

Headspace-GC analysis of dissolved gases in transformer oil according to ASTM D-3612C

Authors: Wenmin Liu¹, Daniela Cavagnino²,
Manuela Bergna²

¹Thermo Fisher Scientific, Shanghai, CN

²Thermo Fisher Scientific, Milan, IT

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Goal

The goal of this work is to demonstrate the performance of the Thermo Scientific™ TriPlus™ 500 Headspace Autosampler coupled to the Thermo Scientific™ TRACE™ 1310 Transformer Oil Gas Analyzer (TOGA) for the determination of the dissolved gases in transformer oil samples, according to the method ASTM D-3612C.¹

Introduction

Uninterrupted production and distribution of electricity relies on proper functioning of electrical transformers. It implies rigorous maintenance protocols and continuous monitoring, particularly for the mineral oils used to maintain the correct insulation of electrical transformers, preventing possible faults and interruption of the electrical power supply. During operation, the insulating oil is subjected to thermal degradation processes responsible for the formation of gaseous by-products that dissolve into the oil, changing its chemical and physical properties, reducing the



expected insulation characteristics, and possibly leading to fault conditions of the transformer.

Dissolved gas analysis (DGA) is one of the most widely used diagnostic tools for detecting and evaluating faults in electrical equipment. The transformer gases formed are hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2) and are found along with light hydrocarbons, such as methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propylene (C_3H_6), and propane (C_3H_8). The identification and quantification of these gases provide an early indication of problems developing in the electrical equipment, allowing a preventive maintenance program.

HS-GC system for transformer oil gas analysis in compliance with ASTM guidelines

The American Society for Testing and Materials (ASTM) offers reference test methods as guidance for performing required routine analysis on transformer oil. To perform this analysis, a sample of the oil is taken from the unit and the dissolved gases are extracted, separated, identified, and quantified. This method is directly applied to oil samples and is applicable to all types of transformer units, detecting all the individual components.

The ASTM methods, including D-3613, D-2945, and D-3612, describe in detail the sampling, gas extraction, and analytical procedures. ASTM D-3612 offers three methods for the DGA analysis¹:

- Method A: Vacuum extraction. Dissolved gases from the transformer oil are extracted by vacuum using a glass apparatus and then analyzed by a GC system.
- Method B: Stripper column method. In this method, gases are extracted by using a high surface area bead stripper column, and the gases from the column are analyzed on a GC system.
- Method C: Head space sampling (HSS) method. In this method, the oil sample is kept in a headspace sampling vial, and the headspace is purged with argon gas, which in turn is analyzed on a GC system.

The procedure and the results shown in this application note are compliant with ASTM D-3612 Method C, requiring a static headspace autosampler based on “Valve and Loop” sample transfer into the GC.

Experimental

Standard sample preparation

Gaseous standard samples were prepared by purging 20 mL headspace vials with a standard mix in argon bulk gas.¹ The composition of the standard gas mixture is reported in Table 1.

Dissolved gas in oil standards were prepared from a certified True North oil standard (Morgan Schaffer, Montreal, Quebec, Canada), by transferring 15 mL of oil into a 20 mL vial, following the ASTM guidelines. The certified composition of the oil sample is reported in Table 2.

Table 1. Standard gas mixture composition

Standard gas mixture – Argon as bulk gas			
Component	Conc. (ppm v/v)	Component	Conc. (ppm v/v)
H ₂	102.3	C ₂ H ₄	100.0
O ₂	10,000	C ₂ H ₆	100.7
N ₂	30,100	C ₂ H ₂	100.0
CH ₄	98.5	C ₃ H ₆	100.3
CO	99.7	C ₃ H ₈	99.7
CO ₂	150.3	C ₄ H ₁₀	100.6

Table 2. True North oil standard certified concentration

Component	Certified conc. (ppm v/v ±5%)	Component	Certified conc. (ppm v/v ±5%)
H ₂	103	C ₂ H ₄	102
O ₂	15,600	C ₂ H ₆	103
N ₂	55,700	C ₂ H ₂	103
CH ₄	102	C ₃ H ₆	102
CO	102	C ₃ H ₈	104
CO ₂	132	C ₄ H ₁₀	102

TRACE 1310 TOGA analyzer

The TRACE 1310 TOGA analyzer connected to the TriPlus 500 Headspace Autosampler is presented in this note (Figure 1), in compliance with ASTM D-3612 Method C.

The TRACE 1310 TOGA analyzer is configured with two 6-port valves and a combination of molecular sieve and porous polymer columns for the separation of all the compounds, which are detected with the in-series TCD-methanizer-FID detection system (Figure 2).



Figure 1. TRACE 1310 TOGA Analyzer connected to the TriPlus 500 HS. The HS transfer line connection to the GC inlet allows manual injection with a gas-tight syringe.

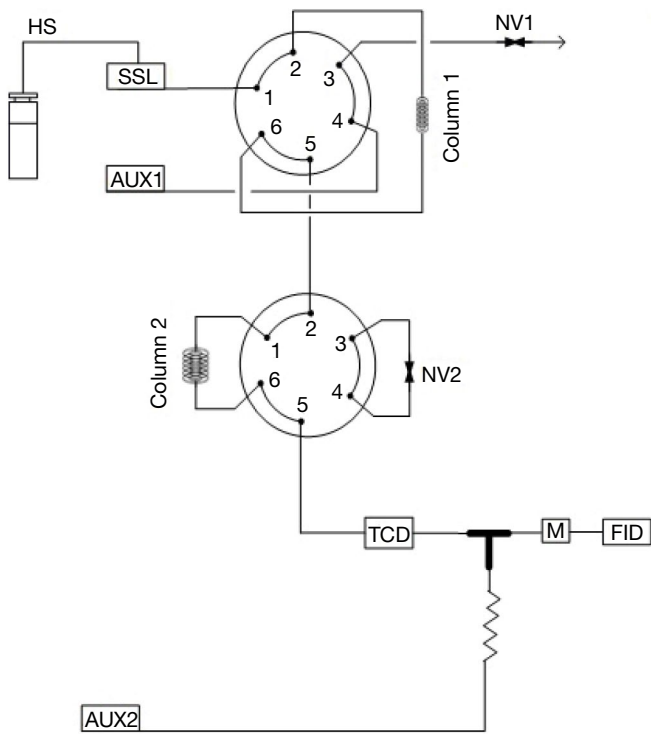


Figure 2. TRACE 1310 TOGA Analyzer configuration

The HS autosampler injects the sample headspace onto the first column to separate the fixed gases from CO₂ and light hydrocarbons. The fixed gases are isolated onto the MoSieve column, leaving the CO₂ and light HCs to reach the detector. Fixed gases are detected by the thermal conductivity detector (TCD) using argon as the carrier gas for the best response of hydrogen. Light hydrocarbons and carbon oxides are detected at low ppm by the methanizer-FID detection system. In the presented method setup, hydrocarbons C₄ and greater are backflushed and not detected. As shown in the inset of Figure 1, the connection of the TriPlus 500 HS to the GC inlet allows direct injection with a gas-tight syringe offering higher flexibility in the operation.

Up to 120 sample vials can be analyzed with the TriPlus 500 HS, with simultaneous incubation of up to 12 vials. In this method, the oil samples were equilibrated at 70 °C for 30 min. Simultaneous vial incubation permits the overall cycle time optimization, injecting the equilibrated sample as soon as the GC is ready for the next run.

The operative conditions used for the HS and the GC systems are listed in Table 3.

Table 3. Operative conditions

TRACE 1310 TOGA parameters	
Column 1	3 m × 1/8" Porous polymer 80/100 mesh
Column 2	2 m × 1/8" MolSieve 5A 80/100 mesh
Carrier gas	Argon
Carrier gas flow rate	26 mL/min - constant flow
GC oven temperature	60 °C (6 min), 10 °C/min, 100 °C (5 min)
Auxiliary oven temperature	115 °C
Inlet temperature	100 °C
Injection mode / Split flow	Split, 5 mL/min
TCD temperature	200 °C
TCD filament temperature	300 °C
Methanizer temperature	360 °C
Methanizer H ₂ flow rate	15 mL/min
FID temperature	300 °C
FID air flow	350 mL/min
FID H ₂ flow	15 mL/min

TriPlus 500 HS parameters	
Sample vial	20 mL
Sample volume	15 mL
Vial incubation temperature	70 °C
Vial incubation time	30 min (for oil samples only)
Vial pressure	100 kPa
Vial pressure equilibration time	0.25 min
Loop/Sample path temperature	150 °C
Loop size	2 mL
Loop pressure	25 kPa
Loop equilibration time	0.25 min
Injection time	0.9 min
Transfer line temperature	150 °C
Auxiliary carrier mode	Constant flow
Transfer flow	25 mL/min

The system is fully controlled by the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS), making the analytical workflow, data analysis, and reporting an extremely simple process.

Results and discussion

Chromatography

The valve switching times were set to allow the elution of the fixed gases and light hydrocarbons including C3, while C4 and heavier hydrocarbons were backflushed and not detected. The complete separation was obtained in less than 15 min. Figure 3 reports an example of separation showing the chromatograms obtained from the TCD and the methanizer-FID detectors.

Repeatability and linearity

The repeatability of the response was evaluated with the injection of six standard gas samples, prepared as described. An average area counts RSD of 0.72% indicates a very good precision of the sample transfer and compounds detection (Table 4).

To check the linearity of the response, the standard gas sample was diluted up to 10 times with argon. A custom diluter was used for this purpose: the diluent gas was controlled by one channel of the auxiliary module installed on the GC, and the standard gas flow was restricted by using a SS restrictor (1/16" o.d., 0.12 mm i.d., 2.7 m L1) installed in the GC aux oven. The diluent and the standard gas were mixed in a 1/16" tee, and the mixed gas flow guided into the sample vial. The flow of the diluent Ar and the standard gas were measured by a flow meter.

The linearity of the response for each compound is reported over one order of magnitude in Figure 4, with a correlation coefficient $R^2 > 0.999$.

Limit of detection

The signal-to-noise ratio (S/N) of each component calculated based on the 10× diluted standard gas sample (Table 5) was used to evaluate the instrument detection limit, considering a S/N=3 (Table 6).

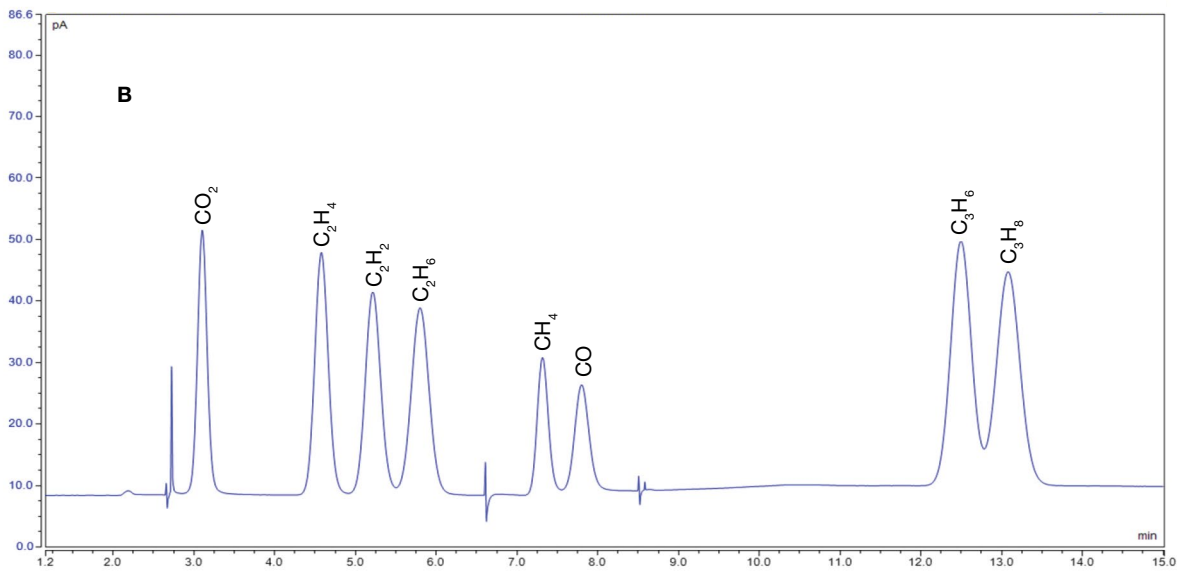
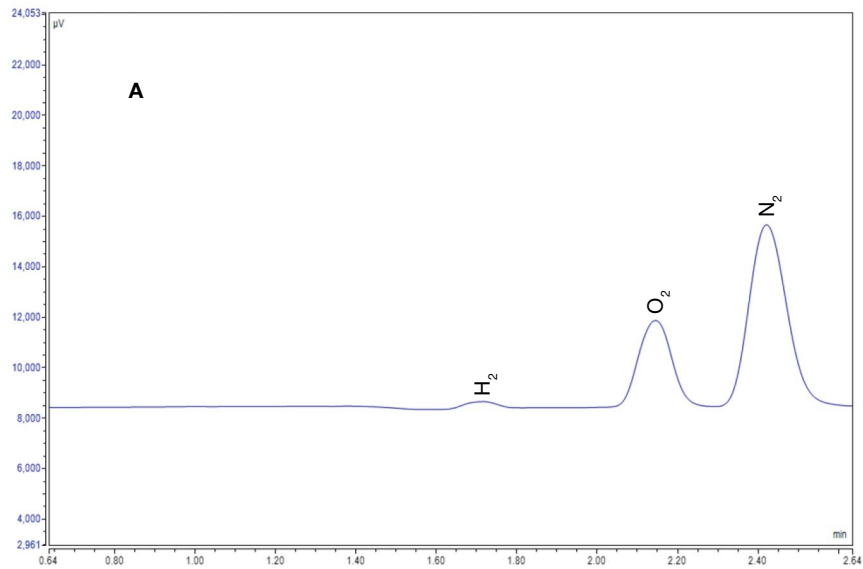


Figure 3. Gas chromatograms for fixed gas from TCD detector (A) and for light HCs and carbon oxides from the methanizer-FID (B)

Table 4. Area counts repeatability for standard gas samples

Injection #	H ₂	O ₂	N ₂	CO ₂	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	CH ₄	CO	C ₃ H ₆	C ₃ H ₈
1	19.61	19.61	602.21	22.39	28.53	28.15	30.61	13.70	13.24	44.29	46.20
2	19.76	19.76	611.08	22.56	28.50	28.13	30.57	13.70	13.28	44.22	46.20
3	19.88	19.88	605.69	22.64	28.58	28.20	30.65	13.74	13.37	44.23	46.27
4	19.83	19.83	624.71	22.89	28.28	27.90	30.35	13.61	13.30	43.87	45.76
5	19.68	19.68	614.86	23.00	28.48	28.09	30.53	13.70	13.42	44.16	45.96
6	19.91	19.91	601.12	22.59	28.41	28.00	30.45	13.65	13.42	44.11	45.75
RSD (n=6)	0.59%	2.00%	1.47%	0.99%	0.37%	0.39%	0.36%	0.34%	0.59%	0.34%	0.51%

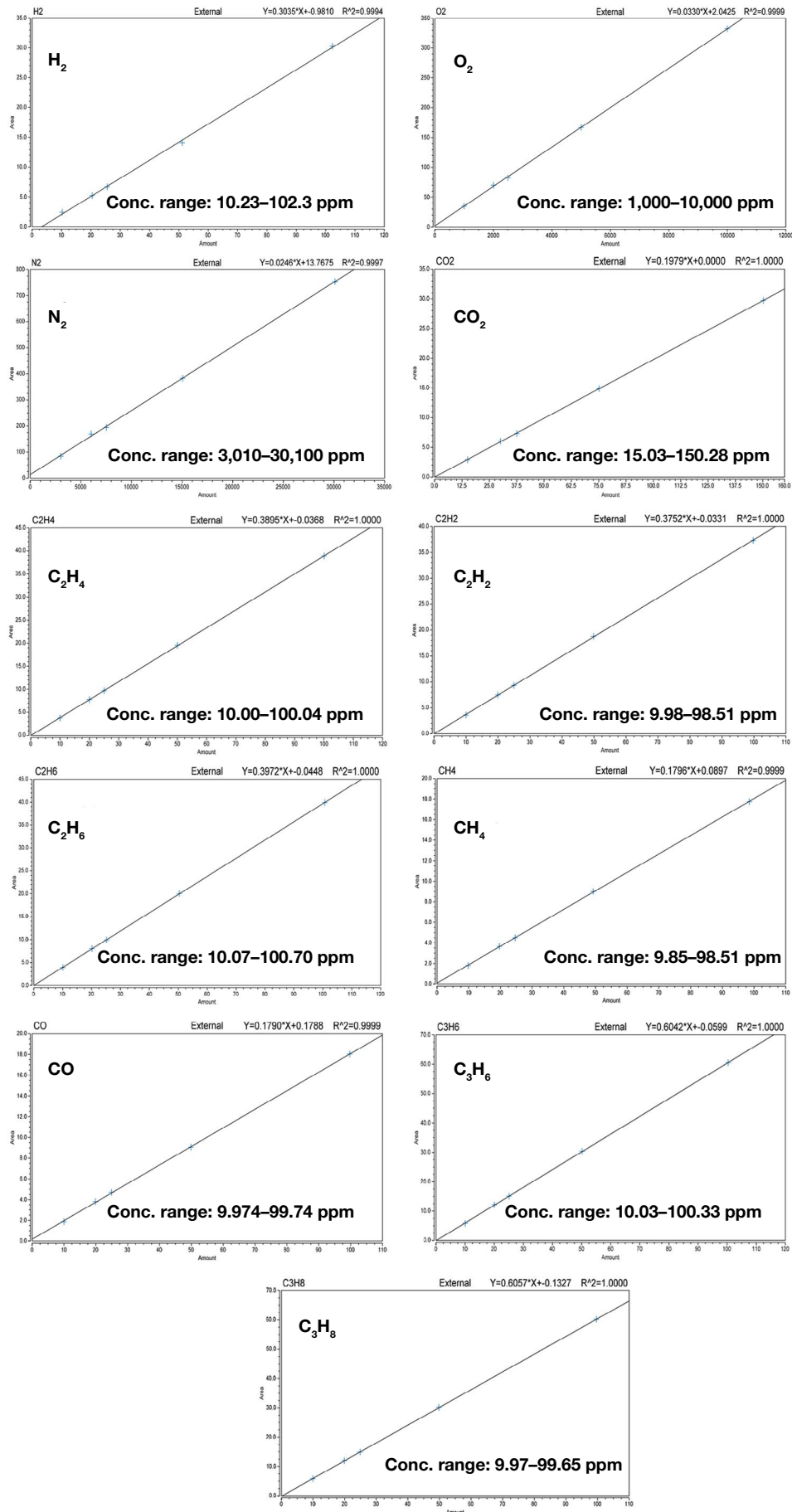


Figure 4. Linearity plots from standard gas samples

Table 5. S/N ratio calculated based on the gas standard sample

	H ₂	O ₂	N ₂	CO ₂	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	CH ₄	CO	C ₃ H ₆	C ₃ H ₈
Sample conc. (ppm, v/v)	10.2	1,000.0	3,010.0	15.0	10.0	10.0	10.1	9.9	10.0	10.0	10.0
Peak height (µV, pA)	23.2	341.2	686.4	17.9	13.5	11.4	11.4	8.9	6.7	13.8	12.8
Noise time range (min)	0.5–1.5										
Noise	4.87 µV				0.024 pA						
S/N	5	70	141	745	561	475	475	370	279	575	534

The LODs in oil samples were calculated from the gas standard LOD considering the partition coefficient K of each compounds at 70 °C¹ and applying the below equation:

$$C_g = \frac{C_o}{(K + \beta)}$$

Where:

C_G = Concentration in the gas phase at the equilibrium

C_O = Initial concentration in the oil (before equilibrium)

K = Partition coefficient

β = Phase ratio (ratio between the sample volume and the headspace volume in the vial). In this case the phase ratio is 0.333.

Considering the C_G at the instrument detection limit, the minimum detectable concentration in the oil was calculated (Table 6).

The certified oil sample was analyzed in the same conditions to compare the extrapolated LOD in oil matrix, considering a minimum S/N=3 (Table 7).

Table 6. LOD in oil sample based on the partition coefficient K at 70 °C

Components	K at 70 °C	Instrument LOD (ppm v/v)	Calculated LOD in oil (ppm v/v)
H ₂	0.074	6.1	2.5
O ₂	0.17	42.9	21.5
N ₂	0.11	64.0	28.4
CO ₂	0.93	0.06	0.08
C ₂ H ₄	1.47	0.05	0.10
C ₂ H ₂	0.93	0.06	0.08
C ₂ H ₆	2.09	0.06	0.16
CH ₄	0.44	0.08	0.06
CO	0.12	0.11	0.05
C ₃ H ₆	5.04	0.05	0.28
C ₃ H ₈	5.37	0.06	0.32

The comparison of the LOD in oil samples, calculated with the partition coefficients from a gas standard and extrapolated from the analysis of a certified oil sample, show a good agreement with the exception of H₂, O₂, N₂, and CO for which the values extrapolated from the certified oil sample are significantly higher (Table 8).

Table 7. Extrapolated LOD (S/N = 3) from the certified oil sample

	H ₂	O ₂	N ₂	CO ₂	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	CH ₄	CO	C ₃ H ₆	C ₃ H ₈
Certified oil nominal conc. (ppm, v/v)	103	15600	55700	132	102	103	103	102	102	102	102
Peak height (µV, pA)	378.3	5393.4	11983.7	126.1	79.7	78.1	51.1	78.0	65.5	31.7	27.8
Noise time range (min)	0.5–1.5										
Noise	5.40 µV				0.023 pA						
S/N	70	999	2219	5482	3465	3397	2223	3389	2849	1380	1209
Extrapolated LOD (S/N=3)	4.4	46.8	75.3	0.07	0.09	0.09	0.14	0.09	0.11	0.22	0.25

This can be due to the labile stability of the oil samples, which may have suffered of loss of components characterized by the lowest partition coefficient.

The LODs extrapolated from the data reported in this application note show a very good recovery and sensitivity considering the use of packed columns and a 2 mL sampling loop. The use of packed columns is preferred in many laboratories to ensure high ruggedness, while still providing very good sensitivity matching the purpose of routine testing of transformer oil.

Oil sample analysis

Transformer oil samples were obtained from a local testing laboratory and analyzed under the conditions listed in Table 2. The preparation of the vials required attention to avoid air contamination of the oil. Thus, the vials were purged in advance with argon and filled with the oil samples. However, a residual air contamination is still visible from the analysis. Figure 5 shows an example of the chromatograms obtained from the TCD and methanizer-FID detectors, while Table 9 reports the quantitative results calculated against the standard gas calibration corrected by the partition coefficient of each compound.

Table 8. Calculated LOD in oil samples

Component	Ret time (min)	LOD in oil* (ppm)	LOD in oil** (ppm)	Detected on
Hydrogen (H ₂)	1.72	2.5	4.4	TCD
Oxygen (O ₂)	2.14	21.5	46.8	TCD
Nitrogen (N ₂)	2.42	28.4	75.3	TCD
Carbon dioxide (CO ₂)	3.09	0.08	0.07	Methanizer-FID
Ethylene (C ₂ H ₄)	4.50	0.10	0.09	FID
Acetylene (C ₂ H ₂)	5.24	0.08	0.09	FID
Ethane (C ₂ H ₆)	5.76	0.16	0.14	FID
Methane (CH ₄)	7.30	0.06	0.09	FID
Carbon monoxide (CO)	7.78	0.05	0.11	Methanizer-FID
Propylene (C ₃ H ₆)	12.50	0.28	0.22	FID
Propane (C ₃ H ₈)	13.10	0.32	0.25	FID

(*) Calculated from the gas standard using the partition coefficient K, considering S/N =3

(**) Extrapolated from the certified oil sample analysis, considering a S/N =3

Table 9. Transformer oil sample quantitative results from the Chromeleon CDS test report page

Integration Results					
Peak Name	Retention Time min	Area μV*min	Height μV	Amount in gas phase ppm	Amount in Oil ppm
H2	n.a.	n.a.	n.a.	n.a.	#VALUE!
O2	2.140	495.526	5119.76	14946.40	7518.04
N2	2.417	893.269	8189.09	35776.71	15849.08
CO2	3.093	45.971	330.78	232.33	314.35
C2H4	4.487	0.013	0.13	0.13	0.23
C2H2	n.a.	n.a.	n.a.	n.a.	#VALUE!
C2H6	n.a.	n.a.	n.a.	n.a.	#VALUE!
CH4	7.318	0.131	0.56	0.23	0.18
CO	7.788	0.268	0.65	0.50	0.22
C3H6	n.a.	n.a.	n.a.	n.a.	#VALUE!
C3H8	13.043	0.093	0.29	0.37	2.13

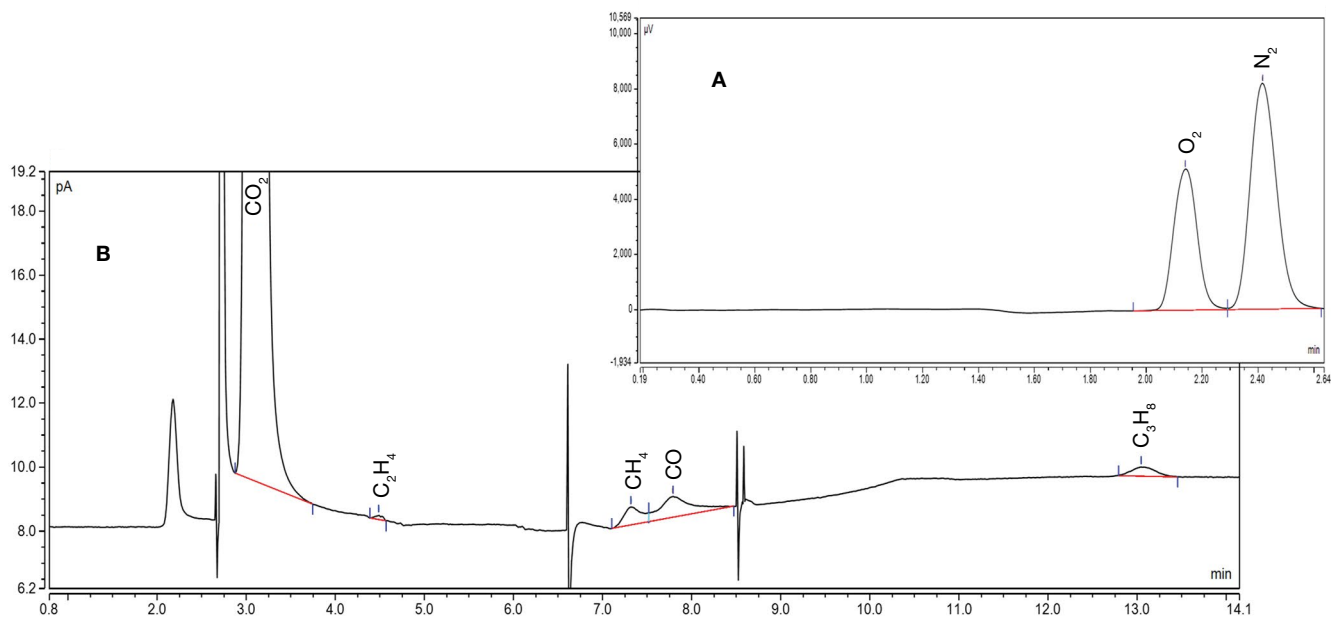


Figure 5. Gas detection from a transformer oil sample. TCD detection (A) and methanizer-FID detection (B)

Conclusions

The TRACE 1310 TOGA analyzer connected to the TriPlus 500 HS autosampler offers a reliable and easy-to-use system capable of providing sensitive and reproducible data for daily monitoring of proper electrical power supply operations, meeting the requirements for Headspace TOGA following the Method D3612 Part C.

The benefits of applying ASTM D-3612 Method C with the use of a headspace system for gas extraction from transformer oil can be summarized as follows:

- Easy to use, reliable, and automated headspace sampling is ideal for high-throughput testing demand.
- There is no use of fragile glassware and highly toxic mercury, as required by the alternative ASTM methods for extraction.

- The system offers the flexibility of using the headspace sampler or manual injection without configuration changes.
- The TriPlus 500 HS ensures high inertness of the sample path during extraction and injection leading to excellent precision in sample transfer.
- The TRACE 1310 TOGA analyzer configuration using packed columns offers the ruggedness and the simplicity required for day-by-day operations, through a turn-key system.
- Instrument control, data acquisition, and reporting are fully automated through the dedicated functionalities of Chromeleon software, simplifying the entire workflow.

Reference

1. ASTM D-3612 – 02 (2017) - Standard Test Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography <https://www.astm.org/Standards/D3612.htm>

Find out more at [thermofisher.com](https://www.thermofisher.com)