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Cellulose Degradation and Transformer Fault Detection by the Application of Integrated Analyses of Gases and Low Molecular Weight Alcohols Dissolved in Mineral Oil

Draginja Mihajlovic *, Vladimir Ivancevic, Valentina Vasovic and Jelena Lukic

Laboratory for Testing and Calibration, Electrical Engineering Institute Nikola Tesla, Koste Glavinica 8a, 11000 Belgrade, Serbia

* Correspondence: draginja.mihajlovic@ieent.org

Abstract: This article presents a method for quantification of methanol and ethanol integrated in the same gas-chromatographic run with a quantification of gases dissolved in mineral oil, making it an integrated tool in transformer diagnostics. The results of aging experiments at 120 °C and 60 °C of Kraft paper, copper, barrier, and pressboard immersed in mineral oil, as well as the aging of thermal upgrade paper in mineral and natural ester oil at 140 °C are presented, in order to investigate correlations between different aging markers and to evaluate their partitioning between oil and cellulose at defined conditions. The results of partitioning experiments at 60 °C showed that re-absorption of methanol from oil to the cellulose materials is faster than the re-absorption of furans. This means that methanol is a paper-degradation marker that can be used in diagnostics over shorter equilibrium times and for the detection of developing faults at broader temperature ranges. Furthermore, a statistical overview of methanol concentration from a database and two transformer fault diagnostic cases are presented. Therefore, in addition to an analysis of gases dissolved in oil, the use of methanol and ethanol in transformer fault and failure investigations should be explored and verified through transformer fault investigations and postmortem analyses.

Keywords: methanol; ethanol; GC FID method; fault detection

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1. Introduction

Insights into the aging of cellulose insulation during a power transformer's lifetime can be gained by measurements of oil-dissolved specific compounds produced by cellulose degradation [1]. Specific compounds which are characteristic for the oil and cellulose aging process in the presence of construction metals of transformers can be more or less selective, dissolved and stable in oil. Therefore, they are used in diagnostics of power transformers' insulation aging by different oil tests. The specific markers for oil degradation are hydrogen, hydrocarbon gases, carbonyl compounds, acids, sulfides, and sludge, whereas specific markers of cellulose degradation are furan derivates. Compounds which are common markers of oil and cellulose degradation are water, carbon monoxide, carbon dioxide (CO_2), and low-molecular-weight alcohols (LMAl), such as methanol and ethanol. For real-time diagnostics of the power transformer condition and aging rate of oil/cellulose insulation, monitoring of the abovementioned compounds is of great importance for the stable and regular operation of the transformer.

Previous studies from the literature have shown that methanol could be a good marker for the early stages of cellulose insulation degradation [2–4] and that methanol and ethanol could be quantified in trace concentrations in the oil by using several detection methods, most of all gas chromatography with mass spectrometer (GC MS) [5–8] and gas chromatography with flame ionization detector (GC FID) [9]. This paper describes the method for LMAl quantification with transformer oil–gas analyzer (TOGA GC FID) and

its practical use as an integrated test with dissolved gas analysis (DGA) in transformer oil, which is commonly used in transformer condition assessments and fault detection.

The possibility of using methanol as an additional marker for transformer fault diagnostics is also shown. Certain authors presented earlier cases where methanol concentration was used to identify transformers with an abnormal paper degradation rate and most of the studies were focused on correlations of methanol and polymerization degree of cellulose insulation [3].

In practice, the difficulties to access thermal faults by using furans were observed, due to their low production in earlier stages of cellulose degradation and low dissolution in oils with low water content and degree of aging. These observations together with a small solid insulation area affected by the fault were found to be restrictions in fault detection which is affecting cellulose insulation. Furthermore, CO_2 is sometimes less sensitive and selective for cellulose degradation, as was observed in some cases wherein high fluctuations of CO_2 were caused by breathing restrictions and not due to aging.

In this paper, our focus was on the trend analysis of methanol and ethanol together with gases dissolved in oil, for the detection of solid insulation degradation, along with all others aging markers. An increase in methanol concentration was observed as a good indicator of failure that affected cellulose degradation of transformer insulation, and this is shown in two transformer cases.

In order to establish threshold values, a statistical overview of methanol concentrations in oil samples from free-breathing in-service transformers was conducted with Kraft paper solid insulation derived from the Electrical Engineering Institute Nikola Tesla (EEINT) database.

Furthermore, in order to analyze the paper aging phenomena in respect to cellulose aging marker production and distribution in paper or oil systems, additional aging experiments were conducted in different oils at two different temperatures (120 °C and 140 °C), including aging markers' partitioning experiments by using the equilibrium of aging markers between paper and oil at 60 °C.

2. Materials and Methods

2.1. Determination of Methanol and Ethanol by TOGA GC FID System

The method for determination of methanol and ethanol was developed in EEINT for the purpose of standard method development, proposed by the IEC TC 10 PT 63025 working group. Alcohols are quantified by using a TOGA GC FID analyzer, with headspace extraction, normally used for DGA analysis. This method for DGA and LMAl quantification has been used in routine laboratory work for several years, as an improved fault diagnostic tool. Dissolved gases, methanol, and ethanol are quantified together in the same chromatographic run, within a standardized method for DGA analysis by using TOGA GC FID (Figure 1).

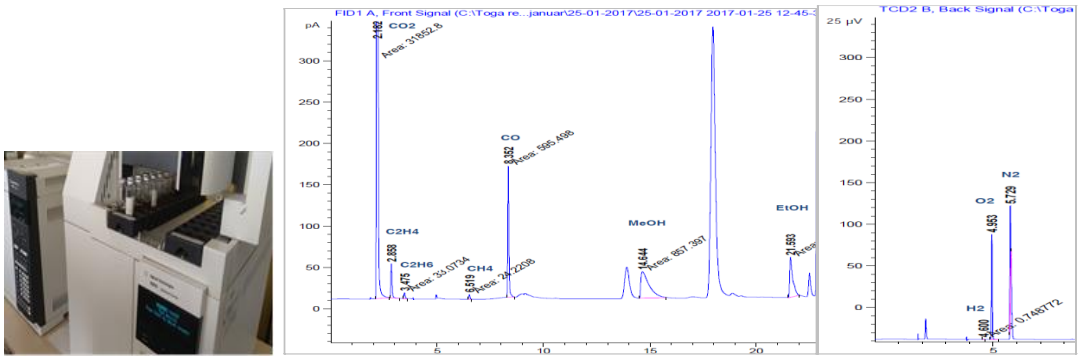

Figure 1. TOGA GC FID analyzer (**left**) and chromatogram of DGA and LMA (**right**).

2.2. Instrument Setup

An Agilent 7890B TOGA system with a headspace autosampler and FID and thermal conductivity detector (TCD) was used. This system has two capillary columns: Plot Q polystyrene-divinylbenzene, 60 m × 20 µm and Molesieve, 30 m × 50 µm. Analysis was performed according to IEC 60567 [10]. Parameters of the headspace and detectors are shown in Table 1.

Table 1. Headspace and detectors parameters.

TOGA System	Parameters	Value
Headspace	Temperature	70 °C
	High shaking	136 shakes/min
	Injection volume	1000 µL
	Vial heating	30 min
	Temperature	70 °C
Detector FID/TCD	Hydrogen flow	50/20 mL/min
	Makeup flow	5/5 mL/min
	Temperature	250/150 °C
	Air flow	400 mL/min

2.3. Standard Solution Preparation

Standard solutions of methanol and ethanol from stock solution were prepared in different concentrations. Calibration standards were made to cover the expected range of concentration in real samples. The quantity of 10 mL of sample was transferred in a conditioned vial crimped with butyl caps by using a syringe equipped with a needle.

2.4. Limits of Detection and Quantification (LOD and LOQ)

LOD and LOQ were evaluated by analyzing ten replicate samples of mineral transformer oil with analytes at a concentration near the expected limits (Table 2). Limits for aged mineral oil from service were also evaluated. Aged oil properties were: acid number 0.87 mgKOH/g_{oil}, interfacial tension 12 mN/m, and electrical dissipation factor 1.043. According to EPA, LOD was calculated as the standard deviation of the mean analyte concentration multiplied by 3, and LOQ as the standard deviation of the mean analyte concentration multiplied by 10 [11].

Table 2. LOD and LOQ of methanol and ethanol, TOGA GC FID method.

Mineral Oil	Alcohol	LOD, ppb	LOQ, ppb	Linearity
New oil	Methanol	2	7	0.02–2.2 (0.9991)
	Ethanol	4	14	0.02–2.2 (0.9994)
Aged oil from service	Methanol	5	15	0.02–2.2 (0.9994)
	Ethanol	7	22	0.02–2.2 (0.9993)

The presented results showed that the proposed method can reach low limits of detection and quantification in the cases of new and aged mineral insulating oils. In order to confirm the applicability of the method, interlaboratory testing and comparison with the GC-MS was performed on three mineral oil samples with different concentrations (Table 3). The first two were spiked (samples S1 and S2), and the last one, AS, was an oil sample from the experimental transformer (aged oil sample). The obtained results showed good agreement of applied methods (Table 3).

Table 3. Comparison of TOGA GC-FID with GC-MS method.

Sample	TOGA GC-FID		GC-MS	
	MeOH, ppb	EtOH, ppb	MeOH, ppb	EtOH, ppb
S1	42	72	47	83
S2	1574	1684	1397	1668
AS	7919	281	8090	241

3. Use of Methanol and Ethanol in Transformer Condition Assessment and Fault Diagnostics

The main factors that have influence on degradation of cellulose insulation of transformers in service are temperature, water, and oxygen. Different aging markers will be formed as degradation products of cellulose insulation. These degradation products behave differently in terms of dissolution, stability, and distribution in the oil/cellulose system. The aging markers ratio and their partitioning gives valuable information for transformer condition assessment and fault detection. Aging experiments and equilibration at certain temperatures were performed in order to get more insight into trends and the relative ratio of produced aging markers. Aging over 60 and 28 days at 120 °C and 140 °C and equilibration at 60 °C for 40 days was performed (Table 4).

Table 4. Experiments overview.

Experiment	Days of Aging/Equilibration	Temperature °C	Materials
I	60	120	Mineral Oil/Kraft paper/pressboard/copper
II	60	120	Mineral Oil/copper
TU–I	28	140	Mineral oil/thermally upgraded paper
TU–II	28	140	Natural ester/thermally upgraded paper
A	40	60	Mineral Oil/Kraft paper/pressboard/copper
B	5 + 40	60 (5 days at 25)	

3.1. Trends of Aging Markers in the Oil

The following materials were used in experiments at 120 °C and 60 °C: paper for barriers (0.25 mm thickness), bare copper conductors with three layers of Kraft paper, pressboard (1 mm thickness), mineral insulating oil (Nynas 4000×) in the following ratios: paper/oil mass ratio: 4%, pressboard/oil mass ratio: 6%, copper/oil surface to mass ratio: 430 cm^2/kg. The initial water content in dried and degassed mineral oil prepared for aging was 8 ppm, and water content in the prepared cellulose materials was approximately 1%. All materials and oil were heated in 50-mL vials sealed with PTFE septa (experiment II). The same experimental setup was used for the system with oil and copper only (Experiment I). Prior to and after aging, the following measurements were performed: degree of polymerization (DP_v) of paper, barrier and pressboard according to IEC 60450, furans dissolved in the oil according to IEC 61198, DGA analysis according to IEC 60567, and methanol and ethanol concentration according to the integrated TOGA GC FID method.

Changes of methanol, ethanol, furans and average DP_v value during cellulose/oil insulation aging in experiment II showed that in the early and mid-phase of cellulose degradation (up to an average DP_v value of approximately 500), an increase of methanol concentration was observed. After 10 days of aging, methanol content was about 3 ppm, whereas furans concentration was still low (0.6 ppm) (Table 5, Figure 2). This was observed elsewhere and can be explained by the degradation of the amorphous structure of cellulose

first [4]. At this point, CO_2 content had maximum value. In the later degradation stage, after 20 days of aging, an increase of furan concentration was observed. In the first 20 days, the rate of DP_v decrease was highest (average DP_v value of approximately 500). Oxygen content in the system during the aging period was in the range of 13,000–6000 ppm. A decrease in methanol concentration in the oil in the later degradation phase was observed, and this was reported by other authors at higher temperatures (over 110 °C) due to its consumption by oxidation byproducts in the oil [12] or by possible consumption in esterification reactions [13]. On the other hand, a lower production rate of methanol at a later degradation stage could be the consequence of lower degradation and stability of remaining crystalline structure of cellulose which has remained as the predominant constituent [4].

Table 5. Change of aging markers concentrations during experiment II (oil and paper) at 120 °C.

Aging Period, Days	MeOH, ppm	EtOH, ppm	O_2, ppm	CO_2, ppm	CO, ppm	Furans, ppm	DP_v Average
initial	0.000	0.000	12,885	288	1	0.00	988
1	0.708	0.020	6385	6224	235	0.02	908
5	2.658	0.150	6161	21,351	889	0.41	646
10	2.994	0.088	7403	21,465	1370	0.64	580
20	3.855	0.133	7155	17,904	1401	2.11	483
30	2.848	0.493	9002	18,522	1891	5.62	351
60	3.741	0.365	7293	14,537	1297	10.61	282

Legend: MeOH—methanol, EtOH—ethanol, O_2—oxygen, CO_2—carbon dioxide, CO—carbon monoxide, DP_v—degree of polymerization.

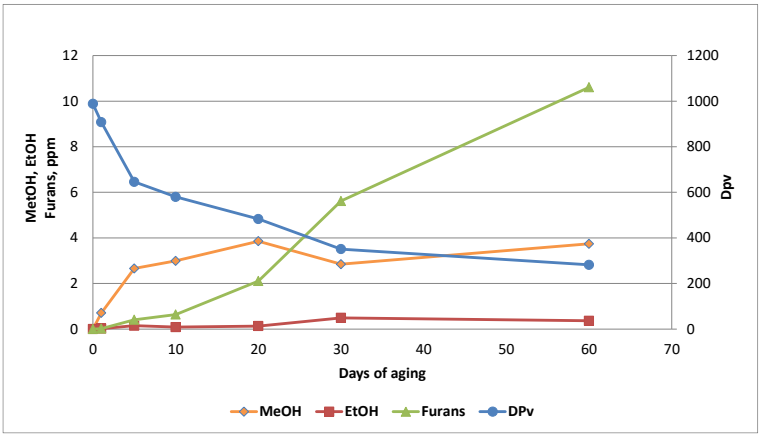

Figure 2. Change of methanol, ethanol and furan concentration and DP_v during aging experiment II at 120 °C.

Concentrations of aging markers during aging in experiments with oil/copper (Experiment I) are shown in Table 6. These results indicate that at 120 °C, including the zone of lower thermal fault temperature range, ethanol is mostly produced from oil aging and is not a very useful marker for paper aging at lower aging temperatures. Literature data showed that in field samples, ethanol was only present at higher pyrolysis temperatures [14].

Table 6. Change of aging markers concentrations during Experiment I (oil only) at 120 °C.

Aging Period, Days	ppm				
	MeOH	**EtOH**	**O_2**	**CO_2**	**CO**
initial	0.000	0.000	12,885	288	1
1	0.022	0.018	11,014	241	24
5	0.069	0.079	15,205	723	125
10	0.061	0.035	17,865	666	155
20	0.082	0.054	15,896	913	299
30	0.112	0.408	14,190	1191	472
60	0.203	0.408	6636	2619	1334

Legend: MeOH—methanol, EtOH—ethanol, O_2—oxygen, CO_2—carbon dioxide, CO—carbon monoxide.

It has been observed that methanol is produced in larger amount in earlier to mid-degradation stages whereas a higher furan concentration was observed in later stages of paper degradation [15–17] and this correlates well with our findings.

In order to investigate methanol formation in system mineral/natural ester (NE) oil and thermally upgraded (TU) papers, aging was performed at 140 °C for 28 days in stainless steel hermetically sealed vessels. The cooling period between cycles was 48 h in order to allow produced and evaporated water to return back from headspace into cellulose materials. All materials were used in same ratios as in the experimental setup previously described. Water content in cellulose insulation was 3%. Dp_v values, water content in cellulose materials, tensile index, and oil properties were analyzed before, after, and during aging, and results are given in [18]. Significantly lower values of methanol concentrations were obtained in natural ester oil rather than in mineral oil. Systems with TU papers and NE oil showed maximum methanol concentration after 4 days of aging (about 1500 ppb and 1700 ppb for Dp_v values 1000 and 1200). Until the end of aging, methanol concentration decreased due to reaction with acids and formation of esters, and this correlated well with previous studies [4]. The trends of methanol concentration for different TU papers in NE oil were similar.

A decrease of methanol concentration in mineral oil was observed at the end of the aging period (Figure 3). A continuous increase of CO_2 concentration in mineral oil was observed. By contrast, a slight decrease of CO_2 concentration in natural ester oil was observed after 4 days of aging [18].

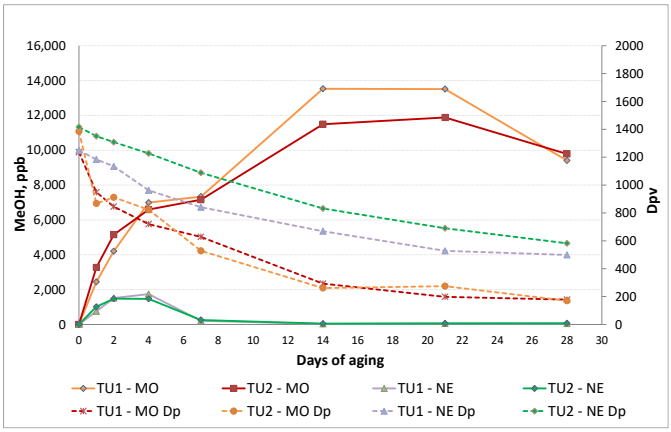

Figure 3. Change of methanol concentration and DP_v during aging experiment (TU papers in mineral and natural ester oil at 140 °C).

Paper aging was more pronounced in system mineral oil/TU with Dp_v values below 200. The highest Dp_v value was at the end of aging of TU_2 paper in NE oil, 582. A decrease

of water content in NE oil/TU paper system during aging was evident, and extremely high values of acid number reported in [18] confirmed the presence of hydrolysis reactions.

3.2. Equilibrium Experiments—Partitioning of Aging Markers

Equilibrium experiments were performed in the experiment with oil, copper, and cellulose materials (paper and pressboard) in vials sealed with PTFE septa at 7, 20, and 40 days at 60 °C. This was done in order to investigate partitioning of LMAl and furans between cellulose materials and oil and to gain better insight into the evaluation of aging marker concentrations in the oil at average transformer operating temperatures of 60 °C.

After initial aging, when paper degradation to certain values of DP_v occurred and a certain amount of aging products were produced, two vials were used for initial measurements and six vials were put at 60 °C for equilibration (two vials for each equilibration period, Experiment A (Table 4)). The remaining eight vials were left for 5 days at 25 °C and after this period, a set of two vials were used for initial measurements, and six vials were put at 60 °C equilibrium for the same duration of 7, 20, and 40 days (Experiment B). All materials were heated in 50-mL vials sealed with PTFE septa. In this experimental setup, high amounts of aging markers were produced by preparative extensive paper/oil aging, and then the diffusion and equilibration of aging markers were observed at normal transformer operating temperature from the oil to the paper. Re-absorption of methanol and ethanol from the oil to the cellulose materials was confirmed after longer equilibrium periods (Table 7). Comparing the initial concentration of methanol in both experiments, a significant decrease was observed after a decrease of temperature from 150 °C to 25 °C during five days. Concentration of methanol in oil continued to decrease after a temperature increase to 60 °C during 7, 20, and 40 days. This is an indication that the migration of methanol, i.e., exchange in the paper/oil system is quite fast, and it was also observed that methanol concentrations were of similar values at the end in both experiments respectively. Such an observation is important in understanding the speed of response/diffusion of produced aging markers in thermal fault conditions and their stability in the oil over time.

Table 7. Changes of concentrations of alcohols and furans during equilibrium at 60 °C.

Experiment	Days of Equilibrium at 60 °C	ppm						
		MeOH	EtOH	2-fol	2-fal	2-acf	5-hmf	5-mef
A equilibrium at 60 °C	initial	8.85	0.24	1.15	31.40	0.27	7.67	0.80
	7	2.32	0.19	1.20	33.57	0.3	4.00	0.88
	20	1.28	0.16	0.97	29.72	0.22	2.58	0.71
	40	1.03	0.13	0.30	27.86	0.21	1.78	0.69
B at 25 °C for 5 days and equilibrium at 60 °C	initial	2.59	0.24	1.11	31.72	0.27	4.26	0.81
	7	1.94	0.19	1.21	34.36	0.34	4.1	0.94
	20	1.85	0.15	1.17	35.42	0.32	3.21	0.98
	40	1.19	0.11	0.12	32.05	0.25	2.32	0.83

Legend: MeOH—methanol, EtOH—ethanol 2-furfurylalcohol (2-FOL), 2-furfural (2-FAL), 2-acetylfuran (2-ACF), 5-methyl-furfural (5-MEF), 5-hydroxymethyl-2-furfural (5-HMF).

Furans were found to be more inert, i.e., slower migration was obvious and re-absorption back into the paper was more pronounced at low temperatures (Table 7, Experiment B, after 5 days at 25 °C). Among all furan derivates, only 5-hmf was absorbed in the cellulose materials significantly, shown as its decrease in the oil over periods of 7, 20, and 40 days.

Intensive absorption of methanol and 5-hmf in the paper was also seen after comparing initial concentrations after five days at 25 °C (Experiment B) and immediately after preparatory aging at 150 °C (Experiment A). The highest rate of decrease from initial concentrations was found in the case of methanol, whereas furans were more inert to diffuse between oil and cellulose materials, so the absorptions processes were much slower.

The maximal change of methanol concentration in the oil due to migration of methanol after being stabilized at operating temperature of 60 °C, excluding thermal fault, was found to be in the range of an approximately 55% change in 33 and 40 days. This confirms methanol capability to migrate easily between oil and paper.

3.3. Statistical Overview and Real Cases

A statistical overview of the EEINT database of methanol concentration in oil samples, from power and distribution transformers of the Electric Power System of Serbia and Transmission System of Serbia is presented at Figure 4. All transformers are free breathing with Kraft paper solid insulation and mineral oil. According to presented results for over 2000 measurements, only 6% of the samples had methanol concentration over 1000 ppb. Therefore, this concentration may be considered as a threshold value for fault detection involving cellulose insulation.

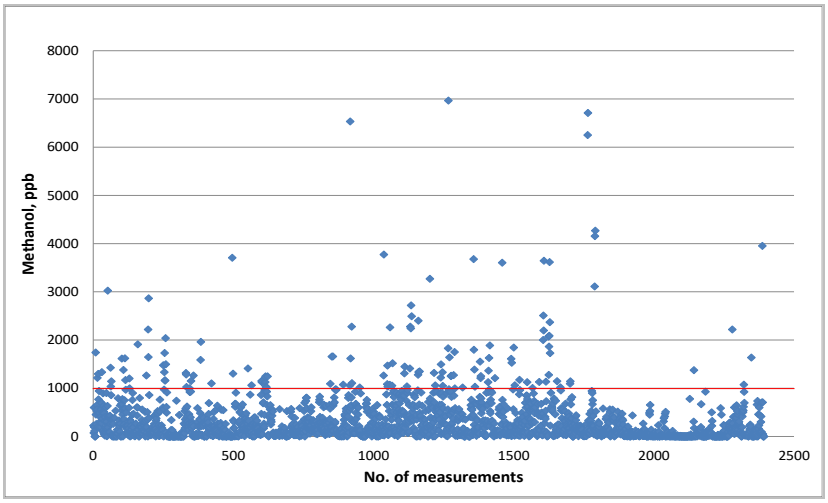

Figure 4. Statistical overview of methanol concentration from the EEINT database.

3.4. Case Studies

In this section, two power transformer failure cases are described. These transformers were free breathing with standard Kraft paper as cellulose insulation. In both cases, monitoring methanol concentration in the oil, along with DGA was observed to be a useful tool with which to diagnose faults involved in cellulose insulation. Data on oil sampling temperature were available, which was of great importance for trending analysis purposes. Factory inspections confirmed given conclusions based on the results of the oil test in the laboratory. Concentrations of other aging markers are shown in both case studies.

Case 1. Results of DGA of oil sampled before and immediately after the failure indicated the presence of an intense electrical failure of the power transformer 120 MVA, voltage 10.5/121 KV with over 40 years in service (Table 8). An analysis of gases, methanol, and ethanol dissolved in the oil were performed by the proposed TOGA GC FID method. Interpretations according to the IEC Standard [19] and the Duval pentagon [20] indicated discharges of high energy, D2. With the increase in concentrations of faulty gases there was also an increase in the concentration of methanol in the same oil sample. On the other hand, the concentration of CO_2 remained the same after the failure. The results of methanol and ethanol analysis, as methanol and ethanol concentration normalized at temperature of 20 °C, are given in Table 8. Normalization at 20 °C, by applying equation and correction factors given in [21], provides better insight into the variation of methanol and ethanol concentrations in the oil. These results indicated that the failure involved solid insulation of the transformer.

Table 8. Case 1—Dissolved gases and methanol and ethanol analysis before (26 May 2017) and after the failure (6 September 2017, 7 September 2017).

Date of Sampling/Level	Temperature °C	DGA, ppm							MeOH, ppb	EtOH, ppb
		H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	CO	CO_2		
26 May 2017/bottom	40	28	19	15	74	15	792	9172	469/195 *	337/167 *
6 September 2017/bottom	/	605	116	354	202	23	1133	10,488	/	/
6 September 2017/middle	/	532	118	361	208	23	1116	11,040	/	/
7 September 2017/bucholz	32	3074	428	513	225	23	1914	11,041	1149/658 *	467/295 *

*—normalized value [21].

Results of electrical testing of transformer insulation after the failure indicated the interruption of one of the HV windings in phase A [22]. Estimated water content according to measured water content in oil (18 ppm at transformer operating temperature of 48 °C) and Perrier–Lukic equilibrium curves for paper and pressboard in mineral oil [23] was 2.3%, and this is in good agreement with water content obtained by the frequency domain spectroscopy (FDS) method, 2.1%. The transformer oil had been regenerated several times and during that process furanic compounds have been removed from the oil. The total cumulative content of 2-furfural in oil was calculated from measured values of 2-fal dissolved in the oil generated during periods before and after oil treatment as is described in reference [24], 2.82 ppm.

The increase of methanol concentration, 2-fal concentration, and estimated water content in cellulose materials indicate an active degradation process of transformer solid insulation, which was confirmed by DP_v values of paper samples taken after postmortem analysis. Measured DP_v values along the height of the windings were from 386 to 422 and show that aging of the insulation was homogenous and that cellulose insulation of the transformer was moderately aged. Estimated DP_v's of 340 and 370 correlated well with the lowest measured value of DP_v = 386, during post-mortem investigation [24,25].

A factory inspection found a breakdown of HV winding, phase A in middle inner part (Figure 5a).

(**a**) (**b**)

Figure 5. Pictures of fault area: (**a**)—Case 1, (**b**)—Case 2.

After rewinding, an increase of ethylene and methanol concentration, indicated a possible development of a new fault in the transformer (Figure 6). It was observed that change in the transformer loading condition and oil temperature was followed by ethylene and methanol concentration change. The methanol response was faster than the ethylene response, confirming observations previously mentioned that methanol migrates quickly between oil and cellulose insulation and can be used as a sensitive marker in fault detection involving insulating paper.

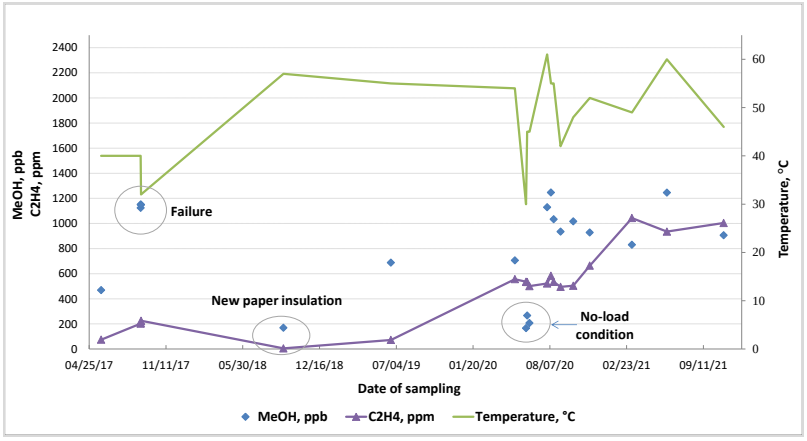

Figure 6. Change in methanol and ethylene concentrations before and after the failure.

Case 2. The results of DGA for the second transformer case before (date of sampling 18 April 2018 and 26 April 2018) and after the failure (date of sampling 5 July 2018 and 6 July 2018) for power transformer unit 360 MVA, voltage level 15/420 kV, with 10 years in service, are shown in Table 9. The measured concentrations of gas in the oil and in the Bucholz gas indicated the extremely rapid fault development. The gas concentration ratios measured in all samples, according to the IEC standard [19], indicated the presence of thermal failure with a temperature over 700 °C. The interpretation according to the Duval pentagon [20] also indicated thermal fault and possible carbonization in the paper.

Table 9. Case 2. Results of dissolved gas analysis and methanol and ethanol before (18 April 2018, 26 April 2018) and after the failure (5 July 2018, 6 July 2018).

Date of Sampling/Level	Temperature °C	DGA, ppm							MeOH, ppb	EtOH, ppb
		H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	CO	CO_2		
18 April 2018/bottom	52	75	439	0	363	149	1332	7931	272/70 *	40/14 *
26 April 2018/bottom	/	91	446	0	378	157	1337	8368	/	/
5 July 2018/bottom	55	2454	6188	23	6346	1473	1146	7017	976/223 *	56/18 *
5 July 2018/top	/	2241	6080	25	6320	1472	1104	6935	/	/
6 July 2018/bucholz	/	2956	6933	30	7048	1638	1102	6816	/	/

*—normalized value [21].

The increase of methanol concentration in the oil sample after the Bucholz alarm (sampling date 5 July 2018), indicated the possibility that the fault involved solid insulation. The measured ethanol concentration was low before and after failure. Electrical testing of the transformer after the failure indicated the possibility of failure located in magnetic core.

The estimated water content according to the measured water content in oil (11 ppm at a transformer operating temperature of 52 °C) and Perrier–Lukic equilibrium curves for paper and pressboard in mineral oil was 1.09% [23], which is in good agreement with the water content obtained by FDS, 1%. The measured content of furanic compounds dissolved in the oil was 0.23 ppm. Unlike the increase of methanol, the CO_2 concentration remained low after the failure.

Failure was confirmed to be located in the magnetic core and burned solid insulation was found during factory inspection (Figure 5b). DP_v measurements of the samples from winding paper were not performed because there was no breakdown in the windings.

The DGA and LMAl method provides an improved tool for fault diagnostics of power transformers, if used as a trend analysis in regular monitoring of dissolved gases and methanol concentration in the oil. These findings can help in anticipating trends and rates of changes to be used in faults detection. It is very important to perform oil sampling when the transformer is in stable operating condition and to record the temperature of oil during

the sampling. For trending purposes, the analytical result of methanol content in the oil at a given sampling temperature can be normalized to a defined standard temperature of 20 °C.

4. Conclusions

The broad use of TOGA systems for DGA gives advantages to this integrated TOGA GC FID method for light alcohol determination in one run with DGA (DGA & LMAl), which is commonly used worldwide in transformer condition assessments and fault detection. Data obtained from equilibrium of methanol at 60 °C revealed that rate of change in methanol concentration in the oil is significant (around 50% rate per month), meaning it is easily migrating between oil and cellulose materials. On the other hand, furans are more inert and are formed in higher amounts in later stages of paper aging, and they can be very useful in life estimations of insulation with Kraft paper. Unlike in system mineral oil/TU paper, much lower concentrations of methanol were measured in experiments with natural ester oil and thermally upgraded paper. This can be attributed to the consumption of methanol in esterification reaction with fatty acids.

The proposed concept is to have more aging markers as complementary tools to improve diagnostics. Based on the presented cases and equilibrium experiments, methanol concentration increases by over 50% in a short period of time together with increases of other faulty gases can be a clear indication that cellulose insulation is affected by fault, whereas absolute methanol values above 1000 ppb can serve as indicators of significant paper degradation.

Further work should be focused on the extensive application of methanol and ethanol in a regular transformer condition assessment and in service diagnostics, to gain a massive number of in-service data, in order to include methanol quantification in standards and guides for interpretation of paper aging markers (forthcoming IEC TC 10 revision of IEC TR 62874—"Guidance on the interpretation of carbon dioxide and 2-furfuraldehyde as markers of paper thermal degradation in insulating mineral oil"), as well as the implementation and verification of methods for methanol and ethanol quantification in transformer fault and failure investigations and postmortem analyses. The proposed integrated LMAl and DGA method was found to be very convenient in practical work and enables continuous and fast updating of in service data.

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