Cellulose Chemical Markers Relationship with Insulating Paper Post-Mortem Investigations

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ABSTRACT

Oil soluble chemical markers such as methanol, ethanol and 2-furaldehyde for assessing the condition of insulating paper still present many challenges for an accurate interpretation in real transformers. Indeed, many conceptual parameters such as design (shell vs. core) or type of cooling are needed for a more accurate interpretation of the data. Moreover, similarly to water, the measured marker concentrations in oil are temperature-dependent, i.e. an existing partition phenomenon between the oil and the solid insulation modify the solubility of the markers, thus changing their apparent concentrations in the oil. Consequently, to follow the real trend of these species during the transformer's service life, it is crucial to correct their concentrations at a specific temperature, as is done for the water content. Knowing these facts and in order to calibrate a predictive model, Hydro-Québec decided to access equipment when dismantled, which enables a large amount of paper to be sampled from different sections of the windings. This allows for a more accurate representation of the transformer paper conditions in relation to transformer design. The paper condition obtained by measuring the degree of polymerization in accordance with the presence of chemical markers is a valuable process. We believe that it is possible to better understand the behavior of the paper insulation and to assess markers concentration thresholds using the oil analysis. This article discusses the recent experience in this field with specific cases.

Index Terms — Transformer, chemical markers, post-mortem, methanol, ethanol, furanic derivatives, degree of polymerization, insulating paper, cellulose, model.

1 INTRODUCTION

THE interpretation of chemical markers for determining the condition of paper insulation in a power transformer is a subject area that still presents many challenges. Oil analysis allows the alcohols and furanic derivatives to be measured and the insulating paper condition to be estimated without any invasive intervention. To date, several accelerated laboratory aging studies involving chemical markers and the degree of polymerization (DP_v) have been proposed, but their application to real equipment is still under investigation. Actually, most of DP_v models are built with lab aging experiments and only based on 2-FAL analysis [1-3]. However, there has not been an attempt to correct concentration based on the design characteristics, the oil temperature or the effect of the physico-chemical parameters. Recently, a consensus about marker interpretation stipulates that it is imperative to compare apparatus with the same configuration (shell vs. core) and the same type of cooling [4-5]. In fact, the quantity of materials implied (oil and paper) is

too different between a shell and a core design to compare these types of apparatus together. Cooling also has an effect on the temperature distribution in the windings, thus allowing a distribution of DP_v values of the paper in the transformer. Moreover, like water, the measured marker concentrations in oil are temperature-dependent. Because of the partition phenomenon between oil and the solid insulation, most of these markers are kept in the solid insulation and are equilibrated with the oil, depending on the temperature and other physico-chemical parameters. In order to follow the real trend of these species during the transformer's service life, it is crucial to correct their concentrations at a specific temperature, as is done for the water content [6]. Recent publications suggest temperature correction factors to take this partition phenomenon into account in the interpretation of alcohols and furanic derivatives [7-8]. Among its fleet of aging transformers, Hydro-Québec has the opportunity to access these devices as they are dismantled and perform post-mortem studies of the scrapped transformers to validate the relationship between DP_v and the presence of chemical markers dissolved in oil. To reduce the associated costs of this initiative, the investigation was conducted jointly by IREQ and the external service suppliers in charge of scrapping. Our

approach consisted in sampling a large amount of paper from each of the different sections of the windings at different locations (top, middle and bottom) for the most accurate representation of transformer DP_v distribution. Prior to this action, representative oil samples need to be collected to assess the oil quality together with the content of chemical markers. These post-mortem data provide a good opportunity to evaluate the viability of these models. This article discusses six specific cases where papers have been sampled with complete chemical data.

2 EXPERIMENTAL

2.1 TRANSFORMER SCRAPPING PROTOCOL

2.1.1   OIL CHARACTERIZATION

Six open-breathing core-type power transformers built in 1958 by the same manufacturer and placed in the same generating station were investigated (see Figure 1). These transformers were initially cooled with OFWF systems and then modified to OFAF cooling systems around the 1990s. They were insulated with standard Kraft papers (0.11% nitrogen content) and filled with inhibited naphthenic insulating oil. The oil was analyzed in the six units before they were scrapped. Upon completion of the analysis, the oil acidities were in the range of 0.012 to 0.017 mg KOH/g of oil. Except for the high values of CO_2 gas, DGA results of Table 1 indicate the transformers had no particular problem and therefore showed no obvious sign of abnormal or accelerated aging of their solid insulation. Nevertheless, it is interesting to note that the overall DGA concentrations are similar for units #1 and #6, and for units #2 to #5. An example of the trend of

Figure 1. Example of (a) the transformer windings investigated and (b) a circumferential disk section of the LV winding.

Table 1. Last DGA results taken before the final outage of the six transformers investigated.

#	H_2 ppm	CH_4 ppm	CO ppm	CO_2 ppm	C_2H_2 ppm	C_2H_4 ppm	C_2H_6 ppm	Post-mortem
1	104	8	597	21376	<LD	54	3	2013
2	10	5	266	9625	<LD	45	3	2014
3	24	4	295	9000	<LD	21	1	2013
4	5	4	245	6395	<LD	33	3	2014
5	22	3	264	10540	<LD	28	4	2012
6	66	7	596	21461	<LD	55	4	N.A.

LD: Limit of detection; N.A.: Not available.

the carbon oxides for unit #3 during 33 years is shown in Figure 2. Note that there is no information in the data bank about any oil reclaiming during the life of these transformers. However, the data bank shows the presence of about 3000 ppm of oil inhibitor 2,6-di-tertiary-butyl-para-cresol (DPBC) added at the end of 1990s. Due to unavailability of paper samples, unit #6 will not be included in this study.
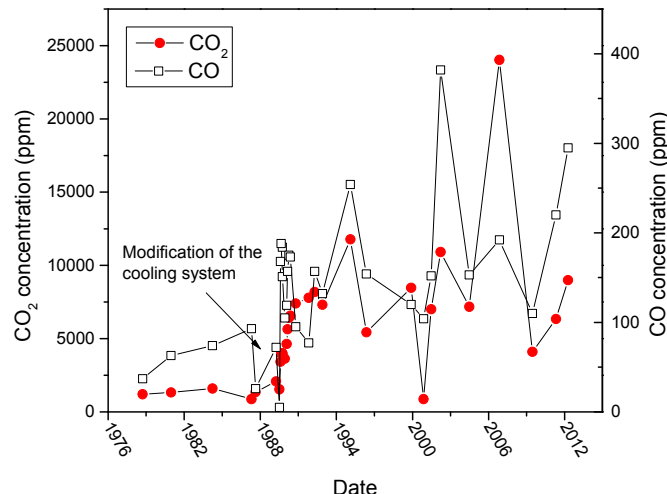

Figure 2. Carbon oxide evolution during the last 30 years for unit #3.

2.1.2   PAPER SAMPLING

We received oil samples from six scrapped transformers; nevertheless, paper samples were only available from the first five units (#1 to #5). The paper was sampled on both the high-voltage (HV) and the low-voltage (LV) of the three-phases (A, B, C). When possible, a complete section of the disk was selected (see Figure 1b) in order to measure the distribution profile of the degree of polymerization (DP_v) across the disk. Moreover, DP_v measurement was performed on the outermost paper layer and on the innermost paper layer. Finally, samples from the top, middle and bottom of each winding were selected. For each unit, there were more than 100 DP_v measurements per transformer.

2.2 APPARATUS AND METHODS

All the measurements (DP_v, acidity, DGA, and furanic derivatives) were determined using normalized methods [9-12]; the alcohols were determined with a method published elsewhere [13].

3   RESULTS AND DISCUSSION

3.1 DP_V MEASUREMENTS

This section presents all the DP_v statistic distributions observed for unit #3 with the corresponding number of samples (n). These distributions are quite similar for the other four units investigated. The total amount of compiled paper samples may differ from one to another due to field sampling conditions.

Figure 3 shows a typical paper DP_v distribution for the three phases of the LV and HV windings. In this figure, the DP_v distribution is considered for all the papers collected in the LV and the HV windings without any distinction as to the phase (A, B or C), position (top, middle or bottom) or paper
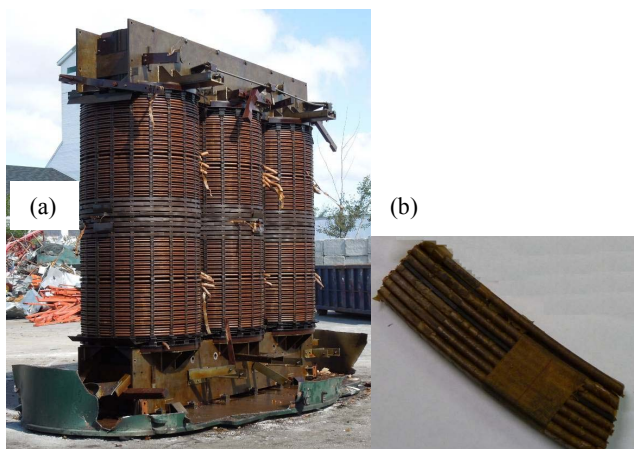
layer (oil or copper side). As observed in several other cases, the DP_v of the LV winding, which is near the end of life, is lower than the one observed for the HV winding. However, in this case, the mean values of both windings exhibit a DP_v of 176 and 306 for the LV and HV windings, respectively. Knowing that this transformer operated with a forced-oil cooling system which provides a more homogeneous temperature distribution along the windings, it could be expected that the DP_v distribution between the top and the bottom would be similar in order of magnitude. Indeed, Figure 4 represents the DP_v distributions of three locations on the HV windings where a small difference is observed. The top shows the lowest mean values with an average of 291 compared to the middle, 305, and the bottom, with an average value of 343.
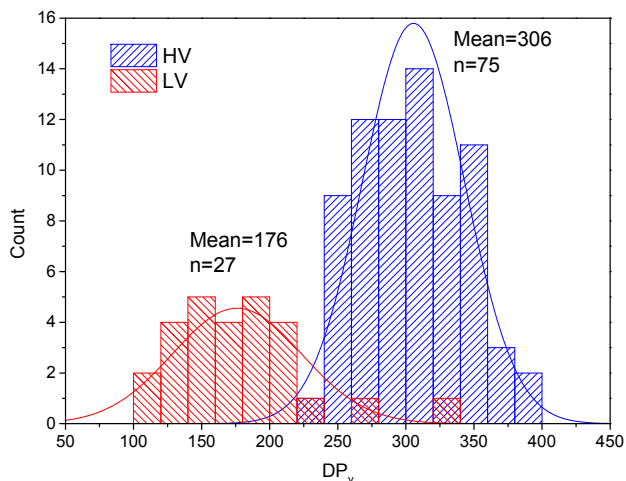

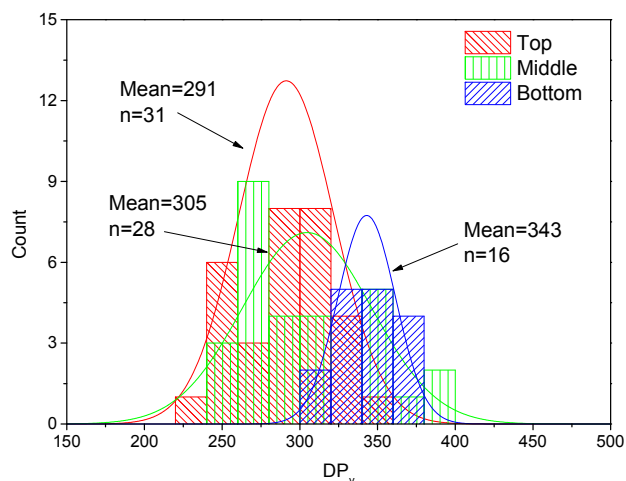**Figure 3.** DP_v distribution for unit #3.

Figure 4. HV DP_v distribution for unit #3 at different winding locations.

Lastly, Figure 5 presents the distribution for the measurement of the DP_v for the paper directly in contact with the oil and in contact with the copper conductor for the HV windings. There are about 14 paper layers. The distributions are quite similar with equivalent mean values (304 vs 310). This may be attributed to the good quality of the oil (acidity of 0.012 mgKOH/g oil) which had no detrimental effect on the winding papers directly in contact with the oil. With respect to LV, it was difficult to count the number of layers because the

papers were stuck to the copper conductors and highly brittle. Even though the papers of these transformers were all near their end of life, particularly for the LV, a statistical approach was used to determine if a difference existed between the units. Tables 2 and 3 summarize all the results and statistics related to the five units studied. Knowing that the number of samples is higher for the HV than the LV, weighted average DP_v values were calculated using equation (1). This method allows taking into account an un-equal number of samples.
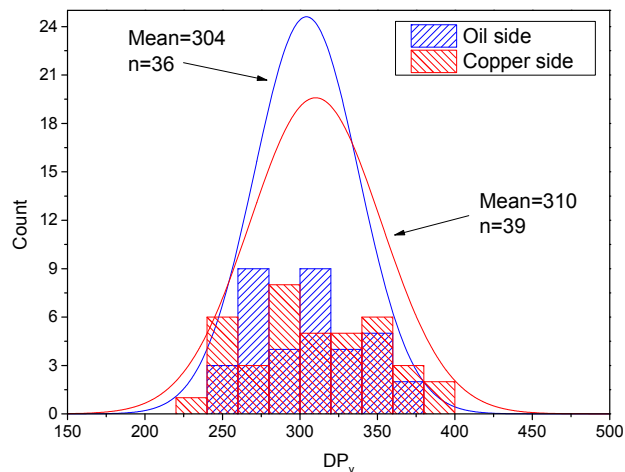

Figure 5. HV DP_v distribution for unit #3 for different paper layers.

$$\text{Weighted average} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} \qquad (1)$$

Where n_1 and n_2 are the number of data with their respective average M_1 and M_2.

Table 2. Average values with their corresponding standard deviations for the high and low voltage conductor paper.

#	High Voltage			Low Voltage		
	Top	Middle	Bottom	Top	Middle	Bottom
1	269 ± 20	272 ± 37	301 ± 35	143 ± 20	161 ± 54	174 ± 85
2	350 ± 43	369 ± 20	428 ± 39	183 ± 16	219 ± 16	214 ± 23
3	291 ± 31	305 ± 42	343 ± 19	138 ± 17	210 ± 42	183 ± 43
4	369 ± 34	352 ± 30	425 ± 35	188 ± 25	241 ± 22	227 ± 28
5	297 ± 20	329 ± 31	360 ± 19	145 ± 20	188 ± 16	217 ± 20

Despite the small differences between the average values, a t-test with a confidence interval of 95% was applied. The results (see Figure 6) show that there is no statistical difference between units #2-4, #3-5 and #4-5. However, #1 is statistically different from all other units. Table 3 shows that bottom HV values are always higher compared to the middle and the top HV values. However, for the LV winding, the results are more homogeneous along the windings.

Table 3. Statistics calculation for the six units studied.

#	Weighted Average	StD	n	Minimum	Maximum
1	236	72	116	118	439
2	328	88	104	150	538
3	272	70	102	120	387
4	310	88	128	145	442
5	293	69	129	118	388

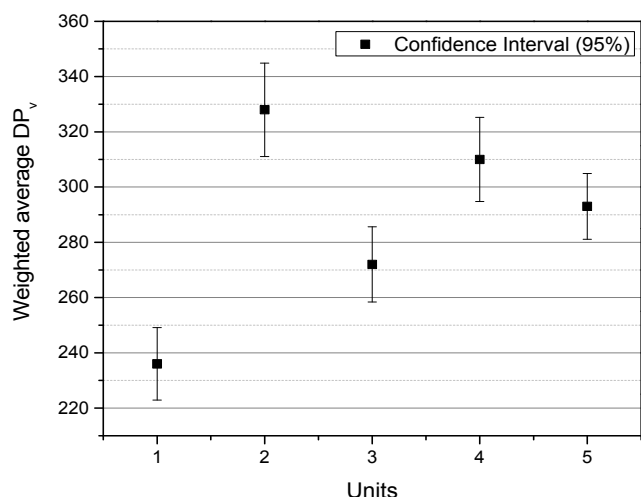StD: Standard deviation, n: Number of samples

Figure 6. Confidence interval for the different units investigated.

3.2 CHEMICAL MARKER MEASUREMENTS

It has been demonstrated that MeOH is directly related to the life of the cellulose by its proportional generation after the opening of the 1.4-β glycosidic bond [14-16]. Moreover, it has been proposed that EtOH might be generated after high-temperature cellulose degradation [17-18]. On the other hand, 2-FAL is generated from the chemical rearrangement of the degraded by-products of the cellulose after the bond scissions and shows an exponential trend for standard Kraft paper that has not been subjected to a thermal upgrade treatment [19].

Table 4 shows concentrations of moisture and cellulose chemical markers together with their corrected concentration values at 20°C. These corrections were obtained using equations published in IEC 60422 [6] and in recent publications [7-8], for moisture and chemical markers, respectively. For the raw data concentrations, assuming that all the chemical species are in equilibrium between the oil and the paper insulation during sampling, a great discrepancy is noted. For example, among all the markers, unit #5 seems to be the worst case with concentration values of 5203, 1034 and 1185 ppb for MeOH, EtOH and 2-FAL, respectively.

Table 4. Moisture and cellulose chemical marker concentrations.

#	Oil temp. °C	H$_2$O ppm	MeOH ppb	EtOH ppb	2-FAL ppb	Weighted Average DP$_v$
1	40	18	3786	1210	1377	*236*
	*20**	*8*	*1582*	*616*	*1108*	
2	37	30	1366	791	575	328
	*20**	*7*	*498*	*364*	*447*	
3	40	16	2697	1040	1491	*272*
	*20**	*7*	*1127*	*529*	*1199*	
4	43	21	1360	793	522	310
	*20**	*5*	*649*	*445*	*434*	
5	60	39	5203	1034	1185	*293*
	*20**	*8*	*977*	*289*	*780*	

* Corrected values

Nevertheless, after correcting the concentrations at 20°C, the worst-case assignation changes, depending on the marker concentration. It is interesting to note that even though these transformers operated under the same loading conditions, units #2 and #4 seem to present less paper degradations based on the MeOH and 2-FAL markers. In the case of EtOH, as observed in lab aging experiments, the MeOH/EtOH ratio is always higher

than one, which implies that no detectable hot spot in these transformers occurred. Indeed, it has been observed in some field equipment that when MeOH<EtOH, is it probably related to a high-temperature area in the apparatus [21].

4 DP$_V$ TREND USING CHEMICAL MARKERS

Knowing that the chemical marker concentrations provide an overall estimation of the cellulose state and even more if the range is very narrow, these data can be used to plot a relation between the chemical markers concentrations and the weighted average DP$_v$. Figure 7 shows these relationships for the two markers. The data symbols representing the transformer numbers are used. The first graph using methanol showed a more scattered relationship before correction, but a linear relationship after correction at 20°C with a coefficient of $R^2 = 0.98357$. This linearity is explained by the fact that the paper is at the end of its life in the asymptotic region when observing DP$_v$ vs. time. In the future, a relationship using the number of scissions instead of the DP$_v$ providing a linear relationship should be used as demonstrated elsewhere [20]. In the case of 2-FAL, the data showed a similar relationship before and after correction with a worst fit. However, it is important to point out that these relationships are valuable for this type of core design with good-quality oil (acidity < 0.017mgKOH/g of oil). More data in a larger range of DP$_v$ are needed to confirm this relationship. Moreover, the comparison of data fitted with already published models using 2-FAL values [6-8] are reported in Table 5 and shows an overestimation of the real average DP$_v$ values of the paper insulation particularly for the De Pablo's models. The equations used are described at the bottom of Table 5. This tendency probably demonstrates the importance of the partitioning effect on the apparent concentrations of the chemical markers measured in the oil.

Table 5. Average DP$_v$ obtained by applying different available models [6-8].

Units	Chendong[1]	De Pablo[2]	De Pablo[3]	Measured
1	392	698	637	236
2	500	757	723	328
3	382	690	626	272
4	512	762	729	310
5	410	711	656	293
6	262	558	462	N.A.

[1]log(2-FAL)=1.51-0.0035DP [6],
[2]DP=7100/(8.88+2-FAL); based on WG 15.01.03 data [7],
[3]DP$_{min}$=800/(0.186*2-FAL+1) [8].

5 CONCLUSION

This paper highlights the importance of normalizing the chemical parameters such as the oil temperature. This correction ensures a more realistic and accurate correlation between the marker concentrations and the DP$_v$ of paper in a transformer. It is also emphasized that a post-mortem analysis in order to draw the complete DP$_v$ profile of a transformer is crucial for the applicability of any model. Lastly, the paper paves the way to establishing concentration thresholds for categorizing the condition of the paper insulation used in transformers in view of more precise asset management.
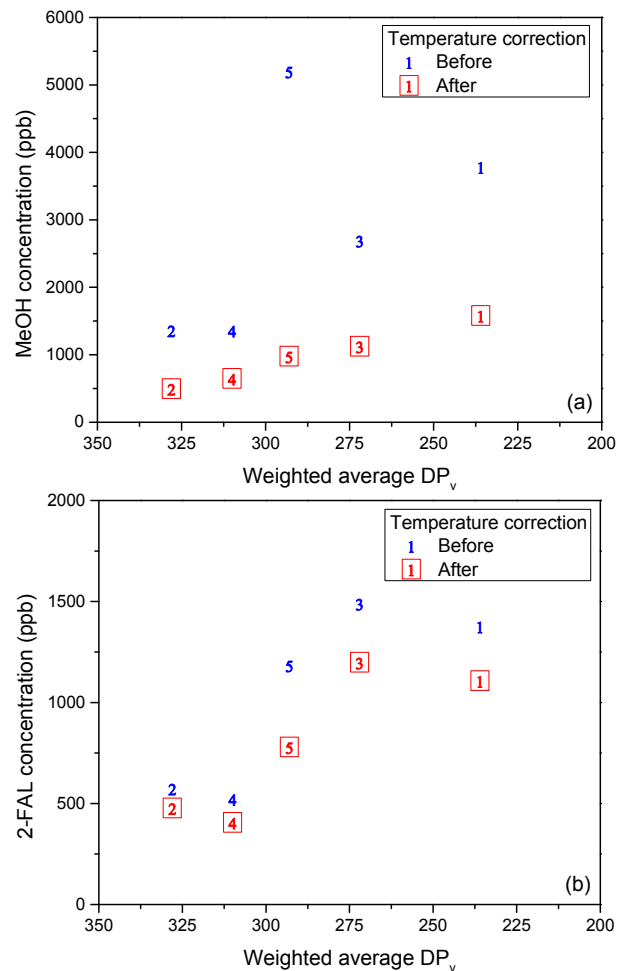
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Figure 7. (a) MeOH and (b) 2-FAL related to weighted average DP$_v$ measurements.

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