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Excellence in Science

A New Approach For Analyzing Water in Petroleum Products

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Agenda

- Water Analysis Background
- Overview of Ionic Liquids
- Millipore Sigma WaterCol Columns
- Overview of BID
- GC Sampling Systems
- Applications
- Conclusions

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Water and Ethanol in Consumer Products

Analysis of ethanol and water in consumer products is important in a variety of processes and often is mandated by regulating agencies:
-Manufacturers want a faster method to analyze for both compounds.
-Water can interfere with the ethanol analysis due to poor efficiency of older GC columns
-Water can affect the taste of the product.

(Source: Rapid Analysis of Ethanol and Water in Commercial Products Using Ionic Liquid Capillary Gas Chromatography with Thermal Conductivity Detection and/or Barrier Discharge Ionization Detection
Choyce A. Weatherly, Ross M. Woods, and Daniel W. Armstrong)

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Water Content in Honey

Water content in honey has both good and bad affects depending on the amount:
-Too little water content (<14%) can cause an increase in viscosity of the honey and form crystalline structures.
- This usually not appealing to consumers as the honey is thought to be old.
-Too much water (>21%) can promote bacterial growth and can lead to illness in humans if consumed.

Water Content in Active Pharmaceutical Ingredients (API)

Water content is typically controlled in commercial active pharmaceutical ingredients:
-Water content can vary during manufacturing, packaging, and shelf life.

- **Water content in an API can be correlated to its chemical stability, the nature of its degradation products, & physical stability***

(Source: Water determination in active pharmaceutical ingredients using ionic liquid headspace gas chromatography and two different detection protocols Lillian A. Frink, Choyce A. Weatherly, Daniel W. Armstrong)

Water in Petrochemical Feedstock

Free water and water vapor leads to Problems:
-Freezing of pipeline and valves
-Blocking by gas hydrates
-Vibration trouble
-Poisoning of catalysts

$15BUSD/year for Corrosion Costs in Oil Refinery Market Globally.
(Source of NACE International)

Comparison of Moisture Analysis Methods

Method	Range(MIN)	Range(MAX)	Solid	Liquid	Gas	Online
Karl Fischer Titration	10ppm	100%	x	x	x	x
Loss on Drying	0.01%	-	x	x		
GC-BID/TCD	1ppm	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
NIR Spectroscopy	0.10%	100%	x	x		x
Colorimetry	0.10%	%	x	x	x	x
Chilled Mirrors(Dew point)	3ppm	%			x	x
Dielectric Constant	1%	10%		x	x	
Electrolytic	ppm	0.10%			x	
Electric Resistance	0.30%	%		x	x	
Distillation(Azeotropic or not)	0.05%	-		x		
Neutron Scattering	%	%	x			
Freeze Valve	10ppm	-		x		x
Centrifuging	%	%		x		

www.metrohm.com

Karl Fischer Titration (KFT)

- **KFT is the leading method for moisture analysis**
  - It has a wide dynamic range (if you have the right sample size, etc.)
  - It can be automated (with autosampler)

- **KFT has some problems**
  - **Side-reactions** can affect results
    - **Sulfur**, ketones, aldehydes, amides, and siloxanes
  - **Labor intensive** and not a high throughput method
  - Need to **control ambient moisture** in both solvents and atmosphere
  - Not accurate for small sample sizes or samples with low water content
    - Coulometric titration can detect 10-99 µg of water but requires 1 g sample
    - Volumetric titration can detect 1 mg and higher water content but requires smaller sample size
  - Samples should be **soluble** in Karl Fischer medium

Pharmaceutical Technology ***2007,*** 31(2), 56–71.
Journal of Pharmaceutical Sciences **2003,** *92* (5), 1058-106

Why water analysis by GC did not work in the past

IL Column can solve these issues

1. Water would degrade the stationary phase.
2. Water would produce ugly peaks difficult to integrate/quantitate
3. Water must be well separated from all solvents (matrices) and an internal standard.

GC-BID/TCD can solve these issues

4. Analysis time was long.
5. Results were inaccurate and not very reproducible.
6. Not effective for a wide range of concentrations

Using the NEW GC method

- IL (ionic liquid) capillary GC column Watercol from MilliporeSigma (Supleco)- Very polar
- Sensitive and reliable GC detectors (BID & TCD)
- Automation by Headspace Sampler (HS-20)
- Automation by Gas/Liquid Valve Sampling

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Ionic Liquids

- A class of ionic solvents with low melting points
- Unique combination of cations and anions that can provide different selectivities when used as stationary phases in GC
- Numerous combinations of cations and anions are possible, allowing for “tailored” selectivity, application or function

Ionic Liquids

Unique Selectivity

The Importance of Selectivity

- A column's selectivity has the greatest influence on resolution
- This is why there are so many GC stationary phases
- Extensive evaluations of ionic liquid GC columns
- Main strength is unique selectivity
- Often resulting in
  - Increased resolution
  - Shorter run times

Desirable IL Properties for GC Use

- **Several properties make ILs desirable as GC stationary phases**
  - Remain liquid over a wide temperature range (Room Temperature→350^{o} C)
  - Very low volatility
  - Highly polar nature
  - Broadest range of solvation interactions of any known solvent
  - Good thermal stability
  - High viscosity
  - Easily tailored to provide different polarities/selectivities

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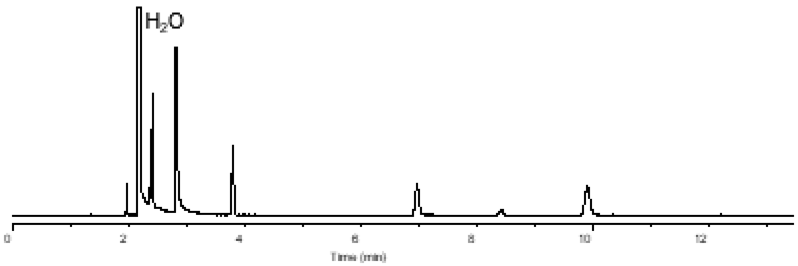
Watercol™ Series (Ionic Liquid stationary phase)

- **Watercol™ series of ionic liquid capillary GC columns**
  - Allows water and organics to be run with one easy GC method
  - Produce a sharp peak shape for water and other small polar analytes
  - Water can be integrated and quantified
  - Water does not interfere chromatographically with many other small polar analytes

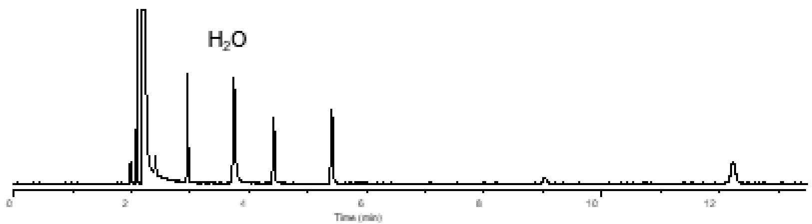
- **Three different chemistries:**
  - **Watercol™ 1910**
  - **Watercol™ 1460 (coming soon!)**
  - **Watercol™ 1900 (coming soon!)**

Watercol™ Selectivity Comparison

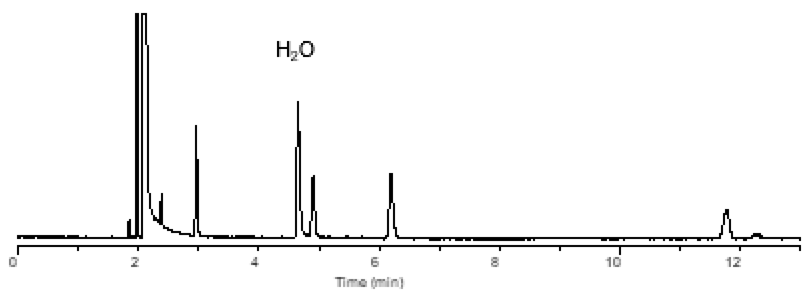
Watercol™1460



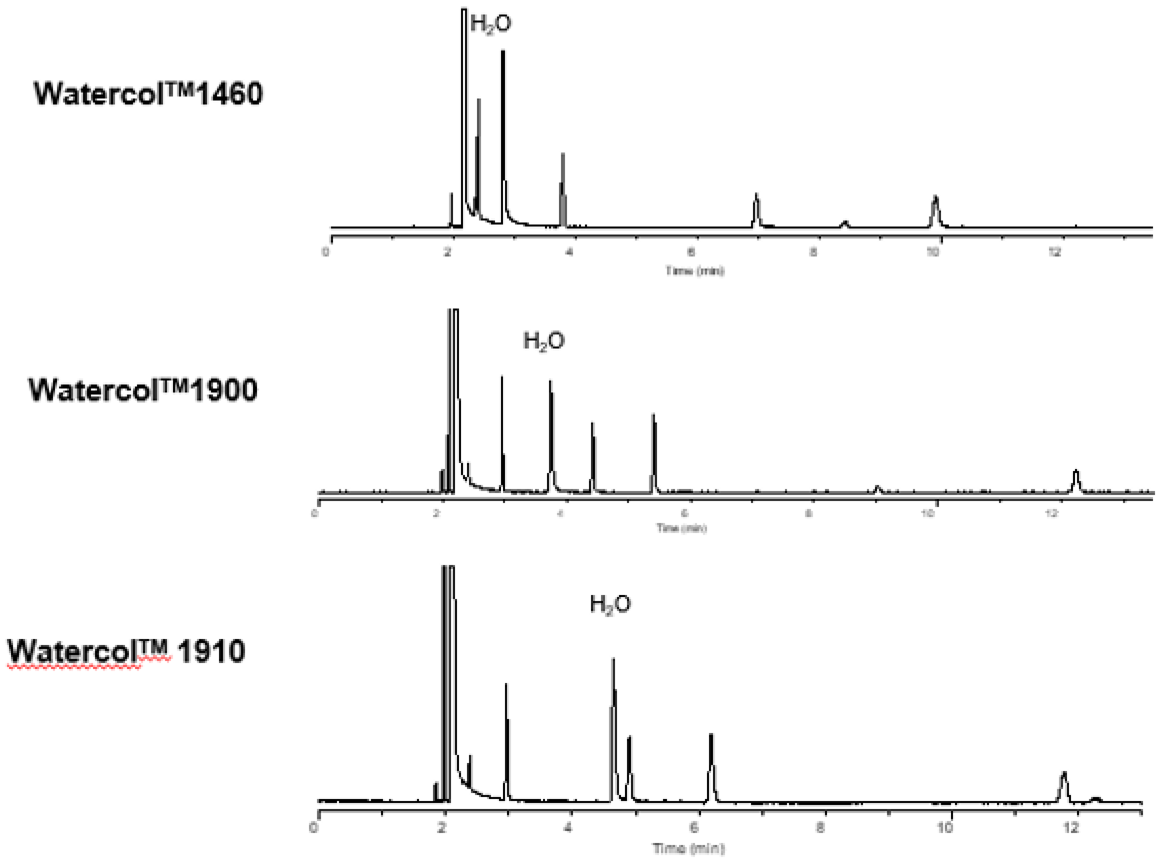
Watercol™1900



Watercol™ 1910



Column Durability- Repeat Water Injections Watercol™ 1460



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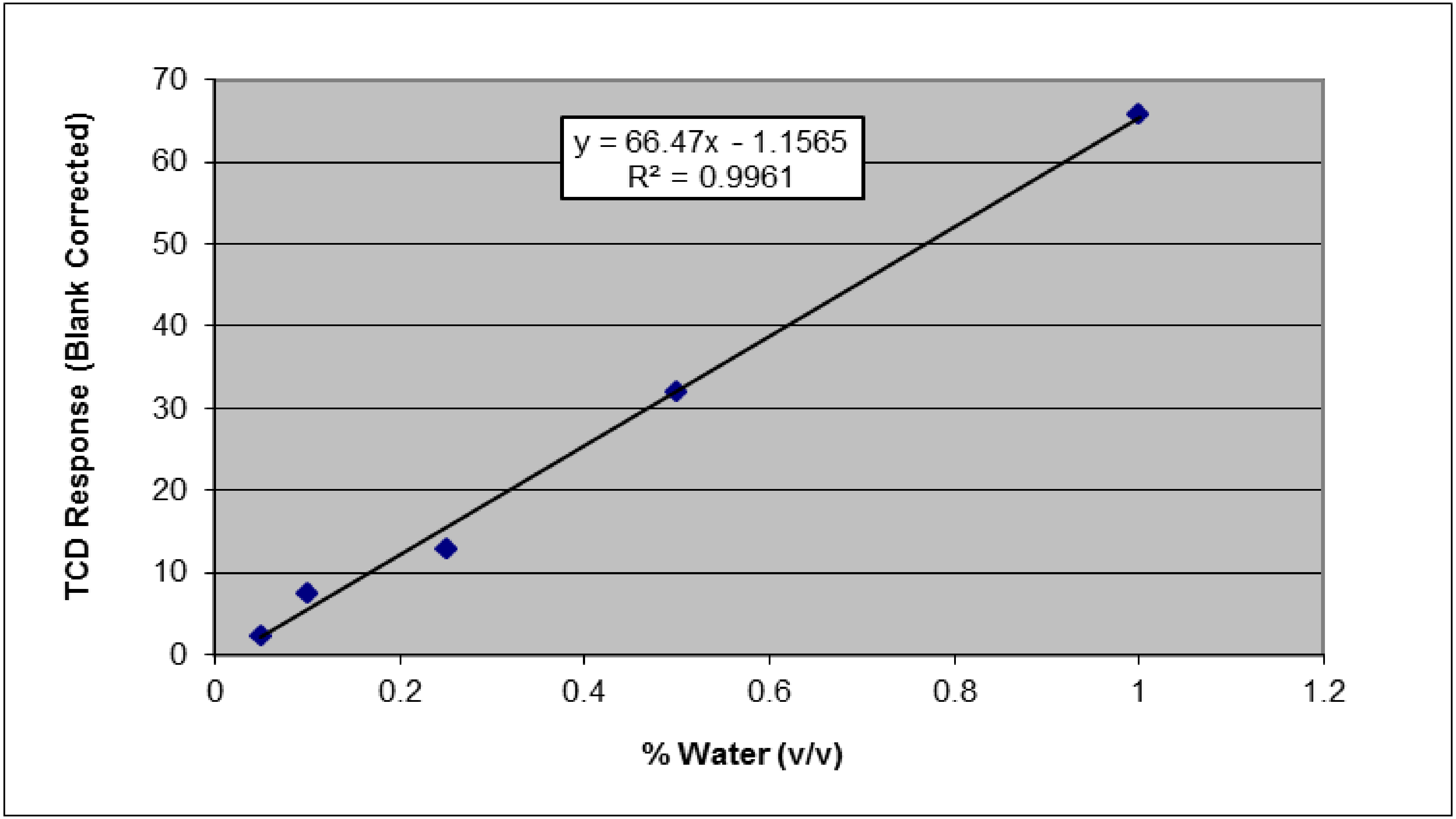
Water Calibration Curve (0.05-1%) on Watercol™1460

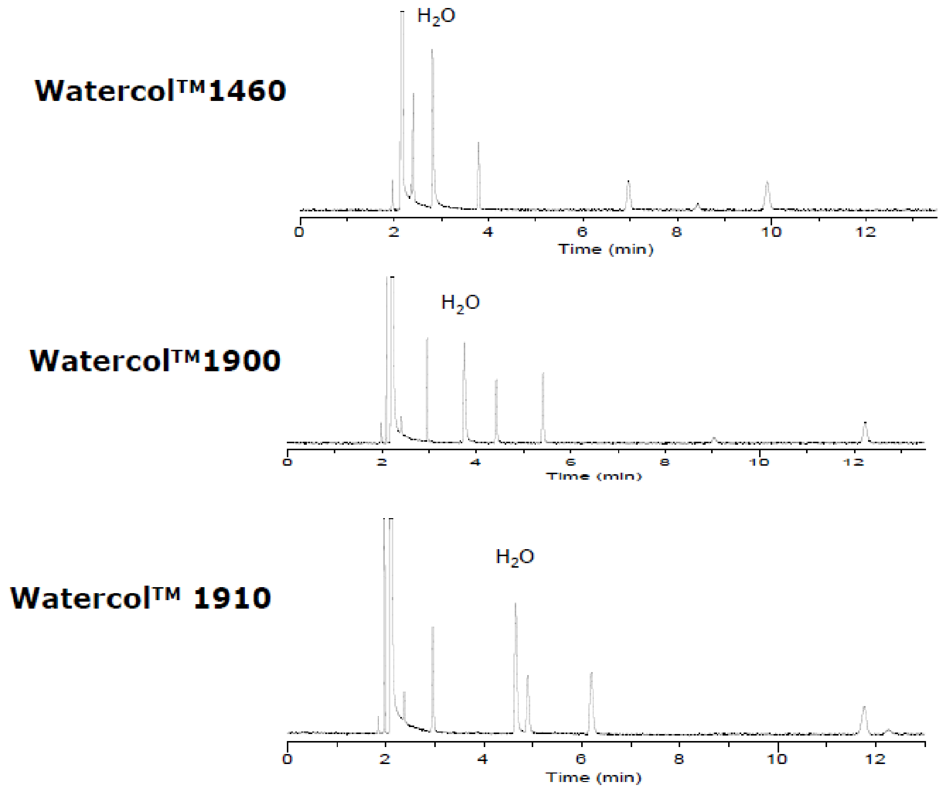


Ionic Liquid Columns from MilliporeSigma

Watercol™ Selectivity Comparison

Why Consider them for GC phases?....

- Remain liquid over a wide temperature range
  - ➢ *extended temperature ranges*
- Highly polar nature
  - ➢ *higher polarity*
- Broadest range of solvation interactions of any known solvent
  - ➢ *unique selectivity*
- Very low volatility
  - ➢ *lower bleed*



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GC Detectors for Water

BID

TCD

PDHID*

MS

VUV*

BID ↘

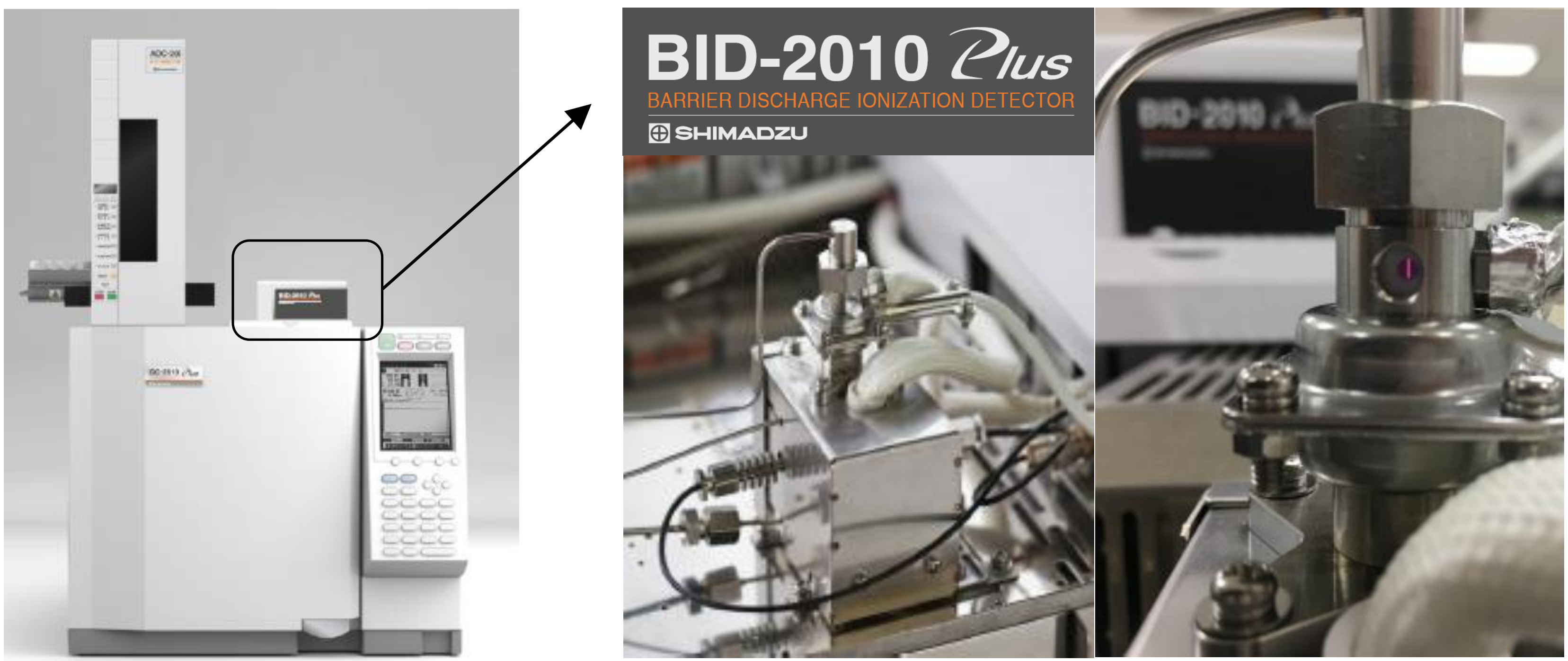
- **Universal detector (Except for He & Ne)**
- **Utilizes cool helium plasma *-Robust-***
- **Highly sensitive *100X more than TCD***
- **Wide Dynamic Range of detection**

* http://www.vici.com/instr/pdd.php , http://www.vuvanalytics.com/

What is BID?

Dielectric **B**arrier Discharge **I**onization **D**etector

- BID is a low-energy plasma detector.
- The plasma is generated via Dielectric Barrier Discharge.
- BID can detect analytes except for He and Ne.
- The BID sensitivity is 100x higher than TCD.



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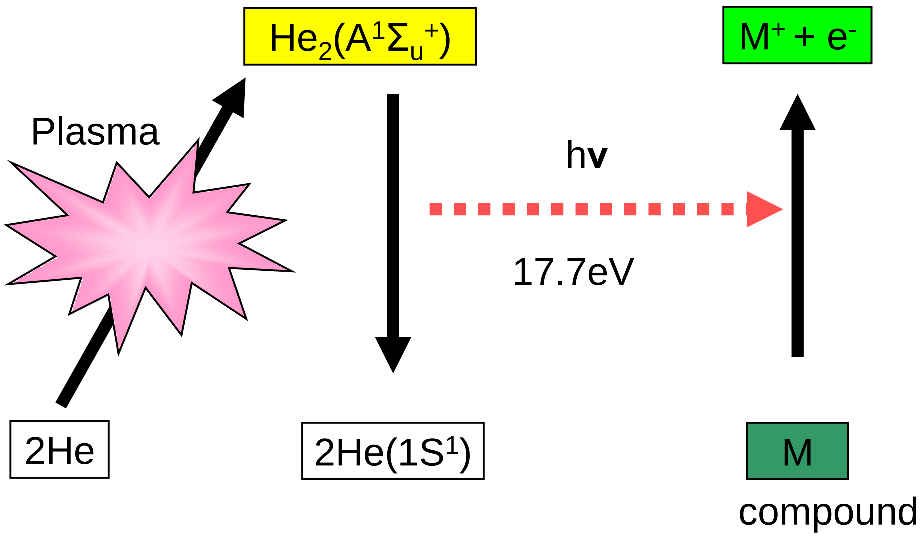
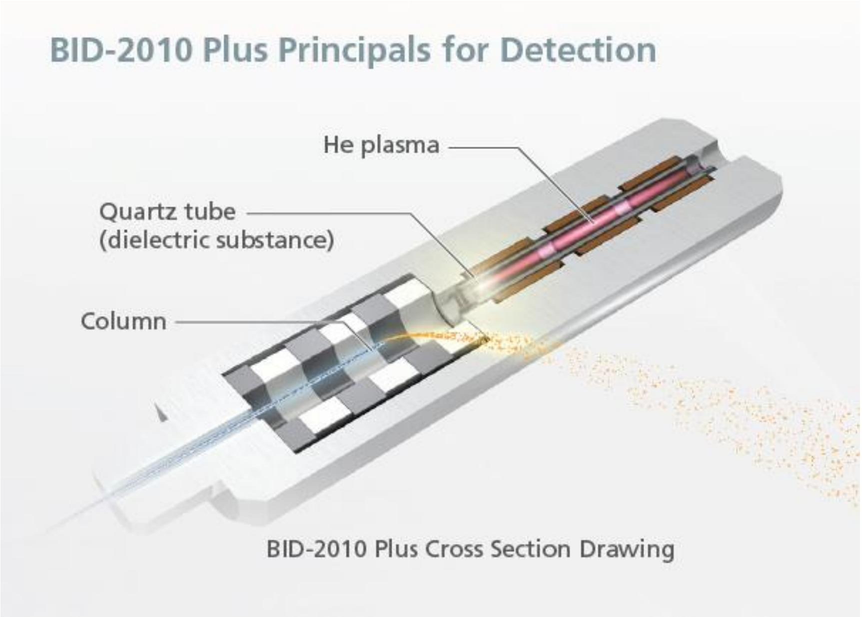
Principle of BID



	Ionization Energy (eV)
Ne	21.56
N_2	15.6
Water	12.6
O_2	12.1
Acetone	9.7
Toluene	8.8

The Ionization Potential of the Helium Photon is 17.7 eV.
Any analyte with a lower Ionization Potential can be detected

What is BID?



Low temperature plasma

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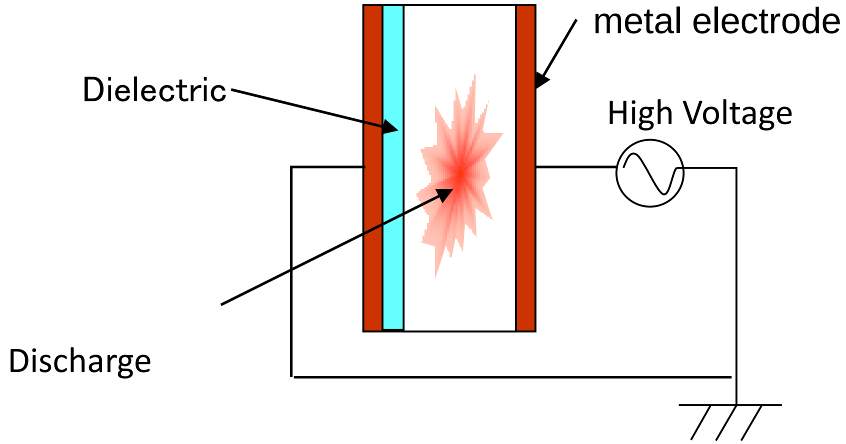
What is dielectric barrier discharge?

Metal electrodes are covered with dielectric proprietary material

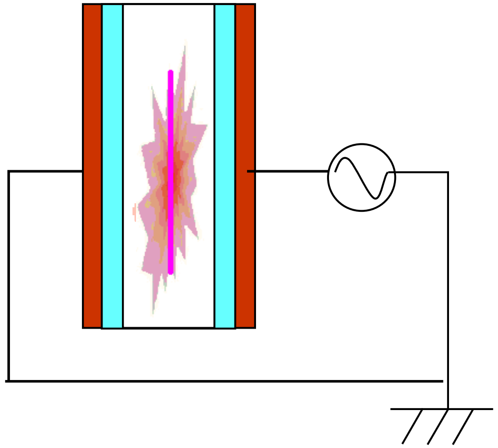
A 3 kV High Voltage is applied to the metal electrode

Dielectric barrier discharge is generated

One electrode Covered with dielectric



Two electrodes Covered with dielectric



Shimadzu BID

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Watercol IL Capillary Column and *Shimadzu* GC-BID/TCD

- Karl Fischer Volumetric (mostly used)
  - 500 ppm is typical detection limit
  - **Watercol + GC-BID/TCD: 100 ppm**

- Karl Fischer Coulometric
  - **5-10 ppm** is typical detection limit
  - **Watercol + GC-BID: 1-10ppm**

GC with Watercol column has several advantages over KFT

- **No unwanted side reactions**
- **No solubility issues**
- **GC requires less hands-on time**
- **Simultaneous analysis of water and volatiles/semivolatiles**
- **Lower volume of chemical waste generated**
- **Reduced amount of sample needed**
- **Less worker exposure to (potentially) harmful chemicals**
- **Reduced costs**

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Shimadzu GC Headspace Sampling Devices

GC-2030 Nexis GC BID/TCD

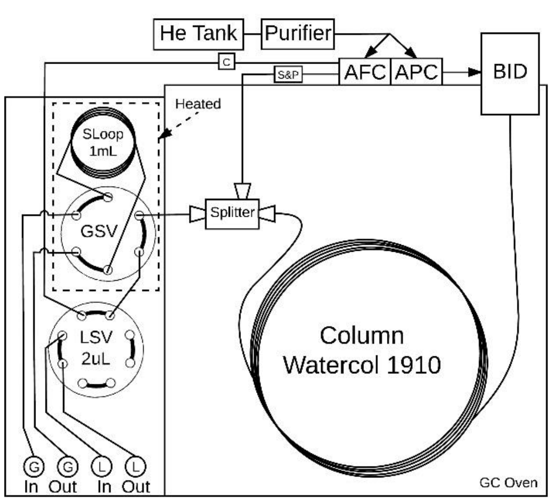
Shimadzu's own unique Technology

HS-20 (90 vials)/ HS-10 (20 vials)

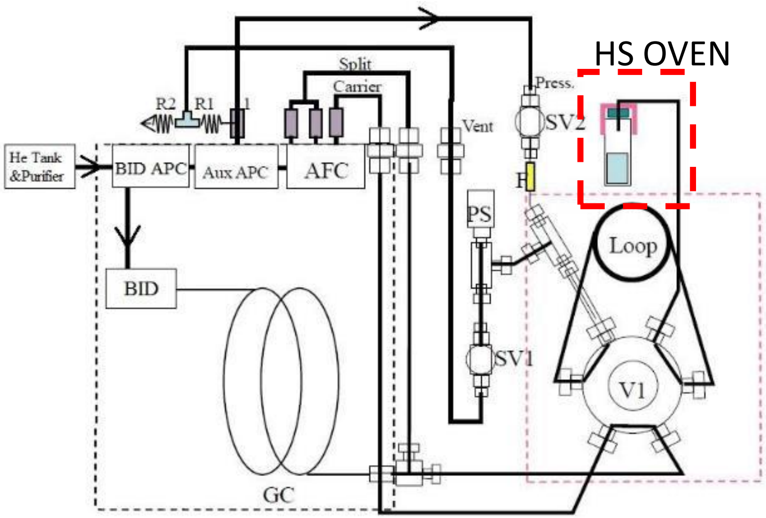
***Advantages*:**

- **High Accuracy (GC Separation RSD% is less than 5%)**
- **No side-reaction and Less Restriction**
- **High Throughput (HS/Valve Sampling)**
- **HS for Solid/Liquid Samples (DR 10ppm-100%)**
- **Sample Introduction Valves for Liquid/Gas Samples (1ppm-100%)**

Flow Diagram of Moisture Analysis System

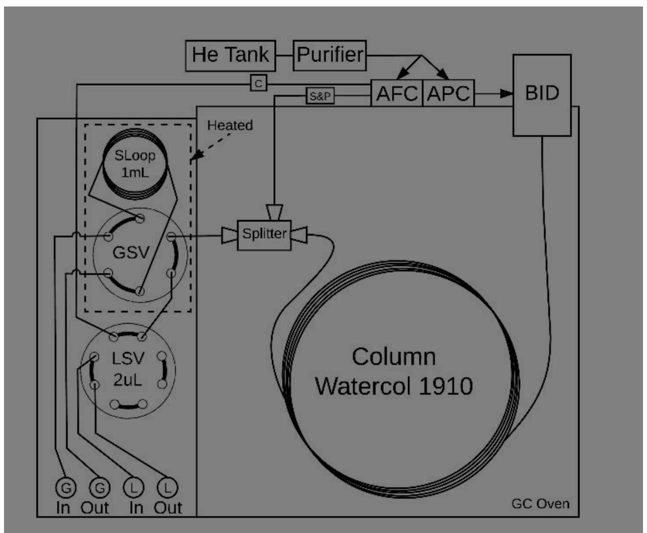


<u>Liquid/Gas Sampling Valve+GC</u>
for Gas/Liquid Products



<u>HS-20+GC</u>
for Liquid/Solid Products

HSGCBID for Liquid/Solid Samples



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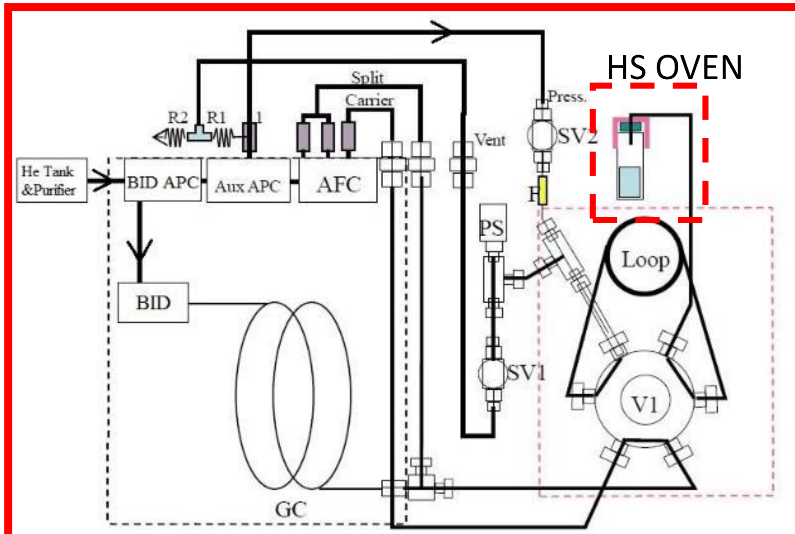
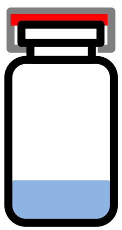


<u>HS-20+GC</u>
for Liquid/Solid Products

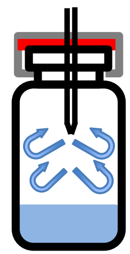
HSGC Method Procedure

Depending on temperature, humidity and air pressure, Air contains **% level of water**. To achieve ppm level of water determination, a purging method must be developed.



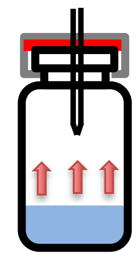
Sample capping

HS is ambient air which contains % level of water.



HS Purging method

HS Oven is still room temp.
Using MHE* function, purge HS air by purified He gas.
Sample water is still not evaporated



Normal HS Sampling

Heat HS Oven Up
Evaporate water from Sample then inject to GC column, separate water and detect water by BID/TCD

Utilizing HS instrument, these procedure are automated.

MHE*: Multiple Headspace Extraction

Purging HS vial

- Multiple Headspace Extraction

$$\text{Purge Efficiency} = \frac{\text{Water peak area after Purge}}{\text{Water Peak Area w/o Purge}}$$

- Comparison of cap/vial/septum

Cap	Vial	Septum	Rubber Thickness (mm)	PTFE Thickness (mm)	Hardness Shore A	MHE 10 Purge Efficiency
Screw	10mL	Red ChloroButyl /Grey PTFE				10
Crimp	10mL	W PTFE /Blue Silicone	3	0.1		30
Screw /Crimp	10mL	Grey Buthyl Stopper	Stopper	-		83
Screw /Crimp	10mL	Trans Silicone Stopper	Stopper	-		63
Crimp	10mL	W Silicone / W PTFE				38
Crimp	10mL	2x W Silicone / W PTFE				58
Crimp	10mL	W Silicone / Natural PTFE	3	0.1		15
Crimp	10mL	W Silicone / Beige PTFE	3	0.1	45	31
Crimp	10mL	W Silicone /W PTFE	3	0.1	45	60
Crimp	10mL	Trans Silicone /Natural PTFE	3	0.1	45	34
Crimp	**10mL**	**Trans Silicone /PTFE**	**2.5**	**0.2**		**6**

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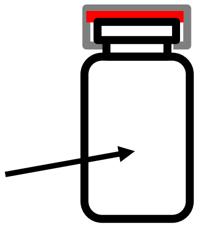
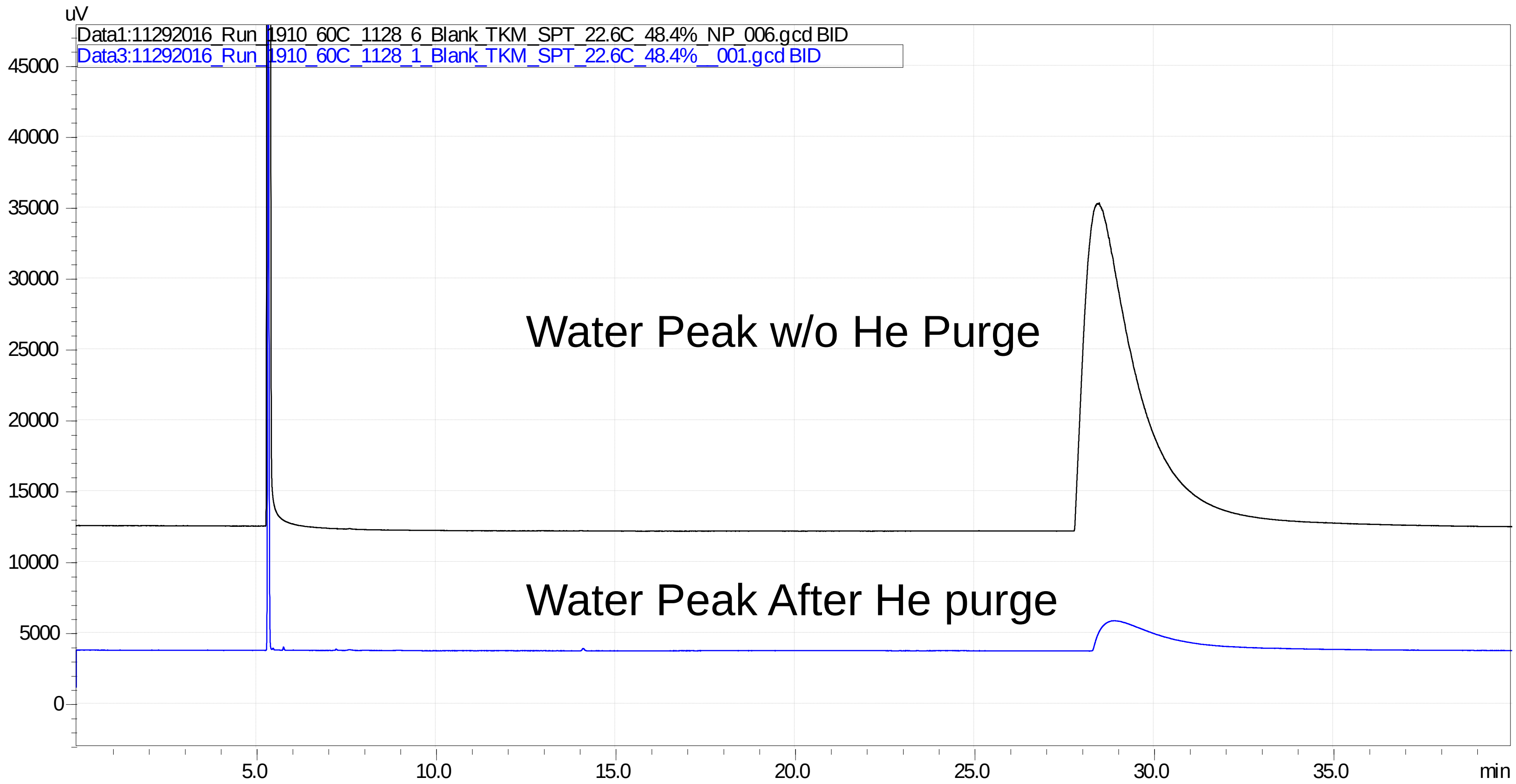
Purging HS Vial

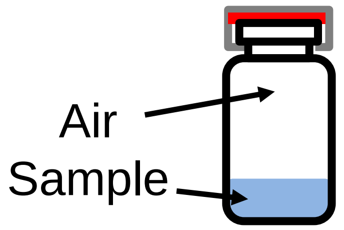
Air



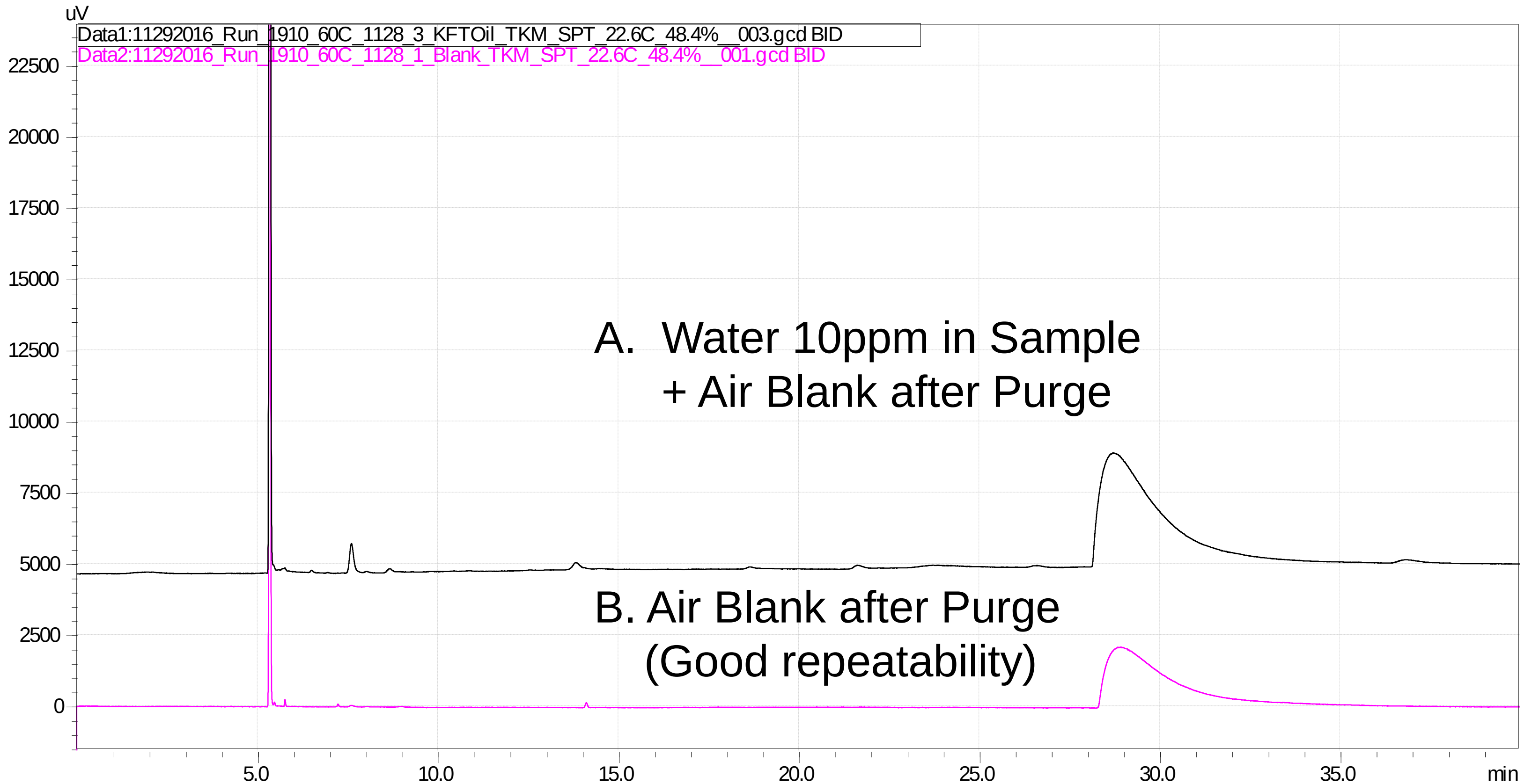
Without any sample, only Air.
Call Air Blank Vial



Determination of water 10ppm in Mineral Oil



With liquid sample with Air.



Conducted Subtraction (A-B) then quantified water amount

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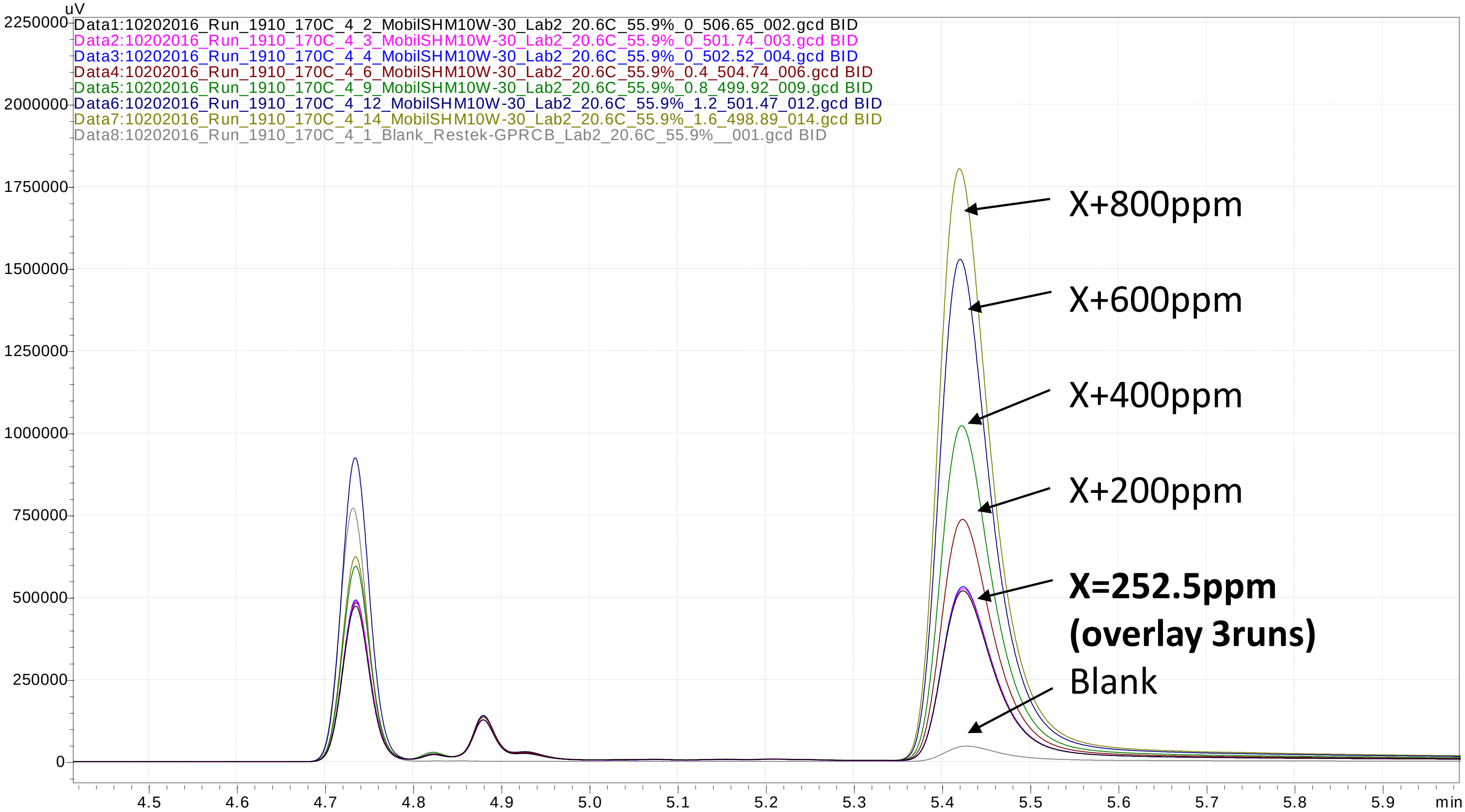
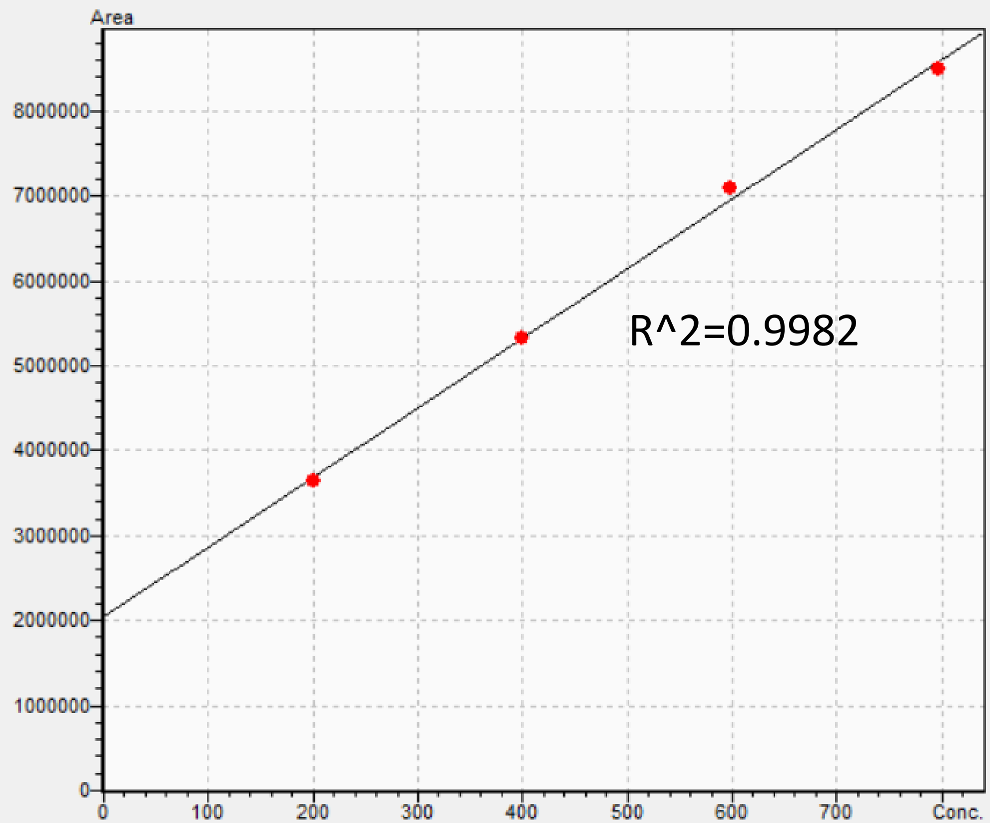
Determination of water 250ppm in Engine Oil (Standard Addition)



Determination of water in Engine Oil (Standard Addition)

Calibration Curve View ◉ Compound ○ Group

#1 Water



Y = aX + b
a = 8199.65
b = 2.04655e+006
R^2 = 0.9981524
R = 0.9990758
RSS = 2.466992e+010

Standard Addition
Calib Curve:Linear
Zero:Not Forced
Weight:None

Mean RF : 1.351070e+004
RF SD : 3.054887e+003
RF %RSD : 22.610879
Date Processed : 10/21/2016 2:28:29 PM

Level	Conc.	Mean Area	SD	%RSD	Area1	Area2	Area3
1	200	3645121	6.581524e+004	1.805571	3607451	3606796	3721117
2	398.9	5316705	4.055857e+005	7.628516	5778008	5016060	5156046
3	599	7084221	3.173696e+005	4.479950	6814853	7434089	7003722
4	797	8497632	2.305720e+005	2.713368	8759640	8407582	8325674

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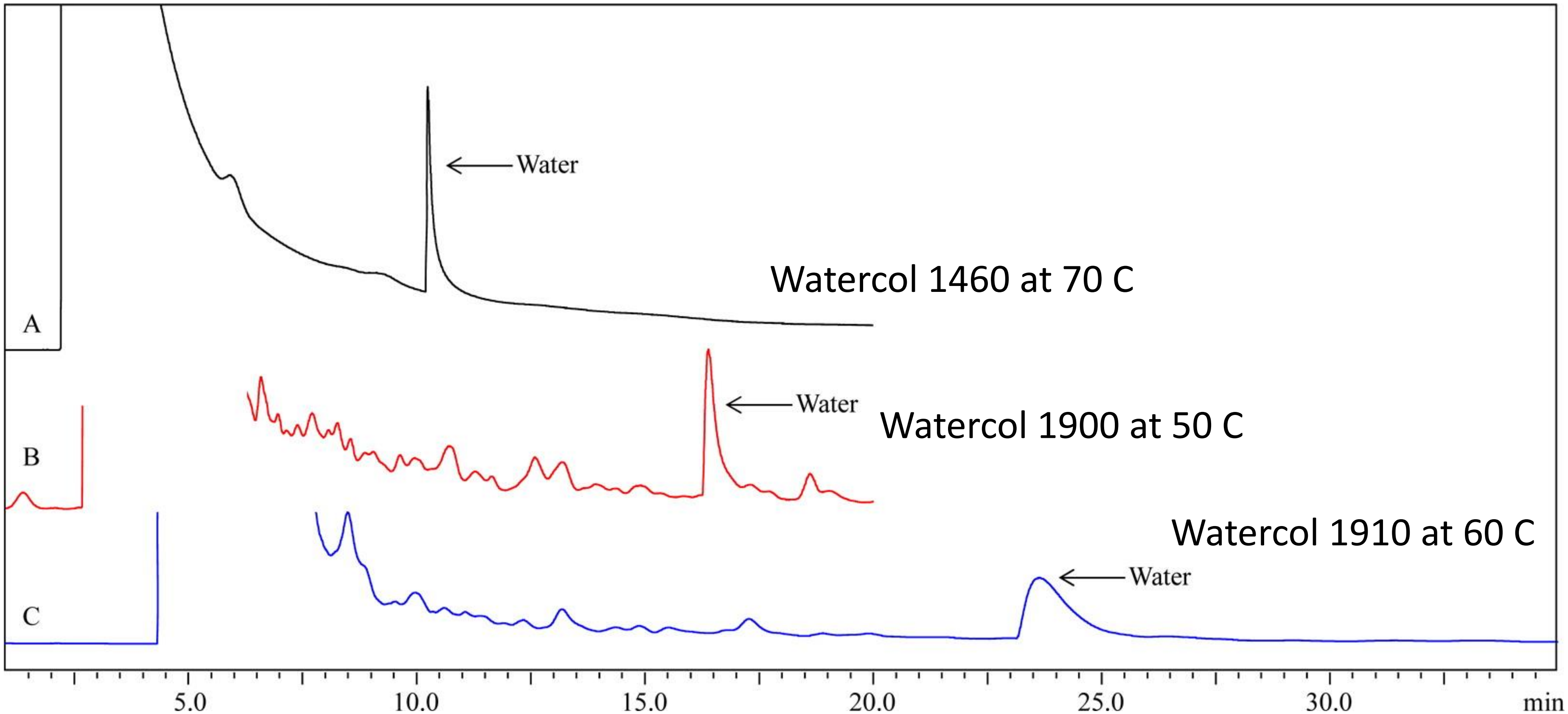
Water in Liquid Petroleum Products

Product	HSGC			Standard Addition
	mg Water Measured [c]	ppm Water	RSD	ppm water
Motor Oil	0.386	770 ± 2.9	0.4	770 [a]
Transmission fluid	0.497	996 ± 9.2	0.9	642
Engine Oil	0.131	261 ± 5.8	2.2	269 [a]
Gear Oil	0.104	207 ± 6.9	3.3	[b]
Power Steering Fluid	0.123	245 ± 5.6	2.3	160
3 in One Oil	0.223	445 ± 21.0	4.7	[b]
M-Pro7 LPX Gun Oil	0.831	1630 ± 15.9	1.0	1540
CLP Gun Oil	1.634	3260 ± 87.4	2.7	[b]
Synthetic Gun Oil	0.117	234 ± 3.4	1.5	[b]
Remington Moistureguard Rem Oil	0.165	330 ± 8.1	2.5	302 [a]
Remington Rem Oil	0.048	116 ± 4.5	3.9	102 [a]
WD-40	0.365	728 ± 5.0	0.7	[b]
Transformer Oil (RM 8506a)	0.0061	12.1 ± 0.8	6.6	[b]
Light Sour Crude Oil (SRM 2721)	0.071	146 ± 7.6	5.2	[b]
Heavy Sweet Crude Oil (SRM 2722)	0.051	102 ± 1.7	1.7	[b]

[a] Standard addition with Aerosol-OT dissolved in water.
[b] Standard addition is not feasible due to the samples high viscosity, complexity of samples and immiscibility with the added water standard
[c] Water measured in a 0.5g sample utilizing headspace gas chromatography

Lillian A. Frink; Daniel W. Armstrong, 8194-8201; *Anal. Chem.* **2016,** 88,.

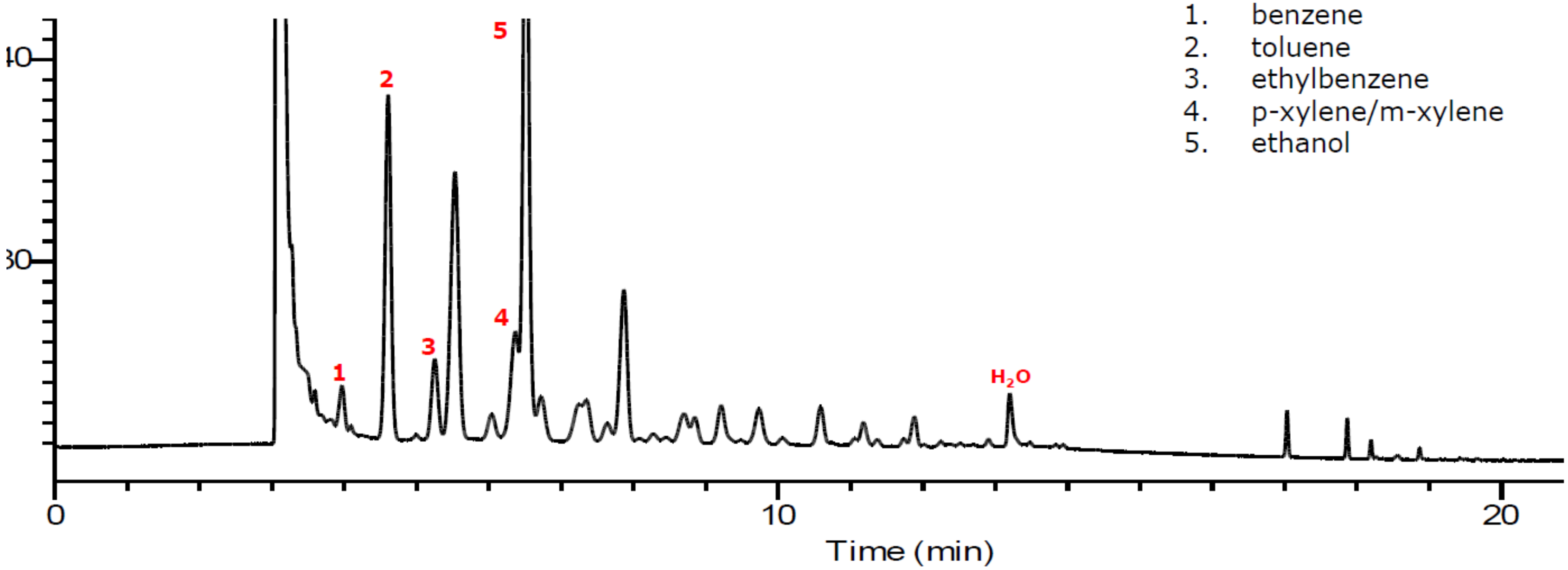
Determination of water in Crude oil (NIST SRM 2722)



Lillian A. Frink; Daniel W. Armstrong, 8194-8201; *Anal. Chem.* **2016,** 88,.

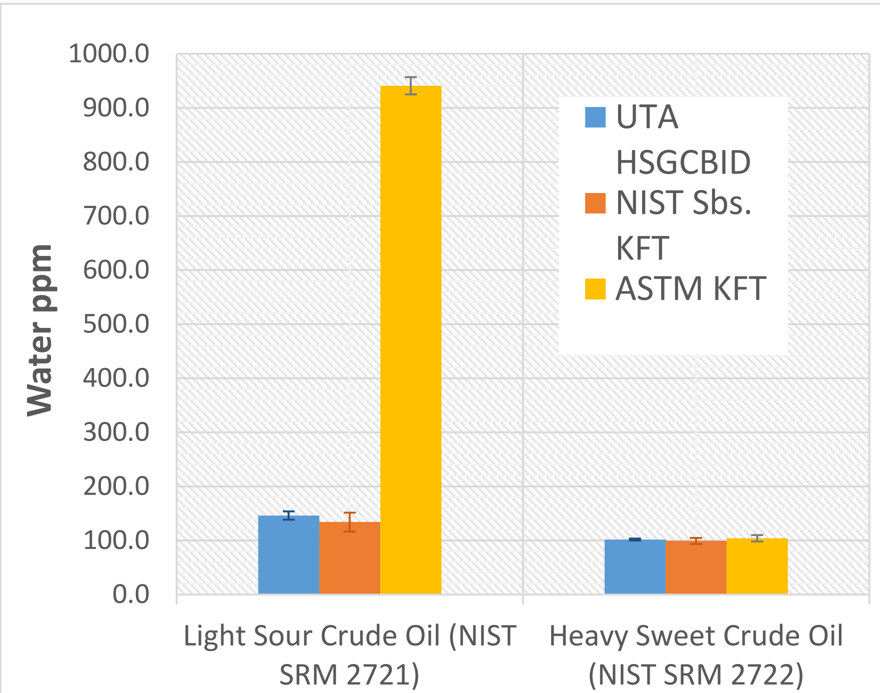
Watercol Series Capillary GC Columns Measure Water in Gasoline (Petroleum Application)

- Water peak is baseline resolved from other gasoline components
- Analysis of BTEX compounds, and oxygenates such as Ethanol are also possible.
- Multiple target analytes can be identified in a single run

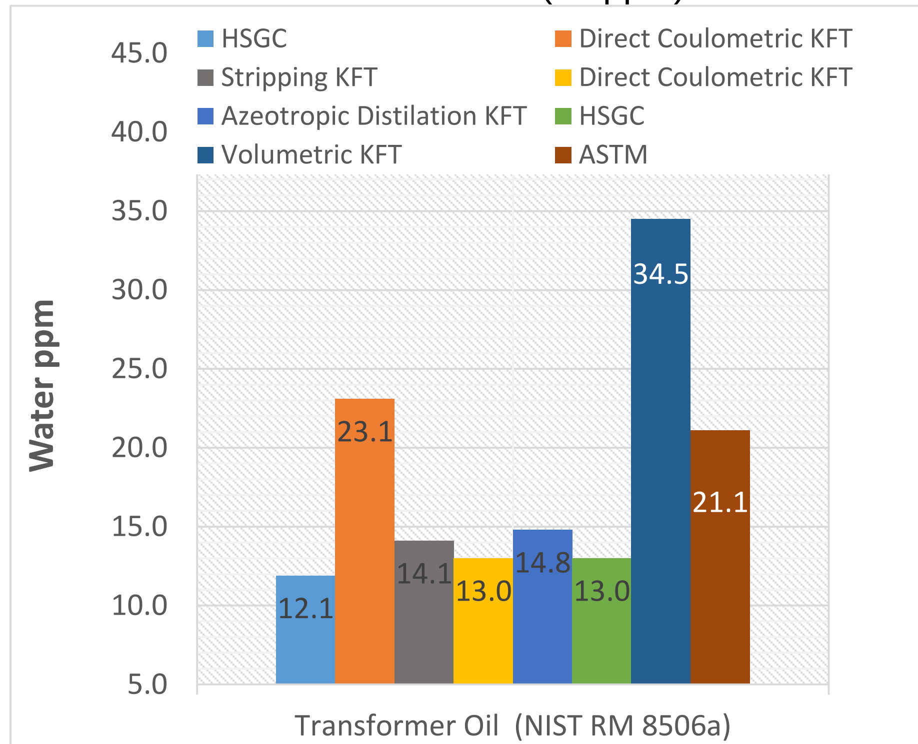


Water Content in Petroleum Products

Crude Oil NIST Standard (100ppm)



Transformer Oil NIST Standard (10 ppm)



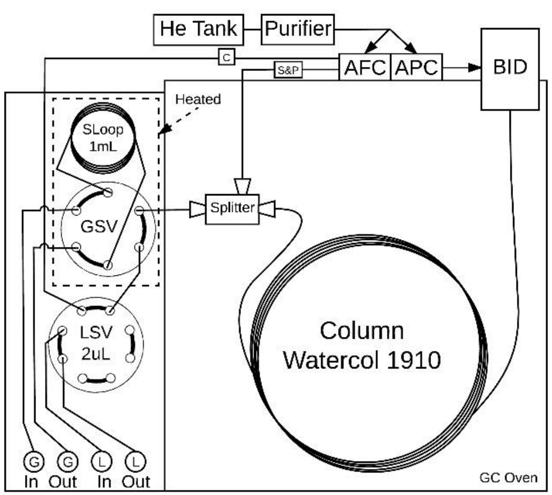
	Light Sour Crude Oil (NIST SRM 2721)		Heavy Sweet Crude Oil (NIST SRM 2722)	
	ppm	RSD	ppm	RSD
HSGCBID	146.1	5.2	101.6	1.7
NIST Sbs. KFT	134.0	13.1	99.0	5.9
ASTM KFT	941.0	1.7	104.0	5.6

Transformer Oil (NIST RM 8506a)		ppm	RSD
Armstrong	HSGCBID	12.1	6.6
Cedefren&Nordmark	Direct Coulometric KFT	23.1	2.6
Cedefren&Nordmark	Stripping KFT	14.1	0.7
Jalbert et al.	Direct Coulometric KFT	13.0	6.2
Jalbert et al.	Azeotropic Distillation KFT	14.8	4.1
Jalbert et al.	HSGCTCD with WAXcol	13.0	3.1
Margolis	Volumetric KFT	34.5	6.4
Margolis Hagwood	ASTM	21.1	9.0

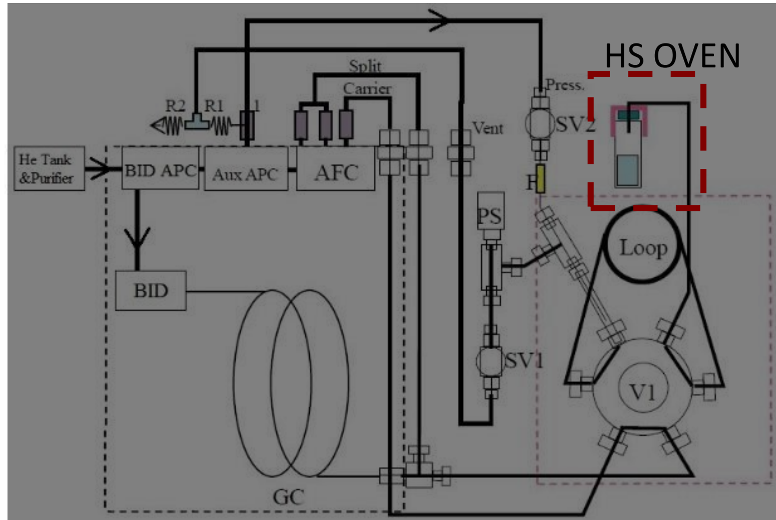
Regarding to KFT, Sulfur components lead to non-accurate result due to the by-reaction.

Lillian A. Frink; Daniel W. Armstrong, 8194-8201; *Anal. Chem.* **2016,** 88,.

SV GCBID for Gas/Liquid Samples

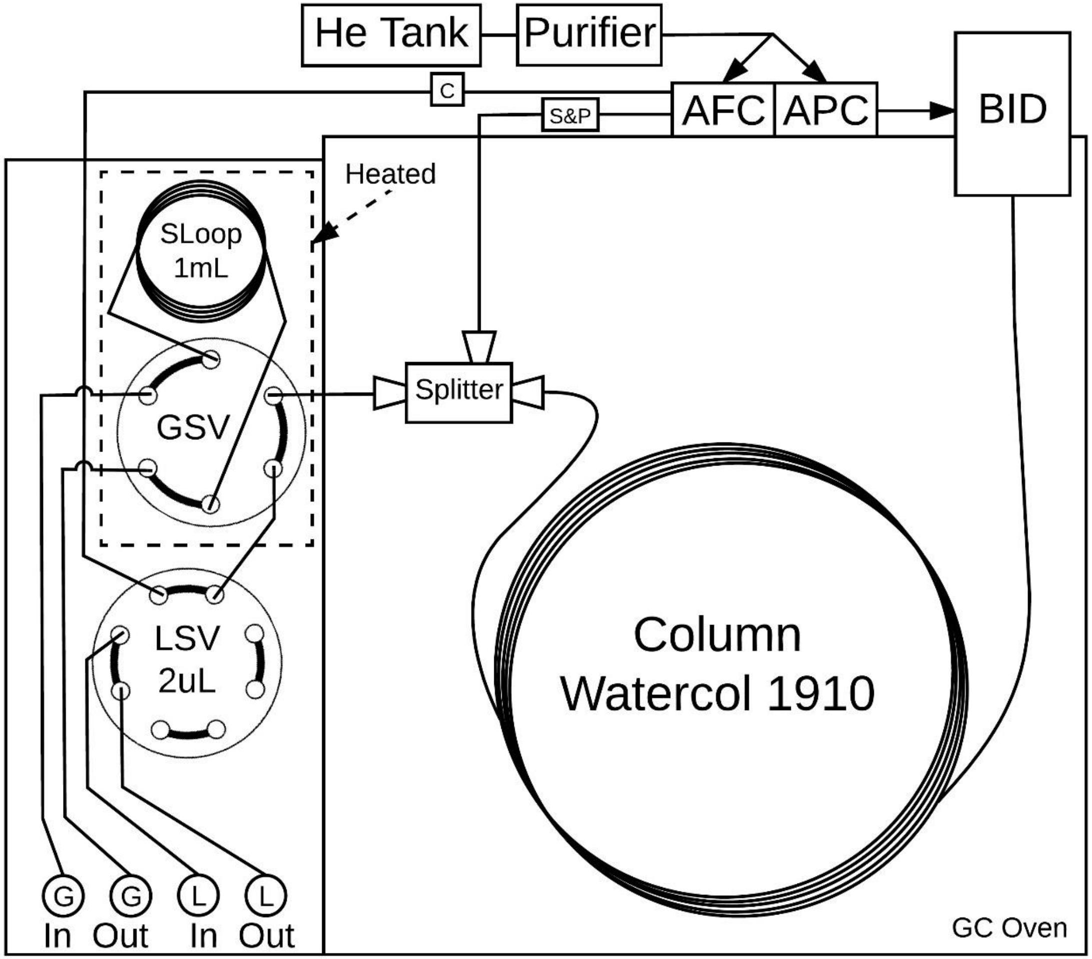


Liquid/Gas Sampling Valve+GC
for Gas/Liquid Products



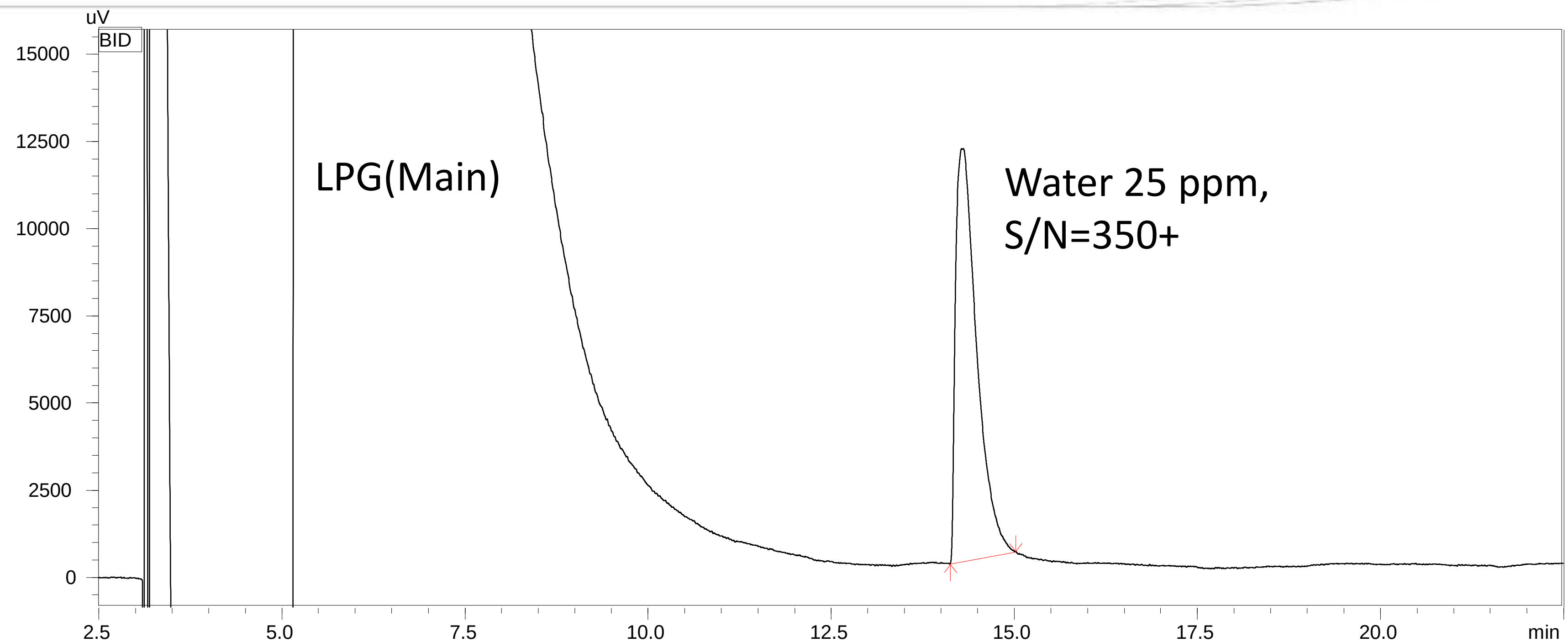
HS-20+GC
for Liquid/Solid Products

SV GCBID for Gas/Liquid Samples



*Vaporizer is also available to introduce liquid samples

Water in Liquid Petroleum Products



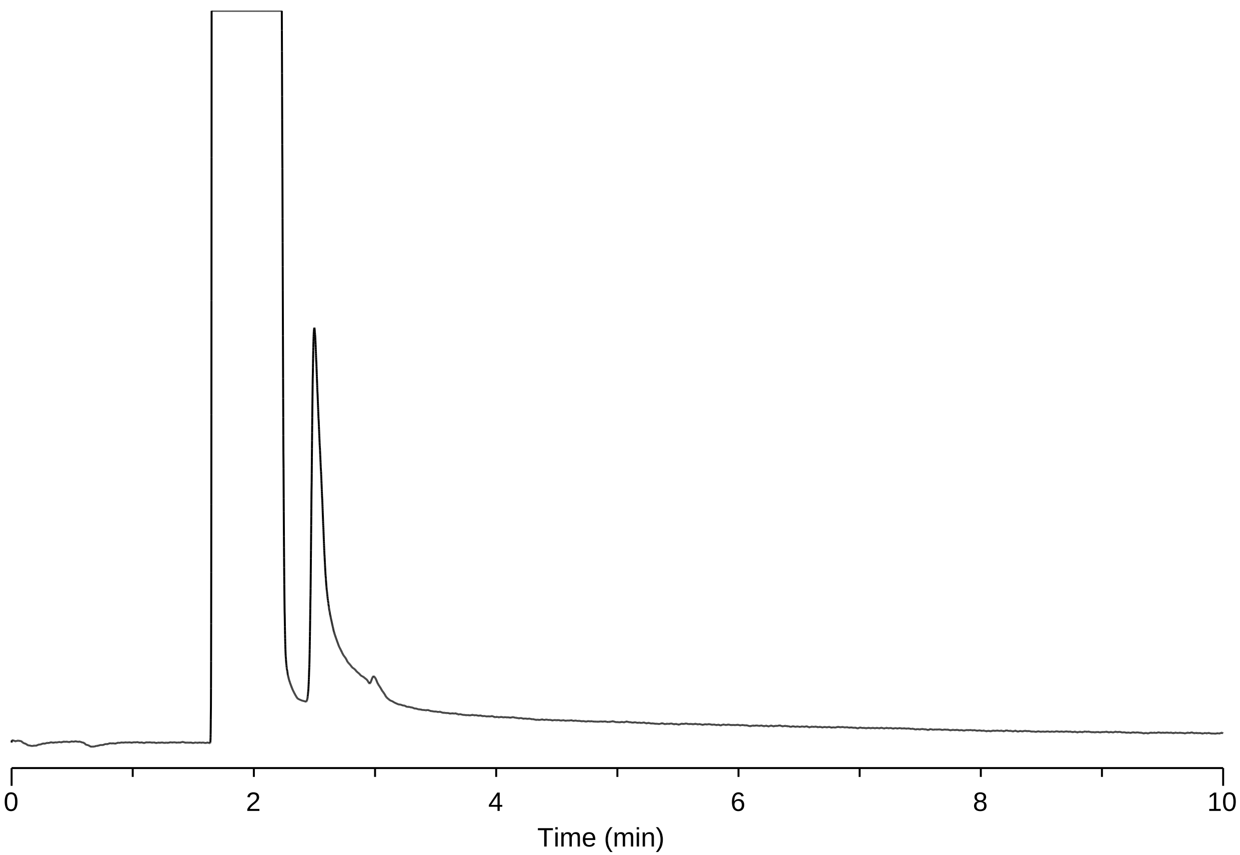
Quantification of Limit(S/N=10) = 0.66 ppm

Detection of Limit(S/N=3.3) = 0.22 ppm

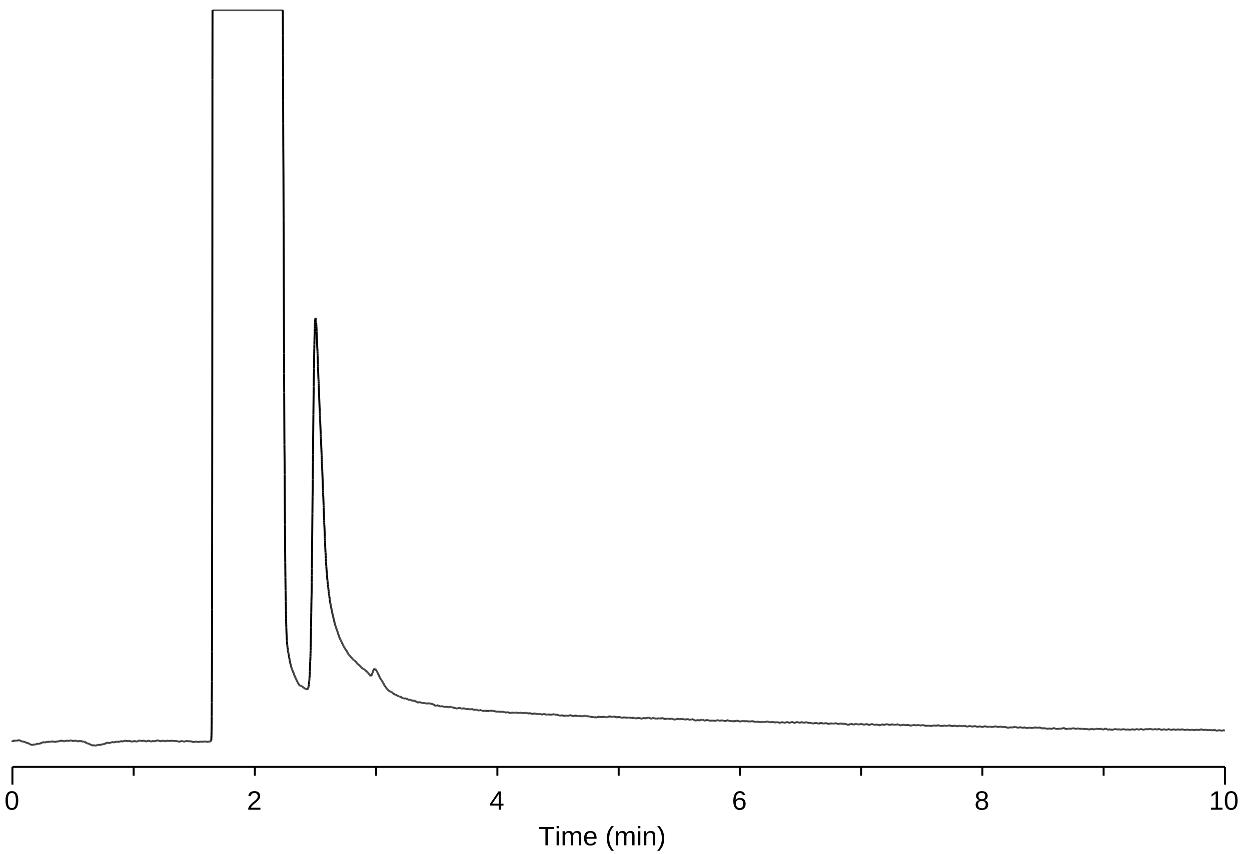
Water	No.1	No.2	No.3	No.4	No.5	**Average**	**SD**	**%RSD**
RT(min)	14.285	14.288	14.286	14.296	14.304	**14.292**	**0.008**	**0.06**
Area(uV・s)	244,037	249,854	246,884	242,950	238,428	**244,430**	**4,296**	**1.76**
Height(uV)	12,418	12,600	12,468	12,045	11,851	**12,276**	**315**	**2.57**
Conc.(ppm)	24.96	25.56	25.25	24.85	24.39	**25.00**	**0.44**	**1.76**

Ethyl Mercaptan(EtSH) coelutes with Propane, No Interference.

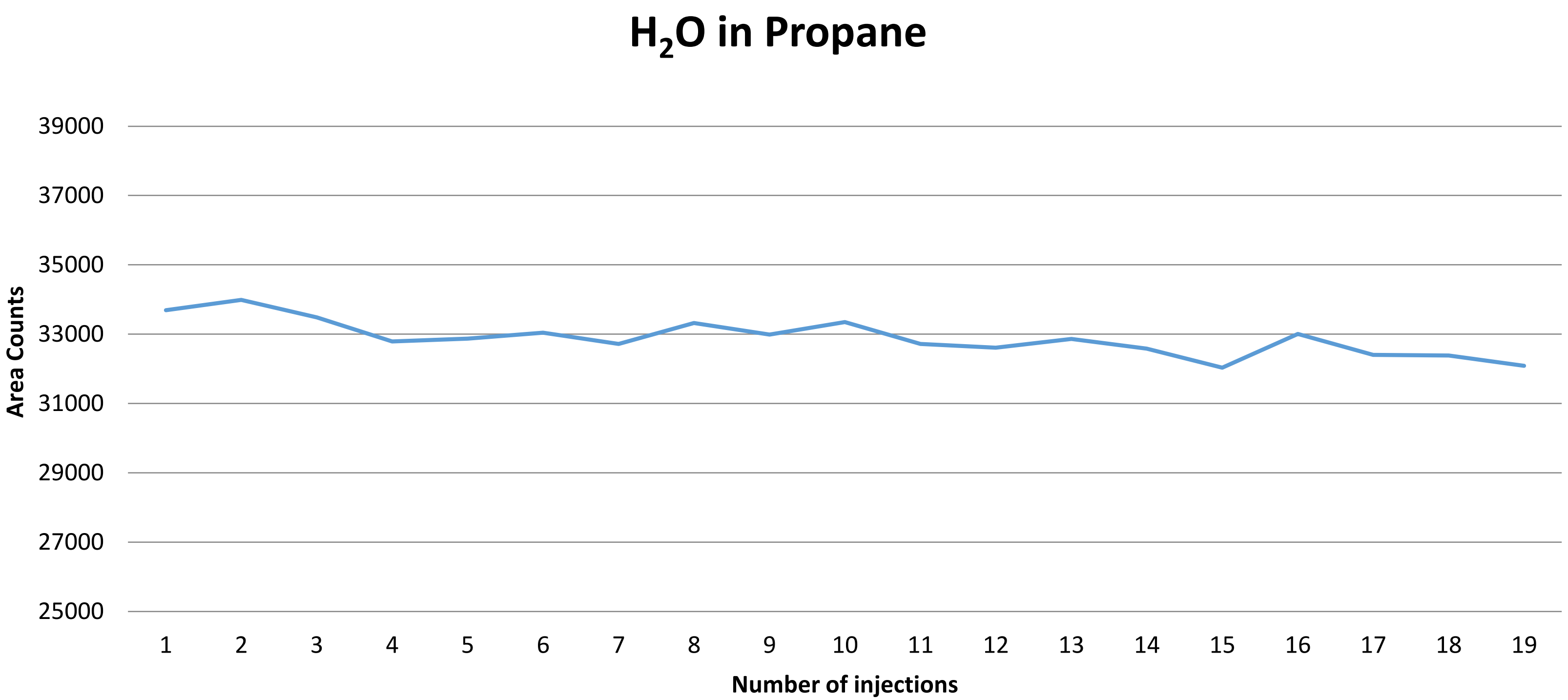
Propane + H_20- Initial Analysis



Propane + H_20- Final Analysis



H_2O in Propane- Statistics



- Average Area Counts- 32889.5
- Standard Deviation 500.1
- % Relative Std. Dev. 1.5%

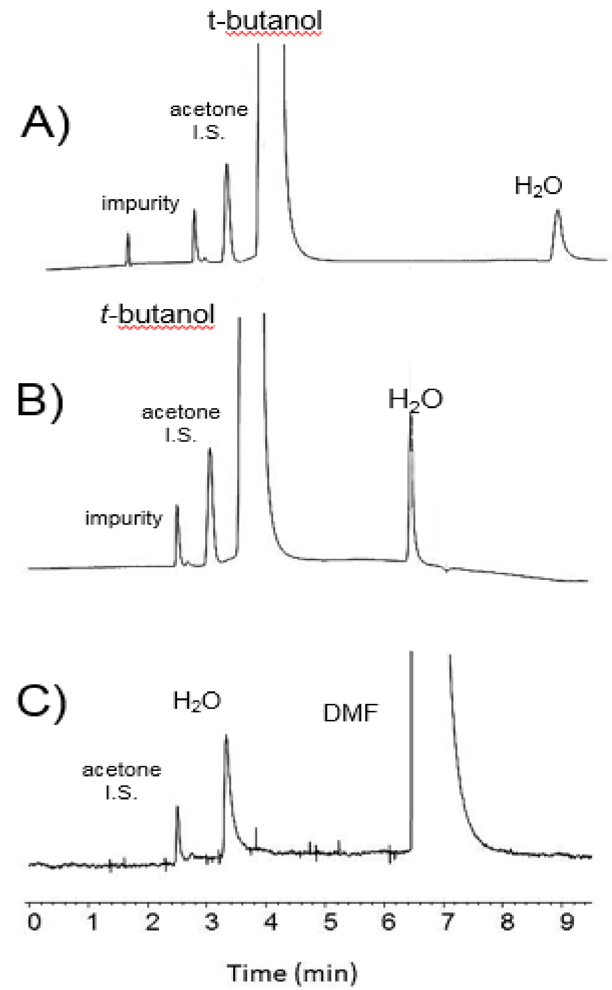
Chromatograms illustrating the separation of water from organic solvents

Chromatograms A and C are isothermal separations. Chromatogram B is for the same sample as in A, however a temperature gradient was used to decrease the analysis time and further "sharpen" the water peak. This enhanced the sensitivity and precision of the method.

Chromatogram A: 1ml injection, 50°C, analysis time: 9 min, Internal Standard: acetone (0.4%)

Chromatogram B: 1 ml injection;50°C (hold 2min), ramp 10dpm to 80°C; analysis time: 6min, Internal Standard: acetone (0.4%).

Chromatogram C: 0.2 ml injection; 110°C, analysis time: 8min, Internal Standard: acetone (0.2%).



LC-GC North America, Vol. 30, April, 2012, pp. 142-158.

Agenda

SHIMADZU

Conclusion

- **Shimadzu's proprietary BID and MilliporeSigma's "Watercol" are combined to separate and measure the Water in Petrochemical Products.**
- **Watercol™ Series**
  - ✓ Watercol 1910
  - ✓ Watercol 1900 (Coming soon!)
  - ✓ Watercol 1460 (Coming soon!)
- **Something totally new and completely different in the world of GC phases**
- **Utilizing HS or Gas/liquid sampling valves, Automated water determination of gas/liquid/solid products can be confirmed.**
  - **ppm-level water detection**
  - **GC-quality repeatability <3%RSD.**
  - **No side reaction**
- **Measurement of water with linearity, great sensitivity, and reproducibility**
- **Less hands-on time compared to other technologies used to measure water**
- **Less volume of chemical waste (which must be deposed of)**
- **Possible to obtain results for water + volatiles/semi-volatiles in same analysis**

New ASTM Method and Shimadzu Branding

ASTM INTERNATIONAL

- Just submitted a new ASTM method as a work item (wk59649)
- D02 H00 Committee – LPG task Force
- D02 Committee- Dimethyl Ether (DME) Task Force
- Replaces the existing Karl Fisher titration methods

Shimadzu Web Page Dedicated to this Technique

Petrochemical Moisture Analysis

http://www.ssi.shimadzu.com/industry/industry_energy.cfm

OR

http://www.analyzeyourgas.com

SHIMADZU

Thank you to Ryo Takechi (Shimadzu Scientific Instruments-Innovation Center) & Len Sidisky- (Millipore Sigma)

SHIMADZU

The New Nexis 2030 GC by Shimadzu

FEATURES

- Analysts will benefit from the touch panel interface, which features clear graphics that display information instantly whenever needed
- ClickTek connectors make tool free column installation a snap.
- Hydrogen Sensor* Monitors Inside the GC Oven
- Minimized Helium Gas Consumption —Carrier Gas Saver Function
- The instrument operating status can be confirmed using the self-diagnostic function (system check)
- 4 heating ports with 3 additional = up to 7 inlets and detectors on one GC

Thank You!

SHIMADZU
Excellence in Science

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