

# **IMPCA METHANOL REFERENCE SPECIFICATIONS**

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## 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° ± 0.1°	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 <sup>-</sup> 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  $\mu\text{m}$  film thickness) or equivalent.
- 4.3 Volumetric flask 100 ml.
- 4.4 Micropipette of 10  $\mu\text{l}$ .

**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  $\mu\text{l}$ .
- 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 contents 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 measured 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

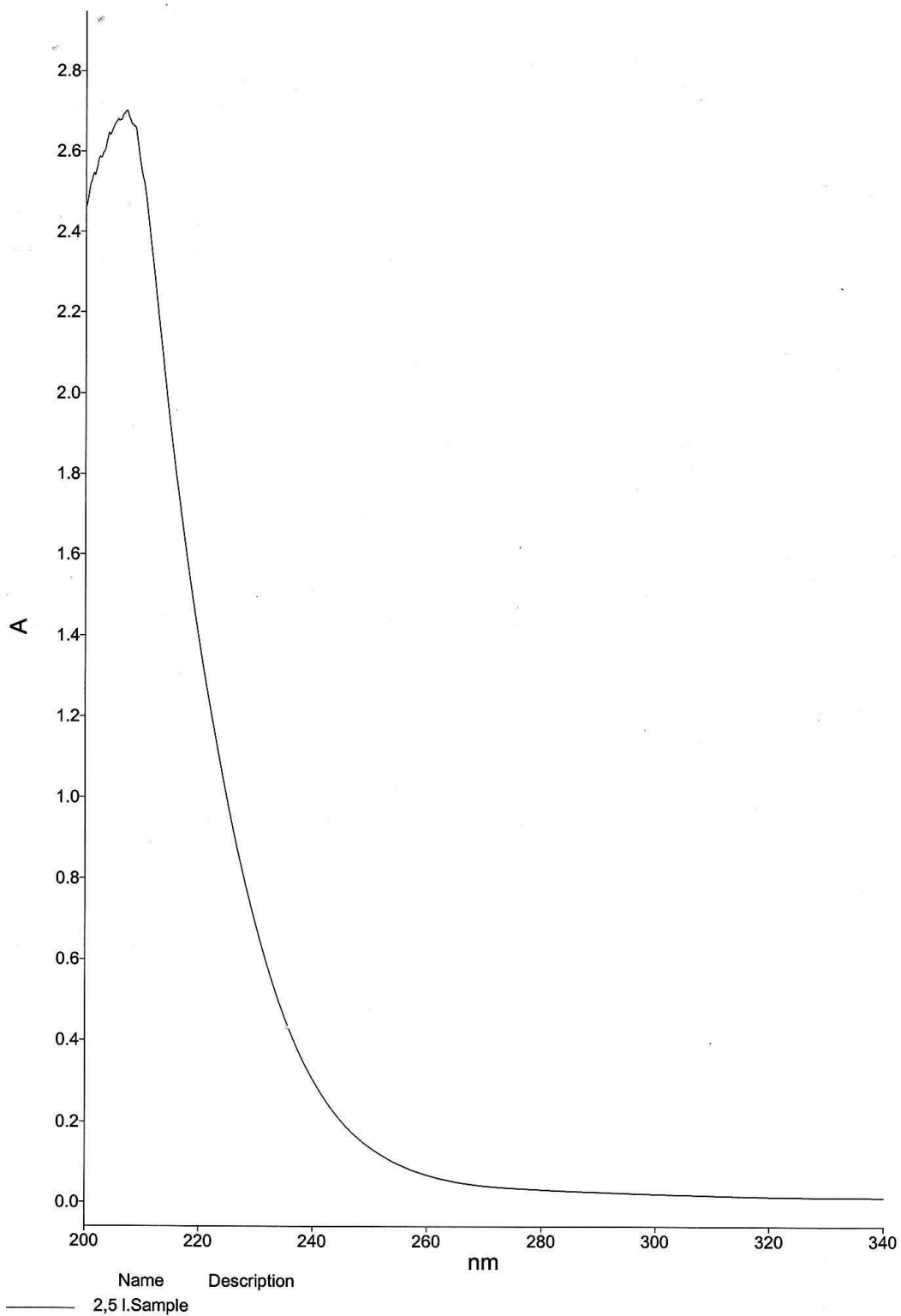
The reproducibility estimate of this determination is based on the results of study iis06C07. In this interlaboratory study three samples with different toluene concentrations (0, 10 and 50 mg/kg) were tested by 11 different laboratories, see below table.

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

## Appendices

1. UV-scan of pure Methanol without contamination with Aromatic compounds
2. UV-scans of pure Methanol without contamination with several Aromatic compounds:
  - A) 1 mg/kg Styrene in Methanol
  - B) 10 mg/kg Phenol in Methanol
  - C) 10 mg/kg Toluene in Methanol
  - D) 10 mg/kg Benzene in Methanol

Appendix 1 - UV-scan of pure Methanol without contamination with Aromatic compounds



Appendix 2 - UV-scans of Methanol contaminated with several Aromatic compounds

