

Introduction

Water in petrochemical feedstocks can cause problems for processors. Freezing of pipe lines and valves and poisoning of expensive catalysts are just a few examples. Monitoring water in petroleum from an upstream source to the downstream processing plant is critical to insure uninterrupted operation. Unlike the commonly used Karl Fischer Titration analysis technique, the Shimadzu water analysis method uses the unique Shimadzu Gas Chromatography (GC) coupled with the proprietary Barrier Dielectric Discharge Ionization Detector (BID) and the unique Merck Supelco WaterCol™ GC column, eliminating the adverse effects of the petroleum matrix which can skew the Karl Fisher results. This GC method can bypass the undesirable chemical interferences due to the column separation technique of a GC. This method provides sensitive and accurate results in concentrations from low ppm to 100%.

Liquid/Gas Sampling valve + GC/BID & HS-20 Headspace + GC/BID

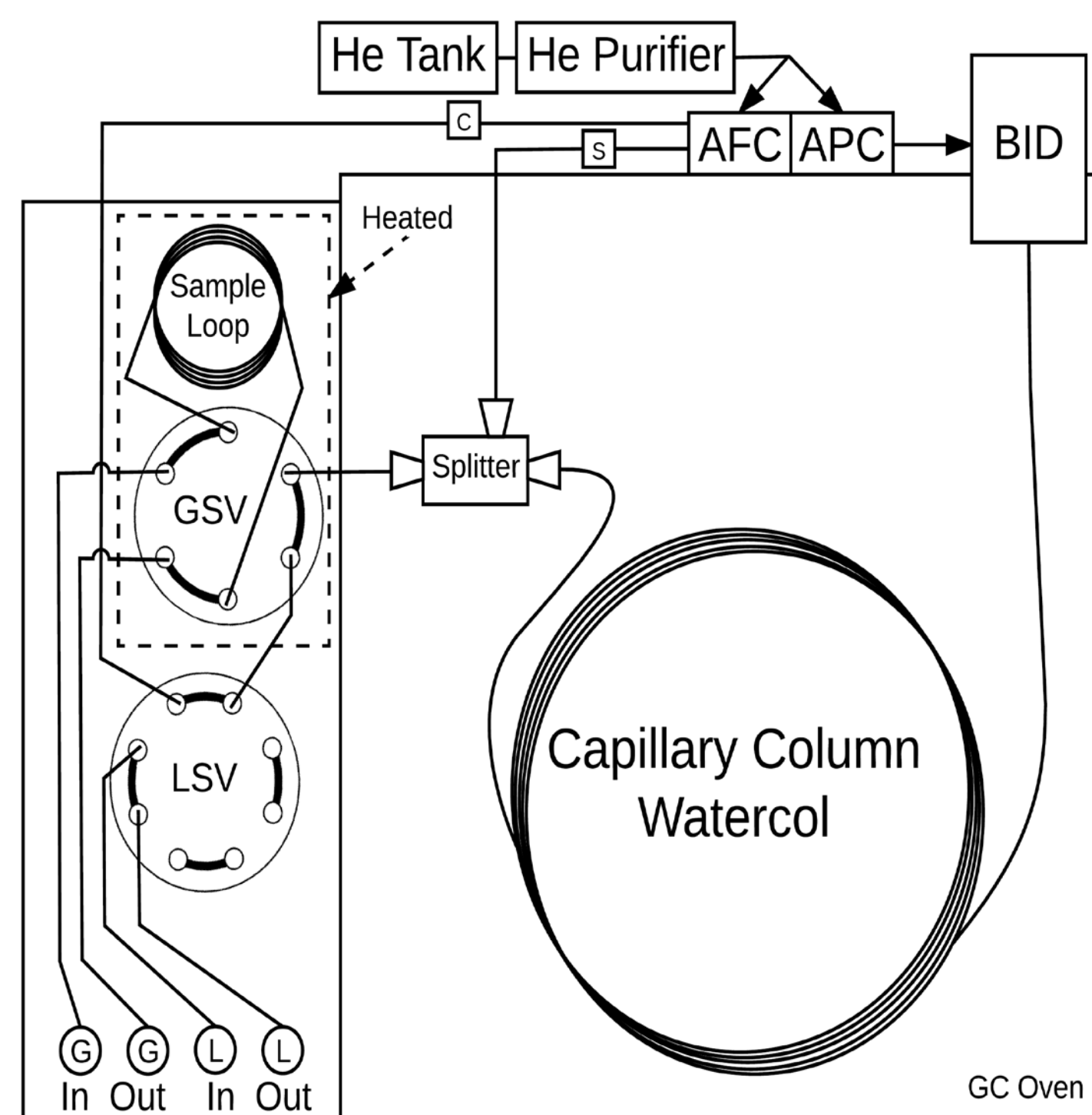


Fig. 1 :Flow diagram of GC configuration.

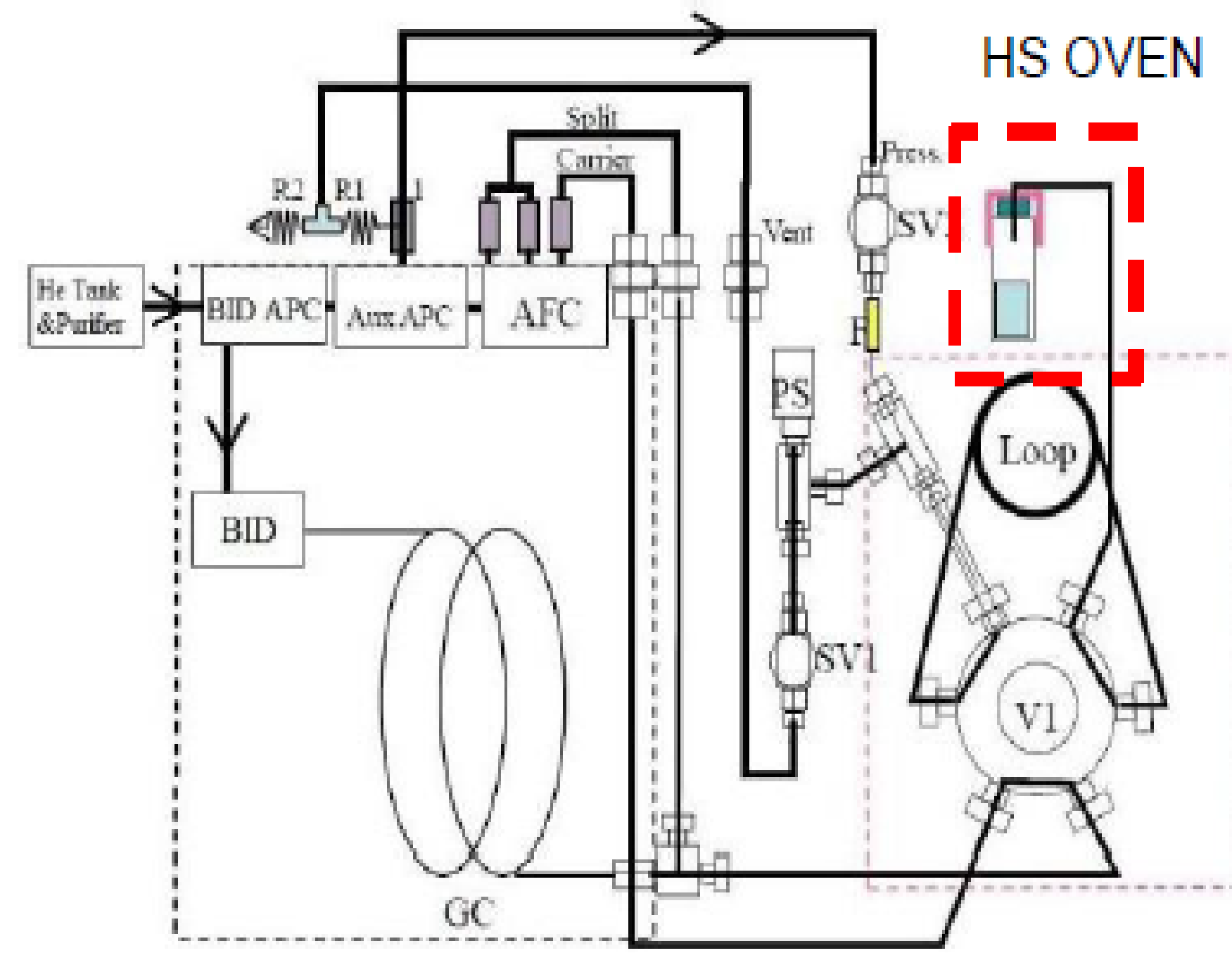


Fig.2 Headspace Sampler HS-20 plus GC/BID.



Fig. 3 Shimadzu NEXIS 2030 Gas Chromatograph

Products	HSGCBID		
	mg Water Measured	ppm Water	RSD%
Motor Oil	0.386	770 ± 2.9	0.4
Transmission fluid	0.497	996 ± 9.2	0.9
Engine Oil	0.131	261 ± 5.8	2.2
Gear Oil	0.104	207 ± 6.9	3.3
Power Steering Fluid	0.123	245 ± 5.6	2.3
3 in One Oil	0.223	445 ± 21.0	4.7
M-Pro7 LPX Gun Oil	0.831	1630 ± 15.9	1.0
CLP Gun Oil	1.634	3260 ± 87.4	2.7
Synthetic Gun Oil	0.117	234 ± 3.4	1.5
Remington Moistureguard Rem Oil	0.165	330 ± 8.1	2.5
Remington Rem Oil	0.048	116 ± 4.5	3.9
WD-40	0.365	728 ± 5.0	0.7
Transformer Oil (NIST RM 8508a)	0.0061	12.1 ± 0.8	6.6
Light Sour Crude Oil (NIST SRM 2721)	0.071	146 ± 7.6	5.2
Heavy Sweet Crude Oil (NIST SRM 2722)	0.051	102 ± 1.7	1.7

Fig. 4 Examples showing precision of technique in various Petrochem products

Analytical Method

Instruments Used

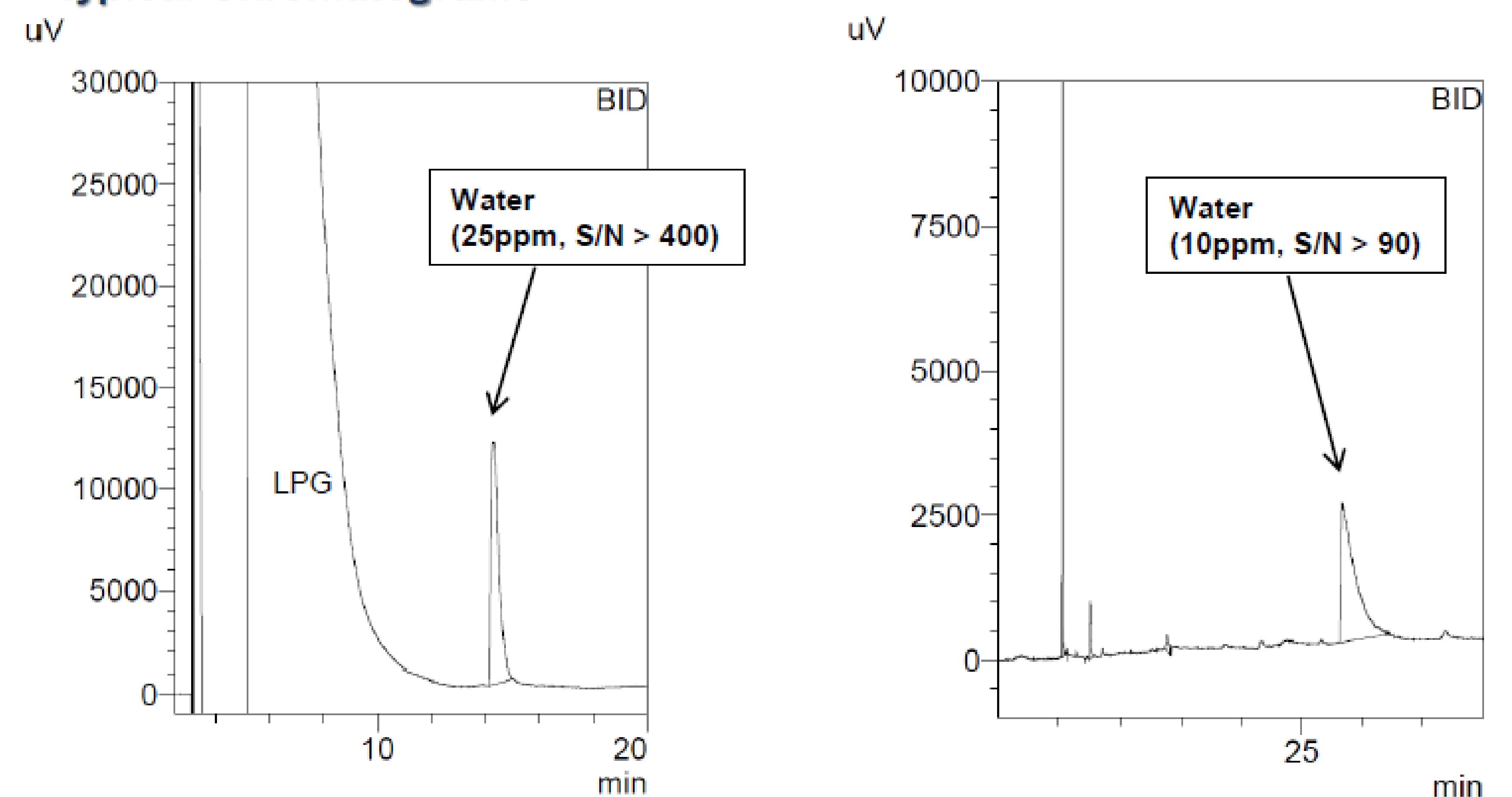
Software	Shimadzu LabSolutions GC NEXIS (GC-2030 + BID)
Gas chromatograph	
Sample injection	Valco Internal Liquid Sample Injector with Splitter Injection Unit
Gas purifier	Supelco High Capacity Gas Purifier (P/N:29541-U)

Analysis Conditions

Column	Supelco Watercol 1910 60 m x 0.25 mm ID, 0.20 μm
Column temperature	35 °C(2.0 min) – 5 °C/min – 150 °C(15 min) Total. 40 min
Carrier gas controller	Constant Linier Velocity
Gas type	Helium(Research grade 99.9999+ %)
Injection volume	2 μL
Split ratio	1:5
Liner velocity	45 cm/sec (Column flowrate 3.78 mL/min)
Transfer line temperature	175 °C (After Internal Liquid Sample Injector to GC column Oven)
Detector temperature	200 °C
Discharge gas volume	50 mL/min(He)

Measurement Results

Typical Chromatograms



25ppm Water in LPG Standard by Liquid Sampling Valve+GCBID (2uL Liquid, Split 1:5).

10ppm Water in Mine Oil (KFT Water Standard) by HS-20+GCBID (1mL Gas, Split 1:100).

Conclusions

Shimadzu's proprietary BID and Millipore Sigma's "Watercol" are combined to separate and measure Water in Petrochemical Products with high accuracy and precision. Utilizing HS or Gas/Liquid sampling valves, one can easily automate water determination of gas/liquid/solid products by:

- Obtaining ppm-level water detection
- Receiving GC-quality repeatability <3%RSD.
- Getting No side reactions

Other benefits include:

- Technicians have less hands-on time compared to other technologies for water measurement.
- Less volume of chemical waste (which is costly to dispose)
- Possibility of obtaining results for water + volatiles/semi-volatiles in same analysis run.