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MONITORING INSULATING PAPER DEGRADATION WITH HIGH PERFORMANCE LIQUID CHROMATOGARPHY DETERMINATION OF FURAN COMPOUNDS

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INTRODUCTION

Monitoring the working condition and life-time of transformers is of vital importance. Nowadays majority of power transformers are exceeding 25 years of service. The actual life time of transformers is highly dependent on the operation, construction and maintenance. The life expectancy of power transformers may be determined by evaluating the state of insulating paper. At working temperatures in transformers (typically between 30 and 60^{o}C) paper degrades slowly, loosing its mechanical and electrical properties. During this decomposition process the degree of polymerization (DP) of insulating paper decreases. DP for new paper is approximately between 1000 and 1400. Values for highly degraded papers are between 240 and 300. Unfortunately, the insulating paper cannot be sampled for analysis while the transformer is working. Thus, the products of paper degradation dissolved in insulating oil have to be analyzed in order to evaluate the paper condition. Trace analysis of furan compounds can be done by High Performance Liquid Chromatography (HPLC) using ultraviolet detection.

CHEMISTRY

Insulating paper consists of cellulose fibers that are made of bundle of cellulose molecules of differing lengths. They are held together by weak hydrogen bonds involving OH- groups on the adjacent molecules. Cellulose itself is linear polymer of glucose molecules, which are linked together through the glycosidic bond. The length of the cellulose molecule is measured in terms of the degree of polymerization (DP). This is the average number of glucose units per cellulose molecule.

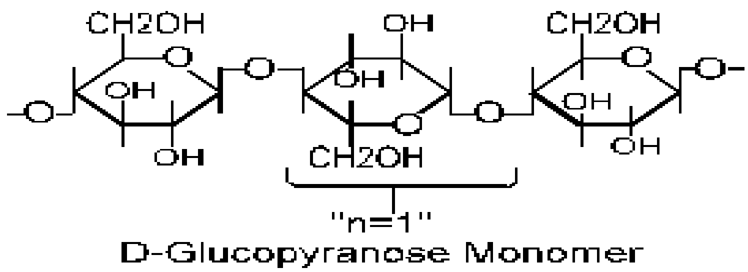

Figure 1. Cellulose polymer

Degradation mechanism and promoting agents

The mechanism of cellulose degradation depends on the conditions to which it is subjected. Main factors which promote cellulose degradation are: elevated temperature, oxygen, moisture and acids formed during the oil aging process. Heating the cellulose to 200°C tends to break the glucosidic bonds and open the glucose rings, producing free glucose molecules, moisture, carbon oxides and organic acids (thermal degradation) /1/.
Moisture is the most powerful degrading agent of paper, promoting the hydrolytic degradation of paper /1/.

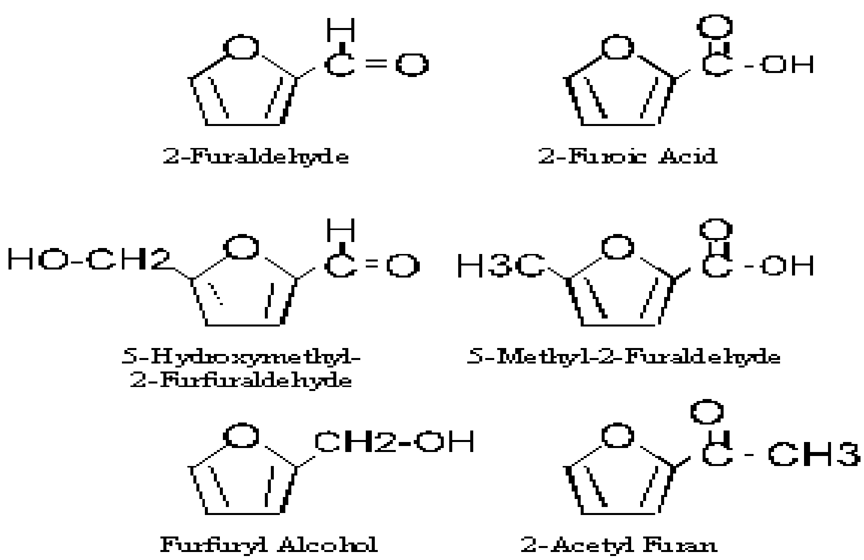

Figure 2. Furan compounds

In the presence of water and acids glucose molecules cleaves (hydrolytic degradation), by ring scission, when furan compounds are produced. These are: 2-furoic acid, furfuryl alcohol, 5-hydroxymethyl-2-furaldehyde, 2-furaldehyde (2-furfural – 2-FAL), 2-acetyl furan and 5-methyl-2-furaldehyde.

DISTRIBUTION OF 2-FAL IN DUAL INSULATING PAPER-OIL SYSTEM

Influence of chemical structure of insulation and water content. All of the furan compounds are mostly absorbed by paper. The amount of absorbed furans depends on the partition coefficients at given temperature and humidity in the paper. 2-FAL has high partition coefficient - 0.83, meaning that 83% of 2-

FAL is dissolved in oil /2/. Because of its higher stability and solubility in oil (partition coefficient) in comparison with other furans (for example: partition coefficient of 5-hydroxymethyl-2-furfural is 0.11, meaning that the 89% is adsorbed by paper and 11% dissolved in oil) 2-FAL is the best compound for diagnostic purposes /2/. More aged oil is better dissolving medium for furans, because of its higher polarity due to higher content of polar aging compounds. The equilibrium in the severe degraded paper-oil insulating system is moved towards higher absorption in oil, having as consequence higher amount of furans detected in oil. The solubility of 2-FAL in oil is increased with increasing amount of aging polar products in oil and water content.

Influence of temperature and working condition. At lower temperatures the adsorption of furans in the paper is higher. The adsorption is enhanced by higher paper water content. The adsorption and desorption process occurs simultaneously, and the thermodynamics of the equilibrium is very complex. Besides the influence of temperature and moisture on equilibrium, very important factor influencing the diffusion of furans between phases is the condition of impregnating oil around the paper.
Stability of furans dissolved in oil is a question for discussion. It is well known that 2-FAL is unstable at the moderate temperatures. It may decompose at temperatures higher than 150^{O}C. Degradation is promoted by oxygen, copper and light. Agent for paper thermal upgrading, dicyandiamide also promotes degradation of furans (3).
At high temperature of thermal or electrical fault, produced furans may degrade. Some investigators point out the increase of CO_2 and especially CO dissolved in oil after failure, while the concentration of 2-FAL was low, due to its decomposition. Correlation between CO_2, CO and furans is denied (4).

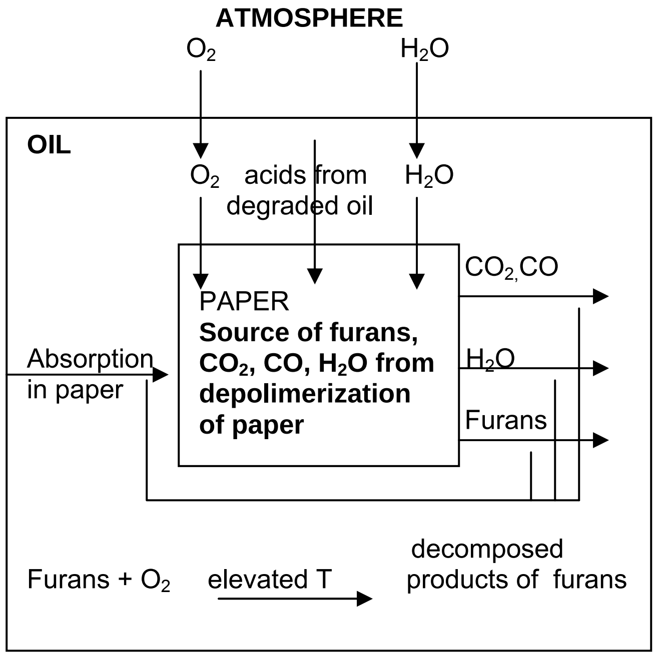

Figure 3. Scheme of simultaneous processes of furans distribution in dual paper-oil system in communication with surroundings

Influence of oil reclaiming and reconditioning. Applied elevated temperature under vacuum during oil reconditioning process influence the higher degradation rate of 2-FAL. Also reclaiming of aged oil also removes 2-FAL from the oil in some extent, due to adsorption on the activated earth. Such facts should be bared in mind when analyzing the data for each transformer. New reference values of 2-FAL concentration should be made.

Correlation with degree of polymerization (DP). In several studies (3) attempt was made to correlate concentration of 2-FAL in oil with DP. Logarithmic function:

$$\text{Log 2-FAL} = -0.00287\ \text{DP} + 3.40$$

and several other logarithmic equations are reported, but there is no justified direct relationship between furans content in oil and DP /3/. Life expectancy of transformers can be evaluated only on the basis of 2-FAL content in oil, looking at the rate of it's increase during service, together with other relevant diagnostic parameters (dissolved gas analysis - DGA, electrical, physical and chemical properties of oil).

EXPERIMENTAL

There are several analytical techniques and methods for determination of furans dissolved in insulating oil, such as: High performance liquid chromatography with ultraviolet detector, static headspace-capillary gas chromatography (7), colorimetry. The results in this paper are obtained with reversed-phase HPLC, according to the IEC 61198/1993 standardized method (6). The chromatographic separation was performed on a reverse-phase C_{18} column under isocratic conditions (flow rate 1.0 ml/min.), with methanol in the mobile phase. Detection was performed using ultraviolet detector at 274 nm (5). Sample preparation, i.e. extraction of 2-FAL was done with acetonitrile in liquid-liquid extraction procedure, according to IEC 61198.

Calibration was done with external standard solutions of 2-FAL in oil. Calibration curve showed good linearity in expected concentration range, with regression coefficient r = 0.9999. The recovery of applied method calculated on several results is between 81 and 89% (Figures 1 and 2) /5/.

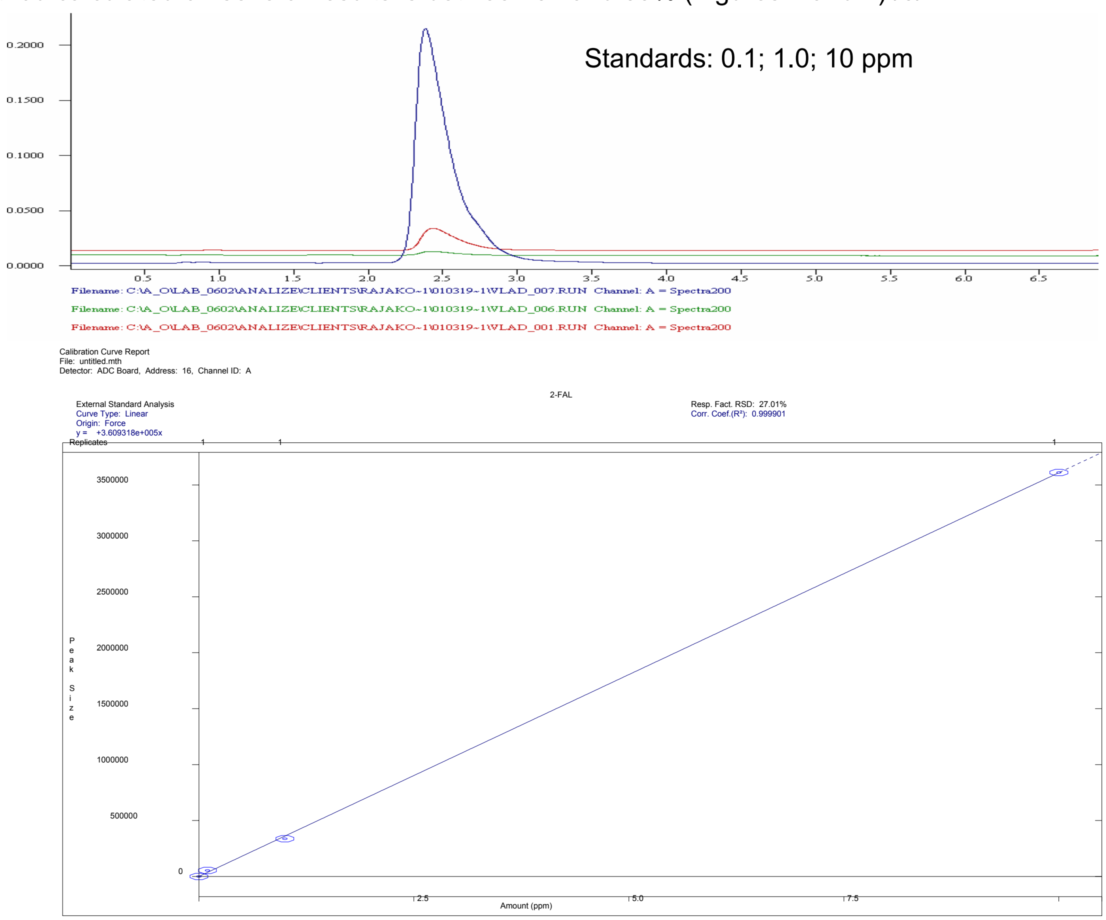

Figure 4. Chromatogram of standard solution of 2-FAL in oil and calibration curve

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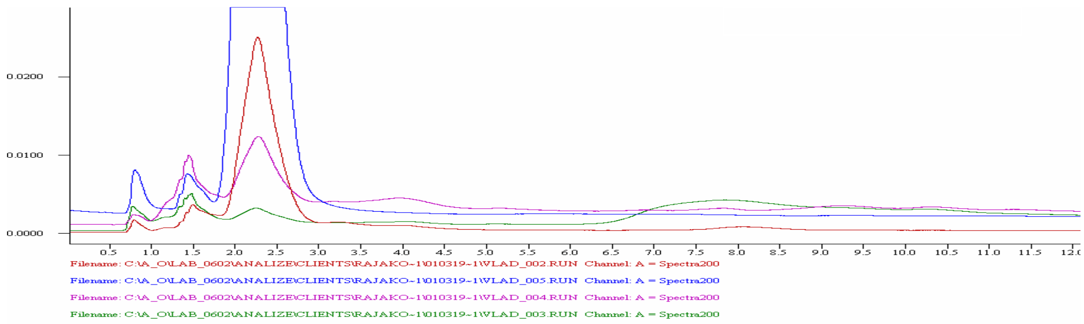

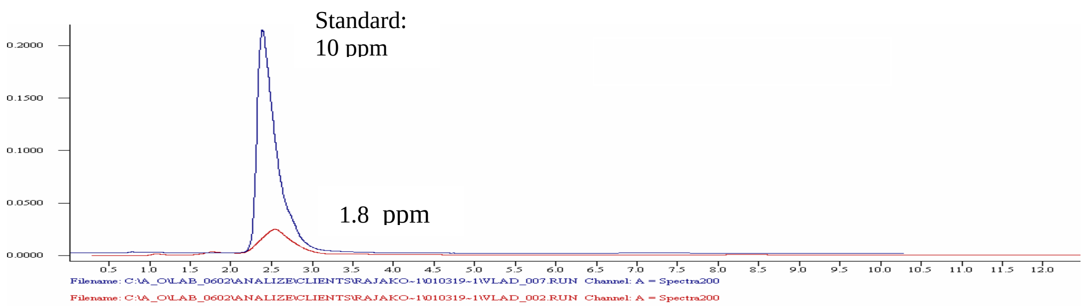

Figure 5. Chromatograms – 2-FAL content of some oil samples

CORRELATION WITH TRANSFORMER YEARS OF SERVICE AND OPERATING CONDITION

Transformer design, operating conditions and frequency of maintenance measurements has a great influence on rate of insulation aging process. On the basis of 2-FAL values from different power station, thermal-power plant (TPP), hydroelectric-power plant (HPP) and 110 kV distribution network, different ranges of 2-FAL content were observed (figures 6, 7 and 8). Highest 2-FAL values in TPP are up to 5 ppm, while in HPP they are only up to 0.6 ppm. In distribution 110 kV network highest 2-FAL values are up to 7 ppm. In TPP working temperatures of transformers are higher than in HPP, mainly due to higher load and air cooling system - OFAF, while in hydro-power plants lower load and water cooling - OFWF is applied. As a consequence, more severe degradation of paper-oil insulation is present in TPP than in HPP. Distribution transformers have unexpectedly high level of 2-FAL values, higher than TPP transformers, as it was observed in other countries utilities and reported in technical papers /3/. It is evident that more cares are taken during the operation of high voltage transformers in power plants in order to ensure reliable function, in comparison with the distribution transformers. Average 2-FAL content for TPP is 0.82 ppm, for HPP the average 2-FAL content is 0.15 ppm. In distribution 110 kV transformers average 2-FAL content is 1.00 ppm, indicating high degree of insulation aging and very old age of transformers. Oil reconditioning and reclaiming processes are removing 2-FAL from oil in some extent, so reference values of 2-FAL content should be carefully selected when analyzing the data and establishing correlations. For example, oil from one power transformer from hydro-power plant had 2-FAL content 0.18 ppm before reconditioning, and afterwards the 2-FAL content was 0.04 ppm. The last 2-FAL value should be new reference value. Some of 2-FAL values in figures 6 and 8 are to low, because oil reconditioning or reclaiming processes were applied during service. In the majority of cases, correlation of 2-FAL content in oil and concentration of CO_2 and CO dissolved in oil was not established. Possible explanation lies in different reaction and mechanism of formation of carbon oxides and furans. Thermal degradation as predominant process yields carbon oxide gases as main products, and hydrolytic degradation which mainly yields furan compounds has to be promoted by presence of water and acids. The extent of dissolution of furans in oil, formed in paper degradation process is dependent on water content of oil and paper, amount of aging polar compounds and working temperature, as previously mentioned.

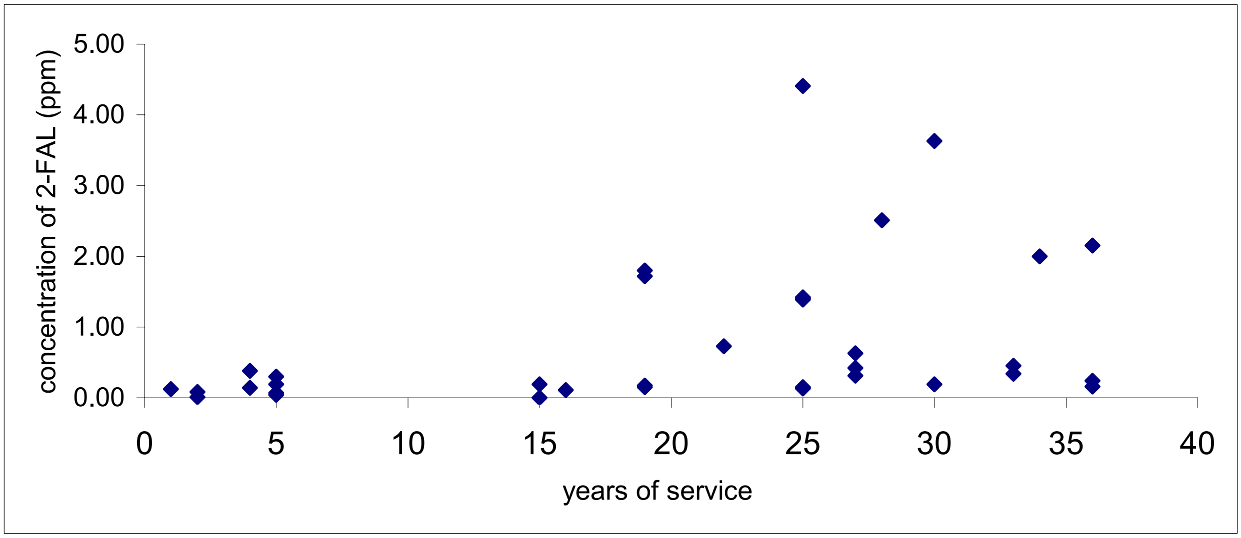

Figure 6. Correlation of 2-FAL content with years of service in thermo-power plant

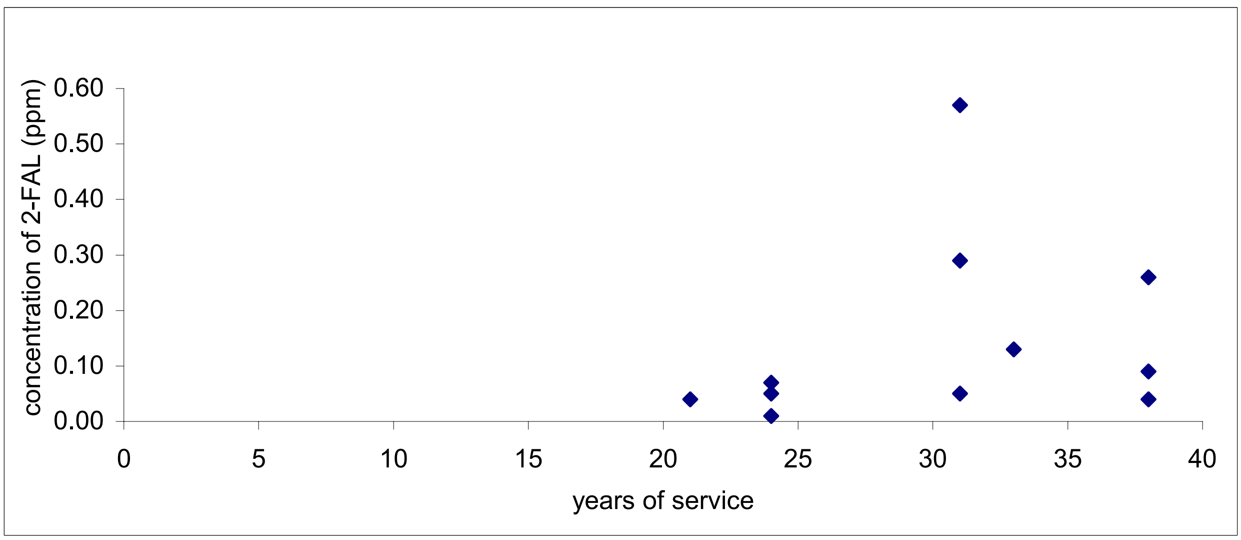

Figure 7. Correlation of 2-FAL content with years of service in hydro-power plant

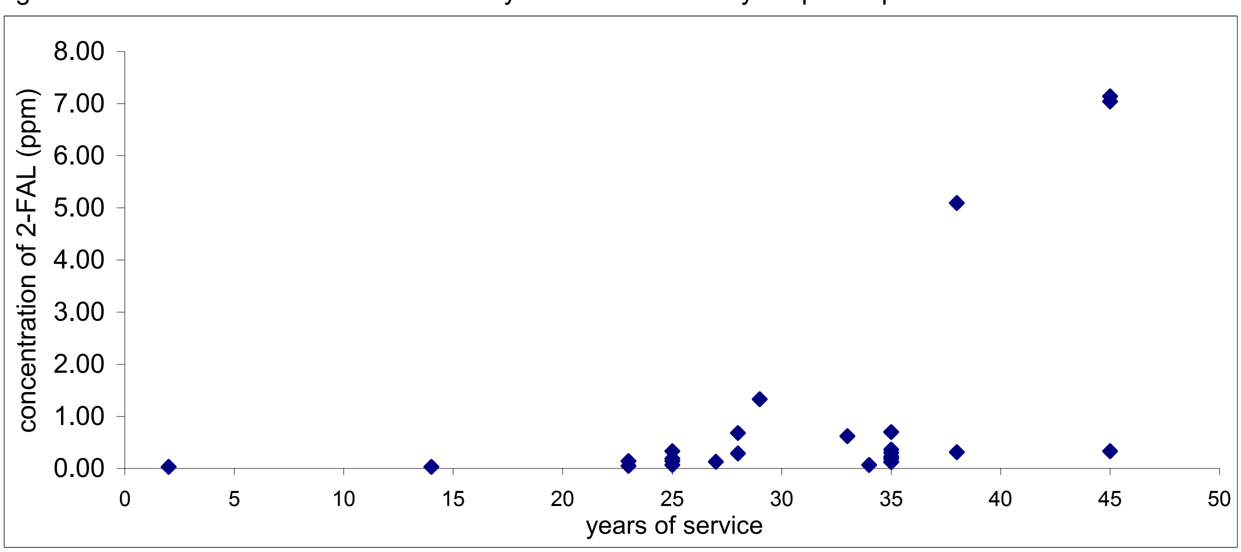

Figure 8. Correlation of 2-FAL content with years of service in 110 kV distribution network

SOME CASE HISTORIES

A few case histories may serve to illustrate the usefulness of 2-FAL as an indicator of cellulose degradation resulting from localized hot spot or more general overheating.

Case I – TPP auxiliary transformer 25/12.5/12.5 MVA, 15.75/6.3/6.3 kV. Measurement of winding resistance indicated bad contact on lower end of a bushing on low voltage side (difference of resistance 8.66 %). DGA indicated normal working regime (table 1.) 2-FAL determination showed great increase comparing with previous result. In 10 months period, 2-FAL concentration rose from 0.3 ppm to 0.7 ppm, indicating high degree of cellulose degradation. After repair of bad contact, the difference of resistance between phases dropped to 0.53% (the acceptance limit is 2%).

Table 1. Case I - DGA and 2-FAL content

Date	H_2 ppm	CH_4 ppm	C_2H_2 ppm	C_2H_4 ppm	C_2H_6 ppm	CO ppm	CO_2 ppm	O_2 ppm	Working regime	2-FAL ppm
31/3/03	15	9	0	75	3	461	4868	6101	normal	0.30
28/2/04	21	7	0	99	4	640	6901	6837	normal	0.70

Case II – TPP auxiliary transformer 35 MVA, 110/36.75/6.3 kV. Due to malfunction of circuit breaker on 110 kV side, transformer remained under short circuit. Results of all electrical measurements were normal (insulation resistance, dissipation factor, leakage resistance, winding resistance, no-load current and losses at low voltage, voltage ratio). Areas of melted paint on tank were observed and gas was accumulated in buchholz relay, due to intensive production of gases. DGA of gas mixture together with calculated equilibrium concentrations (Ce) showed enormous production of hydrocarbon gases, especially carbon oxides. There was combination of thermal and electrical fault (overheating combined with partial discharges), with IEC code 121 (table 2). Great production of carbon oxides indicated thermal degradation of cellulose. Measured 2-FAL content proved suspected cellulose degradation (table 2). Sharp increase of CO showed the cellulose involvement in fault /4/. The transformer was sent to factory for repair.

Table 2. Case II - DGA and 2-FAL content

Date	H_2 ppm	CH_4 ppm	C_2H_2 ppm	C_2H_4 ppm	C_2H_6 ppm	CO ppm	CO_2 ppm	O_2 ppm	IEC Code	2-FAL ppm
9/9/03	39	18	8	64	6	899	13146	11210	normal	0.11*
6/2/04d.n.	923	1522	27	192	217	4869	23707	10982	120	1.80
6/2/04 g.n.	1004	1675	29	212	242	5225	26424	11480	120	1.72
6/2/04 g.b.r., %	1.776	0.673	0.002	0.013	0.010	10.271	2.786	11.502		/
Ce	888	2692	24	182	180	12325	27860	19553	121	

* date of 2-FAL analysis was 12/2001

Case III – TPP step up transformers (1) 240 MVA, 15.75/235 kV, (2) 360 MVA, 15/407 kV. DGA of transformer (1) in contrast with previous case showed low concentrations of carbon oxides and thermal fault with high temperatures of hot spot, above 700°C producing ethylene as key fault gas (table 3). 2-FAL content showed high degradation rate of cellulose, as it was expected due to existing thermal fault. Further development of the fault with increase of gas concentrations and several buchholz relay alarms prompted the repair. The fault was found in core (short circuited laminations and carbonized solid insulation of bolts). Since transformer was in service only for three years before the failure, production of 2-FAL and degradation of cellulose insulation was very intensive, due to existing fault.
Second case (2) is an example of healthy transformer according to DGA, and also with low values of carbon oxides. 2-FAL analysis showed that solid insulation is highly degraded, due to normal aging process.
Both examples of transformers, one in normal working regime, and one in fault condition, showed that there is no correlation between carbon oxide gases dissolved in oil and 2-FAL content. From these cases it is obvious that DGA can not serve as diagnostic tool for monitoring solid insulation degradation, both in

fault and normal working condition of transformers. Better knowledge of solid insulation condition is achieved by means of furan compounds analysis.

Table 3. Case III - DGA and 2-FAL content

date	H_2 Ppm	CH_4 ppm	C_2H_2 ppm	C_2H_4 ppm	C_2H_6 ppm	CO ppm	CO_2 ppm	O_2 ppm	IEC Code	2-FAL ppm
(1) /05/01	32	324	0	917	273	400	3628	16076	022	3.63
(1) /06/01	789	1483	28	3061	611	693	5253	16805	022	/
(2)19/3/04	27	25	0	7	7	925	3934	2972	normal	1.42

CONCLUSION

HPLC analysis of 2-FAL dissolved in oil is improving the maintenance of power transformers. The state of cellulose insulation can be estimated by 2-FAL determination and afterwards, the life expectancy of power transformers can be judged. The 2-FAL analysis showed its benefits through application in power plants and in also in distribution network. Introducing this analysis in periodic control, better insight in processes in transformers can be achieved and prevention of failures, as it was shown through previous case histories. Distribution network transformers showed surprisingly high 2-FAL levels, leading to conclusion that in maintenance program 2-FAL analysis should be introduced for all 110 kV transformers.

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ABSTRACT: The evaluation of power transformer remaining life time is determined by the state of insulating paper. Insulating paper consists of linear polymer of cellulose. Cellulose degradation can be monitored by determination of degradation products dissolved in oil. High performance liquid chromatography (HPLC) of furan compounds is a diagnostic tool for evaluating the degree of cellulose degradation. 2-furfural (2-FAL) is main degradation product of cellulose because of its high solubility in oil and stability in comparison with other degradation products.

In this paper chemistry of cellulose degradation is presented, together with short analytical method description. Factors influencing thermodynamics and equilibrium of furan compounds distributed between oil and paper is discussed.

Correlation between 2-FAL content and years of transformers service was determined in order to evaluate the transformers age. Ranges of 2-FAL values were much higher in thermal-power plants than in hydro-power plants, due to higher load and OFAF cooling design. 110 kV distribution network transformers had surprisingly high 2-FAL values. Maintenance of those transformers should be set to higher level applying 2-FAL analysis in periodic control of power transformers. Correlation between 2-FAL content and carbon oxides was not established.

Through some cases of transformers from power plants, the importance of 2-FAL analysis is emphasized. The importance of 2-FAL analysis was pointed out through cases of healthy transformers and those with thermal fault, where DGA did not indicate cellulose involvement in fault according to carbon oxides concentrations dissolved in oil. High 2-FAL values indicated presence of intensive cellulose degradation, either as a result of normal aging or overheating of insulation due to existing thermal fault.

Together with dissolved gas analysis (DGA), electrical, physical and chemical measurements, furan compound analysis is improving maintenance program of power transformers.

Key words: paper-oil insulation, cellulose degradation, 2-furfural, HPLC, DGA, transformer age