in the vapor space of the drum. Replace the bung with a threaded, alcohol compatible hose. Be careful not to breathe the escaping vapors, which are toxic, and may be flammable. Methanol can be removed from the drum in a controlled manner by carefully rolling the drum to the side so the small bung is in the 1 o'clock position, slightly below the liquid level within the drum. Methanol will now flow out of the drum in a controlled manner. Flow can be terminated by returning the drum to the 12 o'clock position. Replace the transfer hose with the bung, and return the drum to an upright position. Extreme care must be taken to not drop or otherwise damage totes, drums, cans, and 1-gallon containers during handling.

Methanol is toxic, especially when breathed or ingested. Siphon transfer of methanol must never be started by mouth-suction. Ingestion of tea-spoon-sized quantities are known to cause blindness. Inhalation of methanol vapor, even in small amounts over short periods of time, is known to produce acute health effects in some individuals. Methanol is toxic. Do not breathe the vapor, ingest the liquid, or allow bare skin to contact the liquid.

**GRAPH 4:**  
**FREEZING POINTS OF METHANOL**  
**-WATER SOLUTIONS, % BY WEIGHT AND % BY VOLUME**



**GRAPH 5:**  
**BOILING AND FLASH POINTS OF METHANOL**  
**- WATER SOLUTIONS**



**GRAPH 3:**  
**FINAL VOLUME WHEN METHANOL**  
**AND WATER ARE MIXED**

