Improved Transformer Oil Gas Analysis (TOGAS) by GC Headspace

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Description

Hydrocarbon-based oils used as insulating fluids in transformers can partially decompose and produce gases such as hydrogen, methane, carbon monoxide, carbon dioxide and C2-C4 species which are all soluble in the oil. Measurement of the concentrations of these gases as well as the concentration of oxygen and nitrogen in the transformer oil can provide useful information about the existence of faults in the transformer, and indicate when preventative maintenance should be performed. Basic methods for this analysis are described in ASTM-D3612 Method A,B and C.

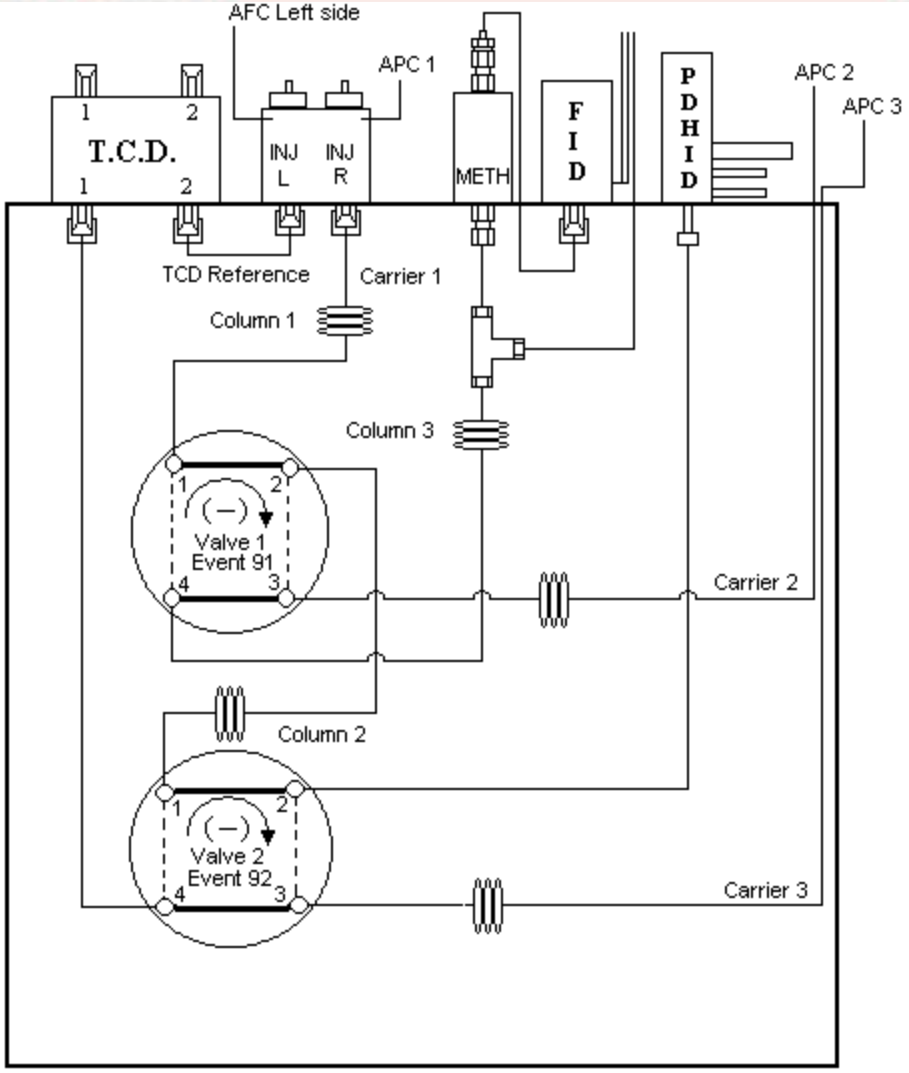
A Gas Chromatograph configured with a headspace autosampler, two automated valves and three detectors will be described. Improvements include detection limits for hydrogen, analysis of hydrocarbons up to n-C4 within 20 minutes, and automated software processing of the data to account for the actual temperature and atmospheric pressure.

In this poster we will examine the methodology from sample prep to GC analysis and data processing.

The System:

- GC with TCD, FID and PDHID
- Tekmar HT-3 Static Headspace Sampler
- Two Valco 1/8th inch 4 port electrically actuated valves
- 5 packed columns
- Data station and software

Plumbing Diagram



Carrier 1: Helium 300kPa

Carrier 2: Helium 301kPa

Carrier 3: Helium 310kPa

Column 1= 2m X 1/8 Hayesep Q 80/100

Column 2= 2.5m X 1/8 MS 5A 60/80

Column 3= 2.5M Hayesep T 80/100

Column 4= 2M restrictor

Column 5= 2M restrictor

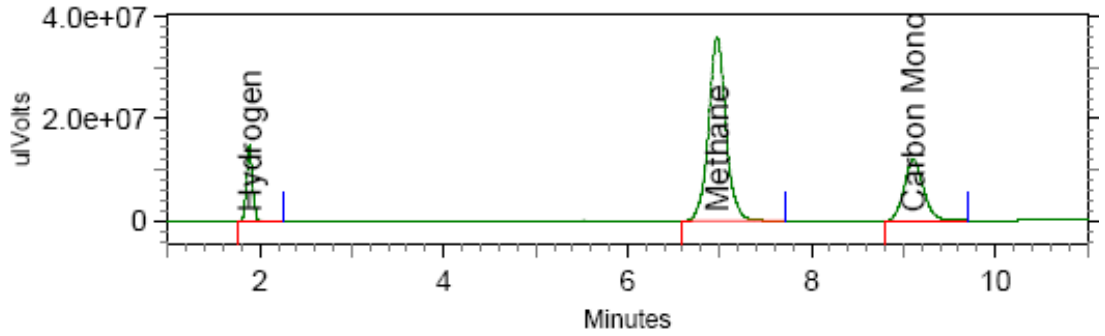
Vial Prep for Gas Standards

- Cap 20ml vial and insert two needles (18G luer lock)
- Connect Argon to one of the needles and purge 2 l/min for 45 seconds
- Connect Helium to the top needle and purge for 2 minutes @ 100 ml/min flow from top to bottom
- Vial is ready for gas standard or oil filling by flowing the standard for 10 minutes at 50 ml/min

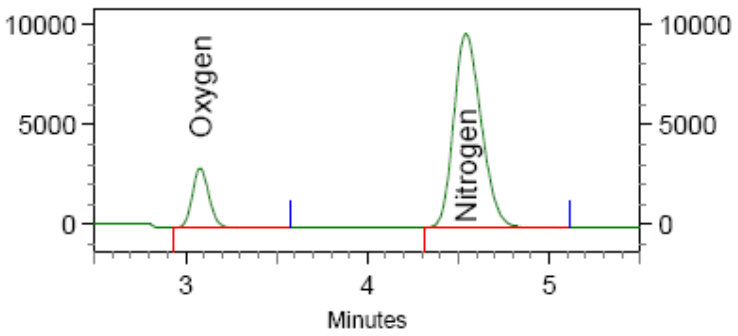
GC Analytical Conditions

	Oven			Time Program		
Rate	**Final Temp**	**Hold time**		**Time**	**Event**	
	75C	4		1.9	91	
10C	165C	8		3.1	92	
				5.9	-92	
	Temp			13.2	-91	
Injection Port	125C			**Gas**	**Press.**	**Flow**
FID	180C		**Carrier 1**	Helium	300kPa	30ml/min
TCD	180C		**Carrier 2**	Helium	301kPa	30ml/min
PDHID	100C		**Carrier 3**	Helium	310kPa	30ml/min

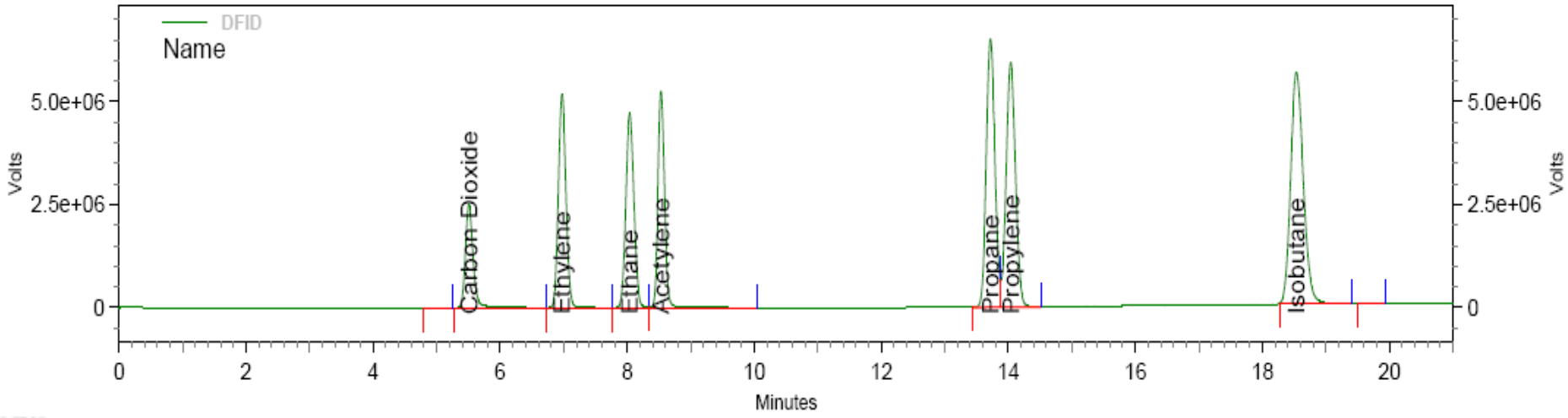
Gas Standard Chromatograms



PDHID



TCD



FID

Gas Standard Precision

- Gas Standards were prepared using the procedure outlined above
- Three concentrations were made:
  - 50ppm
  - 500ppm
  - 5000ppm
- Five vials of each concentration were loaded on the HT-3 and analyzed; results are shown in the table

Gas Standard Precision

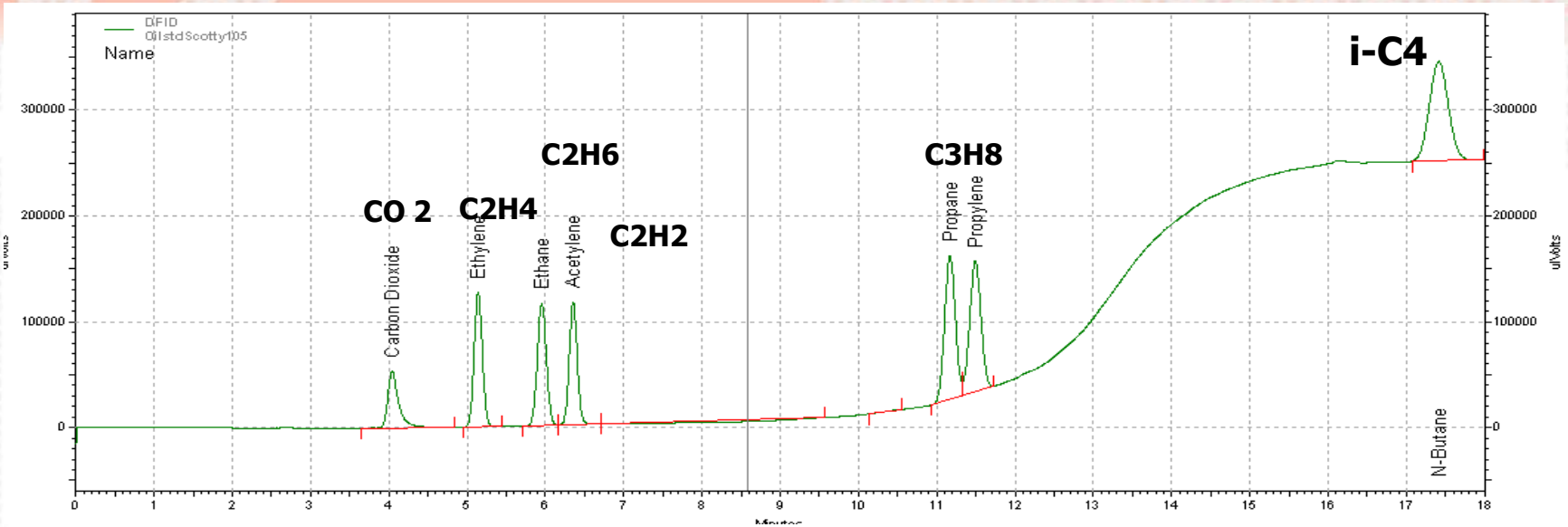
N=5	H2	O2	N2	CH4	CO	CO2	C2H4	C2H6	C2H2	C3H8	C3H6	i-C4H10
50ppm Mean	53	N/D	1267	49	77	54	51	51	48	50	51	50
STDEV	0.84	N/D	549.82	0.30	8.15	0.84	0.24	0.22	0.44	0.26	0.24	0.36
%RSD	1.60	N/D	43.38	0.62	10.6	1.55	0.47	0.43	0.92	0.52	0.47	0.72
500ppm Mean	697	842	5959	560	708	997	492	494	472	497	541	504
STDEV	4.71	240.95	208.18	2.58	4.41	5.99	2.75	2.85	7.45	3.23	3.29	2.87
%RSD	0.68	28.62	3.49	0.46	0.62	0.60	0.56	0.58	1.58	0.65	0.61	0.57
5000ppm Mean	4376	9654	50525	4014	4439	5068	5112	5139	5111	5099	5124	5020
STDEV	34.8	151.39	214.31	48.85	34.40	23.76	24.52	25.11	66.16	21.23	31.21	23.74
%RSD	0.80	1.57	0.42	1.22	0.77	0.47	0.48	0.49	1.29	0.42	0.61	0.47

Oil Sample Prep Procedure

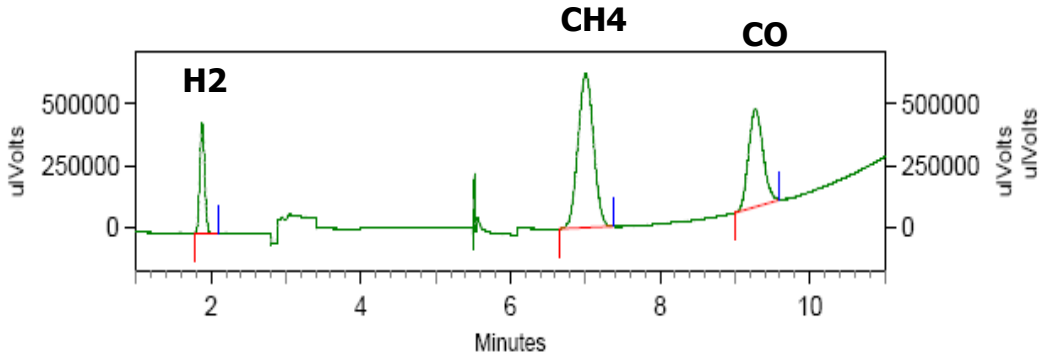
SHIMADZU

- Vials are prepared as per the gas standard procedure outlined above
- 15ml of oil from the sample syringe is injected into the vial
- Once 12mls have been transferred to the vial, the “vent needle” is removed and the last 5 ml is filled, leaving the vial slightly under positive pressure

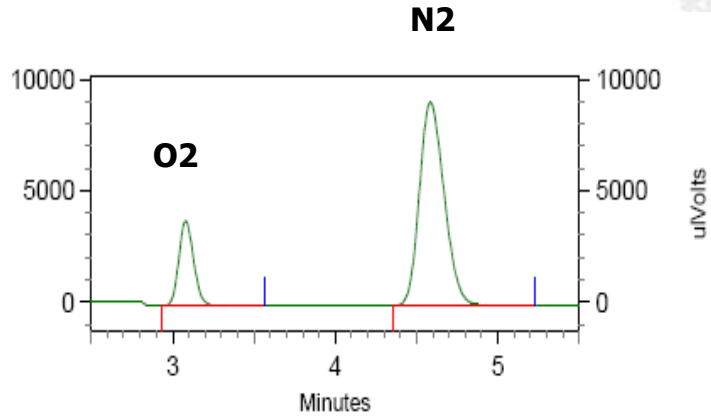
Oil Sample Chromatograms



FID



PDHID



TCD

Oil Sample Reproducibility

n=32	*Hydrogen*	*Methane*	*Carbon Monoxide*	*Oxygen*	*Nitrogen*	*Carbon Dioxide*
Mean Conc ppm	32	435	877	4755	102454	4576
STDEV	2.1	25.1	81.2	4173.5	20635.5	124.9
%RSD	6.6	5.8	9.3	87.8	20.1	2.7

n=32	*Ethylene*	*Ethane*	*Acetylene*	*Propane*	*Propylene*	*Isobutane*
Mean Conc ppm	192	102	0	62	29	11
STDEV	5.4	2.7	0.0	2.0	0.9	2.6
%RSD	2.8	2.6	N/A	3.2	3.1	24.3

- A single lab analyzed the oil from a single transformer
- 16 syringes each in duplicate for 32 total analyses
- Acetylene was determined to not be present in this oil sample

Advanced report

- An automated report is generated at the end of each analysis
- This report corrects for actual temperature, pressure, sample amount and the solubility coefficient of each analyte

Toga Analysis Report

SAMPLE ID	True North 100 A inj 002
Analysis Date and Time	39776.862835648
File Name:	True North Multiple Run 025.dat
Baro Press in. Hg	1
Vol of Headspace	7.8
Vol Of Oil (Vo)	14
Rm Temp F	1
Baro Press (Pa)	3.4
Rm Temp (K)	255.93
Ideal Temp	273
Ideal Press	760

DFID

Peak Name	Area	Raw Conc	K	Corrected Conc.	Final Result STP ...
Hydrogen	1978131	99.77	1.00	155.36	5.56
Methane	8902112	64.52	1.00	100.47	3.60
Carbon Monoxide	5289223	90.90	1.00	141.54	5.07

TCD-L

Peak Name	Area	Raw Conc	K	Corrected Conc.	Final Result STP ...
Carbon Dioxide	384561	71.90	1.00	111.96	4.01
Ethylene	279463	39.42	1.00	61.39	2.20
Ethane	220962	32.11	1.00	50.00	1.79
Acetylene	283997	47.34	1.00	73.72	2.64
Propane	171587	16.65	1.00	25.92	0.93
Propylene	0	0.00	1.00	0.00	0.00
Isobutane	0	0.00	1.00	0.00	0.00

PDHID

Peak Name	Area	Raw Conc	K	Corrected Conc.	Final Result STP ...
Oxygen	24225	14836.94	1.00	23103.23	826.95
Nitrogen	96870	54989.86	1.00	85627.06	3064.92

Combustible Gas		22
Atmospheric Gas	%	0.39

Reviewed_____

Conclusion

- Acceptable reproducibility can be obtained with this method for all target compounds except for Oxygen
  - Oxygen is not a critical component in evaluating transformer health
- Hydrogen sensitivity is better with PDHID than by TCD
- The analysis can be automated by the HT-3
- The separation design protects the MS column from absorbing H2O and CO2.
- C4 which may be present will elute within 19 minutes avoiding ghost peaks
- Continued work is suggested to further optimize the method precision and accuracy.