Application News

System GC

Analysis of Trace Water in Oil Matrices using the Nexis GC-2030 Gas Chromatograph

User Benefits

- A GC-2030 system configured for water analysis in mineral oil is a suitable technique, free from common interferences, for determining trace water in heavy hydrocarbon matrices.
- Use of the Barrier discharge Ionization Detector (BID) and ionic liquids column allows for detection of water with no matrix interference.
- The system is suitable for other heavy hydrocarbon containing samples such as crude oil.

■ Introduction

Water can be found in a multitude of different hydrocarbon matrices, including natural gas, gasoline, mineral oil, and crude oil. Given the non-combustible and corrosive nature of water, it is closely monitored in hydrocarbon feed stocks. The concentration of water in oil matrices is typically under 500 ppm, which necessitates the need for highly sensitive techniques for detection.

Karl Fischer titration is the most used technique for water determination but is subject to interference from alcohols and sulfur species, both of which are commonly found in crude oil. Gas chromatography has been shown to be a viable method for water analysis by employing a Barrier discharge Ionization Detector (BID) with a Supelco Watercol1910 column for gaseous and liquified petroleum gases (LPG). The ionic liquids column lacks the temperature range to meet the analysis in heavier hydrocarbon streams such as crude oil and mineral oil. The heavy hydrocarbon content of these oils is best introduced into a gas chromatograph via an on-column injector (OCI) with temperature programming.

It has been previously demonstrated that the light ends of a middle distillate sample can be repeatably quantified on a GC with an OCI and flame ionization detector (FID) using a backflush to side vent. This application explores using a GC configured with an OCI and a BID to analyze trace water in mineral oil using a backflush to side vent.

■ Samples and Analytical Conditions/Experimental

The evaluation was completed using a GC-2030 equipped with an on-column injector (OCI), a BID, and a backflush to side vent. A 1 m section of 0.53 mm deactivated metal guard column was installed into the OCI. The backflush column was a Restek MXT-1 30 m x 0.25 mm x 0.25 um column housed in the GC oven. The analytical column was a Supelco Watercol1910 30 m x 0.25 mm x 0.25 um column. The instrument schematic is shown in Figure 1. Analysis was performed using an AOC-20i equipped with a tapered syringe. The injection volume was 1 uL for each sample. Method parameters for the analysis are listed in Table 1.

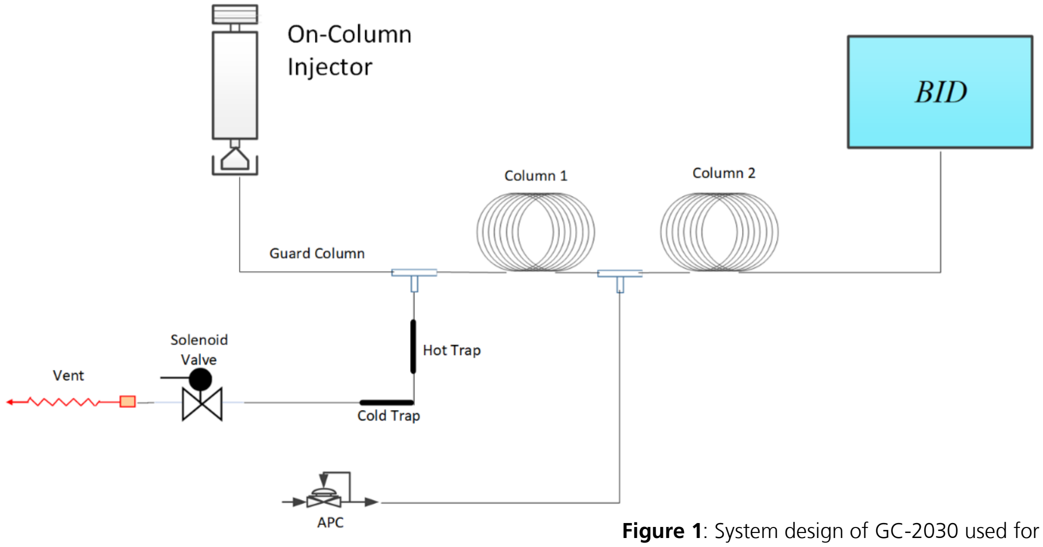

Figure 1: System design of GC-2030 used for this analysis.

Table 1: Instrument parameters

Parameter	Value
Instrument model	GC-2030AF with BID and OCI
Autoinjector type	AOC-20i
Injection volume	1 uL
Injection port type	On-column Injector
Carrier gas type	He
Carrier gas pressure	300 kPa, 5 min, -100 kPa/min, 250 kPa, 19.5 min
Injector temperature	50 ºC, 1 min, 50 ºC/min, 400 ºC, 17 min
Auxiliary Pressure Controller	265 kPa
Oven temperature	80 ºC, 6 min, 20 ºC/min, 400 ºC, 3 min
Auxiliary oven temperature	100 ºC
Transfer line temperature	125 ºC
Columns	MXT-1 30 m x 0.28 mm x 0.25 um Watercol 1910 30 m x 0.25 mm x 0.2 um
Detector	BID
BID Temp	250 ºC
BID Discharge Gas Flow	50 ml/min He
Backflush event time	5 min

A qualitative saturated water in isooctane:hexane mixture was used to determine the backflush timing to ensure the total water peak was captured. Hydranal 1.0, Hydranal 10.0, and Hydranal Water Oil standards were injected to confirm the resolution and retention time for water. A mineral oil sample was injected to confirm the elution of water was free of any interferences and to optimize the backflush time for heavy hydrocarbon samples. A water saturated mineral oil sample was generated by introducing an excess aliquot of water into mineral oil, agitating the mixture, and removing the mineral oil fraction for injection. Triplicate injections each of the Hydranal 1.0, Hydranal Water Oil standard, mineral oil, and mineral oil saturated with water were injected.

Figure 2 shows a representative chromatogram for each. The retention time for water was determined to be 6.7 minutes. Figure 3 shows a representative chromatogram for the Hydranal 10.0 standard. This standard is above the 2% quantitative limit for the BID and is not suitable for quantitative purposes in this application.

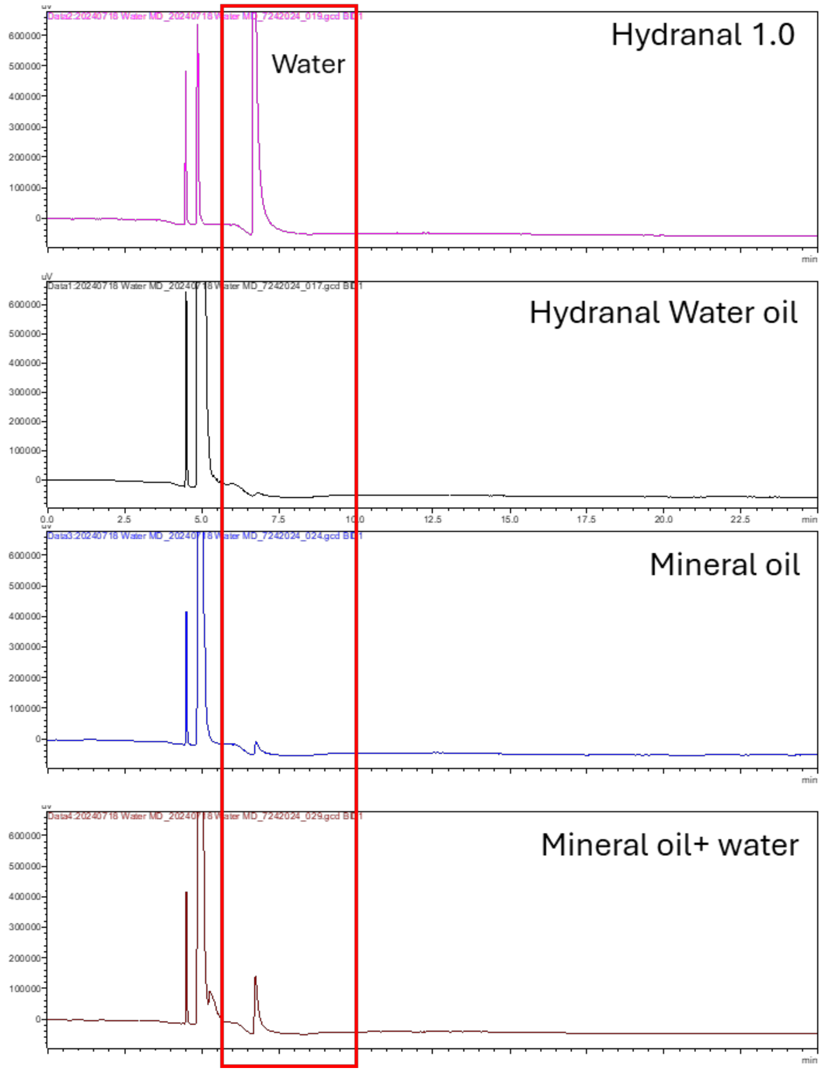

Figure 2: Stacked chromatograms of the Hydranal 1.0, Hydranal Water Oil standard, mineral oil, and mineral oil saturated with water.

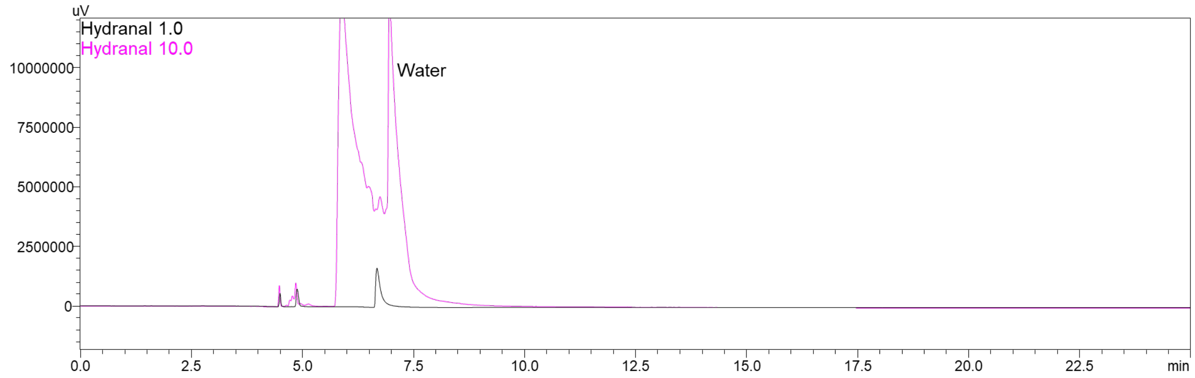

Figure 3: Overlay chromatograms of the Hydranal 1.0 and 10.0 standards.

Quantitative analysis was completed using the Hydranal 1.0 standard to generate a single point calibration. Repeatability under 2% was established for the Hydranal 1.0 standard with a calculated limit of quantitation (LOD) of 6 ppm and a calculated limit of detection (LOD) of 2 ppm. The unknown concentration of water in the mineral oil and mineral oil saturated with water was calculated to be 41 ppm and 142 ppm, respectively. The concentration of water in the Hydranal Water Oil standard was calculated to be 11 ppm which agrees with the reported water concentration on the certificate of "< 50 ppm water". The results of the replicate injections and single point calibration are shown in Table 2.

■ Conclusion

The Shimadzu GC-2030 Nexis gas chromatograph system configured for water analysis in mineral oil is a suitable technique, free from common interferences, for determining trace water in heavy hydrocarbon matrices. The implementation of an OCI and a backflush to side vent aids in the range of matrices that can be used. Excellent repeatability indicates that the design is robust and rugged against clogging. The use of the BID and ionic liquids column allows for highly sensitive detection of water with no matrix interference. This design was evaluated using mineral oil but is suitable for other heavy hydrocarbon containing samples such as crude oil.

Table 2: Summary table of repeatability, concentration, and calculated limits of detection (LOD) and quantitation (LOQ) for sample and standard injections.

Sample	Retention Time (min)	Average Area	RSD% (n=3)	Concentration (ppm)	Calculated LOQ (ppm)	Calculated LOD (ppm)
Hydranal 1.0	6.71	114228654	1.9%	1000	6 (+/- 0.6)	2 (+/- 0.2)
Hydranal Water Oil	6.82	146643	5.7%	11 (+/- 0.6)	9 (+/-2)	3 (+/- 0.5)
Mineral Oil	6.77	569022	3.5%	41 (+/-1)	10 (+/-0.2)	3 (+/-0.1)
Mineral Oil + Water	6.75	1965337	1.8%	142 (+/-3)	6 (+/-0.7)	2 (+/-0.2)

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