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Water in Liquefied Petroleum Gas

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Water in Petrochemical Feedstock

- **Water Damage**
  - Freezing of pipeline and valves
  - Blockages by gas hydrates
  - Vibration Trouble
  - Catalyst Poisoning

Focus is on Liquefied Petroleum Gases (LPG)




Qualitative Water Analysis Methods

Method	Range(MIN)	Range(MAX)	Solid	Liquid	Gas	Online
GC-BID/TCD/VUV	1ppm	100%	x	x	x	x
Karl Fischer Titration	**10ppm**	**100%**	**x**	**x**	**x**	**x**
Quartz Crystal Microbalance	**1ppm**	**1000ppm**			**x**	**x**
FTIR Spectroscopy	**10ppb**	**%**	**x**	**x**	**x**	**x**
TDLA Spectroscopy	**10ppb**	**-**			**x**	**x**
CRDS spectroscopy	**0.1ppb**	**-**			**x**	**x**
Chilled Mirrors(Dew point)	**ppm**	**%**			**x**	**x**
Electrolytic	ppm	0.10%			x	
NIR Spectroscopy	0.10%	100%	x	x		x
Colorimetry	0.10%	%	x	x	x	x
Dielectric Constant	1%	10%		x	x	
Loss on Drying	0.01%	-	x	x		
Electric Resistance	0.30%	%		x	x	
Distillation(Azeotropic or not)	0.05%	-		x		
Neutron Scattering	%	%	x			
Freeze Valve	**10ppm?**	**-**		**x**		**x**
Centrifuging	%	%		x		

Pass
(no frost)

Fail
(frost)

Easy to use, but releases propane as part of the test.

ASTM D2713 (Propane only)

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Centrifuging	%	%		x		

ASTM D7995

Common for Breathing Air

KFT
www.metrohm.com

Shimadzu
Loss on Drying

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Karl Fischer Titration

- **Karl Fischer Titration is the leading method for moisture analysis**
  - Wide dynamic range
- **Challenges of Karl Fischer Titration**
  - Susceptible to side reactions from sulfur, ketones, aldehydes, amides, and siloxanes
  - Need to control ambient moisture in solvents
  - Not accurate for small sample sizes or samples with low water content
  - Need an idea of the range of water content in the sample
  - Samples should be soluble in Karl Fischer medium
  - Labor intensive and not high throughput
  - Requires harsh/halogenated chemicals

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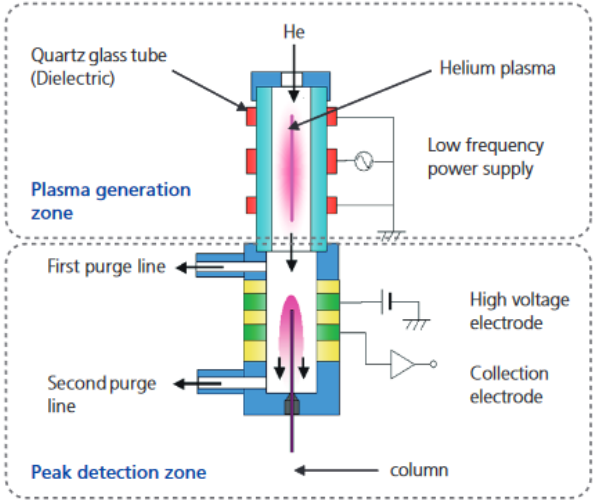
Green Water Analysis by Gas Chromatography

- **Gas Chromatography with Barrier Discharge Ionization Detector**
  - Detection down to 1 ppm water
  - No unwanted side reactions
  - No solubility issues
  - Less hands-on time
  - Minimal chemical waste generated
  - Reduced amount of sample required
  - Less worker exposure to harmful chemicals
  - Reduced cost

Barrier Discharge Ionization Detector (BID)

- **Barrier Discharge Ionization Detector**
- **Virtually universal detection (can detect everything except Ne and He)**
- **Low Energy and Low Maintenance**
- **Only requires Helium for operation → No flammable fuel gases required**
- **100x more sensitive then a TCD**



Three electrodes are placed on the quartz tube. High voltage is applied to electrodes, and plasma is generated

Compounds are ionized by plasma, and signal is collected at collection electrode

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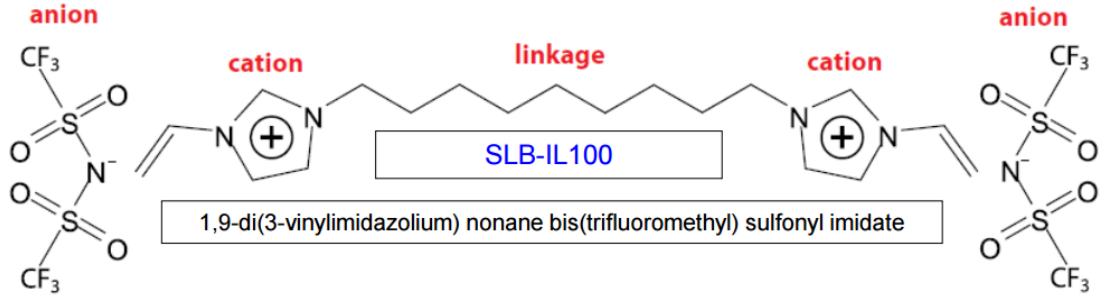
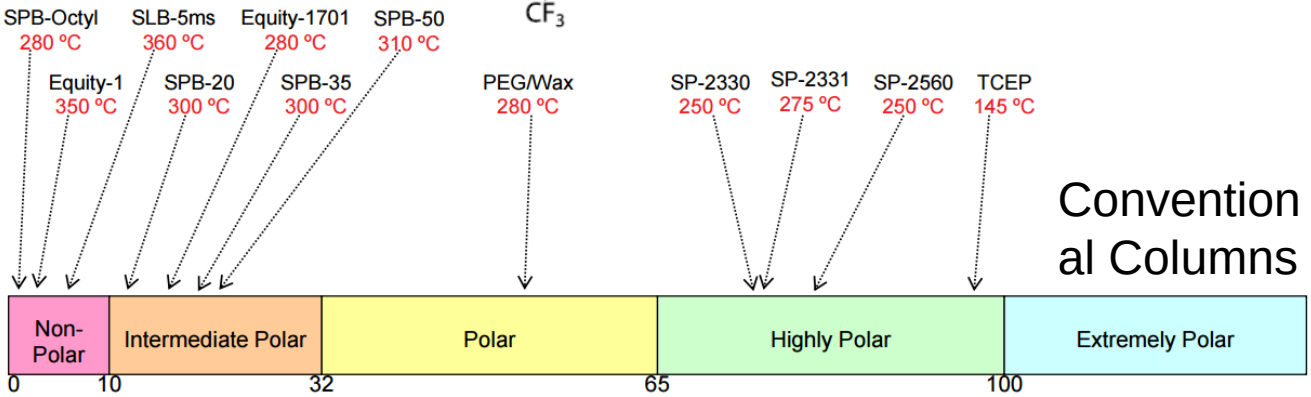
Ionic Liquid Column

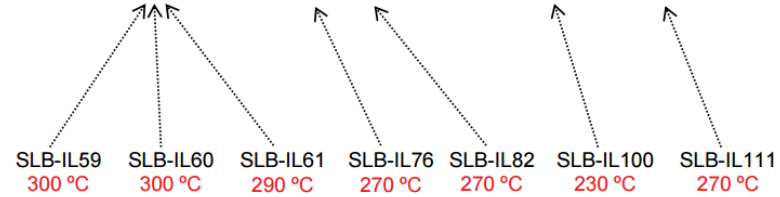
Example Structure of an Ionic Liquid Phase



Conventional Columns

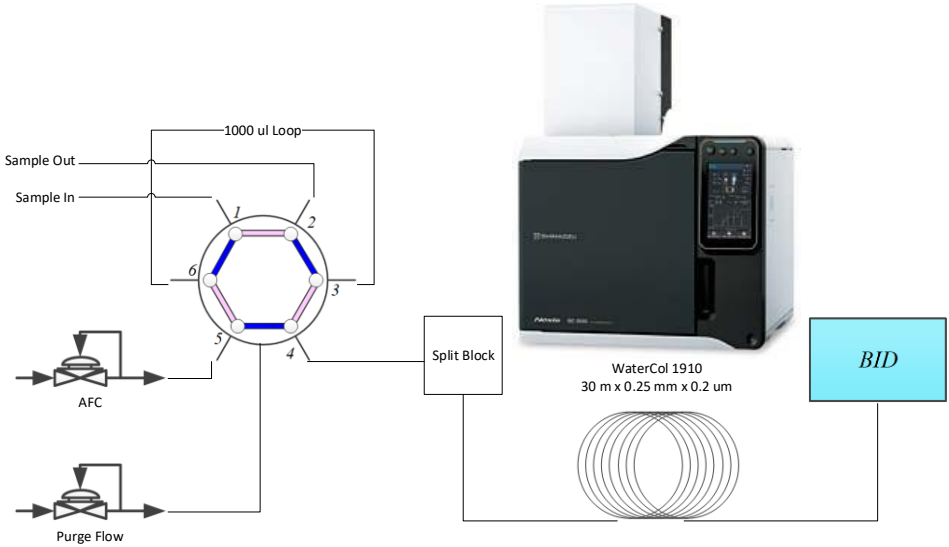


Ionic Liquid Columns

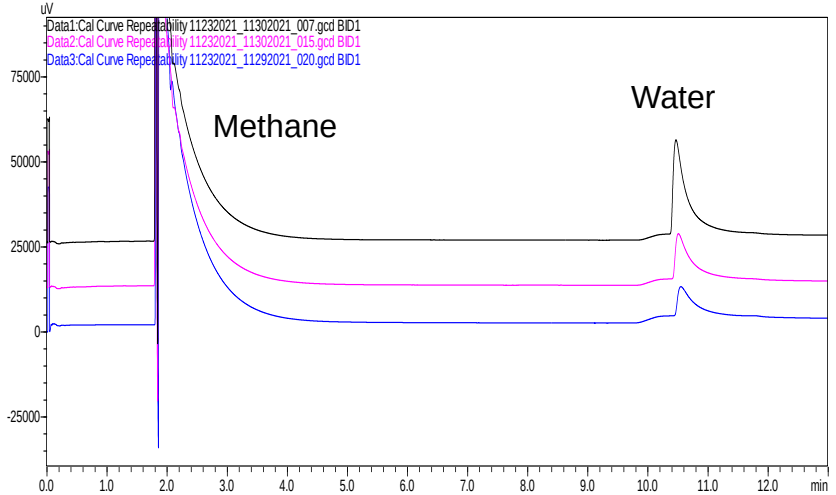


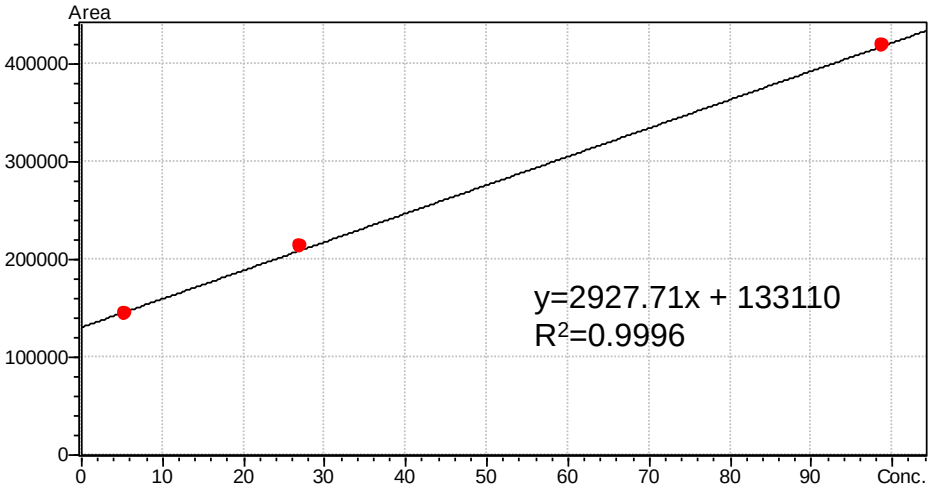
Analytical Conditions

Model	**GC-2030 Nexis** **6 port gas sample valve, Split block and BID**
Column	**Supelco WaterCol 1910** **30 m x 0.25 mm x 0.2 um df**
Column Temp	**<u>Gradient</u>** **35 ºC (2.0 min)→5 ºC/min →90 ºC**
Injection Mode	**Split 7:1**
Carrier Gas Controller	**Constant Linear Velocity Mode (He)**
Linear Velocity	**38.6 cm/sec**
Discharge Gas	**50 mL/min (He)**
Injection Volume	**1 mL**



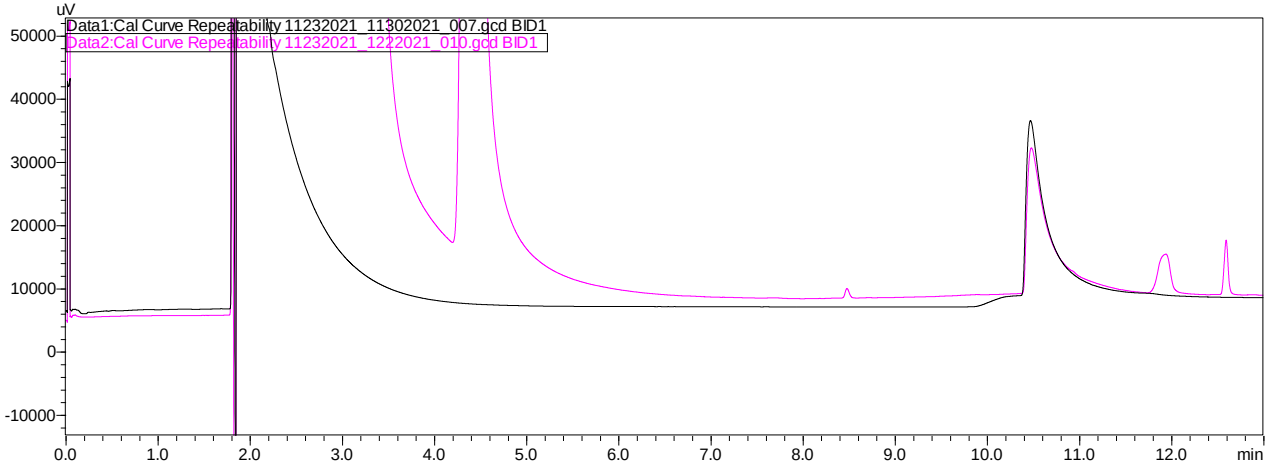
Calibration With Gases





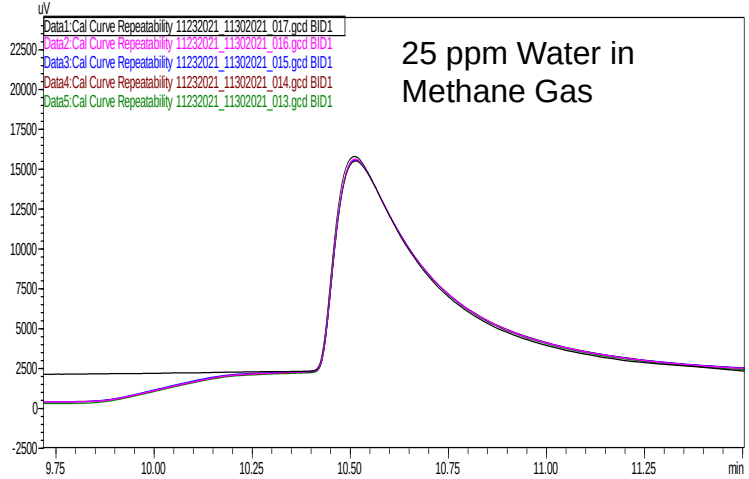
Level	Conc. (ppm)	Mean Area	SD (n=5)	%RSD
1	5.411	146425	1.61E+03	1.10%
2	27.11	215770	1.89E+03	0.88%
3	98.9	421896	4.47E+03	0.58%

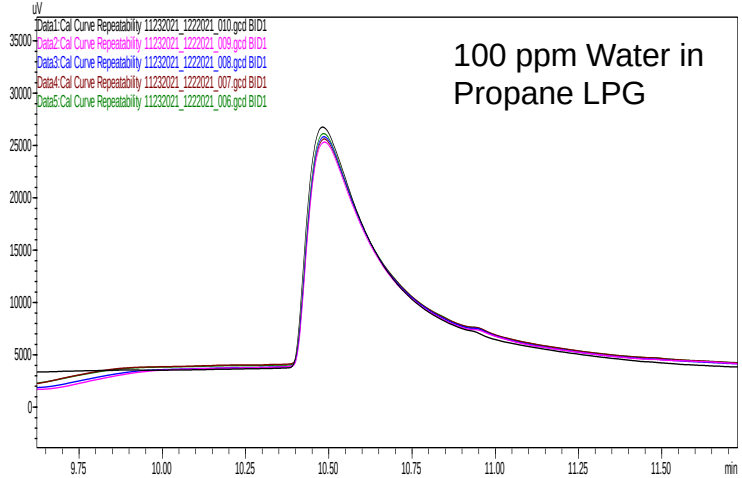
Comparison of Gas to Liquid



Standard Type	Calculated Conc. (ppm)	Conc. Recovery	Average S/N	Average LOQ (ppm)	Average LOD (ppm)
Gas	28.2 (±0.6)	112.80%	140 (±32)	2.12 (±0.6)	0.70 (±0.2)
LPG	75.9 (±0.8)	75.90%	775 (±132)	1.01(±0.2)	0.33(±0.06)

Repeatability

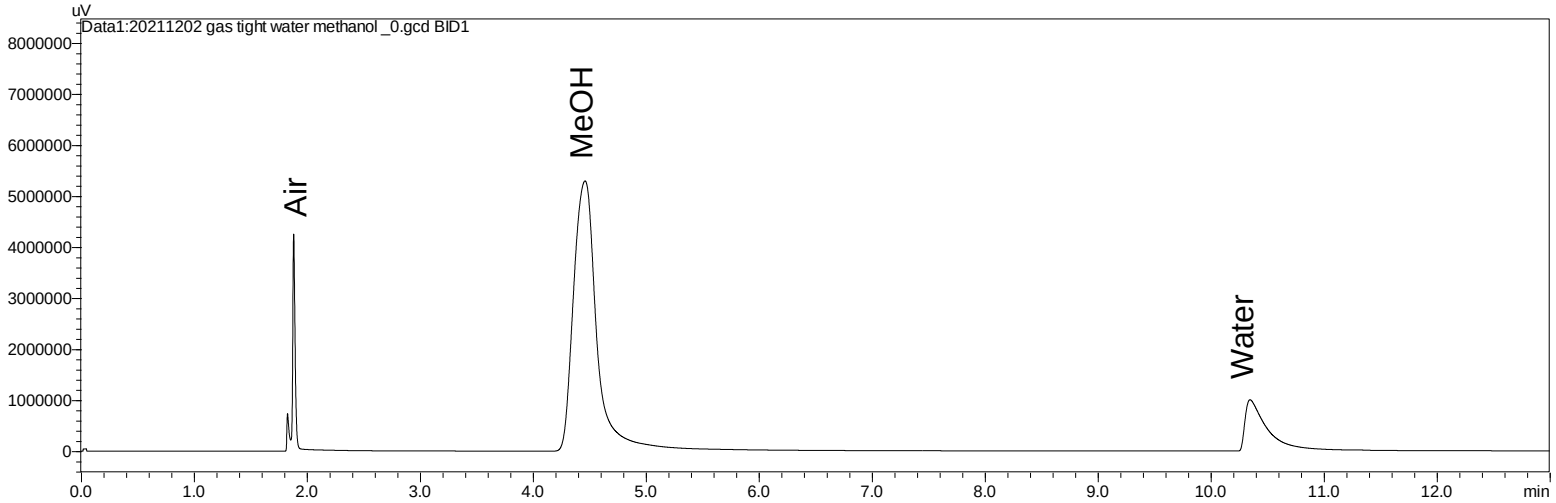




Standard Type	Standard Conc. (ppm)	Retention Time (min)	Average Area	%RSD (n=5)
Gas	25 ppm	10.514 (±0.001)	215769 (±1891)	0.88%
LPG	100 ppm	10.486(±0.001)	10.486(±0.001)	0.67%

Selectivity

- Methanol is commonly present in LPG
- Separation indicates that this setup is transferable to the analysis of water in breathing air



Summary

- Water present in petrochemical feedstocks is responsible for billions of dollars of damage and environmental releases every year
- Active ASTM Work Item for new method
- Environmentally friendly method
- Highly sensitive, repeatable, robust analysis
- Easy quantification of water in petrochemical streams
  - Eliminates the need for environmentally hazardous analysis techniques
- No interference of Sulfurs or alcohols in the analysis
- Simple sample introduction with the vaporizer
  - No sample preparation or hazardous chemicals required

Questions?

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