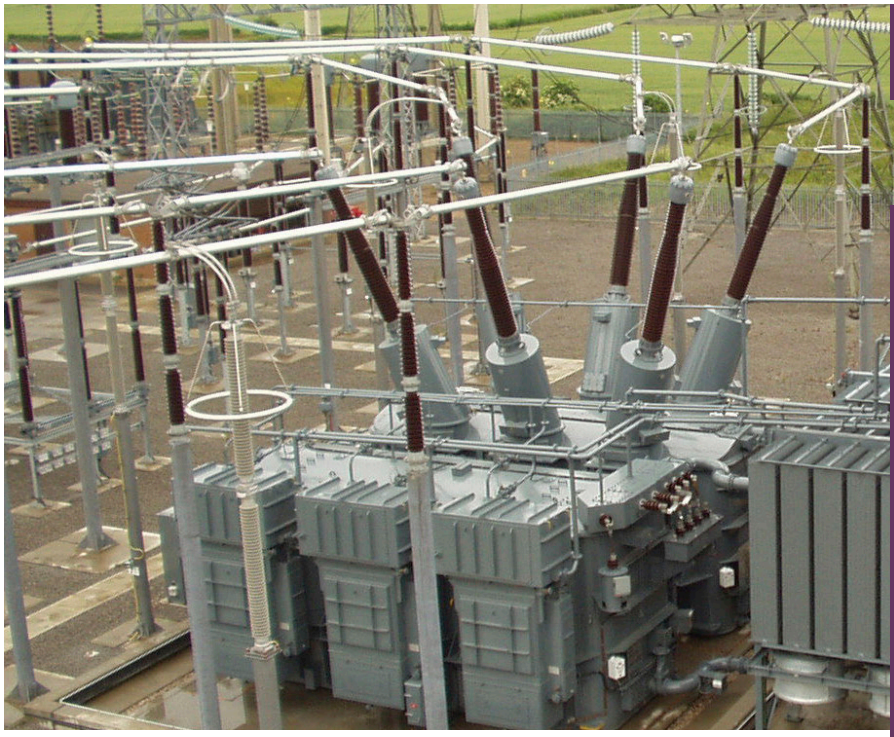

APPLICATION NOTE

Gas Chromatography

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Dissolved Gas Analysis in Transformer Oil Using Transformer Oil Gas Analyzer and TurboMatrix HS Sampler

Introduction

Nearly 90% of the world's population does not know life without the ubiquity of electricity. It is a luxury that gets taken for granted by most people every day. Panic often ensues when the electricity supply is interrupted, as witnessed in Manhattan during the July 13, 2019 blackout that left over 73,000 people without electricity for several hours. While no injuries or fatalities were reported in this case, history offers many accounts of chaos and safety risks following blackouts of this magnitude, especially in a major metropolitan city. To prevent such interruptions in electrical power, transformers must be properly maintained and monitored. An effective means of conducting routine monitoring towards this goal of reduced blackouts includes the analysis of oil insulting the transformers.

Acting as both an insulator and coolant, insulating oil in electrical transformers is expected to meet demanding chemical, electrical, and physical properties to ensure proper functioning of the transformer and its internal components. The American Society for Testing and Materials (ASTM) offers reference test methods as guidance for performing required routine analysis on the oil. As the insulating oil is subjected to high intensity thermal and electrical conditions, decomposition occurs over time and forms gases that dissolve into the oil. ASTM D3612 Method C is a standard test method using a headspace sampler to extract these dissolved gases for GC analysis. Dissolved gas analysis (DGA) is performed on the oil to identify the gases and their concentrations. Analyzing the changes in these concentrations over time is useful in determining preventative maintenance as high quantities of specific gases signify different problems that need to be addressed. A failing transformer can be identified and replaced without a power loss, or the potential of a serious explosion, increasing the lifespan of a transformer and saving time and money.

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Experimental

Instrumentation

PerkinElmer's Transformer Oil Gas Analyzer (TOGA) system, comprised of a Clarus® 590 GC coupled with a TurboMatrix™ Headspace sampler, offers the capabilities to perform ASTM D3612 Method C for the detection of H_2, O_2, N_2, CH_4 (methane), CO, CO_2, C_2H_2 (acetylene), C_2H_4(ethylene), C_2H_6(ethane), C_3H_6 (propylene) and C_3H_8(propane). Figure 2 illustrates the main features of the TOGA analyzer, which include a packed column injection port, a purged housing multifunction gas sampling valve plumbed with a late backflush to vent, a six-port valve plumbed for column bypass, an Elite® Mole Sieve 5A 30 m X 0.53 mm (Column 2 p/n NR210040), and an Elite-Q PLOT 50 m X 0.53 mm (Column 1 p/n N6107408). The late back flush configuration for the first valve ensures that heavier components are back flushed to vent, and not allowed to pass through and poison the molecular sieve from column 1.

Figure 1. Model 4087 TOGA.

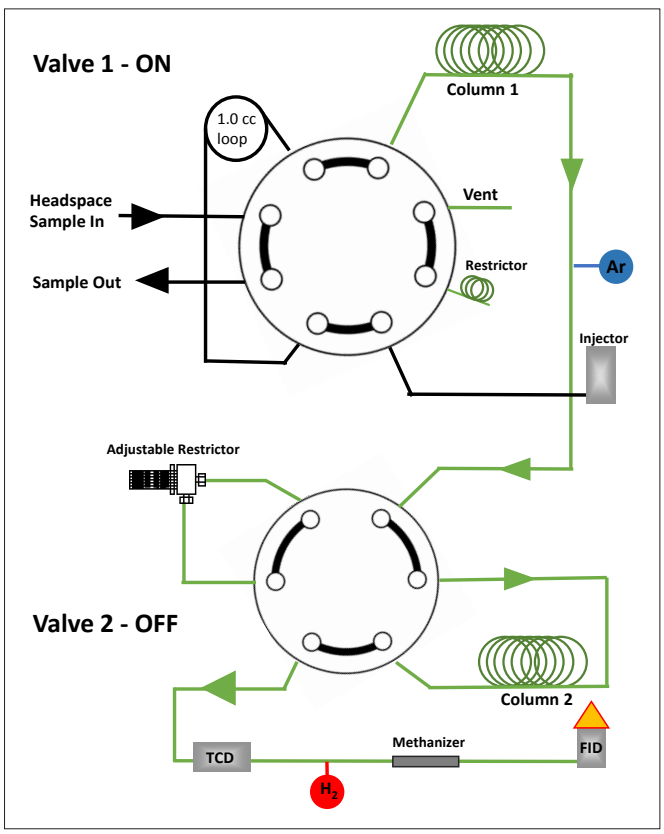

Figure 2. Valves and column set for Transformer Oil Gas Analyzer.

Analysis

Two 18G1 needles were inserted into the septum of a sealed 20 mL headspace vial; one needle attached to an Argon gas line supplying a constant flow of Argon, and the other served as an outlet for the gas. The vial was purged for two minutes. The inlet needle was then removed, followed by the outlet needle, to allow pressure to build in the vial. The oil calibration standards were received in glass syringes equipped with a three-way plastic stopcock. Once it was ensured that no bubbles were present in the sample syringe, a clean 18G1 needle was secured to the stopcock and inserted through a new point in the septum, along with an outlet needle. Once roughly 8 mL of oil were in the vial, the outlet needle was removed. When the vial was filled with 10 mL of oil standard, the stopcock was returned to the closed position allowing the vial to equilibrate to atmospheric pressure, and then the needle removed.

The headspace and GC analytical parameters are presented in Table 1. The sample was heated in the headspace vial oven, allowing the dissolved gases in the oil to partition into the headspace of the sealed vial. Once equilibrium was reached, the needle injected the gas into a sample loop in the GC. The sample filled the loop, and then flowed into the analytical columns. H_2, O_2, N_2, CH_4 and CO eluted from the Elite-Q PLOT where they are captured by switching the 6-port valve (valve 2). While valve 2 is in bypass position, CO_2, C_2H_2, C_2H_4, and C_2H_6 passed through the non-destructive thermal conductivity detector (TCD), allowing them to be detected by the Flame Ionization Detector (FID) at sub-ppm levels. The FID is selective for hydrocarbons, therefore, converting CO and CO_2 to CH_4 in the methanizer by catalytic hydrogenation makes sub-part per million (ppm) detection limits possible for these gases. The timing for valve 2 and the temperature programming allow the components in the molecular sieve to elute between the elution of ethane and propylene peaks. Eluting H_2, O_2, N_2, CH_4 and CO between the ethane and propylene peaks allows for the collection of a single chromatogram for the TCD and FID channels for easy and convenient data reporting. Once all analytes of interest for D3612 successfully eluted, the system backflushes the heavier compounds out to vent.

Table 1. Headspace and GC parameters.

Headspace Parameters	
Sample Pressure	3.5 psi
Temperature	80 °C
Pressurizing Time	1.00 min
Inject Time	1.00 min
Needle Withdrawal Time	0.00 min
Thermostat Time	30.0 min

GC Parameters	
Injector Temperatures	Inj A 100 °C Methanizer (Inj B setting) 400 °C
Detector Temperatures	FID 250 °C, TCD 200 °C
Oven Program	Initial temp: 40 °C Initial hold: 11.00 min Ramp 12.0 0/min to 150

Column Set	
Column 1	Elite-Q PLOT 50 m x 0.53 mm
Column 2	Mole Sieve 5A 30 m x 0.53 mm
Column Flow	Aux 3 27 psig; Aux 4 19 psig
Timed Events	V1 On at 0.50; V2 On at 3.85 min; V2 Off at 8.00; OUT1 set to DetB at 8.01 min; OUT1 DetA at 11.00 min; V2 On at 16.00 min

Results and Calibration

A 5-point calibration curve was performed with concentrations of 5, 10, 50, 100, 500 and 1000 ppm. Linear regression for all nine components were greater than 0.999. A single calibration standard at 100 ppm was used for oxygen and nitrogen.

Table 2. Linear regression for components.

Component	R-squared
Carbon Dioxide	0.999464
Ethylene	0.999859
Acetylene	0.999745
Ethane	0.999986
Hydrogen	0.999874
Methane	0.999230
Carbon Monoxide	0.999331
Propylene	0.999892
Propane	0.999935

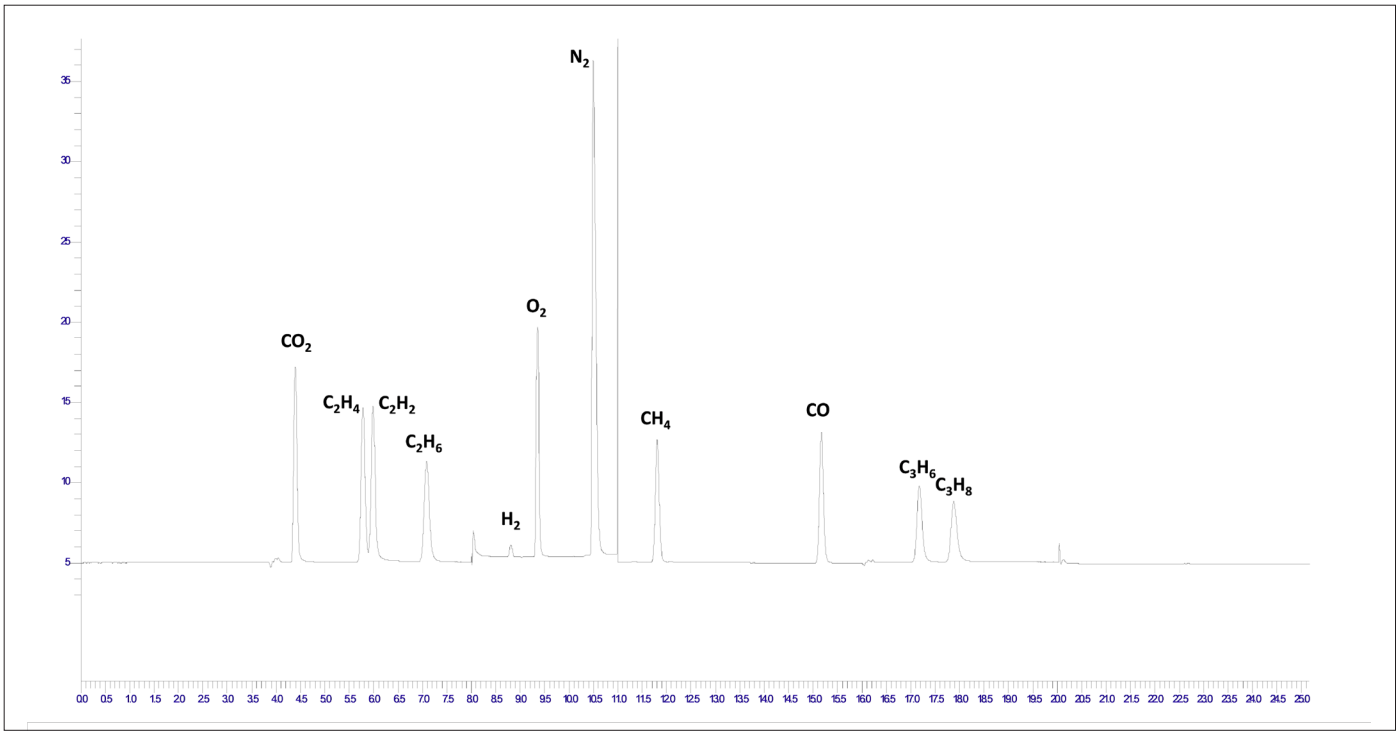

Figure 3. True North 100 ppm Transformer oil.

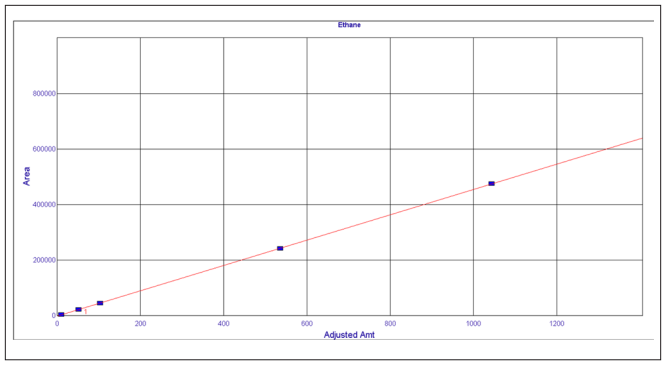

Figure 4. Ethane five point calibration plot.

The detection requirements for ASTM D3612 end with C3 components, however, by increasing the oven temperature to 200 °C and holding it for 10 minutes, this column set can successfully detect out to hexanes.

Conclusion

In addition to heart cutting techniques to save valuable time, the TurboMatrix™ Headspace sampler offers overlapping thermostatting, on HS40 and HS110 models, maximizing theoretical productivity. The column set installed in the PerkinElmer Clarus 590 GC offers excellent peak detection into the hexane range with minimal contamination to the column. PerkinElmer's transformer oil gas analyzer system excels in terms of throughput, precision, and endurance making it a top choice for dissolved gas analysis of insulating oil, ensuring the functionality and longevity of electrical transformers.

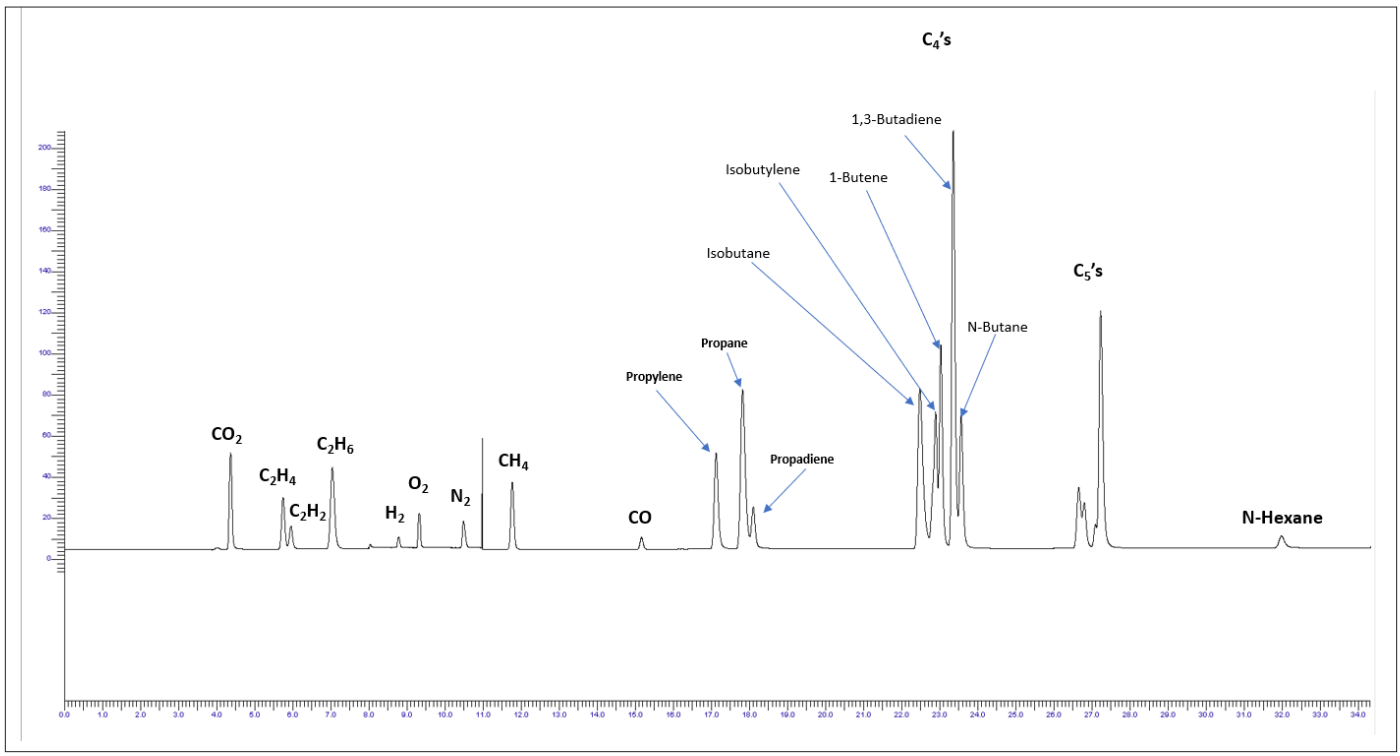

Figure 5. Refinery Gas Mixture range 46-1673 ppm in Argon with extended oven program.

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