The Quantitative Measurement of Water by Gas Chromatography Using Ionic Liquid Capillary Columns

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Abstract

The determination of water content in solvents, alcoholic beverages and various consumer products such as foods, pharmaceuticals, fuels, and petroleum products is one of the most common types of chemical testing. Many techniques such as gravimetric analysis, Karl Fischer Titration, near infra-red spectroscopy, gas chromatography (GC) and others have been used for water quantification with good results. [1] However, the limitations of these approaches can include high limits of detection, large sample sizes required for trace analysis, side reactions, the use of expensive consumables, and the production of chemical waste. Previous work by Prof. Daniel Armstrong and co-workers has described the use of ionic liquid GC capillary columns for the trace analysis of the water content in a wide variety of solvents. [2] These columns were capable of providing a rapid and quantitative determination of water contents using very small sample amounts. Recent studies have focused on developing a method for the analysis of water in liquefied petroleum gases. This presentation demonstrates the capability of the ionic liquid capillary columns for the GC analysis of water in a number of samples.

References

[1.] S. Inagaki, et. al., Anal. Methods, 2015, 7, 4816-4820
[2.] R. Woods, et.al., LCGC Europe, Vol. 24, Issue 10, 2011

Introduction

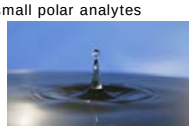
Watercol series of ionic liquid capillary GC columns are characterized by their ability to produce a sharp peak shape for water and other small polar analytes. The water peak shape is sharp enough so that:

Water can be integrated and quantified

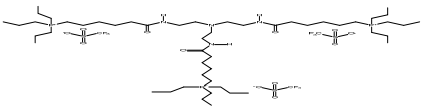
Water does not interfere chromatographically with many other small polar analytes

Three different chemistries available:

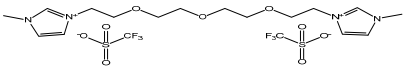
Watercol 1460, Watercol 1900, and Watercol 1910



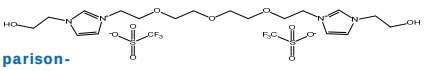
Watercol 1460



Watercol 1900

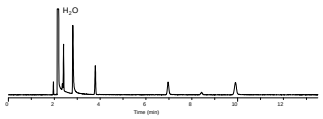


Watercol 1910

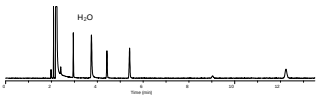


Watercol Selectivity Comparison-
The three different selectivity's for the Watercol columns will provide different elution patterns for the sample components. The Watercol 1460 is the least polar of the columns and elutes water after the C14 n-alkane at 100°C. The Watercol 1900 will elute water about the same retention time as a C19 n-alkane at 100°C and the Watercol 1910 will elute water after the C19 n-alkane. The following figures shows how the water peak shifts its elution on the three different columns.

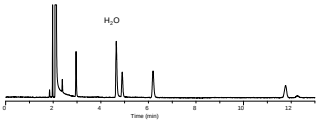
Watercol 1460



Watercol 1900

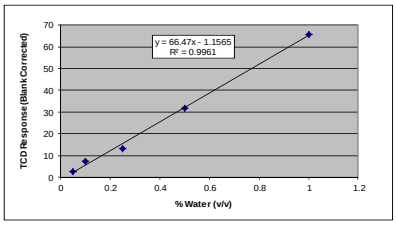


Watercol 1910

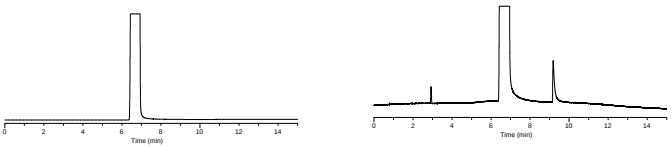


Experimental

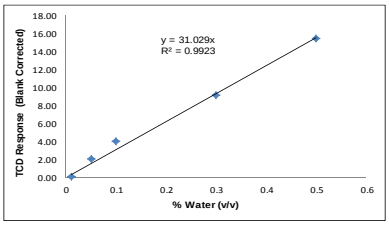
Water Calibration Curve (0.05-1%) on Watercol 1460



Water Standard (0.25% in Ethanol) on Watercol 1460



Water Calibration Curve (0.01-0.5%) on Watercol 1910



Analysis of water in Liquid Petroleum Products

Supelco's Watercol Column + Shimadzu's BID

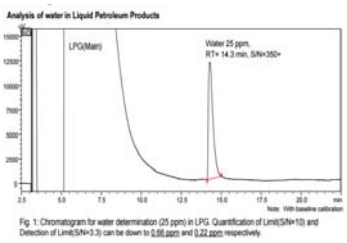


Fig. 1: Chromatogram for water determination (25 ppm) in LPG. Quantification of Limit(S/N=10) and Detection of Limit(S/N=3.3) can be down to 0.66 ppm and 0.22 ppm respectively.

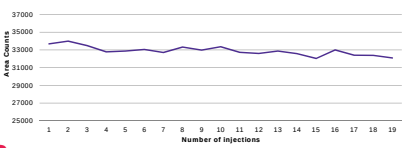
Submitted a new ASTM method as a work item (wk59649)

D02 H00 Committee – LPG task Force

Replaces the existing Karl Fisher titration methods

H_2O in Propane- Statistics

H_2O in Propane



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

Summary

- Something totally new and completely different in the world of GC phases.
- Have the opportunity to impact current GC and GC-MS practices along several paths.

Watercol 1460 **Watercol 1900** **Watercol 1910**

Ionic liquid GC phases based on new selective combinations of cations and anions have been tailored to produce capillary columns that can be used for the quantitative evaluation of water in various samples. Three new selectivity's have been demonstrated, offering the ability to resolve water and other organic compounds in a wide variety of sample types. This makes GC a viable approach for the analysis of water; giving laboratories the option to avoid the use of techniques which produce chemical waste and/or are more expensive to perform.

Acknowledgements

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Ryo Takechi & Mark Janeczko- Shimadzu

www.sigma-aldrich.com/watercol