

# Using a Barrier Ion Discharge Detector for Trace Water Analysis: An Alternative to the Karl Fischer Titration Technique

Kyle O. Reddick, Yuan Lin, Nicole Lock, Andrew Fornadel  
Shimadzu Scientific Instruments, Columbia, MD, USA (800) 477-1227

## 1. Introduction

### Traditional Moisture Analysis Techniques

The determination of water content in a sample is among the most widely used analyses. Water within a sample can provide positive benefits as well as negative impacts on goods depending on its abundance. In polymer and plastics manufacturing, including polysiloxanes, excess water in precursor components can negatively impact the desired structural properties of the final product and be detrimental to its visual properties.

It is of great industrial importance to have a quantitation method that is fast, easy, robust, sensitive, has a wide range of concentrations it can measure, and spans all phases of matter. Various techniques that have been used for this purpose are shown in Table 1. Companies have been looking toward gas chromatography (GC) for its simplicity with minimal sample preparation, but until the released of the Shimadzu Barrier Discharge Ionization Detector (BID), the Thermal Conductivity Detector (TCD) was the only option. The limited sensitivity of the TCD coupled with the fact that water shortens the lifetime of the detector is what has made the use of this detector somewhat unappealing for this application. Incompatibility of water with most column stationary phases has also been a deterrent for the use of GC in this analysis.

### Karl Fischer Titration (KFT)

The most common moisture analysis technique is known as a Karl Fischer Titration (KFT). Although this technique can be automated with instrumentation and has a wide dynamic range, it is not without some significant downsides. The reagents used in KFT are very toxic and incompatible with many sample matrices. Samples containing compounds with functional groups that are capable of undergoing reduction (ketones, aldehydes, amides, sulfurs, etc.) are difficult to analyze using KFT because of side reactions. Although KFT has a wide range of concentrations it can analyze, a large mass of sample is required for low level quantitation using the coulometric technique (~5 gram of sample for 10-100 µg of water).

Method	Concentration		Solid	Liquid	Gas	Online
	Low	High				
GC-BID	1 ppm	100 %	X	X	X	X
GC-TCD	100 ppm*	*	X	X	X	X
Karl Fischer Titration	10 ppm	100 %	X	X	X	X
Loss on Drying	0.01 %	-	X	X		
Quartz Crystal Microbalance	1 ppm	1000 ppm			X	X
FTIR Spectroscopy	10 ppb	%	X	X	X	X
TDLA Spectroscopy	10 ppb	-			X	X
CRDS Spectroscopy	0.1 ppb	-			X	X
NIR Spectroscopy	0.10 %	100 %	X	X		X
Colorimetry	0.10 %	%	X	X	X	X
Chilled Mirrors (Dew Point)	3 ppm	%			X	X
Dielectric Constant	1 %	10 %		X	X	
Electrolytic	ppm	0.10 %			X	
Electric Resistance	0.30 %	%		X	X	
Distillation (Azeotropic and Not)	0.05 %	-		X		
Neutron Scattering	%	%	X			
Freeze Valve	10 ppm	-		X		X
Centrifuging	%	%		X		

Table 1: Various moisture quantitation techniques with their usable water concentration range.

## 2. Experimental

### Supelco WaterCol™ Column

Traditional column stationary phases have been significantly less than ideal when it came to their compatibility with water. Water's small molecular size and noteworthy polarity would cause it to adhere to and embed into the stationary phases of these common columns and cause them to degrade. When water would elute from the column, the increased interaction with the stationary would cause the resulting chromatogram to have very broad peaks with irregular peak shape. This would lead to a decrease in the sensitivity of the analysis (decrease in signal-to-noise ratio) and a greater potential for coelution with other peaks.

The commercial introduction of ionic liquids to be used as column stationary phases by Supelco has eliminated this water incompatibility issue. Large cationic and anionic molecules make up the ionic liquid such that it has a high glass transition temperature, very low vapor pressure, and is a polar stationary phase that does not dissolve water. These characteristics make ionic liquid stationary phases appealing to be used with water analysis as they retain the water long enough to pull it away from dominating solvent peaks while still yielding a sharp Gaussian peak in the chromatography. After determining which ionic liquids were best for water analysis, Supelco released the WaterCol™ series (1460, 1900, and 1910) that are numbered based on their retention indices of water.

### Shimadzu Barrier Discharge Ionization Detector (BID)

The BID uses low-energy plasma that is generated by a dielectric barrier discharge (as opposed to heat) to detect analytes with a lower ionization potential than that of helium (17.7 eV). All analytes have an ionization potential lower than that of helium with the exception of neon. The mechanism of the detector and select ionization energies (including that of water) is shown in Figure 1.

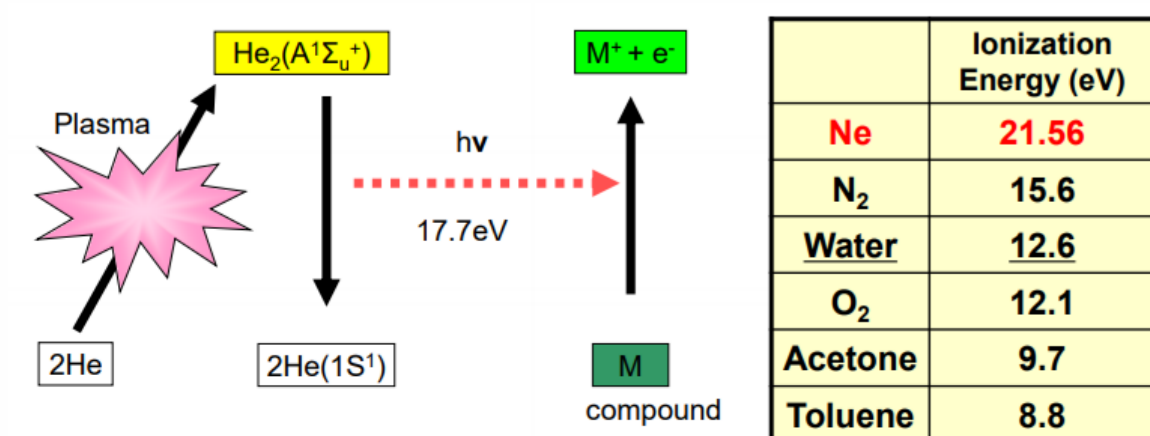


Figure 1: Mechanism of Shimadzu's BID Detector

### Instrumentation and Method

A 0.5 µL liquid sample made primarily of tetramethyldisiloxane (TMDSO) was analyzed for its moisture content using a liquid injection into the split inlet. A Honeywell "hydranal" KFT standard (cat. # 34693) with water at 1.0 % (w/w) was used to give a calibration point. It is difficult to find water standards at single digit ppm levels; this continues to be a goal for this project.



Figure 2: Shimadzu Nexis GC-2030

Trace Water Method Parameters	
Inlet	Split/Splitless; 175 °C; Split Ratio 100:1
Column	WaterCol™ 1910 30 m × 0.25 mmID × 0.25 µm film
Carrier	Helium; Constant Linear Velocity 45 cm/s
Oven	100 °C Isothermal Analysis
BID	200 °C; He discharge gas at 50 mL/min

Table 2: Nexis GC-2030 Analysis Conditions

## 3. Results / Discussion

### Honeywell Hydranal Standard

One of the notable challenges of trace water analysis by GC lies with the inability to find water standards in a suitable matrix to conduct a liquid injection experiment as opposed to other sample introduction techniques (i.e. headspace analysis). What adds to this challenge is the fact that it is virtually impossible to do a serial dilution of a standard given that the dilution solvents likely have trace amounts of water in them. Techniques to dry solvents for this purpose require an elaborate apparatus or do not dry the solvents to suitable (sub ppm) levels.

The stacked chromatograms for the Honeywell KFT standard run in triplicate is shown in Figure 3. The %RSD for the area of the water peak is 1.06 % indicating that the data is very reproducible. A one-point calibration curve was generated from this standard in order to compare the TMDSO sample (Figure 4) water content between the KFT and GC-BID techniques.

### TMDSO Sample

The water content in the samples is at a much lower concentration than the standard, therefore slight variability in area counts has a greater impact on the %RSD. This, coupled with the fact that it is common that the first analysis of a set of analyses provides a slightly false positive or slightly false negative value, explains the increased %RSD of 3.18% for this TMDSO sample.

Table 3 shows the water content of the TMDSO sample in each of the three analyses as according to the one-point calibration curve generated from the Hydranal standard. According to a separate analyst, the concentration of the TMDSO sample by KF coulometric titration was 6 ppm. It is important to consider that this value may be low due to the possibility that the KF reagents reacted with the siloxanes in the sample.

Data File Name	Water Concentration (ppm)
_008	7.255
_007	7.294
_006	7.682
<b>Average</b>	<b>7.410</b>
<b>Standard Deviation</b>	<b>0.236</b>
<b>%RSD</b>	<b>3.186</b>

Table 3: Water Content in TMDSO Sample from GC-BID

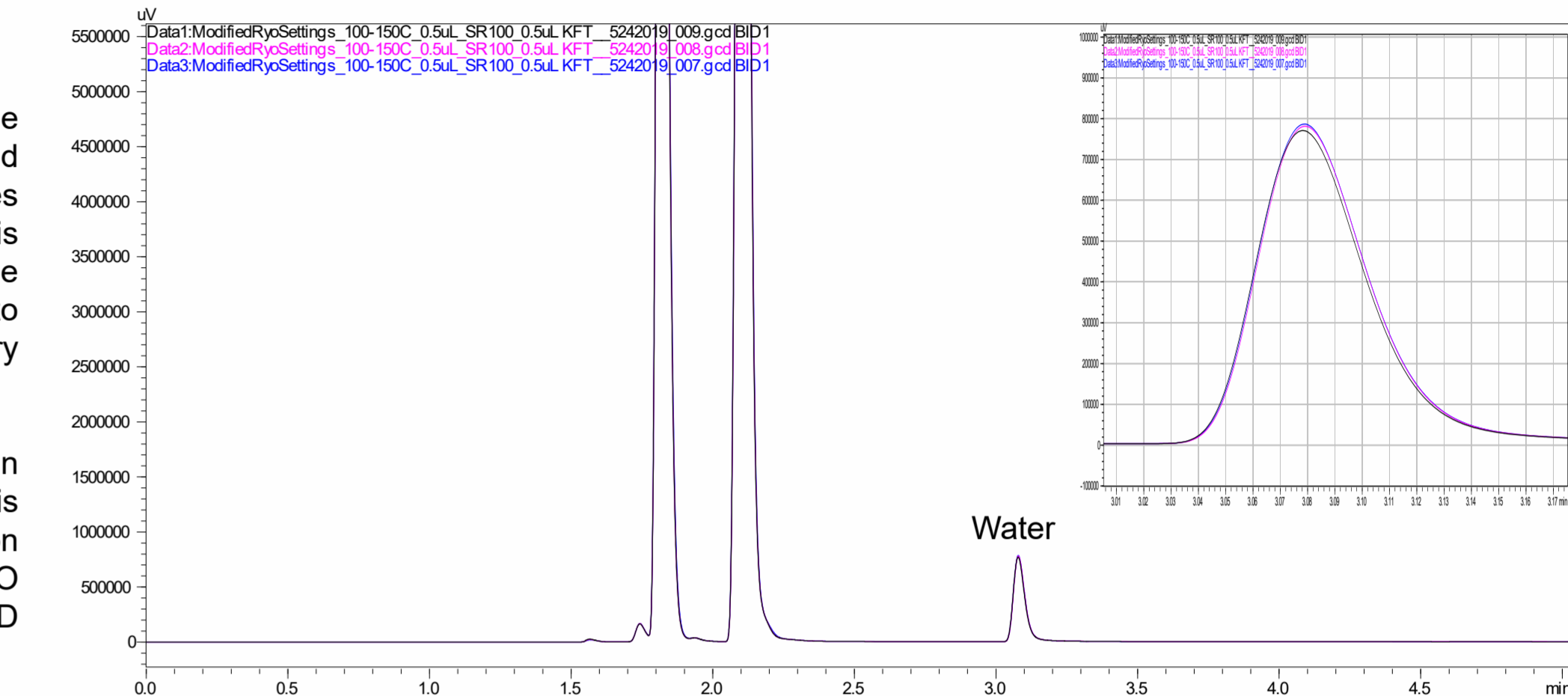


Figure 3: Chromatogram of Honeywell "Hydranal" Standard with 1.0 % (w/w) Water

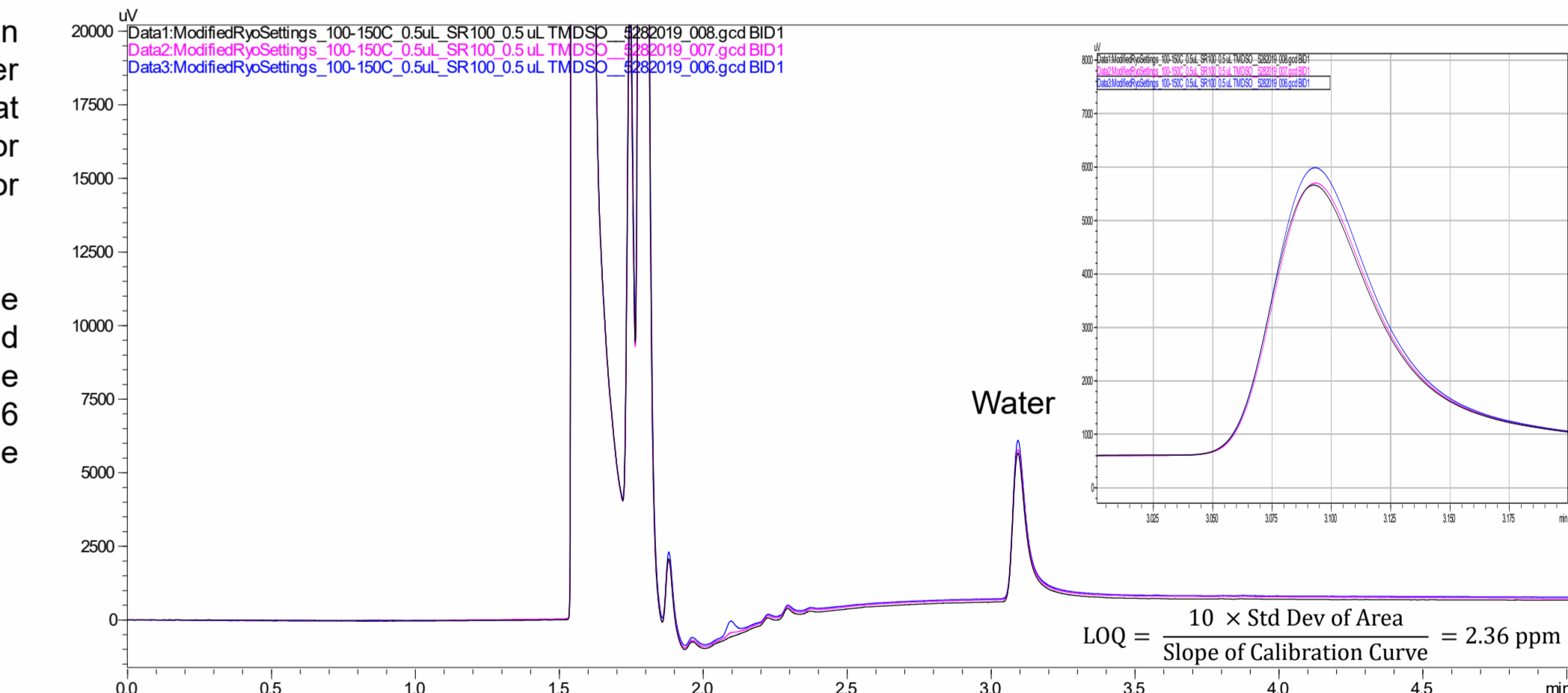


Figure 4: Chromatogram of TMDSO Sample

## 4. Conclusion

- Shimadzu's proprietary Barrier Discharge Ionization Detector (BID) coupled with Supelco's WaterCol™ column is a great alternative to the Karl Fischer Titration technique for trace moisture analysis. The use of GC significantly decreases the sample preparation time that is required by KF, does not generate caustic waste that is expensive to dispose, and does not use chemicals that could interfere with other components in the sample matrix to yield a false value.
- The area counts that were obtained from the BID are very reproducible. A larger set of analyses would allow for the consideration that the first analysis of TMDSO was an outlier that led to a higher %RSD value than could be true while using this detector.
- The calculated water concentration was slightly higher than what was reported by the KF titration, but it is very likely that the KF reagents reacted with the siloxanes in the sample to yield a lower result. Using additional standards that have concentrations of water that are closer to the single digit ppm level will provide more confidence in the results and will likely result in a lower LOQ value.