Applications of Methanol as an Innovative Ageing Marker for Transformer Insulating-Paper Diagnosis

IERE Joint R&D Project Final Report 2017

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EXECUTIVE SUMMARY

In 2012, IERE launched a joint R&D program amongst its members entitled “Transformer Insulating Paper Diagnosis for a Worldwide Application of Methanol as an Innovative Marker”. The R&D program was led by Hydro-Québec’s research arm – IREQ. Initially, there were six IERE members participated in the joint R&D program, including Hydro-Québec, Prolec-GE, Taipower, CLP, NTPC and Toshiba, and the inaugural meeting was held in Montréal, Canada in 2012. In the past three years, annual review meetings were held in Hong Kong (2013), Mexico (2014) and finally concluded in Taiwan (2015). Four members, including Hydro-Québec, Taipower, Prolec-GE, and CLP, with the continuous support from IERE Central Office, successfully brought this multi-national, multi-year research work to a satisfactory conclusion. This is the final report prepared by the joint R&D Program participants.

The end of the useful-life of power transformers is strongly correlated to the condition of its insulation paper. Traditionally, we have been using the concentration of carbon monoxide and carbon dioxide, furan compound (2-furfuraldehyde) as indicators. However, these indications and methods also have their limitations. In recent years, methanol has been identified as an additional ageing marker that aids the insulation paper diagnosis. It has received much attention in the industry and active research works were also conducted in different parts of the world. Hydro-Québec is a front runner in developing and applying the new technology and a wider population of transformer testing is desired in order to build up the scientific case of its applicability and effectiveness for the industry.

With participation of a transformer manufacturer (Prolec-GE) and a couple of utilities (Taipower and CLP), led by the methanol research experts (IREQ), a multi-national and multi-year research work was conducted. Over a thousand transformers were selected and their oil samples were tested in laboratory conditions. Their traces of methanol (MeOH) and ethanol (EtOH) were analyzed. The objective is to examine and compare the behavior of methanol and ethanol contents in different operating conditions and geographical areas.

From our studies, it was shown that there is sufficient evident that the methanol was detected in transformers after they were in services for at least a few years (e.g. > 10). Detection of methanol was also observed in temperature and overload tests for new transformers at the manufacturer level. The detection of methanol was also appearing earlier than the conventional method such as 2-FAL by at least 3-5 years, rendering it being a potentially more sensitive ageing and fault detection marker. Although traces of ethanol were also detected in the field, it is not clear how the ethanol reading can be effectively utilized as yet. It is however quite promising as research work seem to indicate ethanol can be used for tracking high temperature faults (e.g. >250°C) in the insulation papers.

Detailed field measurement studies were also carried out by Taipower showing how nominal maintenance done on the transformers such as degassing and oil filtering could also “reset” the methanol and ethanol readings. This is also true for CO_2 and moisture while 2-FAL readings remain relatively stable. This is of importance in practice as detailed recording of equipment maintenance and having multiple markers are important.

In essence, the R&D program was conducted successfully, thanks to the continuous supports from IERE and Hydro-Québec. The learnings from the field tests and sharing at the annual review meetings were found most useful. To go further, Hydro-Québec has proposed to ask the IERE members pooling their scrapped transformers for post-mortem diagnoses. By examining in details what the real ageing conditions of the papers are when we do the post-mortem, we can then further develop a credible model that can predict the life expectancy of transformers based on the level of methanol and ethanol detected.

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1. INTRODUCTION

An electrical transformer is a major component in any power system and its main function is to convert electrical energy from one voltage to another suitable for transmission and distribution purposes. Typical transformers normally work continuously and their life expectancy range from 30-50 years. To maintain a high reliability and avoid any catastrophic failure, utilities normally have equipment health check programs set up to monitor, assess and diagnose the condition of transformers such that ageing or early fault symptoms can be detected before significant degradation and/or major failure happens.

For transformers, the end of the useful-life is strongly correlated to the condition of its insulation paper. Traditionally, we have been using the concentration of carbon monoxide and carbon dioxide, furan compound (2-furfuraldehyde) as indicators. However, these indications and methods also have their limitations when applied in the field. Recently, methanol has been identified as an additional ageing marker that can be used to aid the insulation paper diagnosis. It has received much attention in the industry and active research works were also conducted in different parts of the world to trial the innovative method. Hydro-Québec is the front runner in applying the new technology and a wider population of transformer testing is desired in order to build up the scientific case of its applicability and effectiveness for the industry.

With the support from International Electric Research Exchange (IERE), a joint research program led by the research arm of Hydro-Québec, IREQ, was launched in 2012. A number of IERE members joined the R&D program. Throughout the period of 2012-2015, the participants were applying the methanol detection method developed by IREQ on various transformers in their own businesses and service areas. The R&D group also met once a year to convene and share their findings.

This final report, applied only for transformers insulated with cellulose based materials (i.e. not Nomex), collected and shared the experiences gained and findings in the field. The participating members in this world-wide study included utilities from Canada, Japan, India, Taiwan and Hong Kong, China as well as a manufacturer from Mexico.

2. TRANSFORMER BASICS

This section describes the principal concepts of a transformer, including its classification, performance, construction, important design parameters, installation, maintenance and general operation.

2.1 Transformer Principle

An electrical transformer is a static device that, by electromagnetic induction, transmits electrical power from one alternating voltage level to another without changing the frequency. It has two or more windings of wire wrapped around a ferromagnetic core. These windings are not electrically connected, but they are magnetically coupled, i.e., the only connection between the windings is the magnetic flux present within the core. In other words, a transformer is a device with no continuously-moving parts, that by means of electromagnetic induction, transfers electrical energy between two circuits at, generally, different voltage between terminals. Figure 1 shows the schematic of the transformer principle.

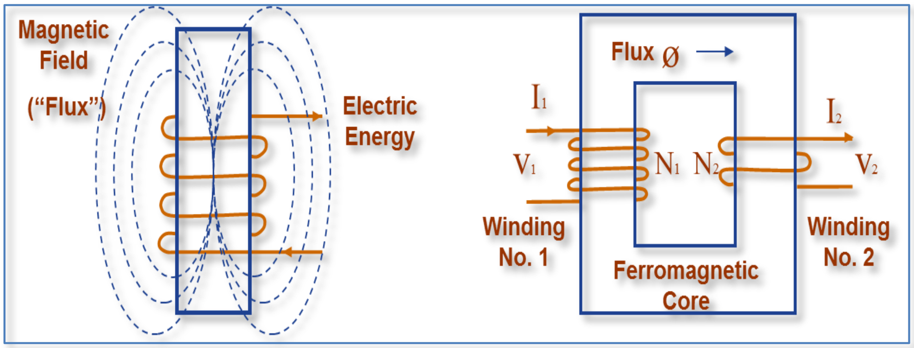

FIGURE 1: TRANSFORMER PRINCIPLE

where:

N = Number of turns of conductor
I = Current
V = Voltage
N1/N2 = Turns Ratio
N1/N2 = I2/I1=V1/V2

The electrical energy received by the primary winding is first converted into magnetic energy which is then reconverted back into a useful electrical energy in the secondary winding (and tertiary winding, if it exists).[1]

In the power industry, the transformers are generally classified depending on its type of core, voltage, number of phases. Table 1 listed the key attributes and classes and the following sections will further explain these classification.

TABLE 1: GENERAL OIL-IMMERSED TRANSFORMER CLASSIFICATION

CLASSIFICATION	DESCRIPTION
Type of transformer	Power (PT) Distribution (DT)
Number of phases	Three Phases Single Phase
Type of Construction	Core type Shell type
Application in the Power System	Substation step down Generator step-up Autotransformer Transmission Reactors Distribution

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[1] **Georgilakis, P.**, *Spotlight on Modern Transformer Design*, Springer, 2009.

	Industrials
Transformer Cooling	ONAN ONAF OFAF OFWF ODAF ODWF
Oil Preservation System	Sealed tank Regulated pressure tank Expansion tank
Transformation Ratio	Load tap changer (LTC)

2.1.1 Number of phases: Single / three phase

Three-phase power is attainable with either one three-phase transformer, which is constructed with three single-phase units enclosed in the same tank or three separate single-phase transformers. The methods of connecting windings are the same, whether using the one three-phase transformer or three separate single-phase transformers

2.1.2 Type of construction: Core/shell type

There are two broad categories of transformer design, shell type and core type. They can be functionally identical, and the choice between the two is basically determined by the design philosophy and know-how of the manufacturer since the two types require fundamentally different design and manufacturing techniques. Figure 2 shows an example of core and shell types.

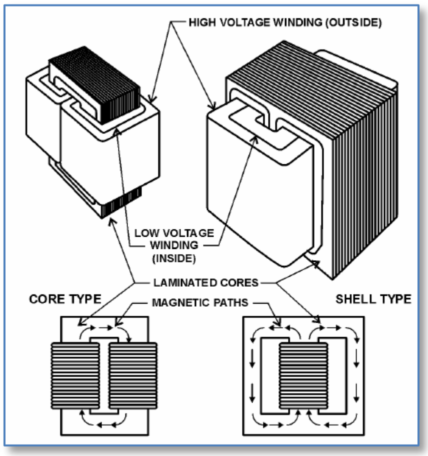

FIGURE 2: MAGNETIC CIRCUIT WITH CORE AND SHELL TYPE

In a shell-type (shell form) transformer, the steel magnetic circuit (core) forms a shell surrounding the windings and the windings are on the inside. In a core form, the windings are on the outside. In power transformers, the electrical windings are arranged so that practically all of the magnetic lines of force go through both the primary and secondary windings. A small percentage of the magnetic lines of force goes outside the core, and this is called leakage flux.

2.1.3 Transformer cooling system

The main source of heat generation in transformer is its copper loss or I^2R loss. Although there are other factors that contribute heat in transformer such as hysteresis and eddy current losses but contribution of I^2R loss dominates them. If this heat is not dissipated properly, the temperature of the transformer will rise continually which may cause damages in paper insulation and liquid insulation medium of transformer. So it is essential to control the temperature within the permissible limit to ensure the long life of transformers by reducing thermal degradation of its insulation system. In electrical power transformer we use external transformer cooling system to accelerate the heat dissipation rate in transformers.

There are different transformer cooling methods available, where the acronym can described its principal characteristic:

- ONAN (Oil Natural Air Natural) - Natural convectional flow of hot oil is utilized for cooling. In convectional circulation of oil, the hot oil flows to the upper portion of the transformer tank and the vacant place is occupied by cold oil;

- ONAF (Oil Natural Air Forced) – With forced air, heat dissipation can obviously be increased. If dissipating surface is increased and forced air flow is applied on that dissipating surface, the cooling can be improved. Air fans are usually employed;

- OFAF (Oil Forced Air Forced) - The heat dissipation rate can be further increased if this oil circulation is accelerated by applying some force. In OFAF oil cooling system forces the circulation within the closed loop of transformer tank by means of oil pumps;

- OFWF (Oil Forced Water Forced) - The hot oil is sent to water heat exchanger by means of oil pump and then the oil is cooled by applying showers of cold water on the heat exchanger's oil pipes;

- ODAF (Oil Directed Air Forced) - Forced circulation of oil is directed to flow through predetermined paths in transformer winding. The cooling oil entering the transformer tank from the cooler or radiator is passed through the winding where gaps for oil flow or pre-decided oil flowing paths between insulated conductors are provided to ensure faster rate of heat transfer; and

- ODWF (Oil Directed Water Forced) – This is just like ODAF and only differs whereas the hot oil is cooled in cooler by means of forced water instead of air. Both of these transformer cooling methods are called forced directed oil cooling of transformer.

2.1.4 Oil preservation system

There are different designs for oil preservation system. A preservation system is essential for a liquid-immersed transformer to allow expansion and contraction of the liquid due to the changes in the temperature without exposing the insulating liquid to external contamination. The expansion space is known as “the oil preservation system”. The following information describes the common preservation systems.

- Free Breathing Sealing - Sealing systems have progressed from early designs of “free breathing” tanks, in which an air space on top of the oil is vented to atmosphere through a breather pipe. The pipe typically is screened to keep out insects and rodents and turned down to prevent rain from entering. If there is one or more of these earlier design transformers, a desiccant type air dryer is usually added to the breather pipe;

- Sealed or Pressurized Breathing – This design is similar to the free breathing type with the addition of a pressure/vacuum bleeder valve. When the transformer was installed, pressurized dry air or nitrogen was placed on top of the oil. The bleeder valve is designed to hold pressure inside to approximately plus or minus 5 psi;

- Pressurized Inert Gas Sealed System – This system keeps space above the oil pressurized with a dry inert gas, normally nitrogen. This design prevents air and moisture from coming into contact with insulating oil. Pressure is maintained by a nitrogen gas bottle with the pressure regulated normally between 0.5 and 5 psi;

- Free Breathing Conservator – This design adds an expansion tank (conservator) above the transformer so that the main tank may be completely filled with oil. Oil expansion and air exchange with the atmosphere (breathing) occur away from the oil in the transformer. This design reduces oxygen and moisture; and

- Conservator with Bladder or Diaphragm Design – The bladder or diaphragm expands and contracts with the oil and isolates it from the atmosphere. The inside of the bladder or top of the diaphragm is open to atmospheric pressure through a desiccant air dryer.

2.2 Important Design Parameters

There are some critical parameters that define the functional capability of a transformer and that are contained in a customer's specifications:

- Load Rating (base and increased cooling)
- Rated Voltages (HV, LV, TV)
- Winding Connection (Y, Δ, Z)
- Temperature Rise (65 °C, 55 °C)
- Impedance
- Ambient Temperature (30 °C Avg., 40 °C max)
- Core excitation: 110% input voltage at no load, 105% output voltage at full load
- Tolerances according to ANSI-IEEE C57.12.00

And, there are other special requirements that could be included in the specifications:

- Core over-excitation
- Overloads with moderate loss of life
- Impedances for multi-windings
- Impedance range for taps
- Extreme ambient temperatures (55 °C…-50 °C)
- Short circuit with overvoltage
- Corrosive operating ambient
- Frequent short circuits or over-voltages
- Reduced tolerances (impedance, losses, turns)
- Reduced dissolved-gas-analysis (DGA) in oil

During the design of a transformer, there are some relevant challenges that should be considered to have the best performance and the best solution to the customer necessity. Some of those challenges are:

- Accurate estimation of losses (No-Load Loss, Load Loss)
- Cooling (Normal and Overload)
    - Accurate estimation of hottest-spot temperatures
    - Limit thermal degradation of cellulose (insulation) and oil
    - Limit winding surface thermal load (W/in^2)

    - Combustible gas generation prevention
- Overvoltage endurance (Impulse, Switching)
    - Limit electrical stress in oil
    - Accurate calculation of voltage distribution
- Mechanical Withstand (Short Circuit, Vacuum, Shipping)
    - Accurate calculation of forces and stresses
    - Estimation of impact strength of materials
    - Limit noise levels to required values

2.3 Construction and Testing

2.3.1 Construction

In essence, there are seven basic stages for the construction of a transformer. Although these stages may vary from manufacturer to manufacturer, the basic stages can be described as:

1. Insulation – Depending on the design, the insulating materials are cut and received for its use in the coils process. Other insulators will be used to drop the coils with the core;

2. Coils and Sizing – Depending on the type (wire, sheet, etc.), the conductor is insulated with paper or any other insulating material to manufacture the coils (single phase or three phases) and put them in the oven to dry the insulators and beginning with the sizing of this components. Some conductors are received with insulator material;

3. Core – The silicon steel is cut in sheets to proper length and stacking to form the core in power transformers. For distribution transformers the silicon steel or amorphous metal is cut to proper length to form the wound core. Some cores are bought ready to be used with the coils;

4. Core and Coil assembly – Both components are dropped and dried. Some internal components could be installed, depending on the specific design;

5. Tank – At the same time of core construction, the manufacturing of the tank starts too;

6. Tanking – Once Core and Coils are dried, those are set up in the tank and all connections should be done; and

7. Final assembly – In this stage, all accessories are installed, the transformer received a vacuum process and it is filled with the dielectric fluid.

2.3.2 Testing

After these steps, the transformer goes to testing and shipping areas. In power transformers, there are some other points to note prior to shipping, namely:

- Perform Frequency Response Analysis Test
- Disassemble Transformer, Final Dry-out Process, And Pressurize With Dry Air to 3-5 psi
- Install Impact Recorders: Digital & Analog Options
- Ship Transformer to Customer

Transformer testing falls into three broad categories:

- Factory testing when the transformer is new or has been refurbished;

- Acceptance testing upon delivery; and
- Field testing for maintenance and diagnostic purposes.

Some tests at the factory are common to most power transformers, but many of the factory tests are transformer-specific. Some tests at the factory are common to most power transformers, but many of the factory tests are specific. In the following figure are shown several typical tests done in transformers.

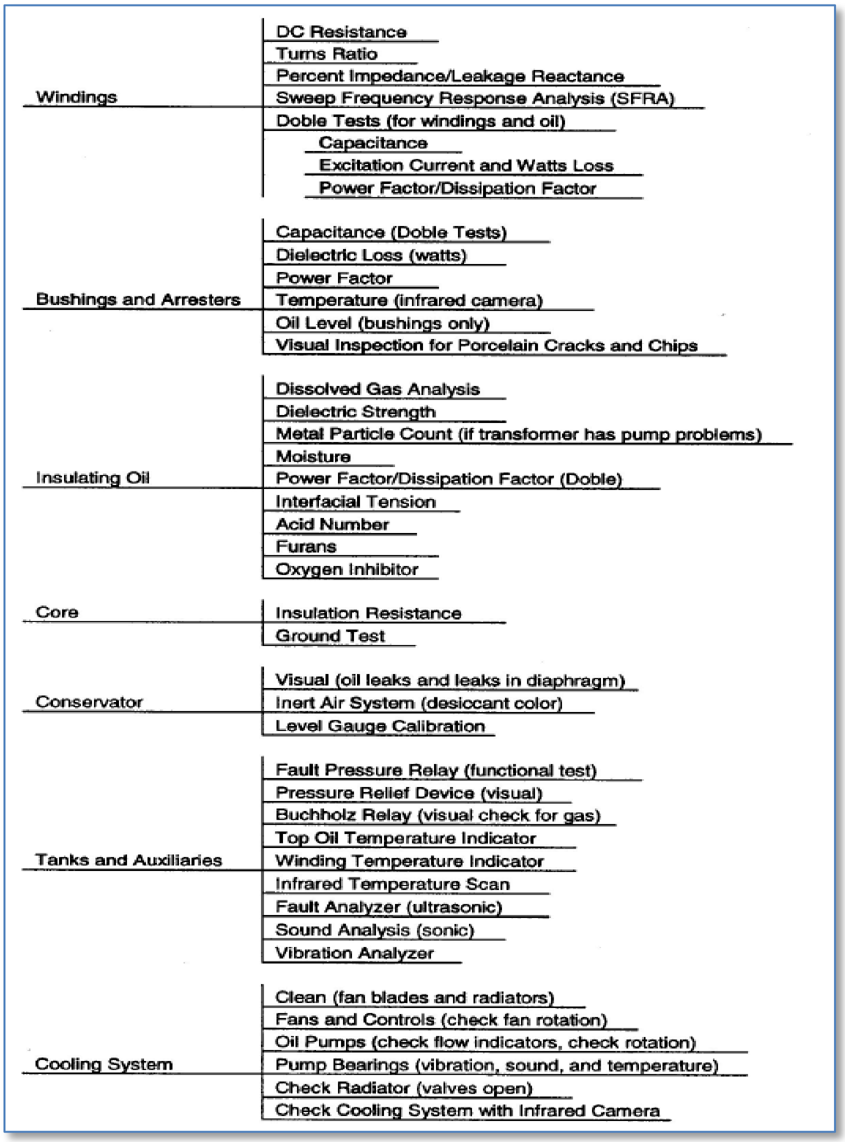

Figure 3: transformer Diagnostic Test Chart[2]

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[2] "Transformers: Basics, Maintenance, and Diagnostics", 2005.

3. CELLULOSE AGEING MARKERS

The end of the useful life of an in-service transformer is strongly correlated to the degree of its insulation paper degradation. On the diagnosis of transformer internal insulation papers, first effort is usually focused on the detection of carbon monoxide (CO) and carbon dioxide (CO_2) quantified by Dissolved-Gas-Analysis (DGA) when ageing begins to show within the paper or oil components. As early as 1981, Tamura *et al.* reported a relationship between the amount of carbon oxides (CO and CO_2) in the oil and the degree of polymerization of insulation papers.[3] However, its applicability was found to be limited considering that these indicators could arise not only from the degradation of paper but also the decomposition of oil during long-term oxidation. The situation is more complex with respect to useful life estimation due to the potentially long ageing time an apparatus may experience, e.g. over 20 years. For example, in open-breathing transformers, the presence of sufficient amount of oxygen is necessary to generate CO/CO_2 in oil and the paper while the paper moisture is also a parameter of prime importance.[4] Moreover, in open-breathing transformers, the carbon oxides (CO/CO_2) can escape from the systems and completely disappear during operations such as oil degassing or regeneration. The low solubility of CO/CO_2 in the insulation paper compared to the one in the oil prevents marker re-equilibration in the oil[5], after which its correlation with the insulation paper degradation becomes meaningless. Since a transformer most likely experiences some maintenance work during its useful life and some leaks may be observed in sealed transformers, the reliance of the CO/CO_2 content to detect or predict the end of useful life becomes questionable sometimes.

An alternative approach is considering a family of furan compounds, especially 2-furfuraldehyde (2-FAL). These compounds are more specifically linked to paper insulation breakdown,[6] though many drawbacks have to be taken into account. In particular, the presence of a very small amount of 2-FAL for thermally upgraded insulation paper (TU paper) renders its detection a laborious process.[7, 8] In addition, the high production rate from hemicelluloses compared to cellulose,[9] the thermal instability of the compound,[10] and the effect of moisture on the rate of production are among the concerns utilities are facing today. Consequently, the use of 2-FAL as a chemical marker for establishing the remaining life of cellulose insulation is also under some scrutiny by the scientific community.

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[3] **Tamura, R., Anetai, H., Ishii, T. and Kawamura, T.** (1981) Diagnostic of ageing deterioration of insulating paper, *JIEE Proc.* Pub. A, 101, 30.

[4] **Stevens GC and Emsley AM**, Review of indicators of degradation of cellulosic electrical paper insulation in oil-filled transformers. *IEE Proc.-Sci. Meas. Technol.* September 1994, Vol. 141, No. 5, pp. 324-334.

[5] **Hisao K, Teruo M, Yoshihiro M, Sadao N and Takashi H**, Absorption of CO_2 and CO gases and furfural in insulating oil into paper insulation in oil-immersed transformers. *Conf. Rec. of the 1994 IEEE International Symposium on Electrical Insulation.* June 5-8, 1994.

[6] **Burton PJ, Carballeira M, Duval M, Fuller CW, Graham J, De Pablo A, Samat J and Spicar E**, Application of liquid chromatography to the analysis of electrical insulating materials, *Proc. CIGRE Conf., Paris.* 1988, Vol. Paper 15-08.

[7] **Griffin PJ, Lewand LR and Pahlavanpour B**, Paper degradation by-products generated under incipient-fault conditions. 1994, Vol. Doble Engineering Meeting, Paper 10-5.1.

[8] **Lundgaard LE, Hansen W, Linhjell D and Painter TJ**, Ageing of oil-impregnated paper in power transformers. *IEEE Transactions on Power Delivery.* January 2004, Vol. 19, 1.

[9] **Scheirs J, Camino G, Avidano M and Tumiatti W**, Origins of furanic compounds in thermal degradation of cellullosic inslulation paper. *Journal of Applied polymer Science.* 1998, Vol. 69, pp. 2541-2547.

[10] **Allan DM and Jones CF**, Thermal-oxidative stability and oil-paper partition coefficients of selected model furan compounds at practical temperatures. *Ninth International Sysmposium on High Voltage Engineering.* 1995.

Three years later, Burton *et al.* (1984) suggested the use of a family of furan compounds that could be directly extracted from the oil to characterize the thermal decomposition of insulation papers.[11] The advantage of such compounds over carbon oxides is that they arise more specifically from the breakdown of the paper insulation. The cumulative amount of the most abundant furan found in transformer oil, 2-furfuraldehyde (2-FAL), was very early related directly to the reduction of the degree of polymerization of the cellulose, both in the laboratory and from in-service transformers.[16, 12] However, considering that 2-FAL could be generated not only from the cellulose degradation but also from hemicellulose (5-membered ring polysaccharides known to possess the lowest stability of all wood-pulp materials), this decreases its value as a chemical indicator (Emsley and Stevens 1994). Moreover, the recent literature is conclusive on the existence of significant differences in the relationship between 2-FAL and DP_v during ageing with the type of paper (ordinary Kraft *vs* thermally-upgraded (TU) Kraft paper), and varying contents of water (Oommen *et al.* 1993[13]; Soares *et al.* 2001[14]; Lundgaard *et al.* 2004[15]). Despite the numerous attempts to correlate 2-FAL with cellulose damage, no satisfactory relationship has yet been established to cover the various in-service transformer conditions.

Cellulose, an unbranched homopolysaccharide composed of β-D-glucopyranose rings joined together by 1,4-β-glucosidic bonds, has been used for over 100 years as electrical insulation in oil-filled transformers (a typical power transformer contains about 12,000 kg of cellulose and 40,000 kg of oil). Its inherent good mechanical and electrical properties, its ease of use in the manufacturing process, and its abundance (obtained from the delignification of wood pulp by the Kraft process) have made it a virtually universal choice. Moreover, this material is generally recognized as the most significant limiting factor in the operating temperature and thermal life of transformers. The combined action of temperature, oxygen and moisture cause the insulation to lose mechanical strength and become weak and brittle. The transformer is then at the mercy of the first short-circuit whose longitudinal electromagnetic stresses crush the paper, in spite of all precautions that may have been taken. Owing to the worldwide growth of large-scale utility systems in the 1950s and 1960s, a large number of transformers now operate at an age beyond the nominal design life. Then, some means of condition monitoring has become essential to promote satisfactory programs of planned maintenance or replacement.

From the standpoint of molecular structure, the ageing of the cellulose fibers is related to the crosswise break of the inter- and intra-molecular hydrogen bonds and the lengthwise break of the molecular chains through the rupture of the 1,4-β-glucosidic bonds. Specifically, the average length of the cellulose chains is the parameter that governs the mechanical strength of the insulating papers. Such a relationship makes the viscometric **degree of polymerization** (DP_v) an appropriate measurement for directly assessing the progress of paper ageing (20% of tensile strength corresponds to $DP_v \approx 200$). This widely used parameter by electric power utilities gives information on the average number of β-D-glucopyranose rings per cellulose molecule. However, the DP_v measurement is impractical in the field due to the need to de-energize the transformer to extract representative paper specimens. To overcome the difficulty, it would be especially useful to identify a relationship between the

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[11] **P.J. Burton, P.J.,. Graham J.,, A.C. Hall , J.A.C., Laver J.A. and A.J. Oliver A.J.**,, "Recent developments by CEGB to improve the prediction and monitoring of transformer performance", *CIGRE Paper 12-09*, 1984.

[12] **Schroff, D. H. and Stannett**, A. W. (1985) A review of paper ageing in power transformers, *IEE Proc.* 132(6), 312.

[13] **Oommen TV, Petrie EM, Breemen RB, Haney CA** (1993) Analysis of furanic compounds from cellulose ageing by GC-MS and attempts to correlate with degree of polymerization,CIGRE Berlin Symposium, Paper 110-02.

[14] **Soares S, Ricardo N, Heatley F, Rodrigues E** (2001) Low temperature thermal degradation of cellulosic insulating paper in air and transformer oil. Polymer Int 50:303.

[15] **Lundgaard LE, Hansen W, Linhjell D, Painter TJ** (2004) Ageing of oil-impregnated paper in power transformers. IEEE Trans on Power Delivery 19(1):230.

cellulose DP_v and a specific product dissolved in the insulating oil that is resulting from ageing. Once established, such a relationship would permit oil analyses to be used to assess the insulating paper condition of transformers in operation.

In 2007, the use of methanol (CH_3OH) was reported for the first time in the literature by Jalbert *et al.* for estimating the degree of cellulose insulation degradation.[16] Laboratory tests showed that methanol is mainly produced during the ageing of oil-impregnated paper insulation at 60-120^{o}C (inhibited naphthenic oil under air), regardless of whether or not the specimens are thermally upgraded. This work revealed the existence of a direct relationship between methanol (CH_3OH) production and the scission of 1,4-ß-glycosidic bonds (bonds that link the cellulose glucose units). Methanol was also detected in the ageing tests in the early scissions of the bonds even at temperatures as low as 60°C. More recently, a kinetics study carried out by the same research group on standard-Kraft paper (std)[17] and on TU-Kraft paper[18]showed that depolymerization and methanol production required an activation energy (E_a) of about 104 $kJmol^{-1}$, thus confirming the link between the two processes. Moreover, the production of methanol and broken cellulose chains showed about the same value for the exponential factors (A_a) of the Arrhenius expression, which introduces the possibility that the rate of production of CH_3OH from chopped chains is much higher than the rate of depolymerization, so that the latter becomes the rate determining step of the overall reaction. This means that contrary to 2-FAL, methanol is instantaneously produced after the opening of the 1,4-ß-glycosidic bonds and, consequently, can be detected earlier in the oil. These authors also demonstrated the role played by both oxygen and moisture on the exponential factors as obtained from the application of different degradation models: pseudo-zero Ekenstam's rate constants,[19] first-order time dependent decrease of k_1,[20] power law[21] and single first-order evolution equation[22] by comparing paper ageing in naphthenic oil under air with paper ageing in uninhibited paraffinic oil under nitrogen. Finally, the oil of pieces of equipment from different utilities (e.g. transformers, shunt reactors, current transformers, etc.) was sampled and assessed for CH_3OH and 2-FAL. The results showed that methanol is detected in the majority of these equipment compared to 2-FAL.

Since the first use of high-performance liquid chromatography (HPLC) by the electric power industry, [16] the research that followed on ageing was for the most part subject to HPLC standard test methods (ASTM D5837 or IEC 61198) for assessing oil samples (giving access to a limited number of molecules of a specific class). This use of an unidirectional analytical approach is at the very least surprising considering that studies in the 1960s in connection with the thermal degradation of pure cellulose indicated for the by-products a large spectrum of low molecular weight compounds starting from small molecules (H_2, CH_4, CO_2) through intermediate-size hydrocarbons, alcohols and carbonyl compounds to 1,6-anhydro-β-D-glucopyranose and other anhydrides equal in weight to the cellulose monomer (Schwenker and Beck 1963[23]; Glassner and Pierce 1965[24]; Shafizadeh

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[16] **Jalbert J, Gilbert R, Tétreault P, Morin B and Lessard-Déziel D**, Identification of a chemical indicator of the rupture of 1,4-β-glycosidic bonds of cellulose in an oil-impregnated insulating paper system. *Cellulose.* 2007, Vol. 14, pp.295-309.

[17] **Gilbert R, Jalbert J, Tétreault P, Morin B and Denos Y**, Kinetics of 1,4-β-glycosidic bonds rupture in cellulose and correlation with methanol formation during ageing of paper/oil systems. Part 1: Standard wood kraft insulation,. *Cellulose.* 2009, Vol. 16, pp. 327-338.

[18] **Gilbert R, Jalbert J, Tétreault P, Morin B and Denos Y**, Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the ageing of paper/oil systems. Part 2: Thermally-upgraded insulating papers. *Cellulose.* 2009, Vol. 17, 2, pp. 253-269.

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[21] **Calvini P**, The influence of leveling-off degree of polymerization on the kinetics of cellulose degradation. *Cellulose.* 2005, Vol. 12, pp. 445-447.

[22] **Ding HZ and Wang ZD**, On the degradation evolution equations of cellulose. *Cellulose.* 2008, Vol. 15, pp. 205-224.

[23] **Schwenker RF, Beck LR** (1963) Study of the pyrolytic decomposition of cellulose by gas chromatography. J Polymer Sci Part C 2:331–340.

1968[25]; Kilzer 1971[26]). During this period, the total number of volatile by-products isolated and identified by gas chromatography was well over 50 and included formaldehyde, acetaldehyde, methanol, acetone, ethanol, glyoxal, 2-butanone and furan. Very little attention in the field has been paid to these molecules over the last 20 years. To our knowledge, only two papers reported the use of such by-products for the assessment of paper insulation, one based on the use of a semiconductor-type sensor in the oil headspace and the other on the determination of acetone in oil (Abe *et al.* 1994[27]; Awata *et al.* 1997[28]).

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[24] **Glassner S, Pierce AR** (1965) Gas chromatographic analysis of products from controlled application of heat to paper and levoglucosan. Anal Chem 37:525.

[25] **Shafizadeh F** (1968) Pyrolysis and combustion of cellulose materials. In: Wolfrom ML, Tipson RS (eds) Advances carbohydrate chemistry, vol 23. Academic press, New York, p 419.

[26] **Kilzer FJ** (1971) Thermal degradation of cellulose. In: Bikales NM, Segal L (eds) High polymers, vol 5, Pt 5, p 1015

[27] **Abe, K., Maeda, T., Shimonaka, T. and Umemura, T**. (1994) A sensing system for degradation diagnosis of oil-filled transformers, *Conf. Record of IEEE Int. Symp. on Electrical Insulation*, p 29.

[28] **Awata, M., Mizuno K., Ueda, T., Ohta, N., Ishii, T. and Tsukioka, H**. (1997) Diagnosis by acetone for determination of breathing transformers containing an adsorbent in the insulating oil, *Trans. IEE Japan* **117-B (5)**, 706.

4. PARTIONING EFFECTS (TEMPERATURE, MOISTURE, ACIDITY ETC)

4.1 Effect of the temperature in the partition of markers[29]

Many efforts have been deployed in the last decades to define the applicability and the limitations of the furanic compounds as chemical markers for the diagnosis of cellulose insulation ageing in power transformers. Indeed, IEEE[30]and CIGRÉ[31] have recently published reports on this topic. Their main conclusion indicates that from the five furan compounds identified by Burton et al.[32] in 1984, 2-furfural (2-FAL) provides the more relevant information on paper degradation. However, transformer differences such as amount of solid insulating material or type of design (ex. shell vs. core) limit 2-FAL interpretation and establishment of typical threshold values. In addition, several physico-chemical parameters such as temperature, humidity, oxygen concentration, etc. influence the concentration of 2-FAL in the transformer oil.[33,34,35]

In the past, it has been difficult to conclude about the reliability of 2-FAL use for transformer diagnosis due to the lack of other equivalent markers. Recently, the methanol (MeOH) marker began to be used in transformer insulation diagnostics.[36,37,38,39,40,41,42] This marker has the advantage of being generated from all types of cellulose based papers e.g. standard Kraft and Thermally Upgraded (TU) papers even at low temperature which is not the case for 2-FAL. There is also a direct link between MeOH generation and the 1,4-β-glycosidic bond rupture of cellulose which has never been demonstrated with any other marker. Therefore, its presence could be associated to the residual life of insulating paper. More recently, ethanol

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[29] **J. Jalbert J. and M-C. Lessard M.C.**,, "Cellulose chemical markers in transformer oil insulation. Part 1: Temperature correction factors", IEEE Trans. Dielectr. Electr. Insul., Vol. 20, No. 6, pp. 2287-2291, 2013.

[30] **L. Cheim, D. Platts, T. Prevost and S. Xu**, "Furan analysis for liquid power transformers" *IEEE Electrical Insulation Magazine*, Vol. 28, No. 2, March-April 2012.

[31] **CIGRE Working Group D1.01.TF 13**, "Furanic compounds for diagnosis", *CIGRÉ Brochure No. 494*, April 2012.

[32] **P.J. Burton, J. Graham, A.C. Hall, J.A. Laver and A.J. Oliver**, "Recent developments by CEGB to improve the prediction and monitoring of transformer performance", *CIGRE Paper 12-09*, 1984.

[33] **J. Kachler and I. Höhlein**, "Ageing of Cellulose at Transformer Service Temperatures, Part 1. Influence of Type of Oil and Air on the Degree of Polymerisation of Pressboard, Dissolved Gases and Furanic Compounds in Oil", *IEEE Electrical Insulation Magazine*, Vol. 21, March/April 2005.

[34] **I. Höhlein and J. Kachler,** "Ageing of cellulose at transformer Service Temperatures. Part 2. Influence of Water content and Temperature on Degree of Polymerization and Formation of Furanic Compounds in Free-Breathing Systems," *IEEE Elect. Insul. Mag.*, Vol. 21, No. 5, (Sept./Oct.), 2005.

[35] **J.A. Lapworth, R. J. Heywood, P.N. Jarman and C. Myers,** "Transformer Insulation: Towards more reliable residual life assessments", *Cigre A2-D1 Colloquium in Brugge*, 2007.

[36] **Jalbert J and Besner S,** "Methanol as a chemical indicator of insulating paper ageing in power transformer", *EJEE*, Vol.13, No. 5-6, 2010.

[37] **Jalbert J., Gilbert R., Tétreault P., Morin B., Lessard-Déziel D**., "Identification of a chemical indicator of the rupture of 1,4-β-glycosidic bonds of cellulose in an oil-impregnated insulating paper system, *Cellulose*, vol. 14, 2007.

[38] **Gilbert R., Jalbert J., Tétreault P., Morin B., Denos Y.,** " Kinetics of the production of chain-end groups and methanol from the depolymerisation of cellulose during the ageing of paper/oil systems. Part 1: Standard wood kraft insulation", *Cellulose*, vol. 16, 2009.

[39] **Gilbert R., Jalbert J., Duchesne S., T.étreault P., Morin B., Denos Y.,** "Kinetics of the production of chain-end groups and methanol from the depolymerisation of cellulose during the ageing of paper/oil systems. Part 2: Thermally-upgraded insulating papers", *Cellulose*, vol. 17, 2010.

[40] **Denos Y., Tanguy A., Jalbert J., Gilbert R., Gervais P., Guuinic P**., "Ageing diagnosis by chemical markers influence of core-type and shell-type technology", CIGRE Session 2010, Paris, France, August 22-27, 2010.

[41] **Jalbert J., Gilbert R., Denos Y. and Gervais P.**, "Methanol: a novel approach to power transformer asset management", *IEEE Trans. Power Delivery*, Vol.27, No. 2, April 2012.

[42] **Schaut A., Stijn A. and Eeckhoudt S.**, "Applicability of Methanol as a New Marker for Paper Degradation in Power Transformers, *IEEE Trans. On Dielectrics and Electrical Insulation,* Vol. 18, No. 2, April 2011.

(EtOH), identified by the same research group studying MeOH, shown a particular behavior in some transformer oil analysis compared to lab ageing experiments.[43] Indeed, during 60 to 210°C lab ageing experiments under air or nitrogen atmosphere, the MeOH concentration was always higher than that for EtOH. Nevertheless, in some real transformer oil analysis from Hydro-Québec and Électricité de France fleet, the EtOH concentration was higher than for MeOH. A recent study in this domain has shown that EtOH acts as a hot spot chemical marker of cellulose insulation. [44] The particularity of the EtOH behavior appears at temperatures over 250°C. At this temperature, the major by-product generated is Levoglucosan (LG) who further decomposes to generate a high amount of EtOH. At this stage, the generation of EtOH becomes higher than for MeOH. This behavior could provide the ability to distinguish between normal and abnormal ageing of the cellulosic insulation and so differencing moderate ageing of a large area to accelerate ageing of a small area of solid insulation.

The first utility of 2-furfural and alcohol markers relies on their ability to provide an insight of the degree of polymerization (DPv) of the windings insulating paper. These markers can also be used to distinguish a normal ageing from a hotspot where a small highly degraded area provides a high yield of marker concentrations. Their combined use may also help the understanding the partition phenomena between the oil and the cellulosic insulation, a key factor when interpreting real transformer data. Knowing that a transformer operates under different loads (e.g. temperatures) and physico-chemical oil conditions (e.g. acidity); like water, the cellulose chemical markers will be equilibrated between the oil and the cellulose. In order to follow the real chemical markers trend during all the transformer life and perform appropriate diagnosis, it is crucial to make adequate corrections to their oil measured concentrations. Also, with the appropriated correction, utilities will count with a normalized cellulose markers concentration for the oil samples they took along the year with varying temperatures.

We propose temperature correction equations for MeOH, EtOH and 2-FAL using modified distribution transformers. These equations which were established from measurements on these units are compared to moisture equations which are already available in the literature.[45]

4.1.1 Model transformer setup

The temperature correction factors were established using three model transformers built with a 100 KVA distribution transformer parts and insulated with Kraft paper (Austral) and filled with a mineral oil (Luminol Tri oil, Petro Canada). This oil has the advantage to be very stable to oxidation minimizing acidity generation that could interfere in this study. Model transformers were built around a 100 KVA distribution transformers tank and core using kraft paper wrapped copper wire as high voltage and low voltage winding.[46] Other pieces of copper wire wrapped with Kraft paper were installed at the top of each tank for paper degradation analysis. The transformers have been modified in order to allow control of the tank temperature using an assembly of heating tape and water circulation, both regulated by electronic controllers (Omega) (see Figure 4). Moreover, these have been modified to breathe through silica gel with a 20 L top oil container. Each model transformer is equipped with electronic sensors (Domino, Doble eng.) allowing to record in real time the temperature and the moisture content.

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[43] **Ryadi M., Tanguy A., Jalbert J., Rajotte C**., “Alcohols based ageing chemical markers for the diagnosis of transformer cellulosic insulation”, *CIGRE A2 & D1 Conference, PS2-O-4*, Kyoto, 2011.

[44] **Rodriguez-Celis, Duchesne S., Jalbert J., Ryadi, M.,** “Understanding ethanol versus methanol formation from insulating paper in power transformers”, *Cellulose* (2015)

[45] *Mineral insulating oils in electrical equipment- supervision and maintenance guidance, IEC 60422*, 2005.

[46] **B. Noirhomme, E. David, H. Garbi, M.C. Lessard, R. Boissoneault**, “Application of dielectric response techniques for the condition assessment of power transformers”, *Annual report Conference on Electrical Insulation and Dielectric Phenomena*, 2005.

FIGURE 4: 100 KVA DISTRIBUTION TRANSFORMER USE FOR THE MARKERS TEMPERATURE EQUILIBRIUM TEST

These transformers were previously used to study the chemical markers under real operating conditions. Table 2 presents the conditions of the previous ageing experiment and Table 3 the state of each transformer at the end of the study. Knowing that a certain quantity of chemical markers has been generated, the transformers were heated from ~20 to ~90°C in order to study different equilibrium situations of these markers between the oil and paper insulation. Note that at 90°C, we limited the equilibrium time to minimize paper degradation which could interfere with this experiment.

TABLE 2: AGEING CONDITIONS

Transformer	Temperature (°C)	Moisture in paper (%)	Time (days)
T-14	92.0	3.7	59
T-15	94.8	2.1	148
T-16	93.9	1.4	199

Oil aliquots were taken at different times using 30-mL glass syringes in order to measure the concentration of the ageing chemical markers. In this manner, it was possible to determine the equilibrium concentrations of the studied markers at a specific temperature.

TABLE 3: TRANSFORMERS CELLULOSIC INSULATION STATE AFTER AGEING

Transformer	DP_v*	2-FAL (ppb)	MeOH (ppb)	EtOH (ppb)	H_20 (ppm)	Oil Acidity (mg KOH/g oil)
T-14	553	1843	814	129	11	0.008
T-15	682	625	394	57	4	0.004
T-16	745	247	172	38	2	0.007

* Measured on the paper stripes coming from the additional piece of wire.

MeOH and EtOH were assessed using headspace gas chromatography equipped with a mass spectrometer. All the experimental parameters can be found in a recent publication.[47] This method allows the measurement of MeOH and EtOH at the low ppb range with an accuracy and precision higher than 94%. The signal was calibrated by injecting a series of dilutions prepared from a stock solution of MeOH and EtOH in oil at a maximum concentration level of 2 ppm (weight/weight, w/w), 6-point calibration curves. Quantification was carried out in extracted ion monitoring mode after the acquisition of the spectrum in total ion monitoring (TIC). 2-FAL was analyzed using high-performance liquid chromatography (from Agilent Technologies) based on the ASTM D 5837 method (direct injection). The signal was calibrated (6-point calibration curves) by injecting a series of dilutions prepared from a stock solution of 2-FAL in oil at a maximum concentration of 2 ppm (w/w). The values for moisture were directly recorded on the electronic sensors installed on each transformer.

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[47] **Jalbert J, Duchesne S., Rodriguez-Celis E., Tétreault P., Collin P.**, Robust and sensitive analysis of methanol and ethanol from cellulose degradation in mineral oils., *J. of Chromatography A*, 1256, 2012.

4.2 Results and discussion

4.2.1 Determination of the correction factors

Figure 4 shows an example of the typical trend observed for each marker and for the water content in one of the transformers.[48] These profiles were obtained after about two years of experiments at different cycling temperatures. If we take the hypothesis that during this period, neither the paper nor the oil has aged significantly; the concentrations measured are directly related to the partition between the oil and the paper. During this temperature cycling period, the rate of the molecules to equilibrate between the oil and the paper was the following:

$$H2O > MeOH \approx EtOH > 2\text{-}FAL$$

For example, on Figure 4, we could observe that at 400 days, by changing the temperature from about 70 to 45°C, the concentration decreased more rapidly for water and equivalently for the alcohols and then for 2-FAL. These results are in conformity with the literature[49] where it is shown that MeOH equilibrates very rapidly compared to 2-FAL in real power transformers.

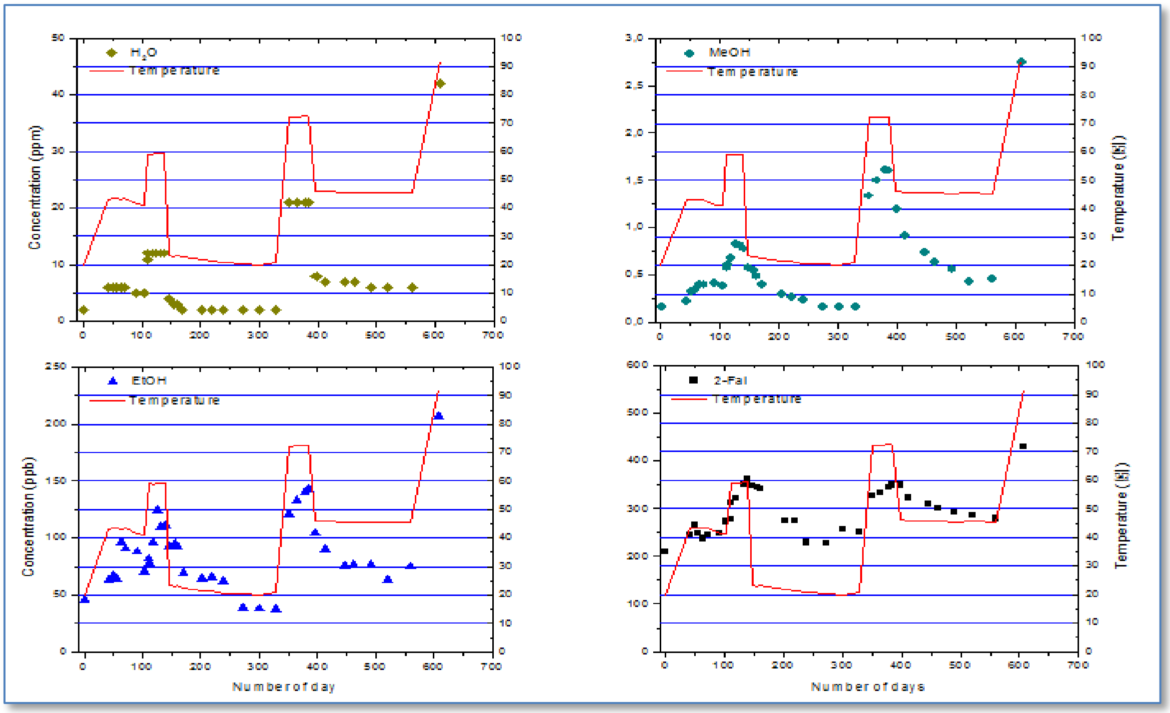

FIGURE 5: TYPICAL TEMPERATURE PROFILE & BEHAVIOUR OF MEOH

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[48] **J. Jalbert, M.C. Lessard and M. Ryadi,** "Cellulose Chemical Markers in Transformer Oil Insulation Part 1: Temperature Correction Factors "Accepted for publication, IEEE Trans. on Diel. and Elec. Insul., Vol.20, No. 6, December 2013.

[49] **Jalbert J., Gilbert R., Denos Y. and Gervais P**., "Methanol: a novel approach to power transformer asset management", *IEEE Trans. Power Delivery*, Vol.27, No. 2, April 2012.

By taking the same approach as the one used in the case of moisture, we can determine, at equilibrium for a specific temperature, a correction factor (Cfx) for each ageing marker (x). This Cfx was calculated by using the mean concentration values under equilibrium at an average temperature around 20°C divided by the one obtained under equilibrium at a specific temperature.

$$Cf_x = \frac{[\mathrm{Marker}]^{20°C}}{[\mathrm{Marker}]^{T_s}} \qquad (1)$$

where [Marker] is the concentration of a specific chemical marker and Ts is the oil sampling temperature.

Figure 5 shows typical Cfx curves obtained for the different markers studied. Each marker is denoted by a specific color and the symbols show some differences in order to represent the three transformers used. From this figure, we note that the most temperature dependent molecule is H2O followed by MeOH, EtOH and 2-FAL. Indeed by varying the temperature from 20 to 90°C, the Cfx of water decreases from 1 to about 0.06 (94%) compared to 1 to 0.44 (56 %) for 2-FAL, under the same equilibrium conditions. By applying a fit function finder to the data points, we obtained, for the three markers and the moisture, the following equation in the form:

$$Cf_x = ae^{-bT_s} \qquad (2)$$

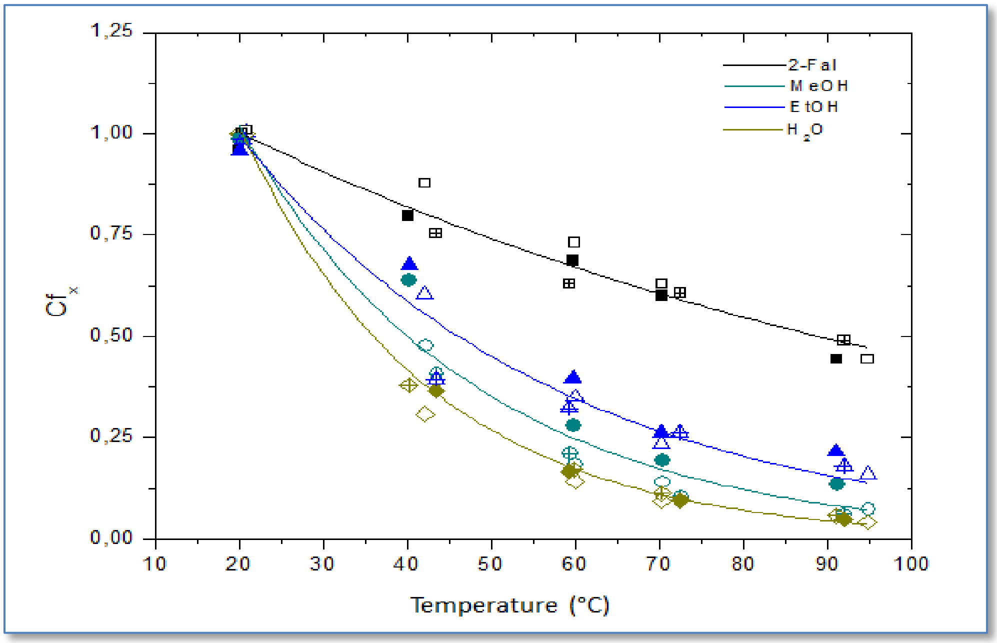

FIGURE 6: CFX OBTAINED FOR THE CHEMICAL MARKER STUDIES

The equation parameters are reported in Table 4. For moisture, there is a good similarity with the literature data[50] with a pre-exponential factor a = 2.59 compared to 2.24 and an exponential factor b = -0.04 for both cases. The best fit (R) was obtained for the moisture followed by MeOH, EtOH and 2-FAL probably due the influence of the equilibrium speed. Thus, in order to follow the real markers trends, public utilities need to use the following equation with the appropriate Cfx.

$$[\text{Marker}]20°\text{C} = [\text{Marker}]T_s{*}Cf_x \qquad (3)$$

TABLE 4: EQUATION PARAMETERS FOR THE CHEMICAL MARKERS STUDIED

Markers	a	b	R
H2O	2.59	0.04	0.998
MeOH	2.06	0.04	0.989
EtOH	1.65	0.03	0.983
2-FAL	1.23	0.01	0.980

The above results are the first step for an accurate and comprehensive evaluation of the cellulose health inside power transformers. Correcting the chemical markers concentrations, may allow the determination of thresholds and the following of the real concentration trends during all the transformer life. In addition, these results demonstrated the importance to register the transformer oil temperature during sampling. To maximize the oil homogeneity, it is recommended to sample the transformer oil on load. This would also allow the markers to be in equilibrium between the two phases (paper/ liquid). These correction equations are usable for oil temperatures over 20°C. Other oil parameters had shown influence on the partition of the markers.

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[50] *Mineral insulating oils in electrical equipment- supervision and maintenance guidance*, IEC 60422, 2005.

5. METHOD DEVELOPMENT

The method for analyzing methanol and ethanol from cellulose degradation in mineral oil was first published by IREQ (Institut de recherche d' Hydro-Québec)[41]. The procedure uses a static headspace sampler coupled with a gas chromatograph equipped with a mass spectrometer. The selected method parameters permitted adequate separation of these two compounds from the complex oil matrix and quantification at ng g−1 concentrations. The applicability of the method to the direct analysis of trace methanol and ethanol in oil from field transformer samples was successfully demonstrated.

5.1 Chemicals

i) Methanol：Sigma-Aldrich (99.9%), ChemService (>95%)
ii) Ethanol：Sigma-Aldrich (99.9%), ChemService (>98%)
iii) Ethanol-d6：Sigma-Aldrich (99.5%)
iv) Non-inhibited mineral transformer oil：YICO (I002)
v) He：>99.9995%

5.2 Apparatus

i) GC：Agilent/ 7890B
ii) MSD：Agilent/ 5977A
iii) Headspace Sampler：Agilent/ 7697A

5.3 Materials

i) Column：Agilent/ VF-624ms (60m)
ii) Syringe：100 mL, 250 µL, 25 µL, 10µL
iii) Connector：Peek, Female Luer × Female 1/4”-28
iv) Septum：3mm × 5mmφ (used between connector and 100 mL syringe)
v) Headspace vial: 20 mL
vi) Vial cap: center hole aluminum crimp cap, PTFE-butyl septum

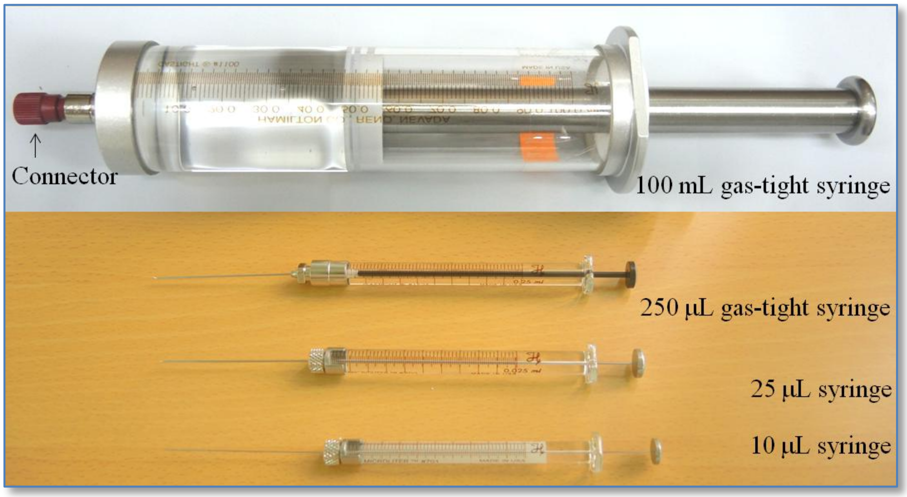

FIGURE 7: SYRINGE OF 100 ML (WITH CONNECTOR)

5.4 Internal Standard Procedure (IS)

To control variability in a quantitative assay, ethanol-d6 was used as an internal standard for methanol and ethanol measurements.[51] Ethanol-d6 was chosen for its absence in natural oil sample and its expected similar behavior to the analytes. The 1800 mg/L internal standard stock solution was prepared by adding 100 µL (~90mg) of ethanol-d6 99.5% to 50 mL of mineral oil in a 100 mL glass gas-tight syringe. All samples, blanks and calibration standards were added a constant amount (5 µL) of ethanol-d6 stock solution. The calibration involved plotting the ratio of the analyte signal (m/z 31) to the internal standard signal (m/z 33) as a function of the analyte concentration of the standards.

5.5 Calibration Standard Preparation

An 80 mg/L calibration stock solution was prepared by diluting 10 µL (~8 mg) of methanol and ethanol in 100 mL of mineral oil. A glass gas-tight syringe was used to perform the preparation process, and no air-filled space was left on the syringe to avoid migration of the analyte toward this region.

Calibration standards were prepared by spiking a specific amount of 80 mg/L calibration stock solution and 5 µL of 1800 mg/L ethanol-d6 stock solution to directly sealed 20-mL HS vials containing 10 mL of blank oil. Calibration standards with concentrations ranging from 0 to 2000 µg/L were prepared and analyzed. A linear regression curve fitting method and inverse of concentration weighting method were used.

TABLE 5: CALIBRATION STANDARDS

Concentration Prepared	80 mg/L Calibration Stock Solution	1800 mg/L IS Stock Solution	Blank Oil (in 20 mL vail)
1951 µg/L	250 µL	5 µL	10 mL
1600 µg/L	200 µL	5 µL	10 mL
1200 µg/L	150 µL	5 µL	10 mL
792 µg/L	100 µL	5 µL	10 mL
400 µg/L	50 µL	5 µL	10 mL
160 µg/L	20 µL	5 µL	10 mL
32 µg/L	4 µL	5 µL	10 mL
16 µg/L	2 µL	5 µL	10 mL

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[51] **J. Jalbert, S. J, Duchesne, E. S, Rodriguez-Celis, EM, Te´treault P,. Tetreault,, Colin P. Collin/ (**2012a) Robust and sensitive analysis of methanol and ethanol from cellulose degradation in mineral oils. J. Chromatogr. A 1256 (2012) :240–-–245. doi:10.1016/j.chroma. 2012.07.069

5.6 Instrumental Setting

This analytical method aims to determine methanol and ethanol in field samples at those low concentrations. Instrumental conditions presented in Table 6 have been selected to ensure appropriate specificity and sensitivity for the determination of methanol and ethanol. For headspace parameters, an equilibration temperature of 90 ◦C was chosen with mechanical shaking, to ensure the migration of the volatile components from the matrix into the vapor phase minimizing contamination of the HS system. The injection loop and transfer line are at higher temperatures (110–120 ◦C) to lessen adsorption of higher molecular weight compounds characteristic of the oil matrix. For chromatographic conditions, a mid-polarity VF-624ms column(6% cyanopropylphenyl, 94% dimethylpolysiloxane) connected to a split/splitless injector was used, and methanol, ethanol, and ethanol-d6 can be separated adequately with good peak shapes.

TABLE 6: INSTRUMENTAL PARAMETERS

Headspace Sampler Parameters		
Temperature	Sample	90°C
	Transfer line	110°C
	Gas sampling valve and injection loop	120°C
Pressure	Vial fill pressure	15 psi
Time	Equilibration at 90°C with shaking	40 min
	Injection	1 min
	GC cycle	45 min
Shaking	Power	136 shakes/min
Gas Chromatograph Parameters		
Column		VF-624ms (60 meters)
Aux 1 temperature		120°C
Aux 2 temperature		250°C
He carrier gas flow		1 mL/min
Split ratio		80:1
Oven run temperature		40°C
Run time		9 min

Oven post run temperature	280°C
Post run time	20 min
MS Parameters	
MS source type	EI (Apply voltage: 70 eV)
Gain Factor	1.000
MS source temperature	230°C
MS quad temperature	150°C
Acquisition type	SIM & Scan
Full Scan Mode Mass range	m/z = 30-300
SIM Mode Mass range	m/z = 31.00 (Dwell time 150 ms) m/z = 33.00 (Dwell time 150 ms)

5.7 Analytical performance

In the total-ion chromatogram (TIC), methanol and ethanol are present at earlier elution times together with other low-molecular-weight volatile carbonyl compounds. A mass chromatogram at m/z 31, characteristic of primary alcohols, was generated (Figure 8) and showed the methanol and ethanol peaks to be free of interferences. Peak identification was performed by comparing their retention times with those of pure components injected separately. Regular analysis of laboratory aged transformer oil, and in-the-field transformer oil samples have shown no other interfering peaks at the elution times of methanol and ethanol. Data is acquired in both full scan mode and selected-ion-monitoring (SIM) mode at the same time. In full scan mode, the full chromatogram fingerprint of the samples was obtained, and that could be useful to check for other molecules present in the transformer oil. To increase sensitivity and eliminate matrix interferences, the calibration and quantification is performed using SIM ion signal rather than extracted-ion signal in full scan mode.

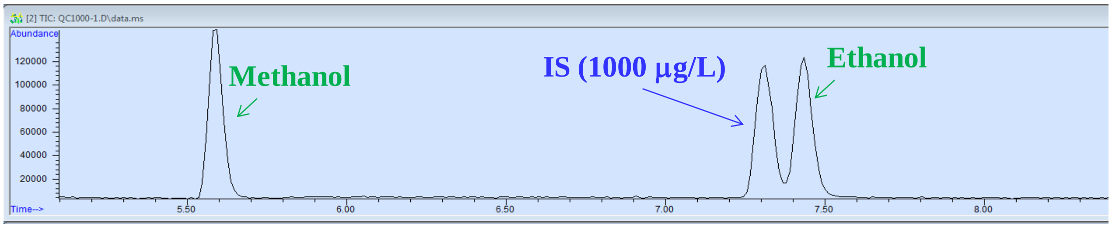

Figure 8: Typical total ion chromatogram of a 1000g/L methanol, ethanol, and internal standard in oil solution

In this study, solutions of approximately 2.4 ng g−1 were prepared and analyzed. The MDL is calculated by multiplying the Student's t-value by the standard deviation of the replicates. For 7 replicates, the t-value is 3.14, which is the value for 6 degrees of freedom at a 99% confidence level. The MDL obtained for methanol and ethanol in transformer oil are 0.23 and 0.59 ng g−1, respectively. These results are presented in Table 6. To the best of our knowledge, these are the lowest MDL reported values for an oil-matrix. Sensitive MDLs are critical for identification of methanol and ethanol as markers of cellulose degradation.

Table 7: Limits of detection (MDL) assay values

		ng/g (□g/L)	
#	Sample Name	**Methanol**	**Ethanol**
1	2.4 STD-1	2.74	2.94
2	2.4 STD-2	2.78	2.45
3	2.4 STD-3	2.72	2.57
4	2.4 STD-4	2.69	2.80
5	2.4 STD-5	2.79	2.67
6	2.4 STD-6	2.83	2.62
7	2.4 STD-7	2.91	2.40
Average		2.78	2.56
Standard Deviation		0.07	0.19
MDL		**0.23**	**0.59**

10 replicates were done in this study to perform the stability assay (Table 7). We got <3%RSD for the response of all the analytes at 1000 ng g−1 of ethanol-d6, methanol, and ethanol, and <1%RSD for the response of both methanol and ethanol to ethanol-d6. Through divided by ethanol-d6 response, the %RSD were reduced by correcting the response variation that came from the instrumental fluctuation or headspace analytes distribution variance. And the results indicate excellent precision based on the low percentage relative standard deviation (%RSD) values.

Table 8: Stability Assay values

QC Standard Concentration：1000 ng/g (µg/L) ※ IS (Internal Standard): Ethanol-d6						
		Response			Response Ratio	
#	Sample Name	**IS**	**Methanol**	**Ethanol**	**Methanol/IS**	**Ethanol/IS**
1	QC1000-1	196999	285979	205000	1.451677	1.040614

2	QC1000-2	192377	279926	198787	1.455091	1.033320
3	QC1000-3	187906	274038	193638	1.458378	1.030505
4	QC1000-4	188548	276436	195334	1.466131	1.035991
5	QC1000-5	187034	275232	194752	1.471561	1.041265
6	QC1000-6	182048	271562	191711	1.491705	1.053079
7	QC1000-7	191241	282692	200237	1.478198	1.047040
8	QC1000-8	187770	278071	196370	1.480913	1.045801
9	QC1000-9	191618	281285	199461	1.467947	1.040930
10	QC1000-10	193021	287417	204089	1.489045	1.057341
Average		189856.2	279263.8	197937.9	1.471065	1.042589
Standard Deviation		4098.9	5165.6	4380.4	0.013838	0.008444
RSD(%)		**2.16**	**1.85**	**2.21**	**0.94**	**0.81**

6. MANUFACTURER'S EXPERIENCES FOR TRANSFORMER ASSESSMENT

6.1 Chemical Markers – Factory Test Experiences

It is well known that the reliability of energy transmission strongly depends on the secure operation of transformer insulating systems, namely cellulose life equates transformer life. Nowadays, the use of chemical markers to indirectly measure the transformer winding paper degradation is no longer an unknown topic. During the last 30 years, MeOH (methanol) and EtOH (ethanol) have been discussed in many papers where traditional markers of insulation ageing are compared with this new tool[52]. Nevertheless, the behavior of these markers is still unknown in new electrical equipment once the transformer is finished its temperature and quality tests.

In this section, it is shown the behavior of those markers in power transformers after its overload temperature tests. Also, an overload test to distribution transformer is presented during different load profiles.

6.2 Overload Temperature Test – Power Transformers

Temperature test in power transformer is moving from being a prototype test to a routine test on many new power transformers where assures the transformer complies with specified limits, verifies the capacity of all conducting elements in a transformer and can include additional overload test to prove the capability of successful operation under overload conditions of 110, 125 or even 140% of rated capacity for certain number of hours[53].

TABLE 9: CHARACTERISTICS OF POWER TRANSFORMERS SELECTED

Transformer	MVA	HV (kV)	LV (kV)	Volume (Gal x 10^2)
XF1	56	115	13	107.75
XF2	27.5	115	13.2	81.47
XF3	28	115	24	37.37
XF4	33.6	115	36.5	52.79
XF5	7.5	44	25	57.7
XF6	33.6	115	13.09	42.3
XF7	45	230	13.8	110
XF8	224	230	115.5	243

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[52] **Castellanos, J. and Betancourt, E.** "Enhanced Field Reliability of Power Transformers by Means of a Low Gas Generation Footprint during Temperature Rise Tests - Improved Reliability Assurance Criteria", 2011.

[53] Ibid.

Since it is well know that this overload test is one of the most severe conditions during factory examinations, it was necessary to record and analyze some power transformers after overload temperature test in order to know if this routine test could be a reference as initial paper insulation degradation and its relation with these new chemical markers.

There were selected eight power transformers filled with mineral oil as dielectric fluid; the main cellulose insulating paper considered in windings was Kraft thermal upgraded paper and standard pressboards to oil ducts. Table 8 shows the characteristics and capacities of the transformers selected.

Power transformers had no conservator tank even pumps for oil forced cooling system were included in the design of those power equipment and non-communication load tap changer cabinet with the main tank was considered. These transformers were tested in overload temperature test; the samples were taken before and after the OL test from each transformer.

In Table 10 are shown the results of chemical markers and some test conditions recorded at the end of the overload temperature test.

TABLE 10: RESULTS OF CHEMICAL MARKERS BEFORE AND AFTER TRAILS

Transformer	**OL %**	T - oil (°C)	HSR-HV (°C)	T - HV Winding (°C)	MeOH (ppb)		EtOH (ppb)	
					Before	**After**	**Before**	**After**
XF1	12	67.2	75	85.6	85.75	83.39	0	0
XF2	25	83.9	75.7	93.9	60.05	57.42	0	0
XF3	25	74.1	73.2	83.3	0	119.04	0	0
XF4	25	75.1	87.8	84.7	77.73	104.62	0	0
XF5	40	78.5	74.8	88.9	25.07	55.68	0	0
XF6	25	92.3	84.2	104.9	0	86.83	0	0
XF7	33	85.9	88.9	101.8	0	0	0	0
XF8	11	87.6	85.3	102.5	0	0	0	0

The maximum overload tested was 40% of the XF5 but XF6 registered the highest winding temperature by high voltage side of all transformers. Samples from XF1 to XF5 were sent at the end of 2013 and the others in 2014. In the first samples 1 to 5 (or XF1 – XF5) sent was observed that there is a little MeOH generation trend with the MVA and HV as can be seen in Figure 9.

There was no generation of EtOH in any transformer sample. This could be compared with a publication[54] that EtOH was not detected at least in the first 75 hrs of heating at 130°C. In these tests, the maximum temperature did not exceed the 120°C. EtOH is not applicable of no high temperature fault is present.

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[54] **Ryadi, M., Tanguy, A., Jalbert, J. and Rajotte, C.,** “Alcohols based ageing chemical markers for the diagnosis of transformer cellulosic insulation”, CIGRE 2011.

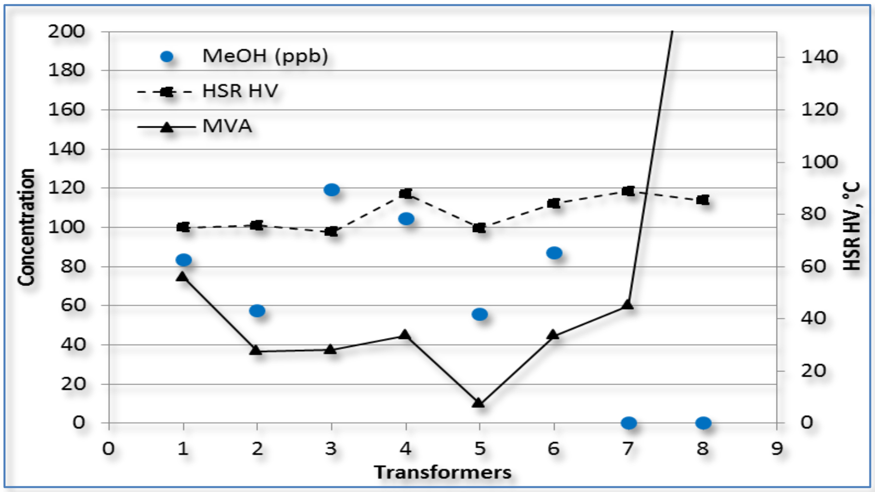

FIGURE 9: MEOH GENERATION IN NEW POWER TRANSFORMERS

The range of parts per billion of these units is similar to the obtained by Ryadi, Jalbert and Rajotte[55]or Annelore et al[56] but for transformers that have up to 25 and 30 years in service, respectively.

With the second samples 6 to 8 (or XF6 – XF8) the behavior is less clear. It can be seen that samples XF7 and XF8 did not present any alcohol concentration despite XF8 was the highest capacity tested. It can't be confirmed a noticeable tendency on the data, more transformers are needed.

Additional comparison was done with dissolved monoxide carbon gas sampled at the end of the overload test. In Figure 10 is shown the behavior of CO and MeOH in all transformers tested. It can be seen a similar tendency of both parameters, it is necessary to increase the samples of new transformers. The other gases did not show any significant tendency.

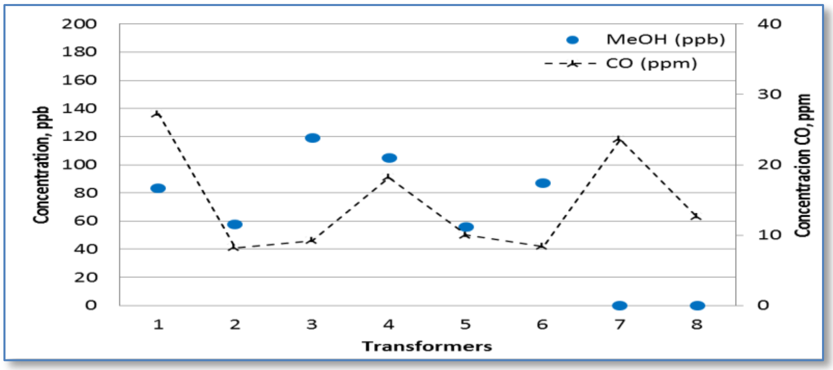

FIGURE 10: GENERATION OF MEOH AND CO IN NEW TRANSFORMERS

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[55] **Ryadi, M., Tanguy, A., Jalbert, J. and Rajotte, C.,** "Alcohols based ageing chemical markers for the diagnosis of transformer cellulosic insulation", CIGRE 2011.

[56] **Annelore, S., Stijn, A. and Steve, E**., "Applicability of methanol as early-stage paper degradation marker", CIGRE 2011.

6.3 Overload Temperature Test – Distribution Transformers

In distribution transformers temperature test is not required for small equipment; some customers demand a heat run test for only one transformer in a lot or representative sample of the same lot.

In this part of the work, the proposal was to evaluate a distribution transformer under different overload tests for understand the behavior of MeOH and EtOH generation when insulation materials are under thermal and electrical stress. In in the next table are shown the principal characteristics of the small transformer.

TABLE 11: CHARACTERISTICS OF DISTRIBUTION TRANSFORMER TESTED

Transformer	Distribution - 3 phases
Capacity	30 MVA HV - 13.2 kV LV – 127 V
Core	Amorphous shell
Insulation	Kraft thermal upgraded
Conductors	HV – Aluminium wire LV – Aluminium sheet
Insulating oil	Mineral type

The load profiles considered for the distribution transformer are listed below,

- Nominal load
    - Over Voltage (24hr)
    - 110%
    - 120%
- Over Load (24hr)
    - 105%
    - 110%
    - 115%

All samples were taken before and after. The concentration obtained of MeOH and EtOH from overload tests is shown in Table 12.

TABLE 12: CHARACTERISTICS OF DISTRIBUTION TRANSFORMER TESTED

CONDITION	T OIL (°C)	H2O (ppm)	MeOH (ppb)	EtOH (ppb)	2-FAL(ppb)
Before test	22.12	6.3	0	0	8
After Nominal load	44.54	6.5	145.82	0	0
After Over voltage 110%	49.28	6.5	18.63	0	0
After Over voltage 120%	53.74	6.8	0	0	0
After OL 105%	54.45	8	61.26	0	7
After OL 110%	68.05	9.8	142.47	0	0
After OL 115%	81.64	11.1	13.79	0	0
After OL and DC	66.61	11.1	37.31	0	7

Since these test were more severe in accordance with overload percentage, furfural compound were analyzed. Temperature profile and behavior of 2-FAL and H_2O are shown in the next figure.

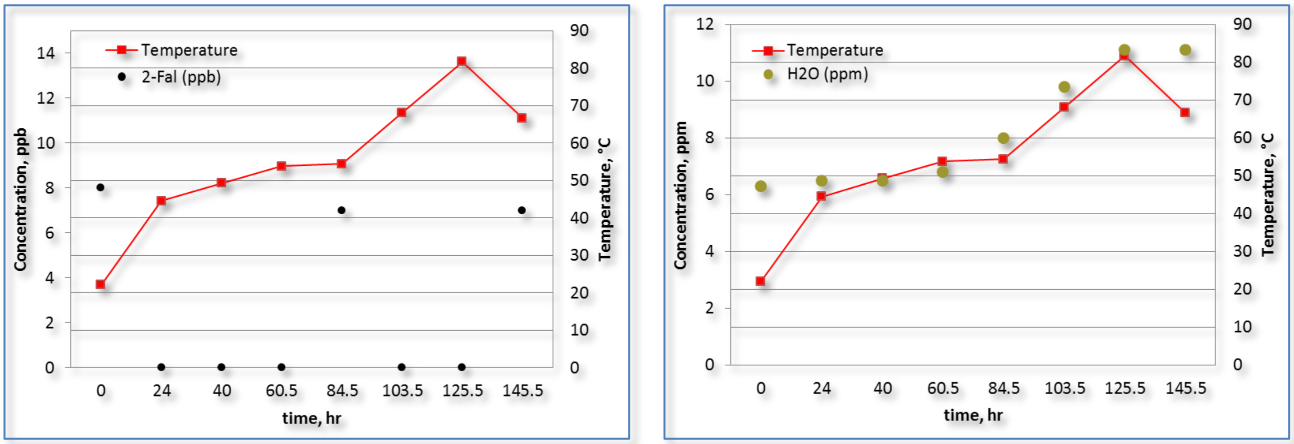

FIGURE 11: TEMPERATURE EFFECT ON FURFURAL AND WATER BEHAVIOR.

It is consider that the transformer is "too" new to can see a generation tendency of 2-FAL. It is possible that the reference for new transformers is cero ppb for this parameter or there is few time to see any strong tendency. Moisture increased according to the increment of the temperature. The concentration moves rapidly for water compared to the other compounds. According to this, in Figure 12, it is shown the generation of MeOH versus temperature.

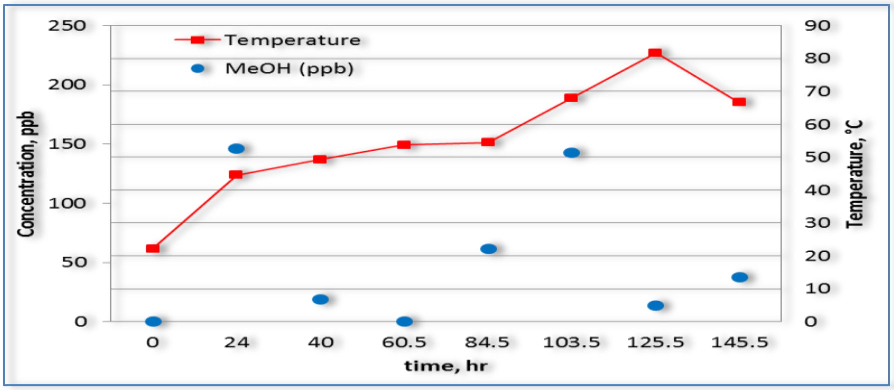

FIGURE 12: MEOH GENERATION DURING TEST PERFORMANCE

Since this transformer was monitored throughout the test, it could be seen the generation of MeOH at different times and conditions in the transformer. When temperature increases, MeOH increases too but takes more time to stabilize at low concentration after a temperature change. This behavior was observed by J. Jalbert and M. Lessard and they determined correction factors that can be applied to H2O, MeOH and 2-FAL, with the following parameters[57],

In Table 12 are calculated all parameters with the correction factors, and it was observed that the higher operation temperature, the lower CFm. That means higher parameter correction is obtained.

TABLE 13: PARAMETERS WITH CORRECTION FACTORS

	T (°C)	H2O (ppm)	CFm	H2O [20°C]	MeOH (ppb)	CFm	MeOH [20°C]	2-FAL (ppb)	CFm	2-fal [20°C]
Before test	22.12	6.3	1.069	6.736	0	0.850	0	8	0.986	7.887
After Nominal load	44.54	6.5	0.436	2.834	145.82	0.347	50.576	0	0.788	0
After Over voltage 110%	49.28	6.5	0.361	2.345	18.63	0.287	5.346	0	0.751	0
After Over voltage 120%	53.74	6.8	0.302	2.052	0	0.240	0	0	0.719	0
After OL 105%	54.45	8	0.293	2.347	61.26	0.233	14.294	7	0.714	4.995
After OL 110%	68.05	9.8	0.170	1.669	142.47	0.135	19.295	0	0.623	0
After OL 115%	81.64	11.1	0.099	1.097	13.79	0.079	1.084	0	0.544	0
After OL + DC	66.61	11.1	0.180	2.002	37.31	0.143	5.353	7	0.632	4.423

6.4 Comments

As could be seen in both distribution and power transformer studies, new chemical markers were evaluated to find their behavior during overload tests. It was found ethanol it is not a marker generated during this part of the manufacture process of a transformer to indicate any degradation of paper insulation.

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[57] **Jalbert J. and Lessard M-C**, “Cellulose chemical markers in transformer oil insulation. Part 1: Temperature correction factors”, IEEE Trans. Dielectr. Electr. Insul., Vol. 20, No. 6, pp. 2287-2291, 2013.

On the other hand, methanol was generated during these tests but the stabilization is slow when a temperature change is registered. Something to remark is that some of the concentrations obtained in these experiments are quite similar to those in the field after some years in operation, while in factory there are only hours of operation. As such, more data are needed to complete these evaluations.

7. FIELD EXPERIENCES

7.1 Taipower Studies

Taipower Research Institute (TPRI) studied over 1,000 units and both transformers and reactors were investigated (Table 14). Most transformers are sealed type and core type units. All units use mineral insulating oil with antioxidants below 0.08% m/m. Most transformers manufactured before 1985 use Kraft insulating paper, and after 1986 use thermally upgraded insulating paper.

A total of 937 Taipower's transformers were studied. Only 5% of transformers are with capacity below 20 Million Volt-Ampere (MVA), which mainly functions as ground potential transformers, station service transformers and auxiliary transformers. The majority 95% of transformers mainly function as distribution transformers in substations, and step-up transformers in power plants. Most transformers studied use Thermal Upgraded (TU) paper.

TABLE 14: THE CAPACITY DISTRIBUTION AND INSULATING PAPER TYPE OF TPC'S TRANSFORMERS

Capacity (Maximum MVA)	<20	≧20, <40 (mainly 25 MVA)	≧40,<100 (mainly 60 MVA)	>100
Number of Transformer	44	346	332	215
% of Transformer	5%	37%	35%	23%

Insulating Paper Type	TU	Kraft	N/ A
Number of Transformer	865	71	7

A total of 133 reactors were studied. Only 17% of the reactors were below 30 MVAr which are mainly used in series or neutral grounding. The majority 79% of reactors are shunt reactors. Most reactors studied also use TU paper (Table 15).

TABLE 15: THE CAPACITY DISTRIBUTION AND INSULATING PAPER TYPE OF TPC'S REACTORS

Capacity (MVAr)	<30	≧30, <60 (mainly 40)	≧60,<90 (mainly 80)	>90	N/ A
Number of Reactor	22	47	55	4	5
% of Reactor	17%	35%	41%	3%	4%

Insulating Paper Type	TU	Kraft	N/ A
Number of Reactor	106	17	10

7.1.1 Methanol/Ethanol/2FAL/CO_2 Analysis

In this transformer's field study, the plot of methanol concentration against years of service in Figure 13 shows a fan-shaped distribution with a slope of 8.2 ppb/year along the fan edge. And the plot of 2-FAL concentration against years of service also shows a fan-shaped distribution, but with a slope of 3.8 ppb/year along the fan edge. As such, it means there might be a positive correlation between methanol concentration and transformer age. But compared to the obvious positive correlation between MeOH and transformer age, 2-FAL seems not so sensitive to age variation, and keep in a relatively low level for most transformers.

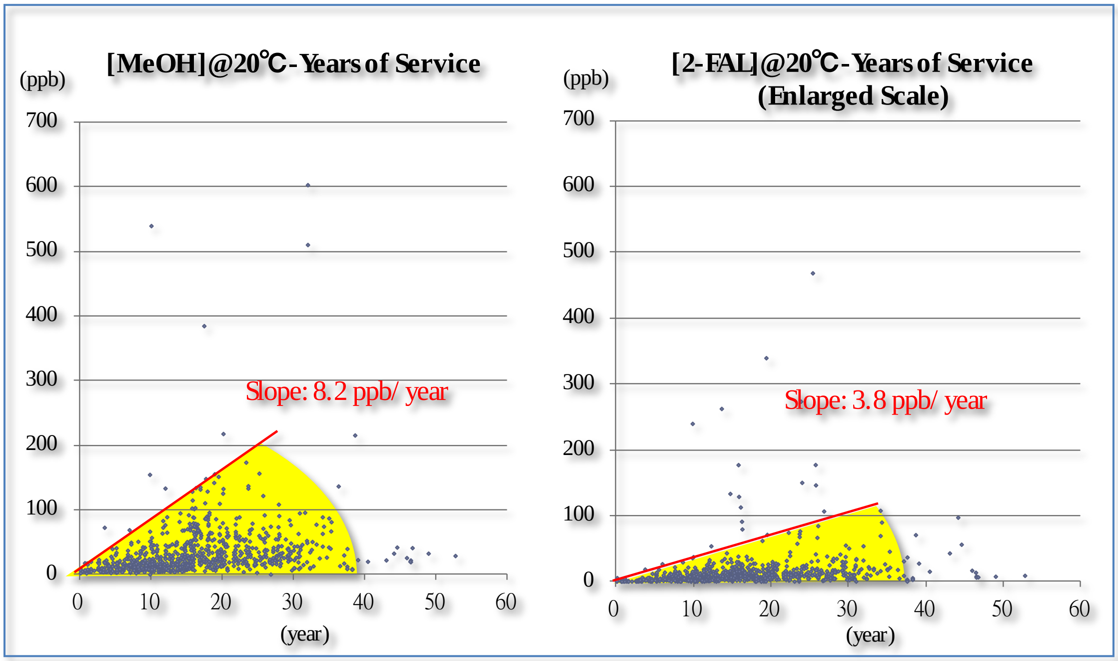

FIGURE 13: THE PLOT OF (A) METHANOL CONCENTRATION AGAINST YEARS OF SERVICE (B) 2-FAL CONCENTRATION AGAINST YEARS OF SERVICE OF TPC'S TRANSFORMERS.

And if we draw the plot of 2-FAL versus methanol concentration, we can find that most methanol concentration is higher than 2-FAL, and lies below the green line. Near the green line, methanol and 2-FAL concentrations are compatible. But near the horizontal-axis, there is some transformers with high MeOH concentration steel keep in a low level for 2-FAL (Figure 14).

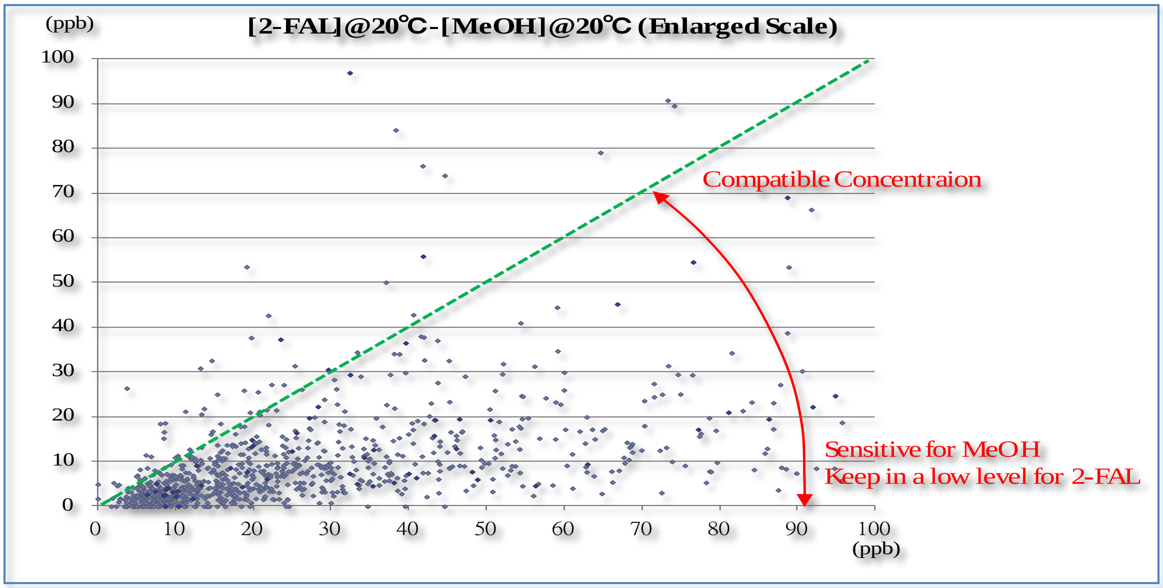

FIGURE 14: THE PLOT OF 2-FAL AGAINST METHANOL CONCENTRATION OF TPC'S TRANSFORMERS.

Ethanol concentration keep in a very low level (<25 mg/L) for most units, and didn't show any significant difference with transformer age variation. Which supports that ethanol has nothing to do with the normal ageing process (see Figure. 15).

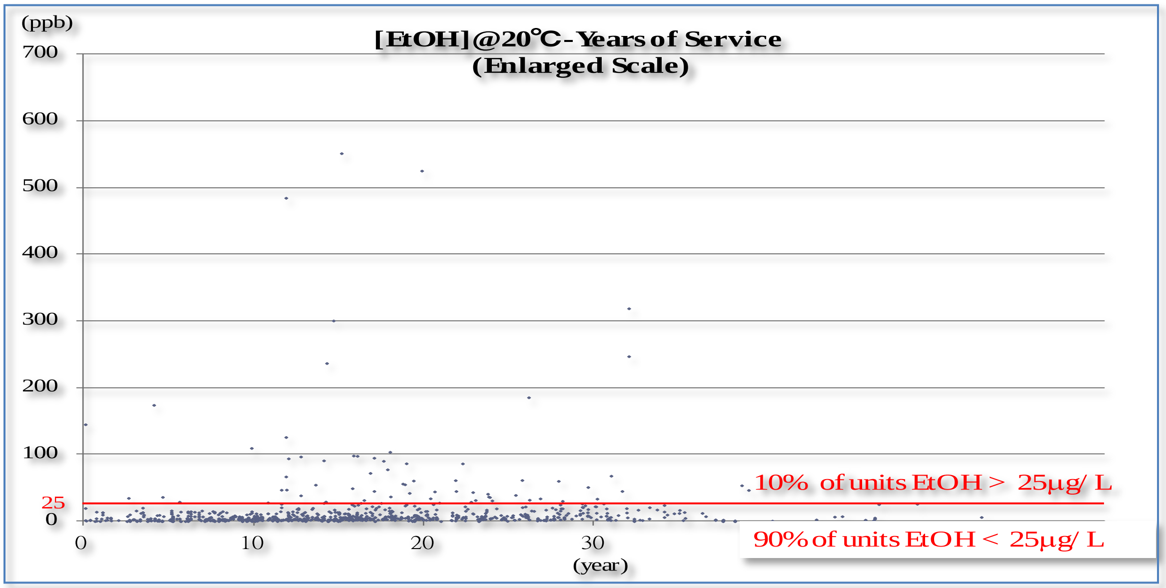

FIGURE 15: THE PLOT OF ETHANOL AGAINST YEARS OF SERVICE OF TPC'S TRANSFORMERS

For most transformers, methanol concentration is higher than ethanol, and lies below the green line. This is reasonable for transformers without paper pyrolysis problem to have the concentration of thermal ageing markers higher than pyrolysis markers, Figure 16 refers.

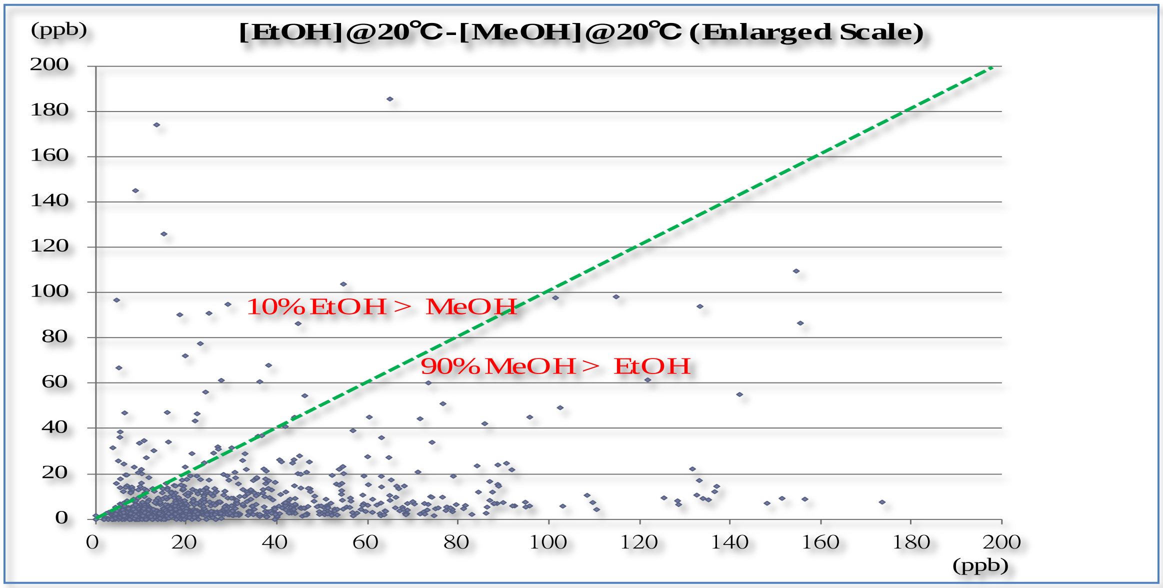

FIGURE 16: THE PLOT OF ETHANOL AGAINST METHANOL CONCENTRATION OF TPC'S TRANSFORMERS

We want to compare transformers with reactors because the loading of transformers could vary from 0-100% but reactors are 100% loading after commission. Therefore, the oil temperature is always higher for reactors and we consider reactors might have an accelerated ageing model.

In Figure 17, the plot of transformer oil temperature shows a normal distribution in our oil samples. A total of 70 transformers were sampled at the temperature of 40°C. However, the plot of reactor oil temperature shows two peaks. One peak is located at 28°C, which is considered to be sampled "off-loading" and the other peak is located at 55°C, which is considered to be sampled "on-loading". We also noticed that there were 7% of reactor oil sampled above 70°C, but there's only 0.1% of transformer oil sampled above that temperature.

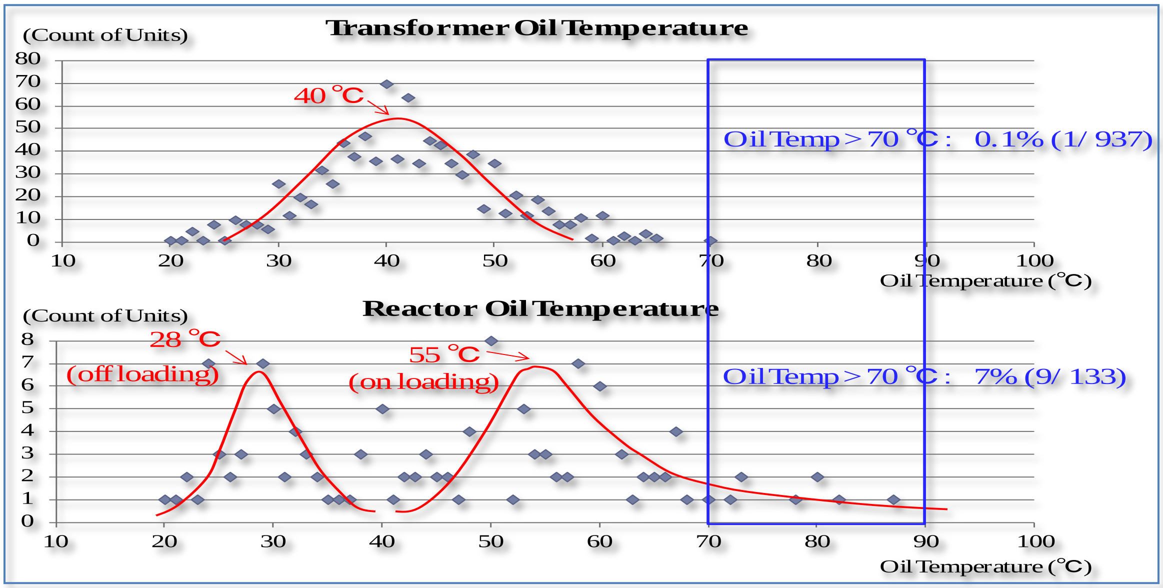

FIGURE 17: TRANSFORMER AND REACTOR COUNT VS. OIL TEMPERATURE

In Figure 18, we observed that the concentration of carbon dioxide (CO_2), methanol (MeOH) and 2-FAL grew faster for reactors than transformers during their early life. That might be attributed to the high loading of reactors (100% of loading) making the oil temperature high enough to give a thermal impact to the insulating paper and thus accelerate the ageing process in reactors. The ethanol (EtOH) concentration for reactors, which are believed as an accelerated ageing model, shows no obvious difference from that of transformers. This is also in agreement with the report of Hydro-Québec presented at the 2014 IERE meeting, i.e. ethanol may be related to paper pyrolysis (Temp >330℃) but not thermal ageing (Temp 60~120 ℃).

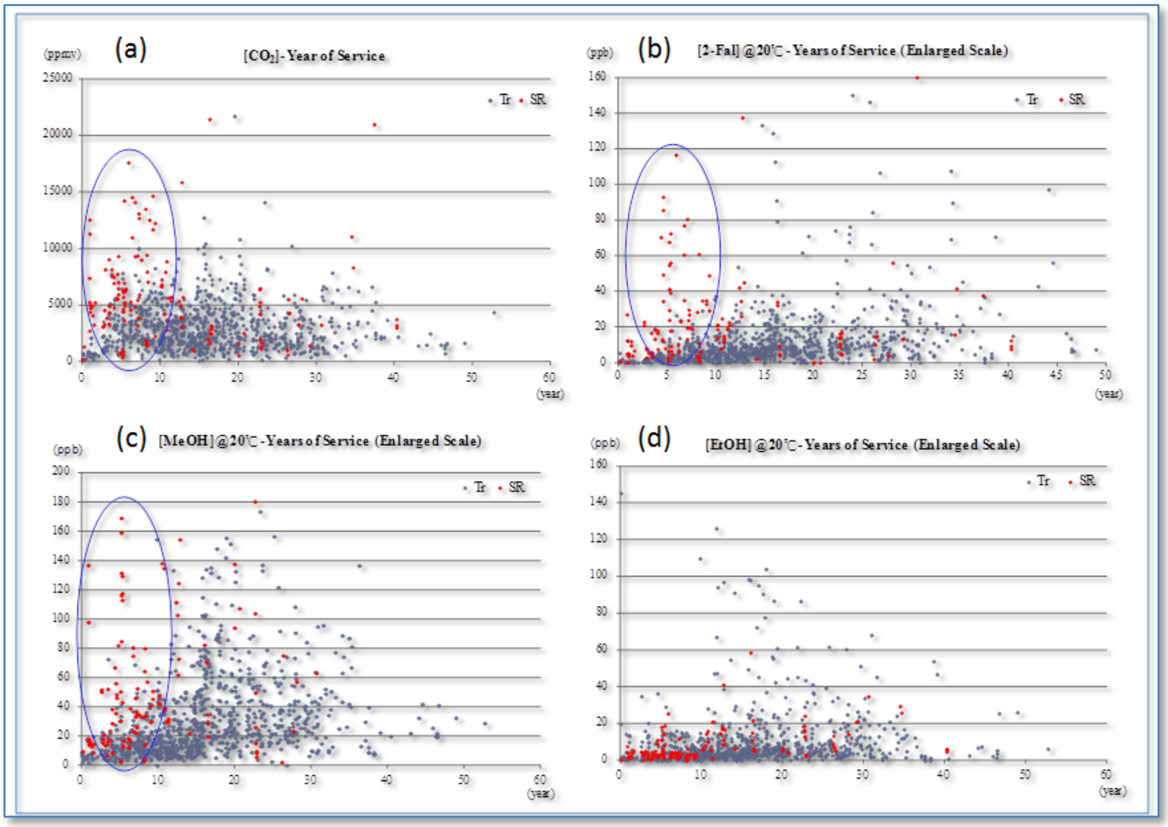

Figure 18: The plot of (a) carbon dioxide (b) 2-FAL (c) methanol (d) ethanol concentration against years of service

7.1.2 Acidity Analysis

We have studied around 400 transformers in Taipower. In Figure 19, the oil acidity keeps in a low level for most of them. But two transformers are found to have an extra high acidity, and they also have high 2-FAL, MeOH, EtOH, and water content. It is reasonable that acidity may affect the ability of chemical markers to be dissolved in oil.

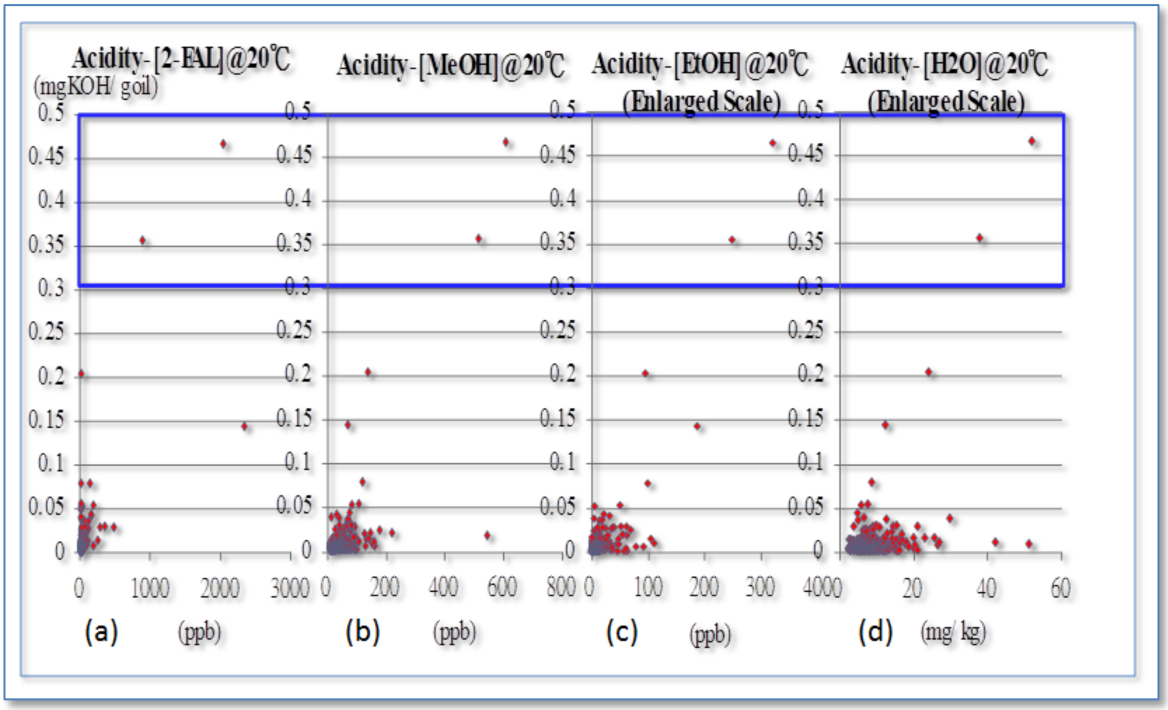

FIGURE 19: THE PLOT OF ACIDITY AGAINST (A) 2-FAL (B) METHANOL (C) ETHANOL (D) H_2O CONCENTRATION

7.1.3 Temperature correction analysis

Temperature correction equation can correct the fluctuation of marker concentration arising from different partition between insulating paper and oil. We want to make sure if temperature correction works helpfully in Taipower' transformer samples. We choose 13 transformers with 2 sampling results, Their oil temperature difference is more than 10 ℃, and their sampling interval range from 3 to 12 month. We compare the results before and after temperature calibration to 20 ℃

We suppose that the transformer ageing rate should not be too fast within one year, and so the two results at different sampling time shouldn't change too much. Based on that, we evaluate the job done after temperature calibration in MeOH and 2-FAL concentration. We calculate the "Growing%" by the following equation:

$$\text{Growing\%}=([\text{Later Sample}]-[\text{Former Sample}])/[\text{Former Sample}]\times 100\% \qquad (4)$$

We consider the correction result is better, when the absolute value of growing% decreased more than 10% after temperature correction. And we consider the correction result is the same, when the absolute value of growing% varied within 10% after temperature correction. We consider the correction result is worse, when the absolute value of growing% increased more than 10% after temperature correction.

In Table 16, the analysis data and their evaluation results of MeOH, we can find that before calibration by temperature correction equation, the absolute value of growing% are large, range from around 50% to 200%. And after calibration, All of the absolute value of growing% decreased, and all calibration results are considered as better.

TABLE 16:THE ANALYSIS DATA AND THEIR EVALUTION RESULTS OF METHANOL

Tr. Code	Sampling Date	Oil Temp. (℃)	MeOH (ug/ L)	MeOH Growing %	MeOH 20℃ (ug/ L)	MeOH 20℃ Growing %	Temp Cal Result Evaluation
D24034	2015/ 06/ 30	55	276	55%	63	-7%	Better
	2015/ 01/ 29	42	178		68		
B13020	2015/ 08/ 05	56	70	75%	15	-21%	Better
	2015/ 02/ 05	37	40		19		
B06119	2015/ 08/ 05	44	30	173%	11	10%	Better
	2015/ 01/ 08	21	11		10		
B06064	2015/ 08/ 05	52	114	90%	29	16%	Better
	2015/ 03/ 03	40	60		25		
B12016	2015/ 06/ 16	60	548	85%	102	-3%	Better
	2015/ 03/ 11	44	296		105		
D43069	2015/ 07/ 01	46	35	46%	11	-8%	Better
	2015/ 01/ 14	36	24		12		
B06075	2015/ 04/ 16	44	155	-38%	55	4%	Better
	2014/ 09/ 24	57	252		53		
B06065	2015/ 08/ 03	42	23	92%	9	0%	Better
	2015/ 01/ 08	24	12		9		
D61018	2015/ 08/ 03	53	131	47%	32	-14%	Better
	2015/ 02/ 10	40	89		37		
B06076	2015/ 04/ 15	40	74	-49%	31	3%	Better
	2014/ 09/ 24	57	144		30		
D57005	2015/ 07/ 22	50	238	92%	66	27%	Better
	2015/ 01/ 07	40	124		52		
B06058	2015/ 03/ 03	29	117	-49%	76	13%	Better
	2014/ 09/ 24	49	230		67		
B09098	2015/ 07/ 27	45	337	204%	115	60%	Better
	2015/ 01/ 28	29	111		72		

In-Table 17, the analysis data and their evaluation results of 2-FAL, we can see that only two calibration results are considered as Better. The other calibration results are considered as the same or worse.

TABLE 17: THE ANALYSIS DATA NAD THEIR EVALUATION RESULTS OF 2-FAL

Tr. Code	Sampling Date	Oil Temp. (℃)	2-FAL (ug/ L)	2-FAL Growing %	2-FAL 20℃ (ug/ L)	2-FAL 20℃ Growing %	Temp Cal Result Evaluation
D24034	2015/ 06/ 30	55	385	13%	273	-1%	Better
	2015/ 01/ 29	42	342		276		
B13020	2015/ 08/ 05	56	6	-40%	4	-50%	Same
	2015/ 02/ 05	37	10		8		
B06119	2015/ 08/ 05	44	1	0%	1	0%	Same
	2015/ 01/ 08	21	1		1		
B06064	2015/ 08/ 05	52	8	-27%	6	-33%	Same
	2015/ 03/ 03	40	11		9		
B12016	2015/ 06/ 16	60	262	-3%	177	-17%	Worse
	2015/ 03/ 11	44	270		214		
D43069	2015/ 07/ 01	46	8	-11%	6	-25%	Worse
	2015/ 01/ 14	36	9		8		
B06075	2015/ 04/ 16	44	14	-22%	11	-15%	Same
	2014/ 09/ 24	57	18		13		
B06065	2015/ 08/ 03	42	2	-33%	2	-33%	Same
	2015/ 01/ 08	24	3		3		
D61018	2015/ 08/ 03	53	134	-1%	97	-13%	Worse
	2015/ 02/ 10	40	136		112		
B06076	2015/ 04/ 15	40	15	-6%	12	9%	Same
	2014/ 09/ 24	57	16		11		
D57005	2015/ 07/ 22	50	321	23%	239	11%	Better
	2015/ 01/ 07	40	262		216		
B06058	2015/ 03/ 03	29	31	3%	29	26%	Worse
	2014/ 09/ 24	49	30		23		
B09098	2015/ 07/ 27	45	164	-2%	129	-16%	Worse
	2015/ 01/ 28	29	167		154		

After temperature correction, MeOH got successfully calibrated to the same base of partition, but 2-FAL didn't work so well after that. We believe that might be attributed to the smaller parameters in temperature correction equation, and the slower response time for 2-FAL. Different from the model transformer, oil temperature of transformers in field vary from day to day, and from season to season. Under such condition, there is not enough time for 2-FAL to get an observable concentration change.

7.1.4 Oil treatment – effect of degassing, filtering etc.

For study the effect of vacuum degassing on markers, we studied our equipment code: D41101 (Table 18). It's a shunt reactor operating at 161 kV and has served for 7 year which was degassed on 2014/12/05.

TABLE 18: SPECIFICATIONS OF EQUIPMENT CODE D41101

Equipment Type	**Shunt Reactor**
Manufactured date (yyyy/mm)	2006/09
Voltage	161 kV
Maximum MVAr	80
Year of Service	7 years
Oil Volume	17500 L
Preservation System type	Sealed

Paper Type	Temperature Upgrade
Degassing Date (yyyy/mm/dd)	2014/12/05

In Figure 20, we found, after vacuum degassing, CO_2 concentration dropped from around 17 thousand to around 200 ppmv, and then grew continuously in the following 9 month. 2-FAL concentration didn't dropped much after degassing, and went back to the original level after 6 month. We didn't get the methanol analysis data before vacuum degassing, but we can see after degassing, methanol concentration increased at first, and then reached a steady state after 3 month.

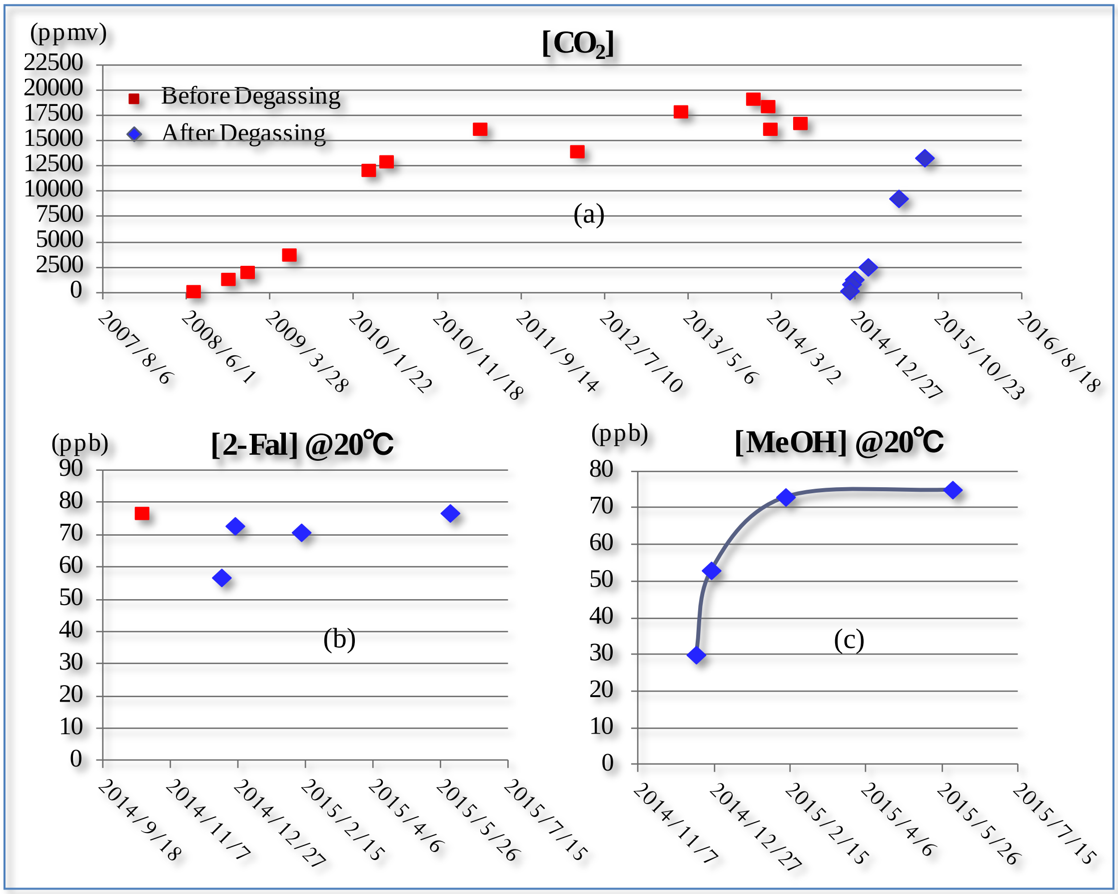

FIGURE 20: (A) CARBON DIOXIDE (B) 2-FAL (C) METHANOL DEGASSING EFFECT OF REACTOR CODE D41101

For study the effect of online drying-out on markers, we studied our equipment code: D51079 (Table 19). It's a shunt reactor operating at 33 kV and has served for 17 years. We use Velcon TDS5 online-Filtering System, to perform the drying out job for a total of 20 day.

TABLE 19: SPECIFICATIONS OF EQUIPMENT CODE D51079

Equipment Type	Shunt Reactor
Manufactured date (yyyy/mm)	1998/06
Voltage	33 kV
Maximum MVAr	40
Year of Service	17 years
Oil Volume	11500 L
Preservation System type	Sealed
Paper Type	Temperature Upgrade
Drying Period (yyyy/mm/dd)	2015/08/27 ~ 2015/09/15

TABLE 20: SPECIFICATIONS OF ONLINE DRY-OUT SYSTEM

Brand	Velcon Systems
Type	TDS5 (without heating & vacuum)
Filter Type	SD1107

TABLE 21: ANALYSIS DATA BEFORE AND AFTER ONLINE DRYING-OUT

	Before Drying		After Drying		After Drying 2 Month	
	Sampling Date (yyyy/ mm/ dd)	Testing Data (20℃)	Sampling Date (yyyy/ mm/ dd)	Testing Data (20℃)	Sampling Date (yyyy/ mm/ dd)	Testing Data (20℃)
Moisture (ppm)	2015/ 8/ 27	**18**	2015/ 9/ 21	**5**	2015/ 11/ 11	**6**
2-furaldehyde (μg/ L)	2015/ 1/ 21	193		203		225
Methanol (μg/ L)		**829**		**179**		**264**
Ethanol (μg/ L)		**22**		**5**		**7**
O_2 (ppmv)		5533		2969		2724
N_2 (ppmv)		44759		44474		41751
CO_2 (ppmv)		**19948**		**16156**		**16907**
CO (ppmv)		215		256		243
H_2 (ppmv)		130		134		115
CH_4 (ppmv)		133		155		155
C_2H_6 (ppmv)		102		121		123
C_2H_4 (ppmv)		11		10		9
C_2H_2 (ppmv)		ND		ND		ND

After drying, moisture, methanol, ethanol, and CO_2 concentration all dropped. Furthermore, the concentration dropped after online drying-out were around 75% for methanol, ethanol, and water, and was around 20% for CO_2. The recovery of dropping value after 2 months was around 10% for methanol, ethanol, and water, and was around 20% for CO_2.

TABLE 22: CONCENTRATION DROPPED AND RECOVERY AFTER ONLINE DRYING-OUT

	Concentration Dropped After Online Drying-Out	Recovery of Dropping Value After 2 Months
MeOH	78%	13%
EtOH	77%	10%
H_2O	72%	8%
CO_2	19%	20%

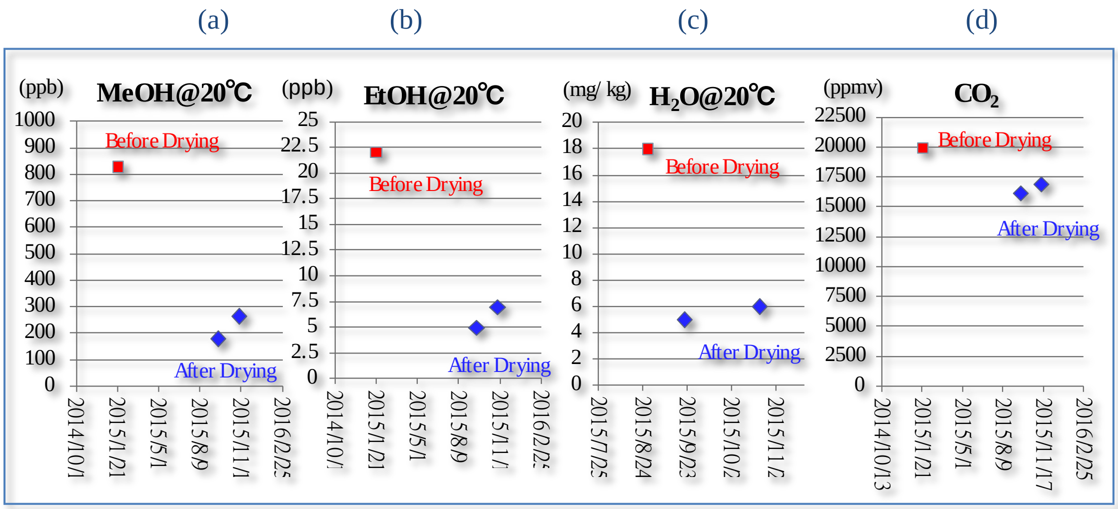

FIGURE 21: ONLINE DRYING-OUT EFFECT ON (A) METHANOL (B) ETHANOL (C) H_2O (D) CO_2 CONCENTRATION

The recovery of dropping value is not so desirable for all markers. That may be caused from the continuously re-equilibrium from insulating paper to oil during the online drying-out period. And hence, there is not so much water left in the paper to recover the concentration lost in the oil after drying.

7.2 CLP Studies

CLP Research Institute (CLP-RI), with the cooperation of CLP Power Hong Kong, intended to introduce this innovative technology for our asset management uses, in particular on transformer health monitoring. While the conventional methods and markers are well established (e.g. furan (2-FAL), CO/CO2, acidity and Dissolved Gas Analysis (DGA)), the new methanol ageing marker for transformers as proposed by Hydro-Québec was considered a low-hanging fruit to learn in order to enhance our early detection and monitoring capabilities.

Since CLP did not have the necessary instrumentation for in-house analysis, the oil samples reported below were sent and analyzed by Hydro-Québec's IREQ. During the period from 2013 and 2014, we sampled 16 and 26 transformers respectively. Among these, 16 transformers were repeatedly sampled. Two reactors were also sampled in this trial.

TABLE 23: CLP METHANOL TEST SAMPLES

Year	Equipment involved	Age	Number of samples	Remark
2013	14 Transmission Tx 2 400kV reactors (total 16)	11 units above 20years old Year of service between 7 – 33	30	More variations in terms of season and time
2014	24 Transmission Tx 2 400kV reactors (total 26)	12 units above 20years old Year of service between 2 – 33	48	Collected over 3 weeks period with most transformers having an am and pm samples

7.2.1 Methanol vs years of service

We observed there were practically no traces of methanol for transformers younger than 10 years old. The concentration in terms of ppb began to increase after around 17-20 years in the 2014 samples (similar in the 2013 samples). The highest range of MeOH was around 400 ppb for a transformer that was 32 years old. Figure 22 below shows the Methanol readings (corrected to 20°C) vs years of service.

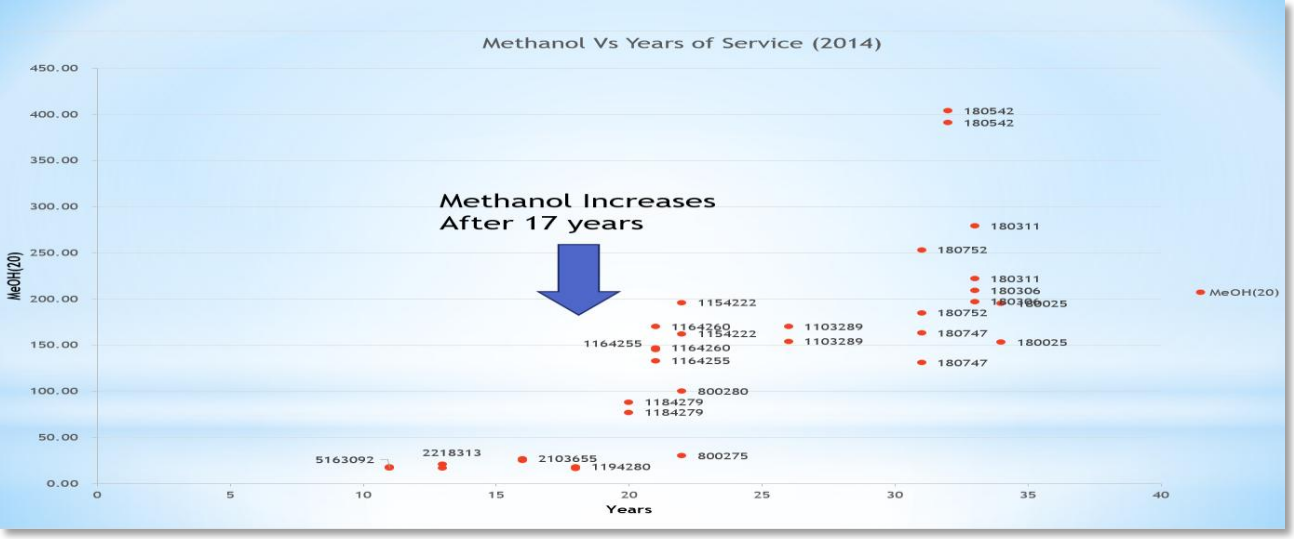

FIGURE 22: METHANOL VS YEARS OF SERVICE

7.2.2 Ethanol vs years of service

On the other hand, ethanol was not detected for any transformers that were younger than 20 years old. It was also observed that the reactor unit had a higher ethanol readings compared to the other transformers. Figure 23 below shows the ethanol vs years of service.

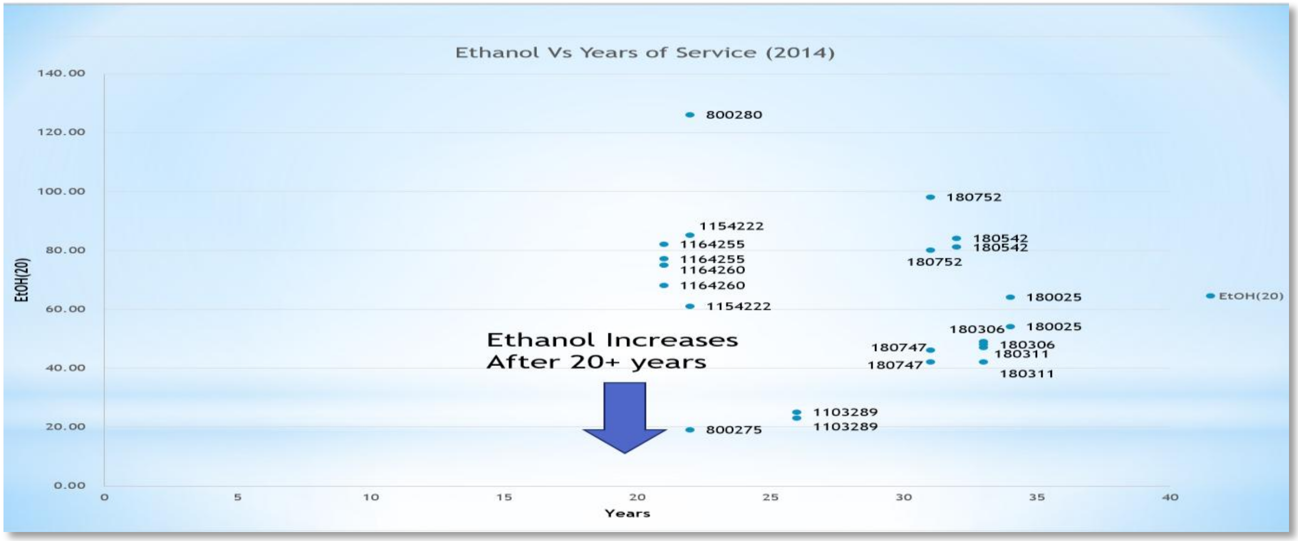

FIGURE 23: ETHANOL VS YEARS OF SERVICE

7.2.3 2-FAL vs years of service

For the conventional measures 2-FAL, it was observed that 2-FAL is usually active after the transformer is old than 20 or even 30 years old. Figure 24 below shows the 2-FAL vs years of service.

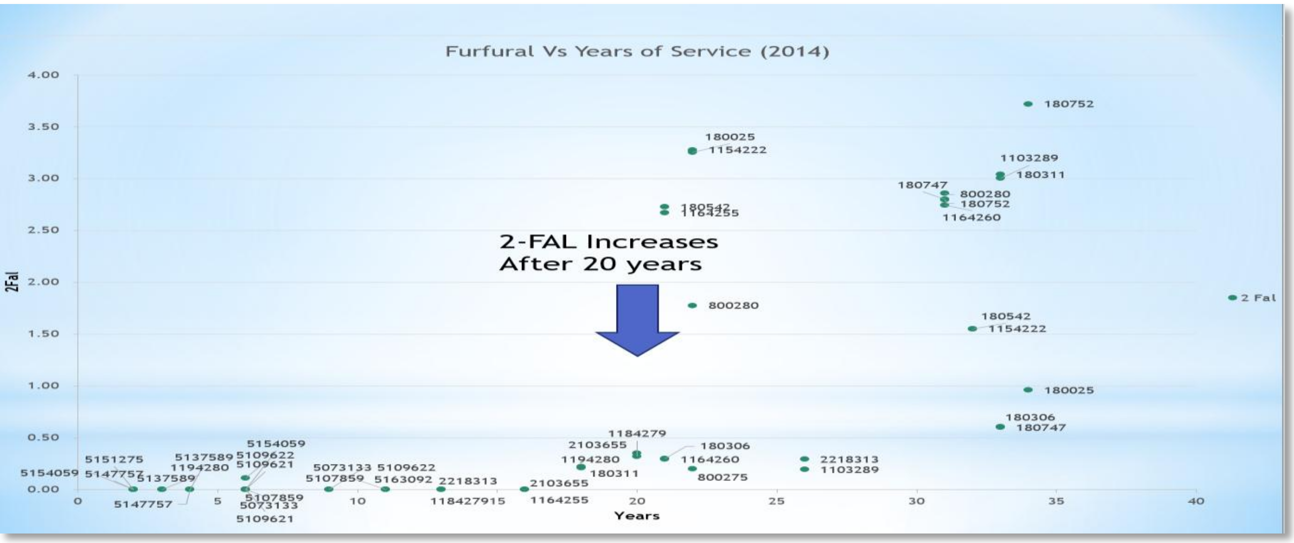

FIGURE 24: 2-FAL VS YEARS OF SERVICE

7.2.4 Comparing Methanol and 2-FAL

We then compared the methanol and 2-FAL readings as shown in Figure 25. It can be seen that except for a couple of outliners, the correlation between methanol and 2-FAL is promising but more samples are desired.

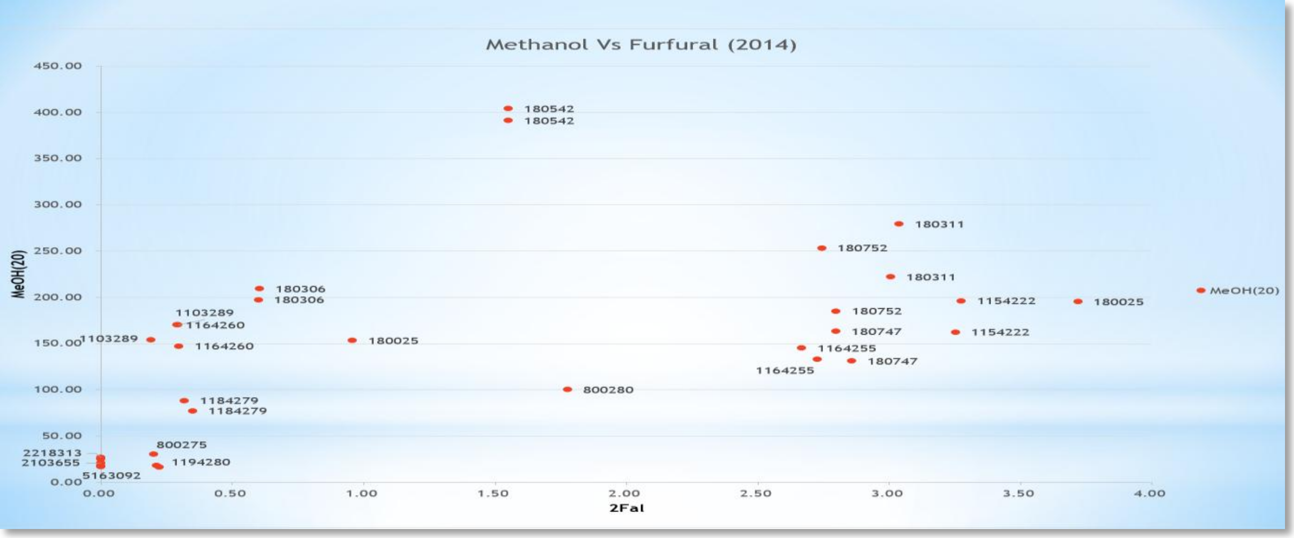

FIGURE 25: METHANOL VS 2-FAL

7.2.5 Comparing Ethanol and DGA

We also looked at the readings of ethanol compared to DGA as shown in Figure 26. Again, aside from an outliner, there seems to have more activities of ethanol when the corresponding DGA reading is low. This may suggest the ethanol could be used as an earlier detector complementing the DGA reading. However, the outliner with higher DGA reading needs to be investigated further.

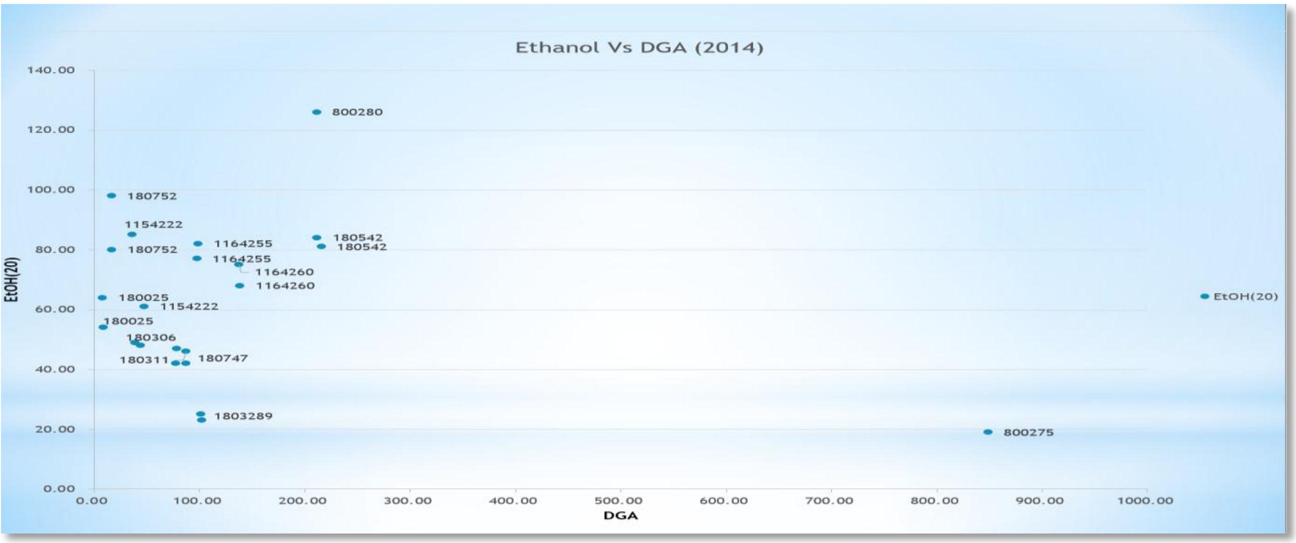

FIGURE 26: ETHANOL VS DGA

7.2.6 General observations and follow-up

We observed that methanol appears to be a good chemical indicator to monitor the ageing of power transformers. However, more tests and experiences are needed to conclude its effectiveness and most importantly how to interpret the level of ageing. Due to its active and easily detectable nature, it could be a good supplementary marker to aid our monitoring and tracking needs.

On the other hand, we did not detect any significant trace of ethanol in our tests and as explained by Hydro-Québec that ethanol could be a marker for high temperature fault (e.g. > 250 °C), it can also be a good additional indicator to track in addition to the conventional DGA method.

With the positive learning from this exercise, CLP Power Hong Kong has acquired the necessary instruments and began testing our oil samples with methanol/ethanol and monitor their performance starting 2016.

Marker for Kraft-paper insulated transformer as both 2-FAL and methanol were not detectable for transformers less than 10 years old. Methanol trace began to show up in different transformers after 17 years and 2-FAL after over 20 years.

8. EXAMPLE OF POST-MORTEM CASES

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 ageing studies involving chemical markers and the degree of polymerization (DPv) have been proposed, but their application to real equipment is still under investigation. Actually, most of DPv models are built with lab ageing experiments and only based on 2-FAL analysis. 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. 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 DPv 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. Recent publications suggest temperature correction factors to take this partition phenomenon into account in the interpretation of alcohols and furanic derivatives. Among its fleet of ageing 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 DPv 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 DPv distribution. Prior to this action, representative oil samples need to be collected to assess the oil quality together with the content of chemical markers. An example of of a post-mortem study is available in the Jalbert et al publication.[58]

This section highlights the importance of normalizing the concentrations of chemical markers with the oil physico-chemical parameters such as the oil temperature. This correction ensures a more realistic and accurate correlation between the marker concentrations and the DPv of paper in a transformer. It is also emphasized that a post-mortem analysis in order to draw the complete DPv 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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[58] **J. Jalbert and M-C. Lessard**, "Cellulose chemical markers relationship with insulating paper post-mortem investigations", IEEE Trans. Dielectr. Electr. Insul., Vol. 22, No. 6, December 2015.

9. CONCLUSION AND RECOMMENDATION

In 2012, IERE launched a joint R&D program amongst its members entitled "Transformer Insulating Paper Diagnosis for a Worldwide Application of Methanol as an Innovative Marker". The R&D program was led by Hydro-Québec's research arm – IREQ. Initially, there were six IERE members participated in the joint R&D program, i.e. Hydro-Québec, Prolec-GE, Taipower, CLP, NTPC and Toshiba, and the inaugural meeting was held in Montréal, Canada in 2012. In the next three years, annual review meetings were held in Hong Kong (2013), Mexico (2014) and finally concluded in Taiwan (2015). Four members, i.e. Hydro-Québec, Taipower, Prolec-GE, and CLP, with the continuous support from IERE Central Office, successfully brought this multi-national, multi-year research work to a satisfactory conclusion. This is the final report prepared by the joint R&D Program participants.

The end of the useful-life of power transformers is strongly correlated to the condition of its insulation paper. Traditionally, we have been using the concentration of carbon monoxide and carbon dioxide, furan compound (2-furfuraldehyde) as indicators. However, these indications and methods also have their limitations. In recent years, methanol has been identified as an additional ageing marker that aids the insulation paper diagnosis. It has received much attention in the industry and active research works were also conducted in different parts of the world. Hydro-Québec is a front runner in developing and applying the new technology and a wider population of transformer testing is desired in order to build up the scientific case of its applicability and effectiveness for the industry.

With participation of a transformer manufacturer (Prolec-GE) and a couple of utilities (Taipower and CLP), led by the methanol research experts (IREQ), a multi-national and multi-year research work was conducted. Over a thousand transformers were selected and their oil samples were tested in laboratory conditions. Their traces of methanol (MeOH) and ethanol (EtOH) were analyzed. The objective is to examine and compare the behavior of methanol and ethanol contents in different operating conditions and geographical areas.

From our studies, it was shown that there is sufficient evident that the methanol was detected in transformers after they were in services for at least a few years (e.g. > 10). Detection of methanol was also observed in temperature and overload tests for new transformers at the manufacturer level. The detection of methanol was also appearing earlier than the conventional method such as 2-FAL by at least 3-5 years, rendering it being a potentially more sensitive ageing and fault detection marker. Although traces of ethanol were also detected in the field, it is not clear how the ethanol reading can be effectively utilized as yet. It is however quite promising as research work seem to indicate ethanol can be used for tracking high temperature faults (e.g. >250°C) in the insulation papers.

Detailed field measurement studies were also carried out by Taipower showing how nominal maintenance done on the transformers such as degassing and oil filtering could also "reset" the methanol and ethanol readings. This is also true for CO_2 and moisture while 2-FAL readings remain relatively stable. This is of importance in practice as detailed recording of equipment maintenance and having multiple markers are important.

In essence, the R&D program was conducted successfully, thanks to the continuous supports from IERE and Hydro-Québec. The learnings from the field tests and sharing at the annual review meetings were found most useful. To go further, Hydro-Québec has proposed to ask the IERE members pooling their scrapped transformers for post-mortem diagnoses. By examining in details what the real ageing conditions of the papers are when we do the post-mortem, we can then further develop a credible model that can predict the life expectancy of transformers based on the level of methanol and ethanol detected.

10. TO PROBE FURTHER

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