

Improved Resolution and Detection of Trace Moisture in A Siloxane Matrix Using GC-BID and WaterCol™ 1910 Column

■ Abstract

The quantification of trace amounts of water in a sample is of great industrial importance and has traditionally been difficult to accomplish, given that there are significant flaws in the techniques used to accomplish this goal. Shimadzu's Nexis GC-2030, with a proprietary barrier ion discharge detector (BID), was used to demonstrate an effective approach to this analysis. A WaterCol™ 1910 column that was manufactured by Supelco was able to separate water from other components, in a siloxane matrix, to yield a sharp, resolved, and Gaussian peak. The percent relative standard deviation values for the water peak in the standard and TMDSO sample (1.060% and 3.180%, respectively) were able to demonstrate the reproducibility of this method. The water concentration of the TMDSO sample was determined to be 7.4 ± 0.2 ppm ($n = 3$). The limit of quantitation for water in this analysis was calculated based upon a signal-noise evaluation method and was determined to be 0.15 ppm. In summary, it has been shown that the use of GC/BID can be used as an advancement over traditional techniques for the quantification of water.

■ Introduction

Companies have been looking toward gas chromatography (GC) for water quantitation due to its simplicity. Unfortunately, the commonly used Flame Ionization Detector (FID) is unable to detect water and the Thermal Conductivity Detector (TCD) is not sensitive enough to detect low level ppm values. The proprietary Shimadzu Barrier Discharge Ionization Detector (BID) is 100 times more sensitive than the TCD and can detect all analytes other than helium and neon.

This study was performed to demonstrate that Shimadzu's proprietary BID detector, coupled with Supelco's WaterCol™ 1910 column, can isolate a water peak and quantify the moisture at low levels. A tetramethyldisiloxane (TMDSO) sample was used for this purpose.

TMDSO has been used as a safe alternative to reducing agents like hydrogen gas and lithium aluminum hydride¹. The presence of water during this synthesis has the potential to produce byproducts and lower actual yields. Thus, it is important to analyze the water content in the TMDSO starting material.

■ Samples and Analytical Conditions/ Experimental

A Shimadzu Nexis GC-2030 with a barrier ion discharge detector was used for this application because of the sensitivity of the detector and its ability to detect water. An AOC-20i+s autosampler was equipped onto the GC to increase reproducibility. A WaterCol™ 1910 column manufactured by Supelco was used for this separation. The temperature of the oven was increased to 180 °C after the water eluted from the column in order to clear the column of analytes with higher boiling points. The analytical conditions for this analysis can be found in Table 1.

Table 1: Nexis GC-2030 method conditions

Nexis GC-2030 Method Conditions	
Inlet	0.5 µL Split Injection; Split Ratio 100.0; Inlet Temperature 175.0 °C
Column	WaterCol™ 1910 30 m × 0.25 mm ID × 0.20 µm film thickness
Carrier	Helium; Constant Linear Velocity 45.0 cm/s
Oven	100.0 °C (4 min hold); 40 °C/min to 180.0 °C (4 min hold)
BID	200.0 °C; Helium Discharge Gas Flow 50.0 mL/min

A Honeywell Hydranal™ 1.0 KFT standard (cat. # 34693) with water at 1.0 % (w/w) (1000 ppm) was purchased and analyzed in order to generate a single-point calibration curve to approximate water content. The tetramethyldisiloxane (TMDSO) sample was obtained by a party that uses the reagent in one of the synthetic processes that ultimately yields their end product.

■ Results and Discussion

The incompatibility of water with most column stationary phases has been a deterrent for the use of GC for moisture applications. When water would elute from traditional columns, the increased interaction with the stationary phase would cause the resulting chromatogram to have very broad peaks with irregular peak shape. Because the BID is a universal detector that can detect all analytes (except He and Ne), it was important to isolate the peak such that it was pulled away from dominating solvent peaks while yielding a sharp, Gaussian peak in the chromatography.

The commercial introduction of ionic liquids to be used as column stationary phases by Supelco has eliminated this water incompatibility issue as certain ionic liquids, like those used in the WaterCol™ columns, produce water peaks of quality.

A representative chromatogram of the Hydranal™ 1.0 standard is shown in Figure 1. A null injection that was obtained immediately after the three standard analyses is included to demonstrate that there is no carry-over. Water peak data from the standard was determined to have a %RSD of 1.060 % (n = 3) and confirms the reproducibility of the BID detector with respect to this application.

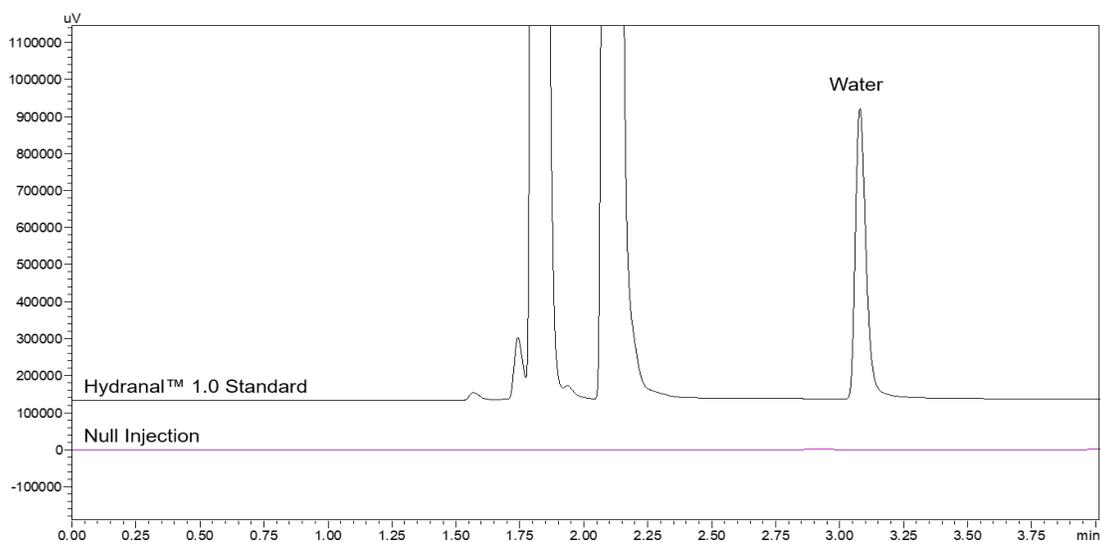
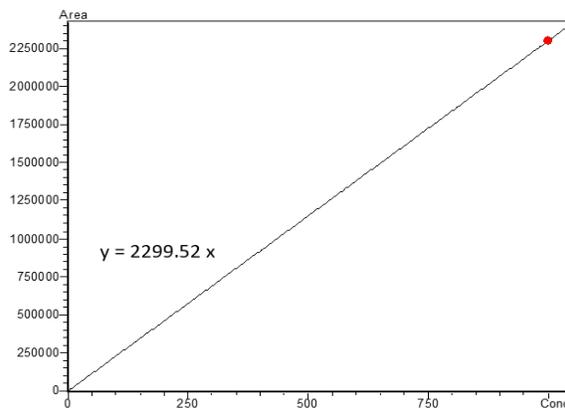


Figure 1: Representative chromatography of the three analyses used to develop a linear calibration curve of the Honeywell Hydranal™ 1.0 water standard. The water peak has been identified. The chromatography of a null injection that took place immediately after the standards were analyzed is included to show that there is no carryover.

A single-point calibration curve was used in order to approximate the water content in the TMDSO sample. The one-point linear calibration curve is shown in Figure 2. If a more precise quantitative result is desired, it is recommended to use additional standards that are closer in magnitude to the water content in the sample. Hydranal™ standards that are lower in concentration (0.1 % and 0.01 %) can be sourced from Supelco.

Figure 2: The linear calibration curve developed from the Hydranal™ 1.0 standard that was analyzed in triplicate. The curve has been forced through zero and the resulting line equation has been displayed.



A chromatograph that was generated from one of the three analyses of the TMDSO sample is shown in Figure 3. Again, a null injection that immediately followed the TMDSO analyses is included to show that there is no appreciable carry-over. Corresponding water data for the TMDSO is included in Table 2. When applied to the calibration curve, it was determined that the water concentration in the sample is roughly 7.4 ppm

Table 2: Data collected and analyzed from the TMDSO sample

Data File	Area Counts for Water Peak	Water Concentration (ppm)
TMDSO Analysis 1	17664	7.682
TMDSO Analysis 2	16773	7.294
TMDSO Analysis 3	16684	7.255
Average	17040	7.410
Standard Deviation	542	0.236
% RSD	3.180	3.186

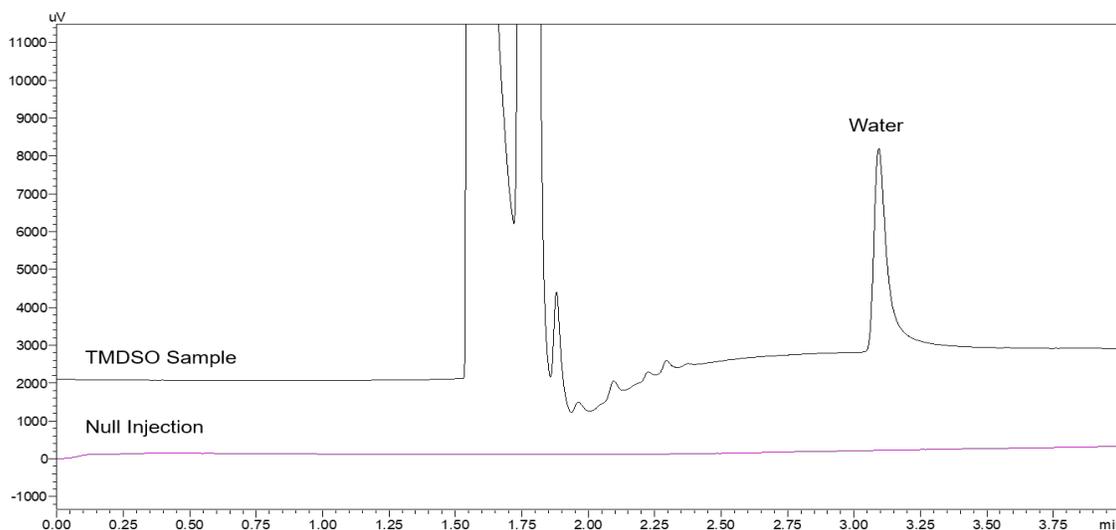


Figure 3. Chromatography for one of the three TMDSO analyses. The water has been identified. A subsequent null injection demonstrates no appreciable carry-over.

In an interest to estimate the sensitivity of the BID for this application, the limit of quantitation (LOQ) was determined in LabSolutions based upon the signal-noise relation (noise collected between 0 and 1 minute). It was determined that the LOQ for water in accordance with this method is 0.15 ppm.

It should be included that all samples for this application were prepared in ambient conditions. Depending on the hygroscopic nature of the matrix being analyzed, it may be important to prepare the samples in a low moisture or moisture-free environment. The chromatogram of a blank, 0.1 μ L air injection has been included in Figure 4 for reference.

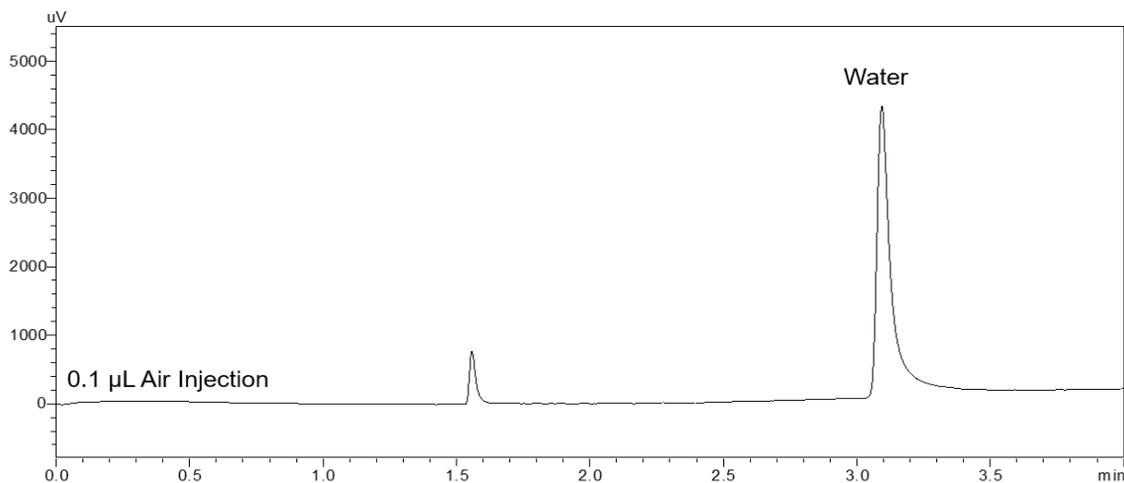


Figure 4: A chromatogram of a 0.1 μ L injection of the ambient laboratory air.

■ Conclusion

The purpose of this study was to demonstrate the capabilities of the barrier ion discharge detector (BID) for trace water analysis using a liquid injection. A fully resolved, Gaussian-shaped, water peak was obtained due to the use of the water-compatible WaterCol™ 1910 column. Low relative standard deviation values demonstrated the reproducibility of the detector with respect to water quantification in this analysis.

The limit of quantitation (LOQ) for water was calculated to be 0.15 ppm, highlighting the sensitivity of the BID detector. It can be concluded that the BID/WaterCol™ combination is an effective technique for determining trace water content

■ Reference

1. Pesti, J.; Larson, G. L. Tetramethyldisiloxane: A Practical Organosilane Reducing Agent. *Org. Process Res. Dev.* **2016**, *20* (7), 1164-1181.

■ Consumables

Part Number	Item Description	
220-97331-31	1.5 mL screw vial kit including vials, caps, and septa (100/pack)	Sample Preparation
220-97331-62	200 µL inserts for 1.5 mL screw vials (100/pack)	
220-91521-10	4 mL screw vial kit including vials, caps, and septa (100/pack)	
221-74469-00	10 µL syringe with PTFE tipped plunger for AOC-20i	Injection Port
227-35007-01	SPL-2030 inlet liner with wool for split injection (5/pack)	
036-11203-84	O-ring for glass liner (5/pack)	
227-35004-01	Premium light green septa rated to 350 °C (50/pack)	Column
221-81162-01	ClickTek ferrules for 0.25 mm ID columns (6/pack)	
220-97352-02	WaterCol™ 1910 Capillary Column 30 m x 0.25 mmID x 0.20 µm film	Gas Filtration
220-97834-01	Valco HP2 Helium Purifier for BID	

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