International Journal of Multidisciplinary Research Education Analysis and Development – IJMREAD

Peer-Reviewed : Open Access Journal

Analysis of Methanol in Water Sample by Gas Chromatography

Dr. Atul Agrawal[1], Dharmendra Kumar Dwivedi[2]& Dr. Hemant Kumar Baghel[3]

1. Sr. Quality Control Manager, Deep Chem Complex Laboratory Bharatpur(Raj.)
2. Head Dept. of Physics, Indira Gandhi Govt. P.G. College Bangarmau (Unnao)
3. Head Dept. of Physics, Goswami Tulsidas Govt. PG College Karwi, Chitrakoot (UP)

Abstract

Methanol typically contaminates the polymer-grade propylene product. The sources of methanol are direct injection into the cold box and cold fractionation areas to remove hydrates and feed stocks containing either methanol or MTBE. A small amount of methanol is produced during the cracking of an impurity- free feedstock in Naphtha cracker and is generally insufficient to cause propylene product purity problems. About 50 to 60% of methanol passes through the furnace unreacted with the balance methanol forming carbon monoxide and hydrogen.

$CH_3OH \rightarrow CO + 2H_2$

Methanol from the furnace enters the process water steam in the quench tower or charge gas condensate of Naphtha cracking units. The majority of methanol in the process water is vaporized in the dilution steam system and recycled to the furnace. Methanol accumulation can be monitored in the process water as early detection of potential propylene-methanol product purity problems.

Methanol in propylene gas is analyzed by test method MTM 151014E. In this test method, a gas sample is injected into the Gas Chromatography by a gas sampling valve and passes through a capillary column to separate the components and FID is used for detection. The concentration of components is calculated by the external standard method. NO test method is available for analysis of methanol contents in water samples.

In the present work, a new method has been developed for the analysis of methanol in water samples by Gas Chromatography.

Keywords- MTBE, Calibration, Drain, FID etc.

Principle:

A small volume of sample is injected into an injector through auto sampler in gas chromatograph and it passes through capillary column DB-624 where separation takes place and the components are detected by FID. The concentration of methanol is calculated by the external standard comparison method.

Reagents and chemicals:

- ☐ Carrier gas: Helium.
- ☐ Air & Hydrogen for the flame.
- ☐ Methanol.

Instrument:

- ☐ Gas Chromatography, Column- DB-624 (30m × 320µm × 1.8 µm) with FID.
- ☐ Syringe 10 µL

Instrument Setting	
Column:	DB-624 (30m × 320µm × 1.8 µm)
Injection Volume :	1.0 µL
Carrier Gas Parameters	
Gas	Helium
Column Flow	1.5 ml/min
Septum Purge Flow	3 ml/min
Split Ratio	10:1
Detector Parameters	
Detector	FID
Temperature	250 °C
Hydrogen	45 ml/min
Air	400 ml/min
Injector Parameter	
Temperature	240 °C
Oven Program	
Initial tem.	35 °C
Initial hold	1 min
Ramp-1	6 °C/min
Final tem.	90°C
Hold	3 min
Ramp-2	70 °C/min
Final tem.	220°C
Total run time	25 min
Calculation type	EXTERNAL STD.

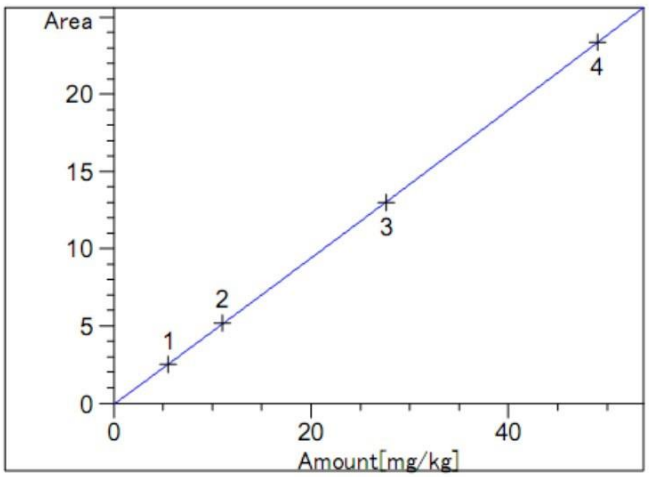
Procedure for Calibration:

- ☐ Prepare the stock solution of 500 mg/Kg methanol standard
- ☐ Take about 1, 2, 5 & 10 ml from the 500 mg/kg stock solution into a 100 ml volumetric flask and diluted with water up to the mark.
- ☐ These solutions contain methanol 5, 10, 25 & 50 mg/kg respectively.
- ☐ Injected 1 µL of calibration mixtures and each mixture was injected three times to get repeatable chromatograms.
- ☐ Calculate the mg/Kg concentration of methanol as follows.
- ☐ Methanol (mg/Kg) = Response × Area of methanol in sample

Calibration Table:

Name	Level	Amount (mg/kg)	Area (I inject Std)	Area (II inject Std)	Area (III inject Std)	Average Area	Response factor
Methanol	1	5.52	2.48026	2.48222	2.51867	2.49371	2.21357
	2	11.04	5.18168	5.18801	5.16714	5.17894	2.13171
	3	27.60	13.08313	13.04045	12.93180	13.01846	2.12007
	4	49.00	23.47897	23.07549	23.54949	23.36797	2.09689

Calibration Curve:

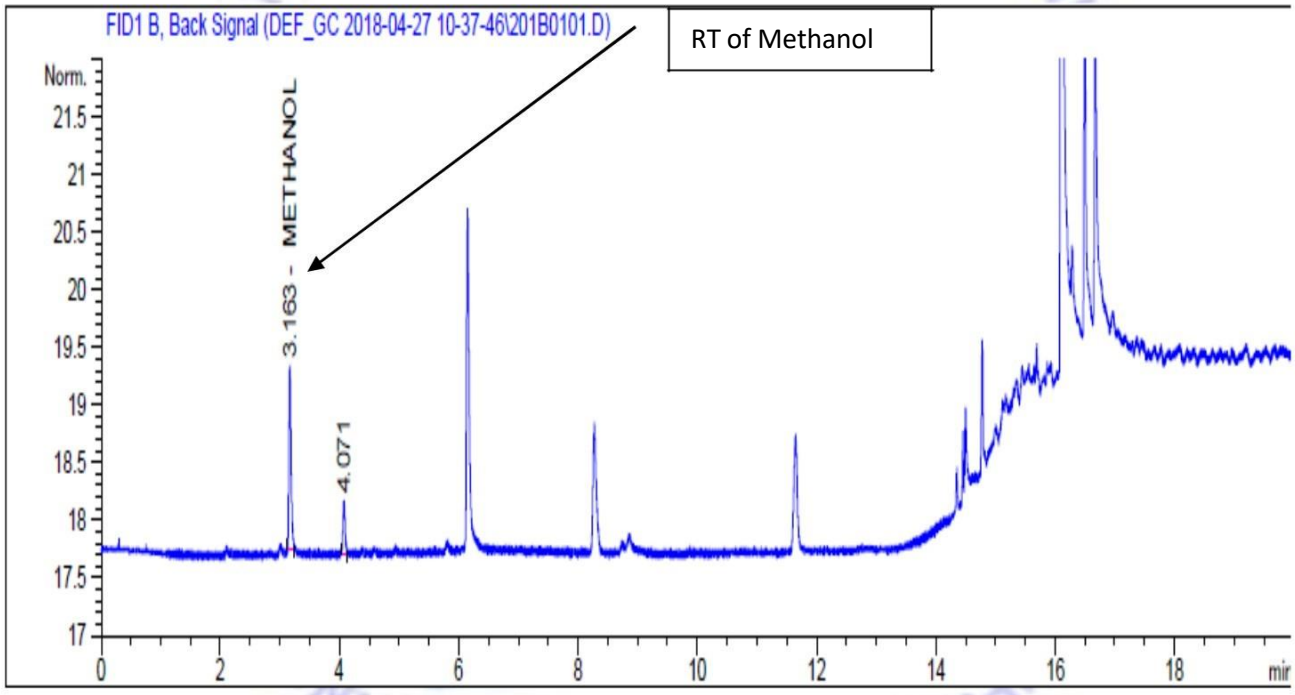


METHANOL at exp. RT: 3.165
FID1 B, Back Signal
Correlation: 0.99999
Residual Std. Dev.: 0.03797
Formula: $y = ax^2 + bx + c$
a: 1.44813e-4
b: 4.71466e-1
c: -8.56911e-2
x: Amount
y: Area

Repeatability of test Method:

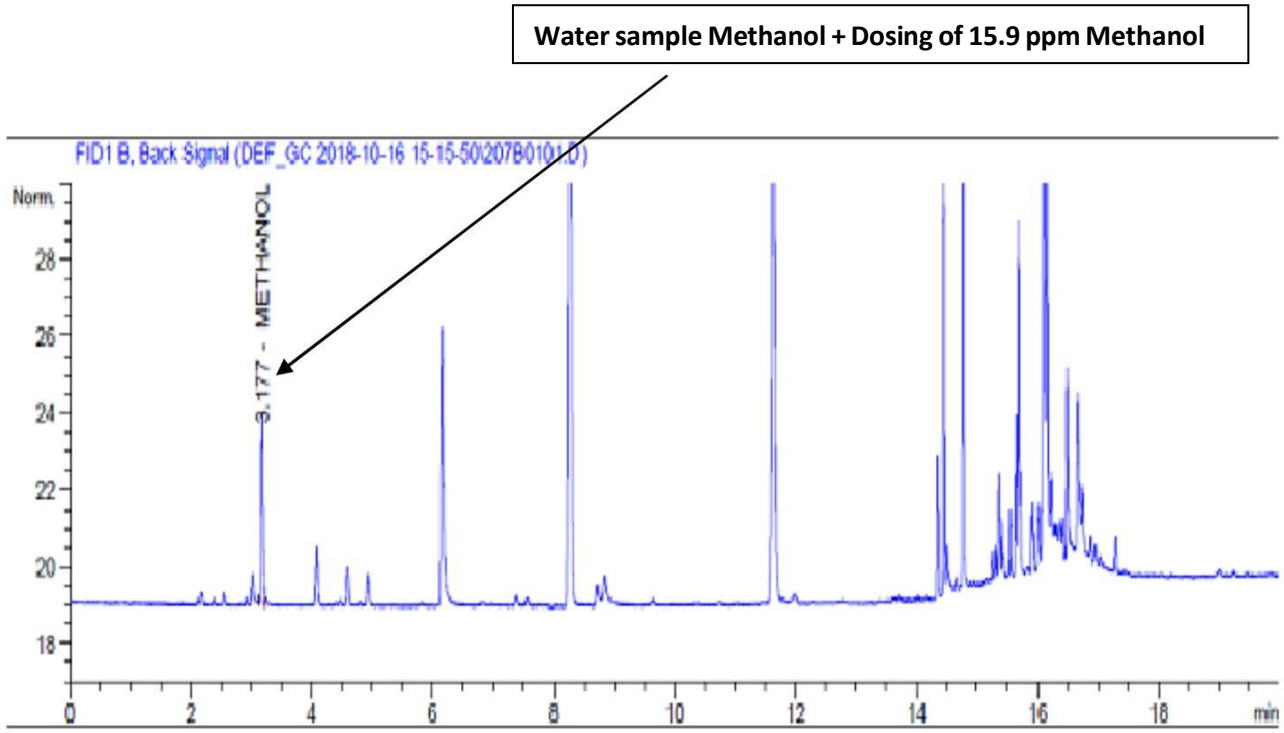
Sr No	Unit Process Water	Test Results (mg/kg)
1	Ist Injection	8.0
2	2nd Injection	8.2
3	3rd Injection	8.2
4	4th Injection	8.3
5	5th Injection	8.1

A standard elution pattern for analysis of methanol in gas sample:



Recovery Check: 15.9 ppm Methanol doses in water sample having methanol 8.57 ppm & test result found 24.03ppm which was in repeatability limit.

RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [mg/kg]	Grp	Name
3.177	BB	11.32785	2.12143	24.03124		METHANOL
Totals :				24.03124		



Test Results: Methanol content (ppm) in water samples & Propylene are as follows:

Methanol Content (ppm) in Unit Water Samples & Propylene

Sl. No.	Date	Samples			
		Process water feed	Process water bottom	Quench water	NCUPropylene product
1	24.04.2018	7	13	16	5
2	25.04.2018	8	15	16	2
3	26.04.2018	7	19	17	8
4	27.04.2018	9	15	15	5
5	28.04.2018	7	14	14	7
6	29.04.2018	9	16	17	10
7	30.04.2018	9	14	14	9
8	01.05.2018	8	16	14	10
9	02.05.2018	11	18	18	5
10	03.05.2018	9	16	15	<2
11	04.05.2018	6	11	12	6
12	05.05.2018	6	12	13	4
13	06.05.2018	6	13	14	6
14	07.05.2018	8	16	21	3
15	08.05.2018	6	11	18	3
16	17.05.2018	3	9	11	<2
17	19.05.2018	4	10	12	<2

18	20.05.2018	4	10	12	3
19	21.05.2018	5	7	10	2
20	22.05.2018	5	9	10	<2
21	23.05.2018	4	9	10	<2
22	24.05.2018	5	10	10	5
23	25.05.2018	4	10	10	3
24	26.05.2018	5	9	10	<2
25	27.05.2018	5	10	11	<2
26	28.05.2018	1	1	2	<2
27	13.06.2018	7	11	11	<2
28	14.06.2018	6	5	11	3
29	15.06.2018	2	11	13	<2
30	16.06.2018	5	11	12	<2
31	17.06.2018	4	11	11	2

Conclusion:

A newly developed method is useful for the analysis of methanol contents (at ppm level) in water samples. Methanol is a polar component with its volatility very dependent on its concentration. At low concentrations, methanol has similar volatility to C3 components and hence most of the methanol travels through the plant with the C3 compounds and ends up in the propylene fractionators. Short-term methanol accumulation within the process of water stream can be reduced by purging to the oily water drain. Methanol is poison for the polymerization of propylene. It should not be more than 5 ppm in propylene feed. If Propylene feed having methanol more than the design specification, it affects the plant operation and causes the variation in Xylene solubility which in turn gives variation in the quality of PP product.

References-

1. Godoy, L. A. F.; Pedroso, M. P.; Ferreira, E. C.; Augusto, F.; Poppi, R. J.; *J. Chromatogr. A* **2011**, *1218*, 1663. [Links]

2 .Goodger, E. M.; *Hydrocarbon Fuels: Production, Properties and Performance of Liquids and Gases*; Wiley: New York, USA, 1975. [Links]

3 .http://legislacao.anp.gov.br/?path=legislacao-anp/resol-anp/2013/outubro&item=ranp-40-2013, accessed in December 2019. [Links]

4. https://www.normasbrasil.com.br/norma/portaria-75-2015_281775.html, accessed in December 2019. [Links]

5 .Agarwal, A. K.; *Prog. Energy Combust. Sci.* **2007**, *33*, 233. [Links]

6 .Oumer, A. N.; Hasan, M. M.; Baheta, A. T.; Mamat, R.; Abdullah, A. A.; *Renewable Sustainable Energy Rev.* **2018**, *88*, 82. [Links]

7 .Naik, S. N.; Goud, V. V.; Rout, P. K.; Dalai, A. K.; *Renewable Sustainable Energy Rev.* **2010**, *14*, 578. [Links]

8 .Nastari, P.; *Eletrificação com Biocombustíveis*; available at http://www.anp.gov.br/images/Palestras/Matriz-Veicular-2019/08-Plinio_Nastari-Datagro.pdf, accessed in December 2019. [Links]

9 .http://legislacao.anp.gov.br/?path=legislacao-anp/resol-anp/2011/fevereiro&item=ranp-8-2011, accessed in December 2019. [Links]

10. http://legislacao.anp.gov.br/?path=legislacao-anp/resol-anp/2015/abril&item=ranp-19-2015, accessed in December 2019. [Links]

11 .Kruse, J. A.; *Intensive Care Med.* **1992**, *18*, 391. [Links]

12 Jahan, K.; Mahmood, D.; Fahim, M.; *J. Pharm. BioAllied Sci.* **2015**, *7*, 60. [Links]

13 .Martins, G. B. C.; Montenegro, M. A.; Suarez, P. A. Z.; *Quim. Nova* **2015**, *38*, 280. [Links]

14 .ABNT NBR 16041: *Fuel Ethanol - Determination of Methanol and Ethanol Contents by Gas Chromatography*; ABNT: Campos Elíseos, SP, Brazil, 2015. [Links]

15 .ABNT NBR 13992: *Automotive Gasoline - Determination of Anhydrous Ethanol Fuel Content*; ABNT: Campos Elíseos, SP, Brazil, 2015. [Links]

16 .Abreu, R. E. L.; Paz, J. E. M.; Silva, A. C.; Pontes, M. J. C.; Lemos, S. G.; *Fuel* **2015**, *156*, 20. [Links]

17 .Pereira, P. F.; Sousa, R. M. F.; Munoz, R. A. A.; Richter, E. M.; *Fuel* **2013**, *103*, 725. [Links]

18 .Silva, A. C.; Paz, J. E. M.; Pontes, L. F. B. L.; Lemos, S. G.; Pontes, M. J. C.; *Electrochim. Acta* **2013**, *111*, 160. [Links]

19 .Carneiro, H. S. P.; Medeiros, A. R. B.; Oliveira, F. C. C.; Aguiar, G. H. M.; Rubim, J. C.; Suarez, P. A. Z.; *Energy Fuels* **2008**, *22*, 2767. [Links]

20 .Silva, A. C.; Pontes, L. F. B. L.; Pimentel, M. F.; Pontes, M. J. C.; *Talanta* **2012**, *93*, 129. [Links]

21. Fernandes, H. L.; Raimundo Jr., I. M.; Pasquini, C.; Rohwedder, J. J. R.; *Talanta* **2008**, *75*, 804. [Links]

22 .Corsetti, S.; Zehentbauer, F. M.; McGloin, D.; Kiefer, J.; *Fuel* **2015**, *141*, 136. [Links]

23. Lutz, O. M. D.; Bonn, G. K.; Rode, B. M.; Huck, C. W.; *Anal. Chim. Acta* **2014**, *826*, 61. [Links]

24 .Mabood, F.; Gilani, S. A.; Albroumi, M.; Alameri, S.; Al Nabhani, M. M. O.; Jabeen, F.; Hussain, J.; Al-Harrasi, A.; Boque, R.; Farooq, S.; Hamaed, A. M.; Naureen, Z.; Khan, A.; Hussain, Z.; *Fuel* **2017**, *197*, 388. [Links]

25 .Milanez, K. D. T. M.; Silva, A. C.; Paz, J. E. M.; Medeiros, E. P.; Pontes, M. J. C.; *Microchem.* **J. 2016**, *124*, 121. [Links]

26 .Concklin Jr., A.; Goldcamp, M. J.; Barrett, J.; *J. Chem. Educ.* **2014**, *91*, 889. [Links]

27. Maldonado, M.; Barreiro, P.; Gutierrez, R.; Vergara, G.; *Fuel Process. Technol.* **2018**, *171*, 287. [Links]

28 .Correia, R. M.; Domingos, E.; Cao, V. M.; Araujo, B. R. F.; Sena, S.; Pinheiro, L. U.; Fontes, A. M.; Aquino, L. F. M.; Ferreira, E. C.; Filgueira, P. R.; Romao, W.; *Talanta* **2018**, *176*, 26. [Links]

29 .Teixeira, L. S. G.; Oliveira, F. S.; Santos, H. C.; Cordeiro, P. W. L.; Almeida, S. Q.; *Fuel* **2008**, *87*, 346. [Links]

30 .Ardila, J. A.; Soares, F. L. F.; Farias, M. A. S.; Carneiro, R. L.; *Anal. Lett.* **2017**, *50*, 1126. [Links]

31. Fortunato, F. M.; Vieira, A. L.; Neto, J. A. G.; Donati, G. L.; Jones, B. T.; *Microchem. J.* **2017**, *133*, 76. [Links]

32 .Xu, Q.; Ye, Q.; Cai, H.; Qu, R.; *Sens. Actuators, B* **2010**, *146*, 75. [Links]

33 .Numata, Y.; Iida, Y.; Tanaka, H.; *J. Quant. Spectrosc. Radiat. Transfer* **2011**, *112*, 1043. [Links]

34 .Ye, Q.; Xu, Q.; Yu, Y.; Qu, R.; Fang, Z.; *Opt. Commun.* **2009**, *282*, 3785. [Links]

35 .Neto, A. C.; Oliveira, E. C. S.; Lacerda Jr., V.; Castro, E. V. R.; Romao, W.; Silva, R. C.; Pereira, R. G.; Sten, T.; Filgueiras, P. R.; Poppi, R. J.; *Fuel* **2014**, *135*, 387. [Links]

36 .Turanov, A.; Khitrin, A. K.; *Fuel* **2014**, *137*, 335. [Links]

37 .Bueno, L.; Paixão, T. R. L. C.; *Talanta* **2011**, *87*, 210. [Links]

38 .Wiedemann, L. S. M.; d'Avila, L. A.; Azevedo, D. A.; *J. Braz. Chem. Soc.* **2005**, *16*, 139. [Links]

39 .Wiedemann, L. S. M.; d'Avila, L. A.; Azevedo, D. A.; *Fuel* **2005**, *84*, 467. [Links]

40 .Wang, M.; Wang, J.; Choong, Y.; *Food Chem.* **2004**, *86*, 609. [Links]

41 .Wang, M.; Wang, J.; Choong, Y.; *J. Food Compos. Anal.* **2004**, *17*, 187. [Links]

42 .Nespeca, M. G.; Munhoz, J. F. V. L.; Flumignan, D. L.; de Oliveira, J. E.; *Fuel* **2018**, *215*, 204. [Links]

43 .Moreira, L. S.; d'Avila, L. A.; Azevedo, D. A.; *Chromatographia* **2003**, *58*, 501. [Links]

44 .Godoy, L. A. F.; Ferreira, E. C.; Pedroso, M. P.; Fidelis, C. H. V.; Augusto, F.; Poppi, R. J.; *Anal. Lett.* **2008**, *41*, 1603. [Links]

45. Dermibas, A.; *Energy Convers. Manage.* **2009**, *50*, 2239. [Links]

46. Pedroso, M. P.; de Godoy, L. A. F.; Ferreira, E. C.; Poppi, R. J.; Augusto, F.; *J. Chromatogr. A* **2008**, *1201*, 176. [Links]

47 .Avila, L. M.; dos Santos, A. P. F.; de Mattos, D. I. M.; Souza, C. G.; Andrade, D. F.; d'Avila, L. A.; *Fuel* **2018**, *212*, 236. [Links]

48 .Kaminski, M.; Kartanowicz, R.; Przyjazny, A.; *J. Chromatogr. A* **2004**, *1029*, 77. [Links]

49 .Saczk, A. A.; Okumura, L. L.; de Oliveira, M. F.; Zanoni, M. V. B.; Stradiotto, N. R.; *Chromatographia* **2006**, *63*, 45. [Links]

50 .Aleme, H. G.; Costa, L. M.; Barbeira, P. J. S.; *Talanta* **2009**, *78*, 1422. [Links]

51. Oliveira, F. S.; Teixeira, L. S. G.; Araujo, M. C. U.; Korn, M.; *Fuel* **2004**, *83*, 917. [Links]

52 .Chen, S.; Wu, H.; Yen, C.; Wu, S.; Lin, S.; Kou, H.; *J. Chromatogr. A* **1998**, *799*, 93. [Links]

****