IMPCA
METHANOL
REFERENCE
SPECIFICATIONS

IMPCA REFERENCE SPECIFICATIONS

	TEST	UNIT	METHOD	LIMITS
1	Appearance		IMPCA 003-98	Clear and free of suspended matter
2	Purity on dry basis	% W/W	IMPCA 001-14	Min 99.85
3	Acetone	mg/kg	IMPCA 001-14	Max 30
4	Ethanol	mg/kg	IMPCA 001-14	Max 50
5	Colour	Pt-Co	ASTM D1209-11	Max 5
6	Water	% W/W	ASTM E1064-12	Max 0.100
7	Distillation Range at 760 mm Hg	°C	ASTM D1078-11	Max 1.0 to include 64.6° +/- 0.1°
8	Specific Gravity 20°/20°		ASTM D4052-11	0.7910-0.7930
9	Potassium Permanganate Time test at 15 °C	minutes	ASTM D1363-11	Min 60
10	Chloride as Cl $^-$	mg/kg	IMPCA 002-98	Max 0.5
11	Sulphur	mg/kg	ASTM D 3961-98	Max 0.5
	Note 1, page 3	mg/kg	ASTM D 5453-12	Max 0.5
12	Hydrocarbons		ASTM D 1722-09	Pass test
13	Carbonisable Substances (Sulfuric Acid Wash Test)	Pt-Co	ASTM E 346-08	Max 30
14	Acidity as Acetic acid	mg/kg	ASTM D 1613-12	Max 30
15	Iron in solution	mg/kg	ASTM E 394-09	Max 0.10
16	Non Volatile Matter	mg/1000ml	ASTM D 1353-13	Max 8
17	TMA Note 2, page 3			optional (see notes for recommended methods)
18	AROMATICS Note 2, page 3			optional (see notes for recommended methods)

Notes:

1. **Sulphur**

Whilst the scope of ASTM D 5453 is stated to be for various fuels containing 1.0 to 8000 mg/kg total sulphur, IMPCA consider this method to be suitable for the determination of total sulphur in methanol provided that the laboratory performing the analysis has demonstrated that it can achieve a Limit of Detection < 0.5mg/kg with the apparatus available to it.

2. **TMA and Aromatics**

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-**15**

PURITY AND IMPURITIES OF METHANOL   METHOD IMPCA 001-14

1. Scope

This method describes a procedure for the determination of the purity and impurities (e.g. acetone, ethanol, BTEX) 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 impurities and purity on dry basis are calculated.

4. Apparatus

4.1   Gaschromatograph with FID detector
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 (minimum purity of 99%)

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   MTBE (methyl tertiary butyl ether)
5.8   MEK (methyl ethyl ketone)
5.9   Benzene
5.10   Toluene
5.11   Ethylbenzene
5.12   Ortho-xylene
5.13   Meta-xylene
5.14   Para-xylene

6. Procedure (Typical Gas Chromatographic conditions)

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: start 5 min. @ 50°C; rise 5°C/min to final temp 1 = 100°C (hold 0 min.); rise 10°C/min to final temp 2 = 250°C (hold 4 min.).
Carrier gas: Helium, Nitrogen or Hydrogen
Split: 50 ml/min

Column pressure: approx. 100 kpa (Helium), 80 kPA (Nitrogen), 45 kPa (Hydrogen)
Injection volume: 1µl

6.2   When the method is first set-up or has not used for a long period, determine the response factors for all impurities (see secton 5) for 2 concentration levels (e.g. 5 mg/kg and 100 mg/kg), relative to sec-Butanol present at a concentration of 10 µl per 100ml.
The difference between the response factors determined at both levels should not exceed 10%.
The average response factors are used for the quantification of the individual impurities.
6.3   Transfer approx 80 ml of sample to a 100 ml volumetric flask
6.4   Add 10 µl of sec-Butanol [5.1] as internal standard and fill up to the mark with sample and homogenize.
6.5   Run the mixture under the GLC conditions as described in par.6.

7.   Calculation

Calculate the concents of the impurities in mg/kg by the internal standard method as follows :

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

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

For unknown impurities (impurities not present in section 5) use RF 1.00 for calculations

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 %W/W as follows :

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

Note that one should not subtract the water content.

8.   Report

The content of impurities should be reported in mg/kg and rounded to the nearest whole mg/kg.
The lower limit of the determination of the ethanol content and other impurities is 5 mg/kg.
The purity on dry basis should be reported in %W/W and rounded to 0.01 %W/W.

9.   Precision

The precision of this determination is yet unknown.

APPENDIX 1.   TYPICAL SETTINGS IMPCA 001   (REVISED FEB 2014)

GC	Agilent 6890, Split/Splitless Injector / FID-Detector
Column	HP-1 60 x 0,32 D_f : 5.0 μm
Injectionvolume	: 1 μL (autosampler)
Run time	: 34 min
Internal Standard	: sec-Butanol 10 μL in 100 mL

Oven
> Initial Temp: 50 °C
> Initial Hold: 5 min
> Rise 1: 5 °C/min
> Final. Temp 1 : 100 °C
> Hold : 0 min
> Rise 2 : 10 °C/min
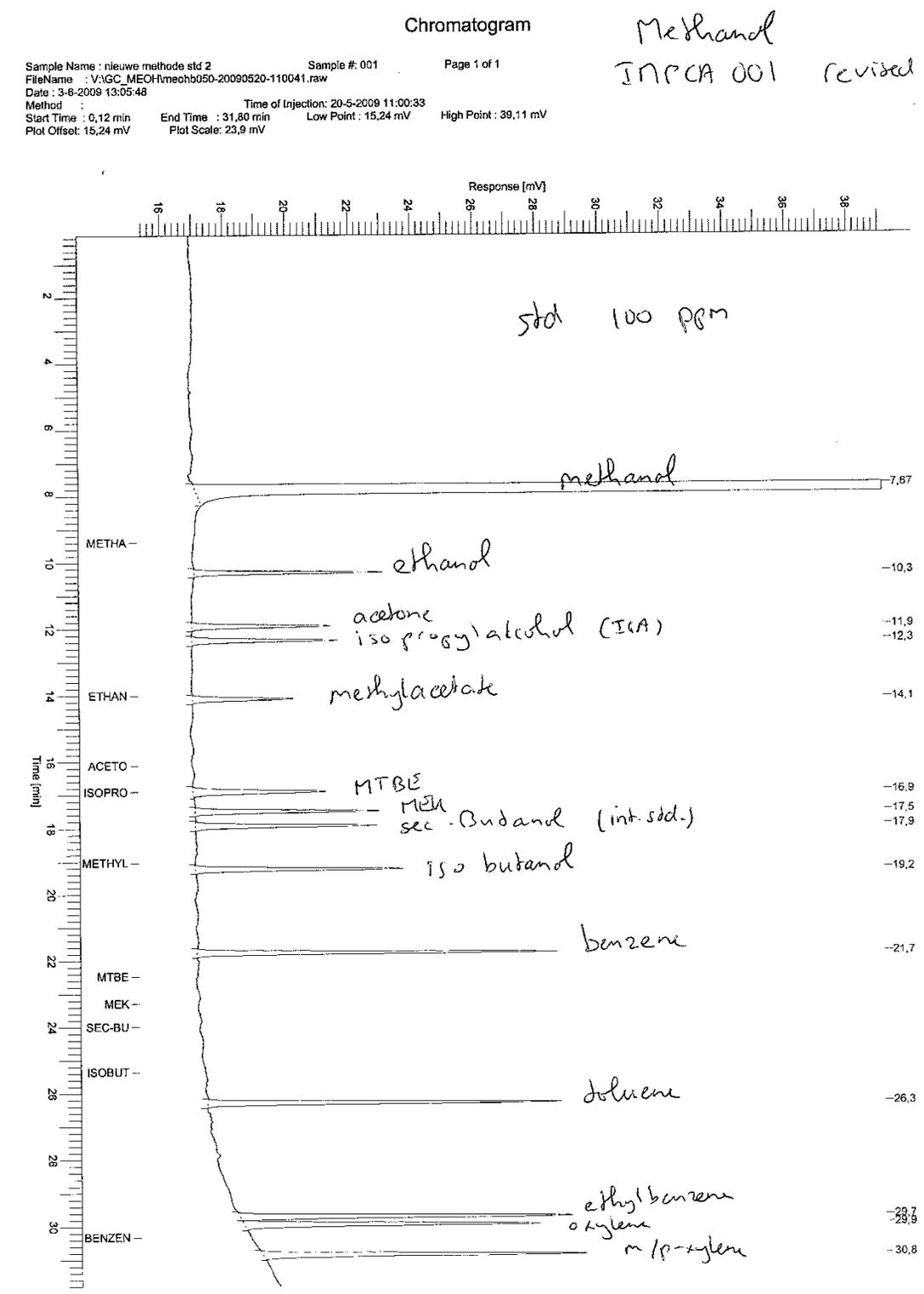> Final. Temp 2 : 250 °C
> Final Hold : 4 min

Injection 275 °C

Detection: 275 °C

Carrier gas: Helium (100kPa), Nitrogen (80 kPa) or Hydrogen (45 kPa)

Split: 50 mL/min

Chromatogram

Methanol
IMPCA 001   revised

Sample Name : nieuwe methode std 2   Sample #: 001   Page 1 of 1
FileName   : V:\GC_MEOH\meohb050-20090520-110041.raw
Date : 3-6-2009 13:05:48
Method   :   Time of Injection: 20-5-2009 11:00:33
Start Time : 0,12 min   End Time : 31,80 min   Low Point : 15,24 mV   High Point : 39,11 mV
Plot Offset: 15,24 mV   Plot Scale: 23,9 mV

std 100 ppm

methanol — 7,67
ethanol — 10,3
acetone
isopropylalcohol (IPA) — 11,9 / 12,3
methylacetate — 14,1
MTBE — 16,9
MEK — 17,5
sec. Butanol (int. std.) — 17,9
iso butanol — 19,2
benzene — 21,7
toluene — 26,3
ethylbenzene — 29,7
o xylene — 29,9
m/p-xylene — 30,8

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 tritration 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 concent in mg/kg for each single determination as follows :

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

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 = *titer, in mol/l, of the standardised aqueous silver nitrate stock 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 ± 0.5 nm or less at 220 nm, wavelength repeatability 0.3 nm or less at
       220 nm and a photometric accuracy of ± 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 ± 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 record the absorption spectrum between 190nm and 350nm. 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 and record the absorption spectrum between 190 nm and 350 nm. Optionally, measure and record the absorbances at 220, 250, 268.5 and 300 nm.

7.5 Print the obtained curve on an A4 or Legal size paper. The scale of the X-axis should be between 190 and 350 nm. The scale of the Y-axis should be between 0 (or -0.05) and 0.4A.

7.6 Compare the curve with the reference methanol scans (e.g. the scan shown in Appendix 1)

7.7 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.

7.8 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**

The result of the UV-scan is qualitative and must be reported as pass or fail only. As a source of supporting evidence for the pass or fail result, optionally report the measured absorbance rounded as X.XXX at 220, 250, 268.5, and 300 nm.
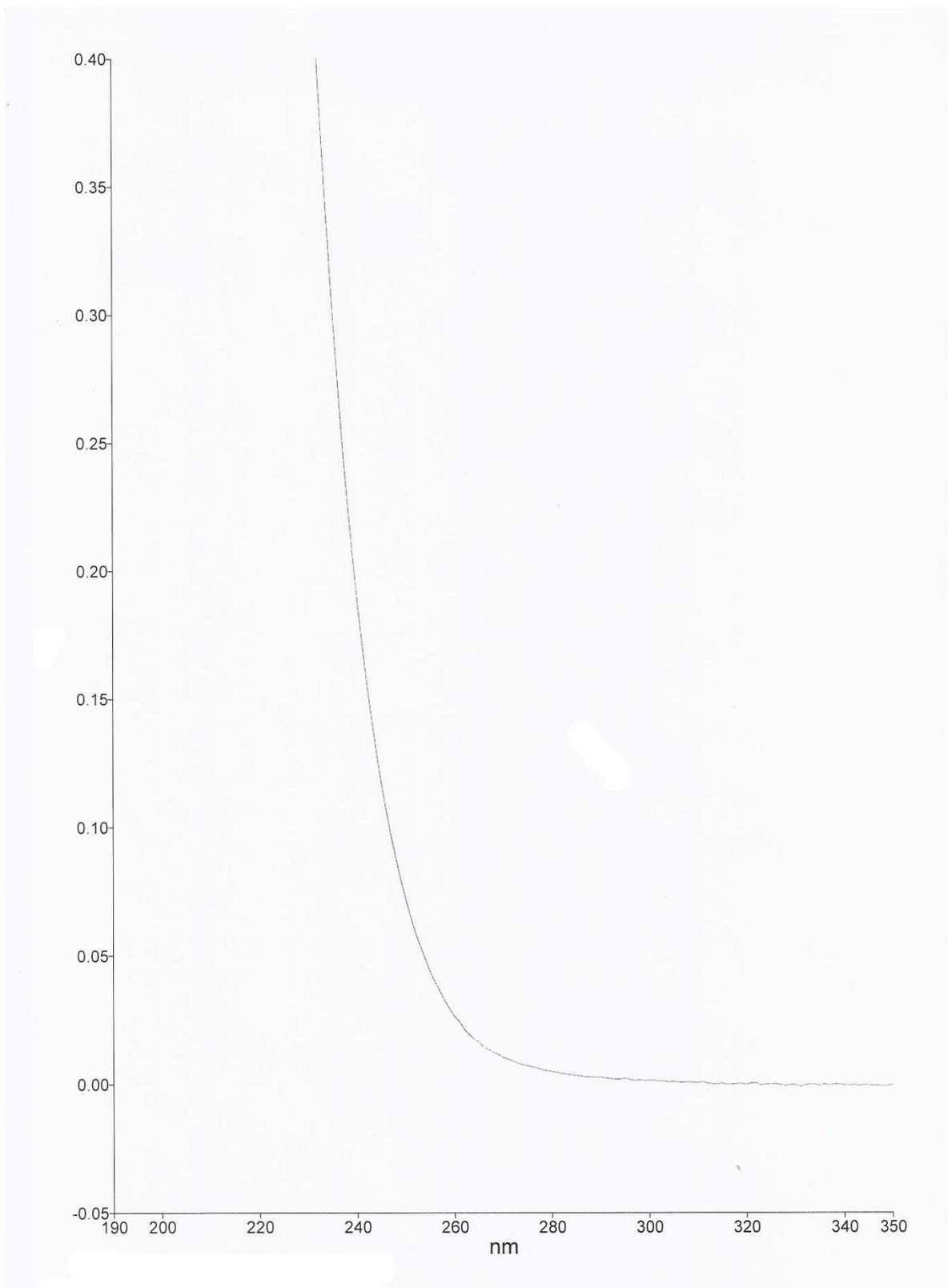
10. **Precision**

The reproducibility estimate of this determination is based on the results of study iis06C07. In this inter-laboratory study, three samples with different toluene concentrations (0, 10 and 50 mg/kg) were tested by 11 different laboratories and a summary of the findings is provided in the following table. Note that this is considered to be a qualitative method and the data table is provided for information only.

Wavelenght	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

Name   Description
—— 1 mg/kg styrene in meoh.Sample
—— 2,5 I.Sample

Name   Description
—— 10 mg/kg phenol in meoh.Sample
—— 2,5 I.Sample

Name   Description
—— 10 mg/kg toluene in meoh.Sample
—— 2,5 I.Sample

Name   Description
—— 10 mg/kg benzene in meoh.Sample
—— 2,5 I.Sample