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Application News

No. GC-2110

System GC

Rapid Dissolved Gas Analysis in Transformer Oils per ASTM D3612 Method on the Nexis GC-2030 Gas Chromatograph

■ Background

As electrical and thermal loads are applied to transformers, the insulator oil and various components can undergo decomposition, the byproducts of which are dissolved into the transformer oil as gaseous compounds. Analyses of these gases, called dissolved gas analysis (DGA), is a common analysis performed on insulator oil sampled from electrical transformers that can indicate the health, longevity, and potential error states of transformers. Given the large and growing number of transformers associated with modern electrical infrastructure, limited throughput for the large number of received samples is a common issue faced by testing labs. ASTM D3612 Method C specifies the use of automated headspace sampling of the transformer oil, which allows for higher throughput over other sampling methods for DGA analyses, such as vacuum extraction or the use of a stripper column (e.g., ASTM D3612 Methods A and B, respectively).

Using current techniques and technologies, this application gas chromatography system increases throughout and serviceability over previous designs.

■ Instrumentation

The GC-2030 Nexis gas chromatograph is equipped with an HS-20 loop model, two capillary columns, one needle valve, one 6-port column switching valve, a thermal conductivity detector (TCD), and a flame ionization detector (FID) with a Jetanizer™, an in-jet methanizer supplied by Activated Research Company (Eden Prairie, MN). An overview of the instrument design is provided in Figure 1.

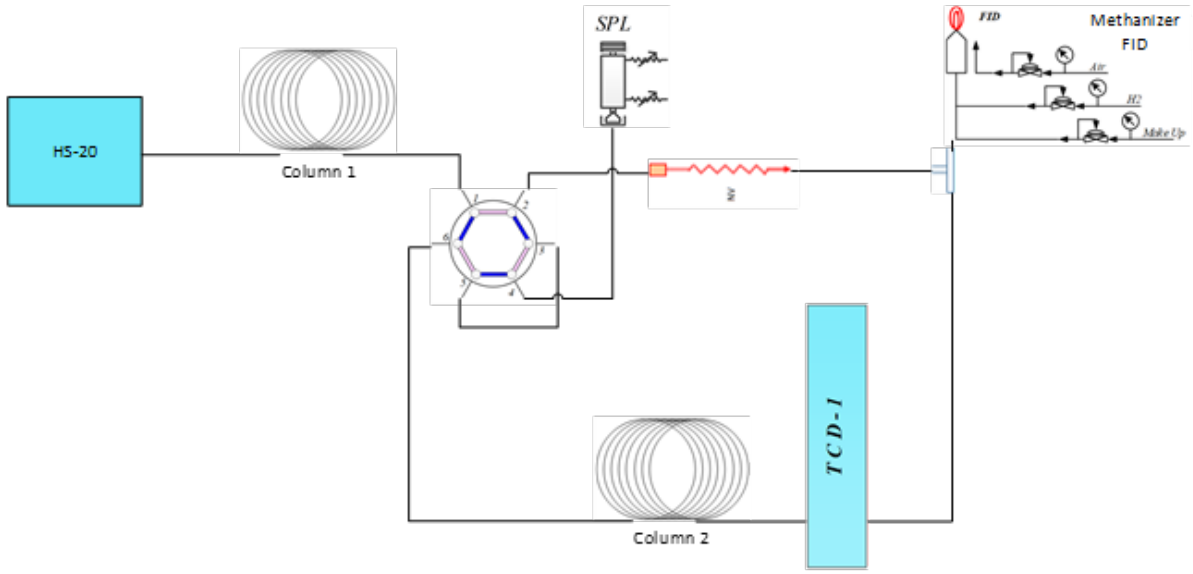

Figure 1: Overview of the system configuration for ASTM D3612 Method C analysis using the GC-2030 Gas Chromatograph

The use of capillary columns provides faster analysis compared to previously used column equivalents while also reducing complexity of the flowpath. The proprietary Jetanizer™ has been shown to be highly resistant to oxygen and other analytes that would damage a traditional methanizer catalyst and demonstrates a wide linear range from ppm to high percent levels with no additional hardware required. By incorporating a split/splitless inlet, the carrier gas flow can be controlled using constant linear velocity regardless of the valve position. This design allows for a more service-friendly unit with higher throughput over previous designs with only a single valve timing required and no peak trapping.

The HS-20 features a short transfer line that connects directly to the column, which reduces travel time between the column and the headspace autosampler, resulting in improved sensitivity, reliability, and peak shape. Given the 90-vial capacity and time-saving measures. such as the vial overlap function, which preheats the next vials to be analyzed, the HS-20 provides for high sample capacity and throughput.

■ Experimentation and Observation

Vials were prepared by 4 alternating cycles of vacuum and argon pressurization to purge ambient gases. To test repeatability of the unit, a 1 mL aliquot of a high transformer gas standard in each of the 22 mL headspace vials was prepared. To determine repeatability, 8 consecutive runs were processed, and the average results were used to generate the reported relative standard deviation and all other analytical figures of merit.

Table 1: Concentrations of Gas Standard Analyzed

ANALYTE	FINAL CONCENTRATION IN VIAL
HYDROGEN (H_2)	229 ppm
OXYGEN (O_2)	229 ppm
NITROGEN (N_2)	44037 ppm
METHANE (CH_4)	229 ppm
CARBON MONOXIDE (CO)	229 ppm
CARBON DIOXIDE (CO_2)	229 ppm
ETHYLENE (C_2H_4)	229 ppm
ACETYLENE (C_2H_2)	229 ppm
ETHANE (C_2H_6)	229 ppm
PROPYLENE (C_3H_6)	229 ppm
PROPANE (C_3H_8)	229 ppm
N-BUTANE (C_4H_{10})	229 ppm

Method Conditions

Method conditions were optimized for separation of the permanent gases, carbon dioxide, and hydrocarbon components. The permanent gases were cut to the molecular sieve column for separation. Hydrogen, oxygen, and nitrogen were detected by the TCD, whereas methane and carbon monoxide were detected by the Jetanizer™-FID.

Table 2: Method conditions and instrument parameters used for analysis

Headspace Parameters	
Parameter	Value
Model	HS-20
Injection mode	Loop
Loop size	1 mL
Vial temperature	70° C
Valve temperature	150° C
Transfer line temperature	150° C
Vial pressurization	75 kPa
Flow rate	7.5 mL/min (constant flow mode), Ar
Split Ratio	2 : 1
GC Parameters	
Parameter	Value
Model	GC-2030
Columns	SH-RT-Q-BOND 30 m x 0.53 mm x 20 µm (P/N 221-75765-30) SH-Msieve 5A PLOT 30 m x 0.53 mm x 50 µ m (P/N 221-75763-30)
Auxillary AFC flow rate	7.5 mL/min (constant flow mode), Ar
Valvebox temperature	75° C
Temperature ramp	35° C hold for 7.0 min, ramp to 125° C at 15° C/min, hold for 10 min
FID temperature	400° C
FID flows	24 mL/min Ar make-up 32 mL/min H_2 flow 250 mL/min air
FID Jet	Activated Research Company Jetanizer™
TCD temperature	100° C
TCD make-up flow	15 mL/min Ar
TCD reference flow	20 mL/min Ar

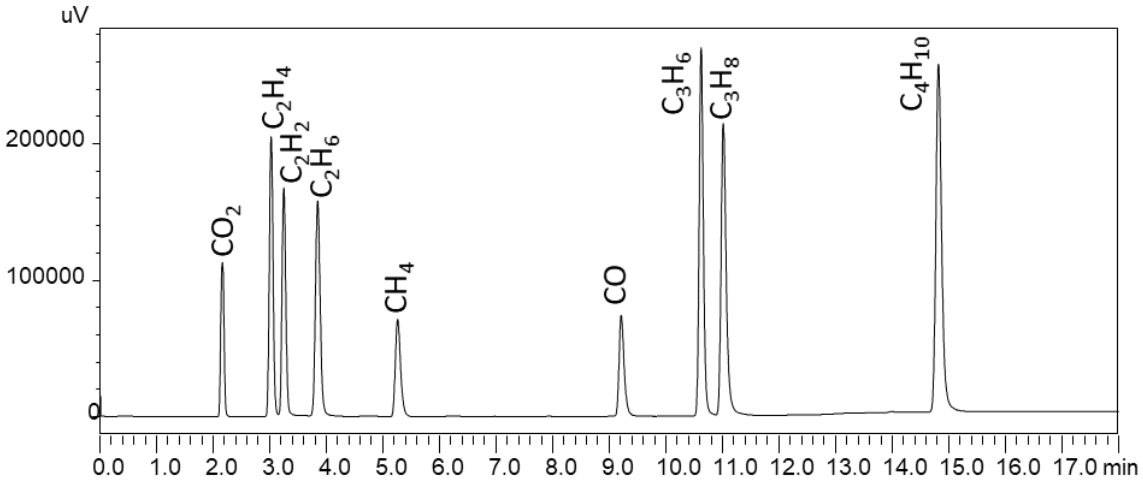

Figure 2: Representative chromatogram of from gas standard injections on FID

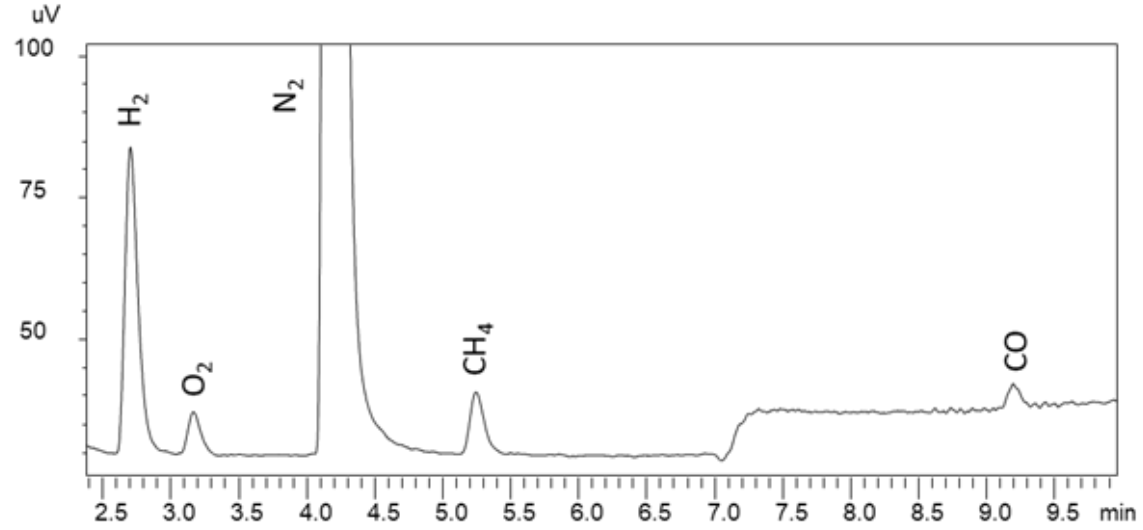

Figure 3: Representative chromatogram from gas standard injections on TCD

Table 3: Repeatability and detection limits from analysis of 8 injections of the gas standard

FID						
ANALYTE	Retention time (min)	Peak Area	RSD% (n=3)	S/N	Calculated LOQ (ppm)	Calculated LOD (ppm)
CO_2	2.16	465630.00	1.29	609.20	3.79	1.25
C_2H_4	3.02	944584.67	0.97	1095.47	2.11	0.69
C_2H_2	3.24	780167.33	0.54	888.18	2.60	0.85
C_2H_6	3.84	917500.67	0.89	839.80	2.75	0.91
CH_4	5.26	462087.33	1.31	381.53	6.04	1.99
CO	9.21	455124.00	0.90	395.26	5.84	1.93
C_3H_6	10.62	1390158.33	0.87	1431.83	1.61	0.53
C_3H_8	11.01	1344958.33	0.78	1136.28	2.03	0.67
C_4H_{10}	14.81	1801425.00	0.67	1345.67	1.72	0.57

TCD						
ANALYTE	Retention time (min)	Peak Area	RSD% (n=8)	S/N	Calculated LOQ (ppm)	Calculated LOD (ppm)
H_2	2.70	363.00	1.38	114.47	20.19	6.66
O_2	3.17	54.67	32.84	17.96	127.71	42.14
N_2	4.18	6067.33	0.92	1736.00	255.61	84.35
CH_4	5.25	77.67	2.68	23.03	100.30	33.10

The GC configuration used for this analysis was able to fully resolve all of the required analytes required by ASTM D3612 with high sensitivity. Analysis up to propane can be completed in under 12 minutes and butane can be completed in just 15 minutes. The Q-BOND column was able to fully speciate ethylene, acetylene and ethane, as well as propylene and propane for a rapid, full speciation of the typical hydrocarbon gases in transformer oil analyses.

Across three injections, all analytes on the FID showed a repeatability under 2% RSD. For carbon dioxide and carbon monoxide, two analytes that require the Jetanizer™-FID detection, a limit of quantitation below 6 ppm and a limit of detection of below 2 ppm were calculated. Methane was separated by the molecular sieve column and yielded a calculated limit of quantitation of just above 6 ppm and a limit of detection of below 2 ppm, which is thought to be the result of mild dilution from the TCD-FID series connection. All other analytes directly analyzed through the Q-BOND to the FID showed a calculated limit of quantitation below 3 ppm and a limit of detection as low as 0.6 ppm, respectively.

On the TCD, hydrogen and nitrogen demonstrated a repeatability below 2% RSD across three runs. Repeatability for oxygen and methane was reported high due to the levels being close to or below the calculated limits of detection. The FID is more sensitive for methane and is used for quantitation rather than the TCD. The HS-20 has the option of larger loop sizes and various other parameters that can be further optimized which means the unit could be modified to further push sensitivity for the permanent gas fraction of the sample.

Methanol Analysis

With an increase in use of more environmentally-friendly FAME-based oils in transformers, methanol is a potential degradation product that may be observed. To demonstrate that this configuration is compatible with methanol analysis, a vial was prepped with 1 mL of gas standard and 0.5 mL of methanol headspace.

As shown in the results, methanol is fully resolved from propane and *n*-butane with a retention time around 12.66 min. With a Q-BOND column, this analysis could be expanded to other light alcohols as they become of interest.

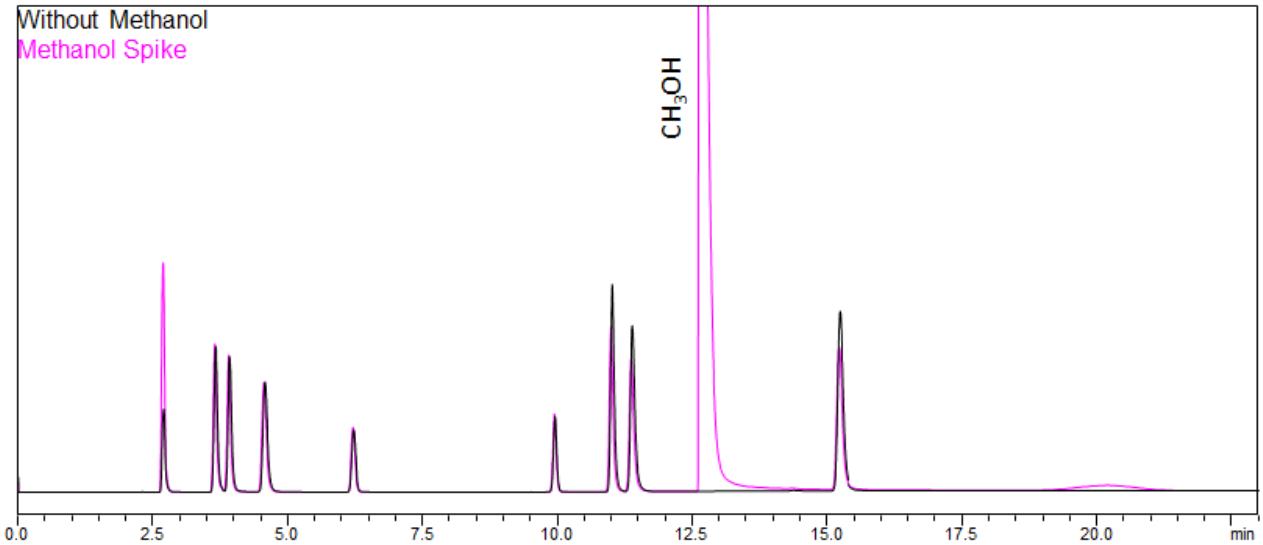

Figure 4: Overlay of FID TOGAS standard data with a standard vial spiked with methanol

■ Conclusion

The GC-2030 Nexis gas chromatograph can be configured to meet the specifications of ASTM D3612 Method C. The simplified system design makes maintenance and serviceability easier over previous designs. The use of Q-BOND and molecular sieve PLOT capillary columns greatly decrease the run time with n-butane completed in just over 15 minutes with full speciation of permanent gases, carbon dioxide, and hydrocarbon gases. For the FID analytes, calculated limits of detection were observed to be below 2 ppm for all analytes, including carbon monoxide and carbon dioxide. The calculated limit of detection on the TCD for hydrogen was around 6.7 ppm and higher concentrations for oxygen and nitrogen.

The HS-20 is an adaptable platform which can be modified to further increase sensitivity for permanent gases as needed. Between the vial capacity and time-saving features of the HS-20 with the faster GC method, higher throughput can be achieved. The system design can additionally be expanded to light alcohols as new, FAME-based oils are adopted more leading to a future-proof unit for dissolved gas analysis.

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