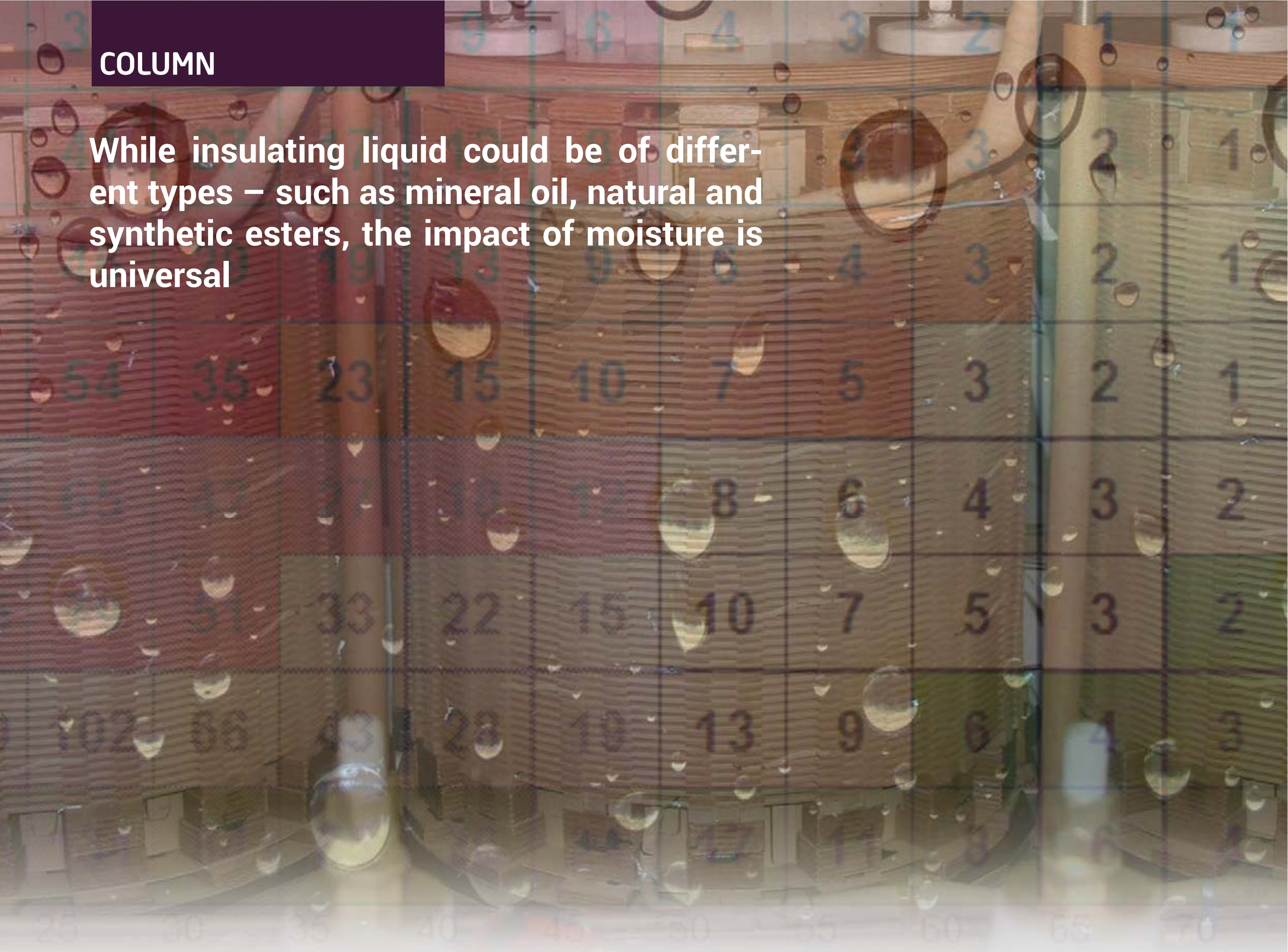

While insulating liquid could be of different types – such as mineral oil, natural and synthetic esters, the impact of moisture is universal

How water affects transformer oil quality and helps monitor its aging

As it is well known, transformer insulation consists of two major components – oil (liquid insulation) and cellulose based solid insulation (also colloquially known as "paper"). While insulating liquid could be of different types – such as mineral oil, natural and synthetic esters, the impact of moisture is universal. For that reason, we will be using the term "oil" throughout this article assuming that the findings here hold true for all types of insulating liquids.

This article, the forth in series of water in transformers column, attempts to explain not only how moisture affects the quality of the insulating liquid, but also how online sensing of moisture parameters can be used in continuous monitoring of oil condition, rate of oil deterioration and aging of both oil and paper insulation. Various definitions related to moisture in transformer used in this article were introduced in previous issues of this magazine [1, 2, and 3] and the reader is advised to refer to these issues to recall some of the concepts and examples. The article also reveals a method of continuous online determination of absolute water content of insulating liquid and the means for determination of minimum reduction of oil dielectric strength – key oil quality parameters.

We should never forget that apart from being an insulator and a coolant, oil is also an information carrier. That information could be related to a condition state of another critically important component - paper, affecting overall transformer performance and its insulation life span.

There are some physical and chemical parameters that characterise oil quality. Among these are dielectric loss factor, thermal and electrical conductance, re-

Apart from being an insulator and a coolant, oil is also an information carrier, and this information could be related to a condition state of paper, affecting overall transformer performance and its insulation life span

sistivity, viscosity, oil chemical composition, colour, acidity, interfacial tension, moisture, and particle content, to name a few. When properly measured, these parameters can form the basis for an integrated diagnosis of oil condition.

As a product, oil is considered to have a good quality if its physical and chemical properties are within specified levels as designated by the respective standards [4, 5]. For IEC followers, some of the key oil quality parameters are summarised in Tables 1 and 2.

It could be argued that these oil quality limits do not have any scientific basis and their correlation to aging is not fully warranted. For example, the authors of the research [6] made the following observation:

"Notwithstanding the ease of comparison to recommended values, doubts still persist on the validity of the recommended values. There is a lack of statistical backup or explicit information on how those values were determined. It is still an open question as to whether the typical value ranges were formed based on substantial technical arguments, economic reasons or international experience". And further: "One thing that can be certain is that wrong classification of transformer condition could induce serious consequences regarding unnecessary maintenance expenses or severe penalty incurred for reduced quality of electricity supply due to transformer failure."

Even if the values in Tables 1 and 2 were perfectly correct, currently it is not feasible to monitor all the tabulated parameters online. Thus, we are sharing here a monitoring solution that offers a continuous online determination of insulating liquid quality in operating transformer.

Water-in-oil solubility as oil quality parameter

Water-in-oil solubility is not part of the oil quality characteristics specified in the standard tests and oil maintenance guidelines. However, we are going to demonstrate that this is one of the most sensitive indicators revealing signs of deterioration of insulating oil from the very early stage to its complete degradation.

As it was defined in [1], water-in-oil solubility (WCO*) is the maximum concentration of water that can exist in dissolved state in mineral oil at thermodynamic equilibrium at specified temperature and pressure.

Table 1. IEC recommended limits for mineral insulating oil after filling in new electrical equipment as related to oil quality [4]

	Limits for highest voltage for equipment (kV)		
Voltage range	**< 72.5**	**72.5 – 170**	**> 170**
Colour (on scale given in ISO 2049)	Max. 2.0	Max 2.0	Max. 2.0
Breakdown voltage (kV) 2.5 mm gap	>55	>60	>60
Water content (mg/kg)	20	<10	<10
Acidity (mg KOH/g)	Max. 0.03	Max. 0.03	Max. 0.03
Dielectric dissipation factor at 90°C and 40 Hz to 60 Hz	Max. 0.015	Max. 0.015	Max. 0.010
Interfacial tension (mN/m)	Min. 35	Min. 35	Min. 35

Table 2. IEC classification of quality for in-service mineral oil by key indicators [4]

Oil test parameter	Voltage class	Condition classification		
		Good	Fair	Poor
Dielectric Dissipation Factor, DDF (40–60 Hz at 90°C)	> 170 kV	< 0.10	0.10 – 0.20	> 0.20
	< 170 kV	< 0.10	0.10 – 0.50	> 0.50
Breakdown Voltage, BDV (2.5 mm electrode gap)	> 170 kV	> 60	50 – 60	< 50
	72.5 – 170 kV	> 50	40 – 50	< 40
	< 72.5 kV	> 40	30 – 40	< 30
Neutralization Number (Acidity) (mg KOH / g oil)	> 170 kV	< 0.10	0.10 – 0.15	> 0.15
	72.5 – 170 kV	< 0.10	0.10 – 0.20	> 0.20
	< 72.5 kV	< 0.15	0.15 – 0.30	> 0.30
Water (mg H_2O / kg oil at transformer operating temperature)	> 170 kV	< 15	15 – 20	> 20
	72.5 – 170 kV	< 20	20 – 30	> 30
	< 72.5 kV	< 30	30 – 40	> 40
Interfacial Tension, IFT (mN / m)	All (Inhibited)	> 28	22 – 28	< 22
	All (Uninhibited)	> 25	20 – 25	< 20
Colour per ISO 2049	All	< 2		> 2

The validity of recommended values of oil parameters from standards are doubtable because there is a lack of statistical backup or explicit information on how those values were determined

Mathematical equation of water-in-oil solubility can be derived from fundamental thermodynamic functions, such as Gibbs energy G, enthalpy and entropy of water in oil solution H and S respectively, more precisely from their respective changes ΔG°, ΔH°, ΔS°:

According to definition of Gibbs energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{1}$$

and relationship between Gibbs energy change and equilibrium constant K_{eq}:

$$\Delta G^\circ = -RT\ln K_{eq} \tag{2}$$

the solubility of water in oil can be determined by combining (1) and (2) and taking into account that WCO* is an equilibrium constant, (WCO* = K_{eq}), we get an equation identical to equation (3) in [2]:

$$\ln WCO^* = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}, \tag{3}$$

where ΔH°, ΔS° and K_{eq} are the standard enthalpy change, standard entropy change, and equilibrium constant of the chemical reaction of water dissolution in oil respectively. R is universal gas constant equal to 8.3145 J mol^{-1} K^{-1}. From now on we are going to drop the superscript nough "°" sign for convenience, but the meaning of change in enthalpy and entropy remains throughout the article.

Assuming that changes in standard enthalpy and entropy are not dependent on temperature, we obtain familiar equation for water in oil solubility:

$$\ln WCO^* = A - \frac{B}{T} \tag{4}$$

where solubility constants

$$A = \frac{\Delta S}{R} \tag{4a}$$

and

$$B = \frac{\Delta H}{R} \tag{4b}$$

Since in reality ΔH and the reaction entropy ΔS do vary with temperature for most chemical processes, equation (4) is considered to be only approximate.

Clarke and Glew [7] have derived mathematical equation (5) for solubility of gases in liquids as function of temperature, which can be used if more accurate assessment of solubility is required:

$$\ln WCO^* = A - \frac{B}{T} + C \ln T + DT \tag{5}$$

In addition to A and B, two more constants are introduced in Equation (5), these are C and D.

However, Tsonopoulos [8] pointed out that for the solubility of water in saturated hydrocarbons, such as alkanes, equation (4) is sufficient, i.e. C and D are equal to zeros.

Roizman and Davydov confirmed this finding in [9] as being applicable to mineral oil.

Equation (4) could also be written in the exponential form as:

$$WCO^* = e^{A-B/T} \tag{6}$$

Two curves for new and severely aged oils according to Equation (6) were shown in [1].

It has been reported in the CIGRE technical brochure [10] and pointed out in [11] that water-in-oil solubility does not remain constant over the life of a transformer. Its temperature dependent characteristic changes so that the water solubility increases as the oil deteriorates (Figure 1), giving a great opportunity to trace oil quality.

Figure 1 is Van't Goff plot of the same solubility curves as shown in Figure 1 in [1]. The fact, that water is more soluble in service-aged oil, can be explained by the decrease in heat energy (enthalpy change) required to dissolve water in oil.

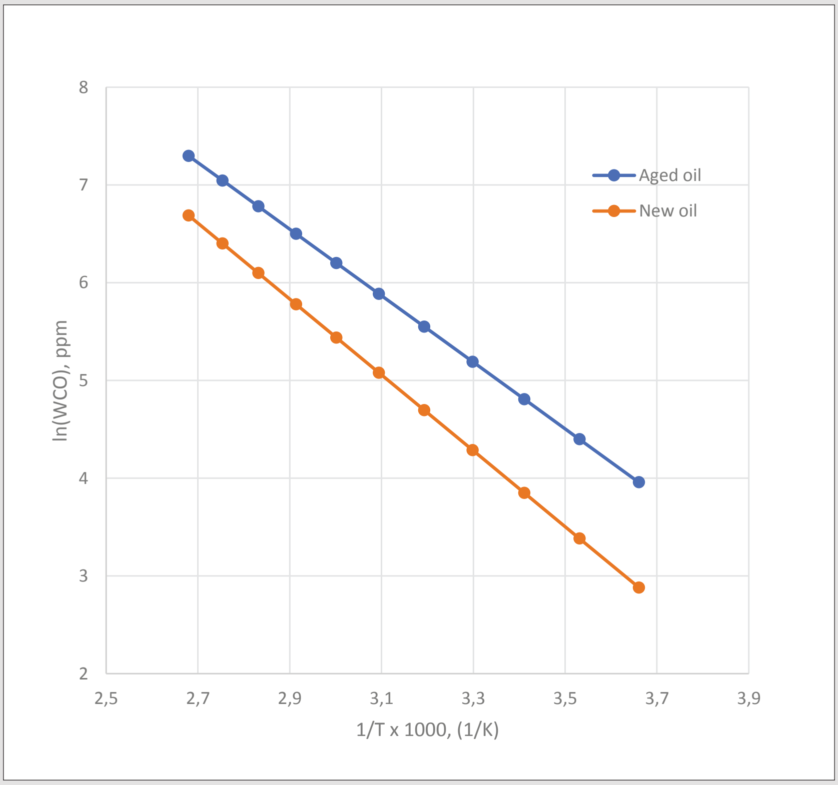

Figure 1. Water-in-oil solubility for new and severely aged oil.

Water-in-oil solubility is one of the most sensitive indicators revealing signs of deterioration of insulating oil from the very early stage to its complete degradation

We know that water-in-oil solubility is a critical parameter when it comes to the determination of absolute water content as described in Equation 7.

$$WCO = \frac{rS}{100} \text{ x } WCO^*, \tag{7}$$

where WCO is the absolute water content in oil in mg / kg (ppm) and rS is the relative water saturation as measured by a moisture sensor and expressed in percentage.

With reference to Figure 2, borrowed from [3], the enthalpy of water-in-oil solution can be determined by solving two simultaneous equations, Equation 8 and 9, by exclusion of WCO.

Provided there is a temperature difference between the top and bottom oil levels, it becomes possible to determine ΔH by measuring rS and T at the bottom and top oil levels of a transformer continuously, as it is shown in Figure 2.

By substitution of Eq. (6) into (7) we get:

$$WCO_{to} = \frac{rS_{to}}{100} e^{A-B/T_{to}} \tag{8}$$

$$WCO_{bo} = \frac{rS_{bo}}{100} e^{A-B/T_{bo}} \tag{9}$$

where W_{to} and W_{bo} are concentrations at the top and bottom oil levels respectively.

Assuming that water-in-oil content in the lower cooler pipe is equal to water content in the upper cooler pipe for any given moment of time, the solubility coefficient B can be determined by equating W_{to} to W_{bo} as:

$$B = \ln\left(\frac{rS_{to}}{rS_{bo}}\right)\left(\frac{T_{to}\,T_{bo}}{T_{to} - T_{bo}}\right) \tag{10}$$

Considering equation 4b, the change in

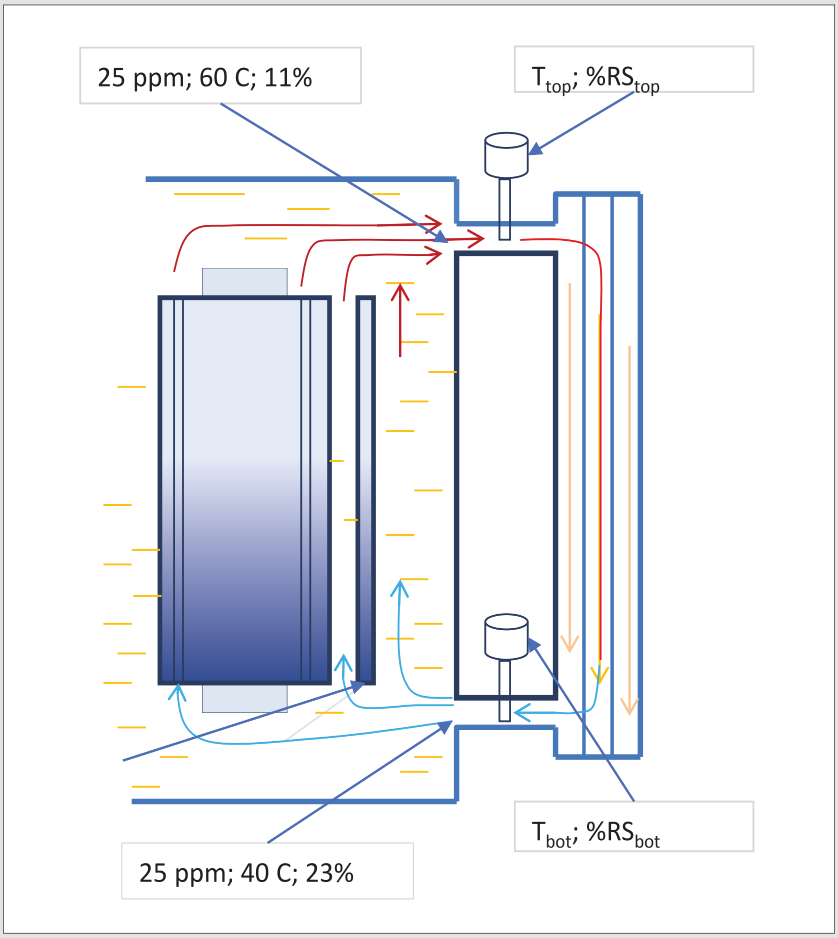

Figure 2. Oil quality monitoring by dual probe moisture/temperature sensors

Annual oil sampling may not be adequate for tracking moisture content, which may lead to misdiagnosis and create the real need for online oil quality assessment

standard enthalpy of water dissolution in oil is obtained as:

$$\Delta H = -B \times R \qquad (11)$$

While R is a constant = 8.3145 J mol^{-1} K^{-1}, the *B* coefficient is not a constant and will experience change due to a change of oil chemical composition over time. Thus, *ΔH* will change too upon any change in oil quality. Oil chemical composition is progressively affected by contaminants, such as low weight molecular acids, resulting in reduction of energy/enthalpy required to dissolve water in oil.

It follows from Equation 11 that the change in *ΔH* is not dependent on the second solubility coefficient *A*, i.e. change in entropy. It is only dependent on *B*. Then the insulating Liquid Quality Index (*LQI*) could be calculated as a linear function of *B*, B_{max} and B_{min}, e.g.:

$$LQI = 1 - \frac{B_{max} - B}{B_{max} - B_{min}}, \qquad (12)$$

or in terms of *ΔH*:

$$LQI = 1 - \frac{\Delta H_{max} - \Delta H}{\Delta H_{max} - \Delta H_{min}}, \qquad (13)$$

where B_{max} and B_{min} are the highest and lowest values of the solubility coefficient *B*, which varies from B_{max}, representing a new clean insulating oil, to B_{min}, representing very aged (end of life) liquid. For transformer mineral oil, these values are found to be 3900 and 3100 respectively [11]. This translates to the range of *ΔH* = [~25 – ~33] kJ mol^{-1}. This dynamic range of *ΔH* is wide enough to establish a correlation of *LQI* and the change in enthalpy.

The question remains as to how we can determine the solubility coefficient *A*, which is needed to devise the absolute water content (*WCO*) per equation (7). There are three methods that can be utilised:

The first method involves Karl Fisher (KF) titration method and *B* value determined by equation (10) mentioned before:

1. Karl Fisher titration

$$A = \ln\left(\frac{W_{KF}}{rS_{bo}} \times 100\right) + \frac{B}{T_{bo}} \qquad (14)$$

where W_{KF} is KF moisture content at thermodynamic temperature *T* and relative saturation *rS*.

2. Without using KF:

$$A = \ln\left(\frac{\Delta W}{\Delta rS} \times 100\right) + \frac{B}{T} \qquad (15)$$

where:

ΔW is the known small amount of water added to water in oil solution,

ΔrS is a change in *rS* due to a small amount of water added.

However, if *A* is required to be determined online, the challenge we promised to take on, then, according to the law of enthalpy-entropy compensation, there is a linear relationship between the two [12]:

$$\Delta H = \alpha + \beta \Delta S \qquad (16)$$

where α and β are constants.

Dividing both sides of Equation (16) by R and taking into account equations 4a and 4b yields:

$$A = \hat{\alpha} + \hat{\beta} B \qquad (17)$$

In order to find $\hat{\alpha}$ and $\hat{\beta}$ for chemical reaction of water dissolution in oil, we used laboratory data from one of the early studies on determination of moisture state and ranking of utility trans-

Table 3: Twelve selected transformers sorted by *B* – factor

Transformer	Serial #	Moisture Solubility Coefficient A	Moisture Solubility Coefficient B	IFT	Acidity	Color
Haw 2	351851	16.647	3703.8	23.2	0.04	1.5
High 3	851219A	16.565	3687.5	21.4	0.05	1.1
Haw 3	C0243852	16.554	3628.8	21.2	0.05	2
Green 8	6536831	16.536	3614.8	23.3	0.04	2
Mon 2	66222	16.445	3603.2	23.6	0.03	1.4
Wood 2	G851287C	16.095	3567.8	27.3	0.01	1
GM 1	0190051	16.311	3386.1	17.8	0.12	3.5
Rop 3	04901515	15.796	3373.5	18.2	0.15	3
Green 7	6536830	15.869	3363.3	18.1	0.13	3
GM 3	6536415	15.698	3348.7	18.8	0.15	4.5
Rop 1	04901514	15.214	3213.7	18.3	0.11	2.5
Green 5	6532689	15.271	3161.8	18.4	0.23	4.5

New oil A=17.08 B=3876

formers based on water contamination. Table 3 is a compilation of the laboratory results from that study.

The study included 20 transformers of different age, designs, and manufactures. Along with conventional acidity, IFT, PF, and colour, water in oil solubility values (*A* and *B*) were also reported. We sorted the records related to each transformer in the decreasing order of parameter *B* to discover a striking correlation of *B* and other oil quality parameters, such as acidity, IFT, and colour. To focus our attention on this correlation, we removed those records which would have fallen into "yellow" category.

Plotting water in oil solubility factor *A* against *B* produced straight line, demonstrating linear relationship between *A* and *B* as predicted by equation (17) and depicted in Figure 3.

Performing linear regression on the data set from the study above, we finally arrive at a relationship between *A* and *B*:

$$A = 6.8444 + 0.0026B \tag{18}$$

> **With periodic sampling it is difficult to see any trends in the degradation of the dielectric strength and oil acidity before the oil reaches a condition of severe deterioration**

Equation (18) concludes the formulation of thermodynamic approach to oil quality and moisture parameters determination for an energized transformer.

These $\widehat{\alpha}$ and $\widehat{\beta}$ constants are valid for mineral oil only, but the same approach can be taken to find these constants for any insulating liquid.

Case study

To demonstrate our approach on operating transformer, we selected a free breathing unit with moderately aged oil. The studied unit is 40 MVA, 66 / 22 kV, ONAN / OFAF distribution transformer. The temperature and relative saturation profile for two weeks of monitoring of this transformer are shown in Figure 4 and Figure 5. Four years worth of oil quality data is summarised in Table 4.

From the analysis of annual oil samples, one can see that the water content was always below the specified limits, according to the IEC guidelines (refer to Table 2). However, examining the data of Figure 6, we can see that on January 8th, water content was 45 ppm, well over limit. This renders annual oil sampling nearly useless as far as water-in-oil assessment is concerned.

Acidity is within the norm, but IFT is borderline between "fair" and "poor". The DBV does not correlate with the age; however, the value of 29 kV registered on February 7th indicates that the oil is "unacceptable" and "poor". The next year

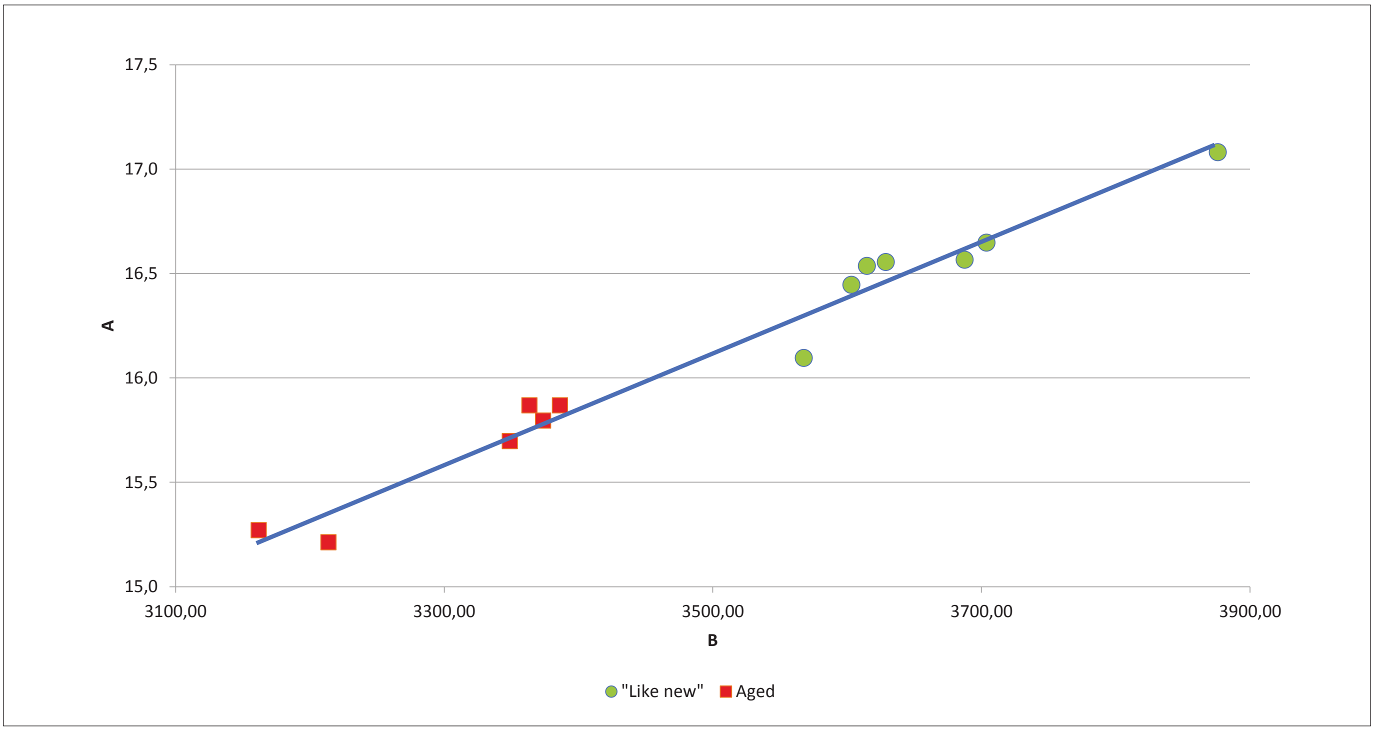

Figure 3. Relationship between and *A* and *B* water in oil solubility coeeficients

> ***LQI*** **is an integral indicator of oil deterioration, which correlates well with both late oil life acidity and IFT**

it is back to a rather high 60 kV (meaning "acceptable" and "good" according to the IEC Guide). The colour is progressively getting worse. Having a value of 2.5 indicates that oil approaches an "unacceptable" level. Indication of value getting close to "unacceptable" level is also supported by the IFT value approaching 22 mN / m.

A comparison of top and bottom calculated values for *WCO* is shown in Figure 6. These two series theoretically must agree, having the same value of ppm taken for top and bottom oil. Also shown (Figure 6) are residuals, which is a difference of top and bottom oil ppm at any given moment of time. One can observe that the average residual is approximately 2.5 ppm and the max is 6 ppm.

And finally, Figure 7 depicts a comparison of estimated top and bottom ppm based on the method proposed in this article. Here we can see that a satisfactory agreement between the two trends is reached with a high level of accuracy. When compared, the estimated online solubility coefficients **A = 6.96; B = -1527** are different from the default values, being **A = 7.37; B = -1662.7**. *The* B coefficient converts into ΔH = 29.2 kJ/mol.

Table 4. Nearly 5 years worth of oil quality data

Sample date	8 Jan 2010	19 Jan 2011	13 Jan 2012	7 Feb 2013	4 Apr 2014
Oil temp., °C	25	16	19	38	19
Moisture bottom, ppm	17	19	17	26	23
Dielectric breakdown 2 mm	56	40	56	29	60
DDF at 100°C	0.01	0.01	0.01	0.01	0.01
Acid number, mg KOH / g	0.06	0.03	0.03	0.04	0.04
IFT	26.9	24.1	26.8	25.1	22.2
Colour	2.0	2.0	2.5	2.5	2.5

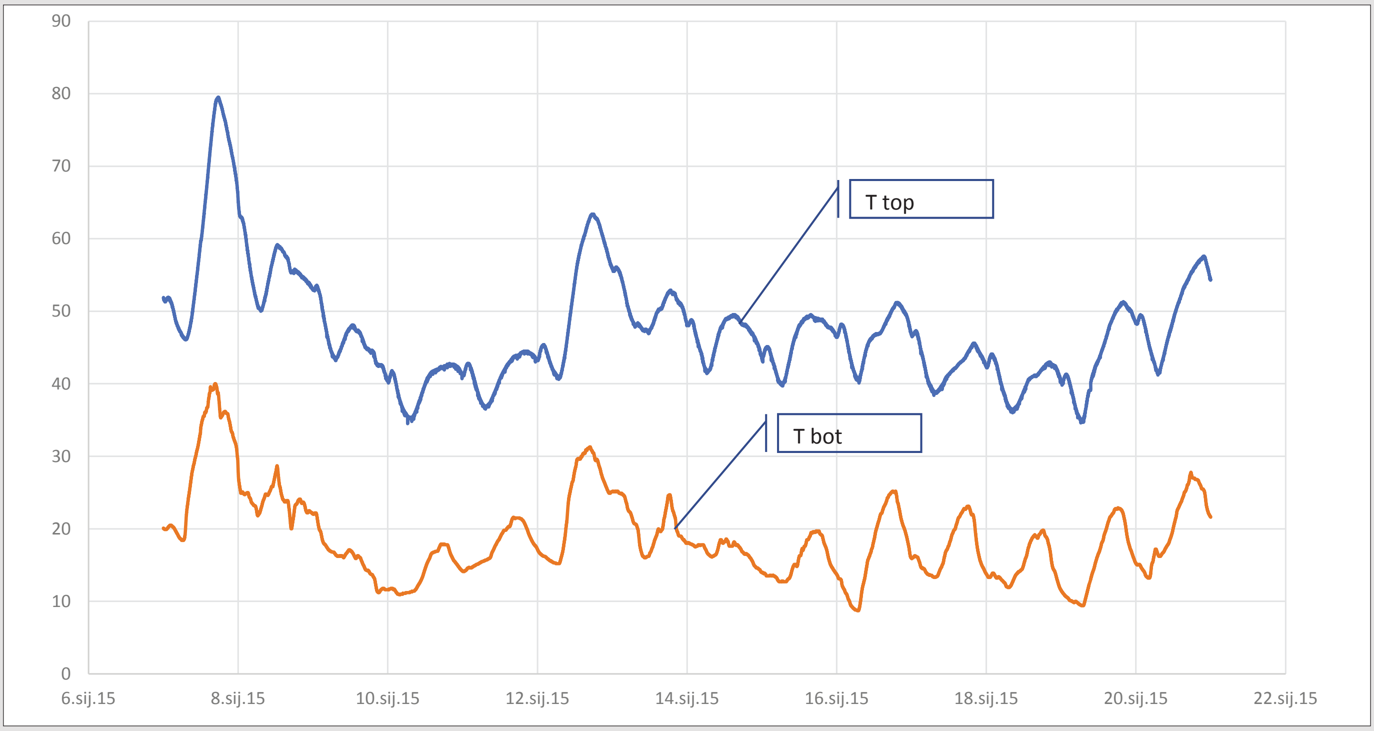

Figure 4: Top and bottom temperature recorded for studied unit during the two weeks period

The Liquid Quality Index *LQI* = 0.52, representing a 50 % deterioration as compared to the new oil. There is not yet an established scale for *LQI* but based on the results with the studied transformers we could offer diagnostic classes as depicted in Figure 8.

Conclusion

Insulating oil is one of the most important and critical natural protective mediums in transformers. It serves many purposes including defending a transformer from dielectric stresses, thermal overheating, and electrical partial discharges and arcing. It also serves as an information carrier. Thus, timely monitoring of transformer oil quality has become one of the emerging requirements of a modern diagnostic and monitoring system.

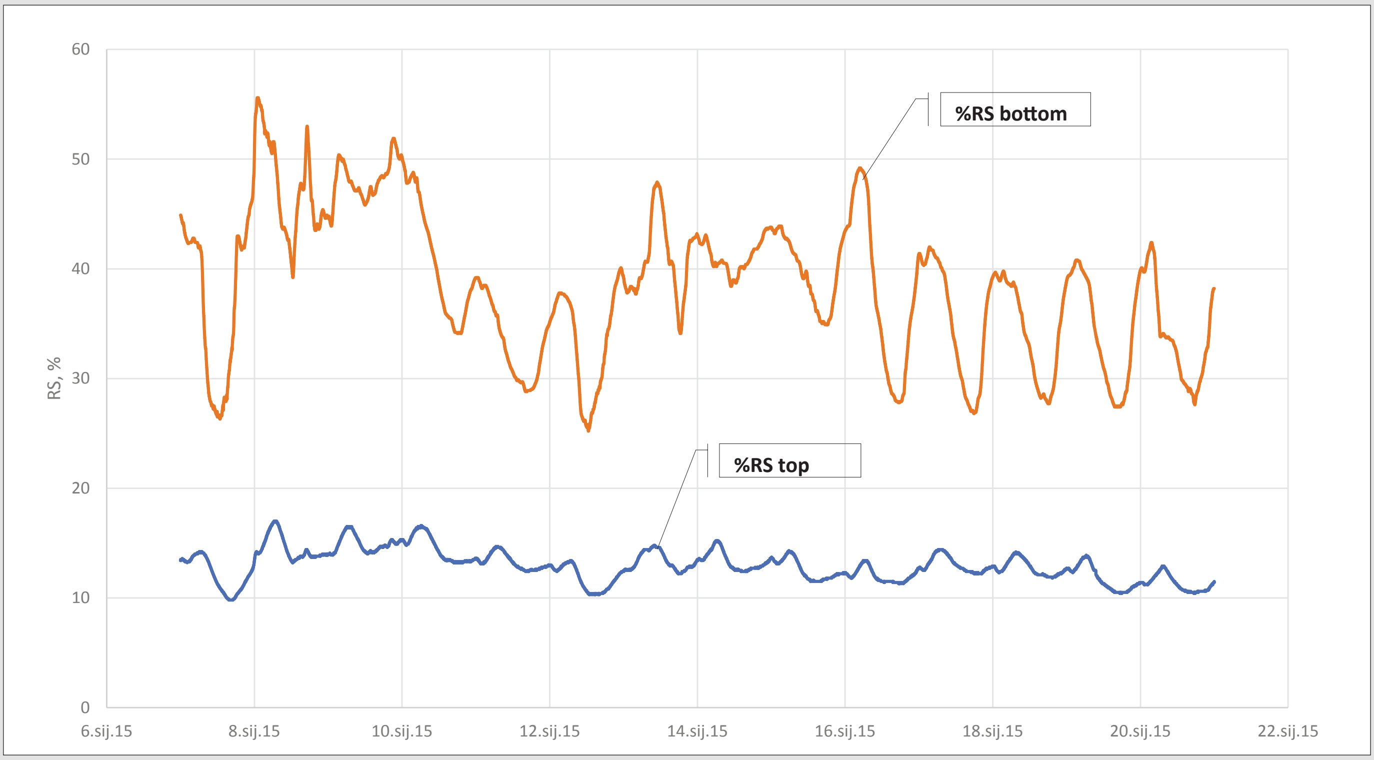

Figure 5: Top and bottom relative water saturation recorded for studied unit

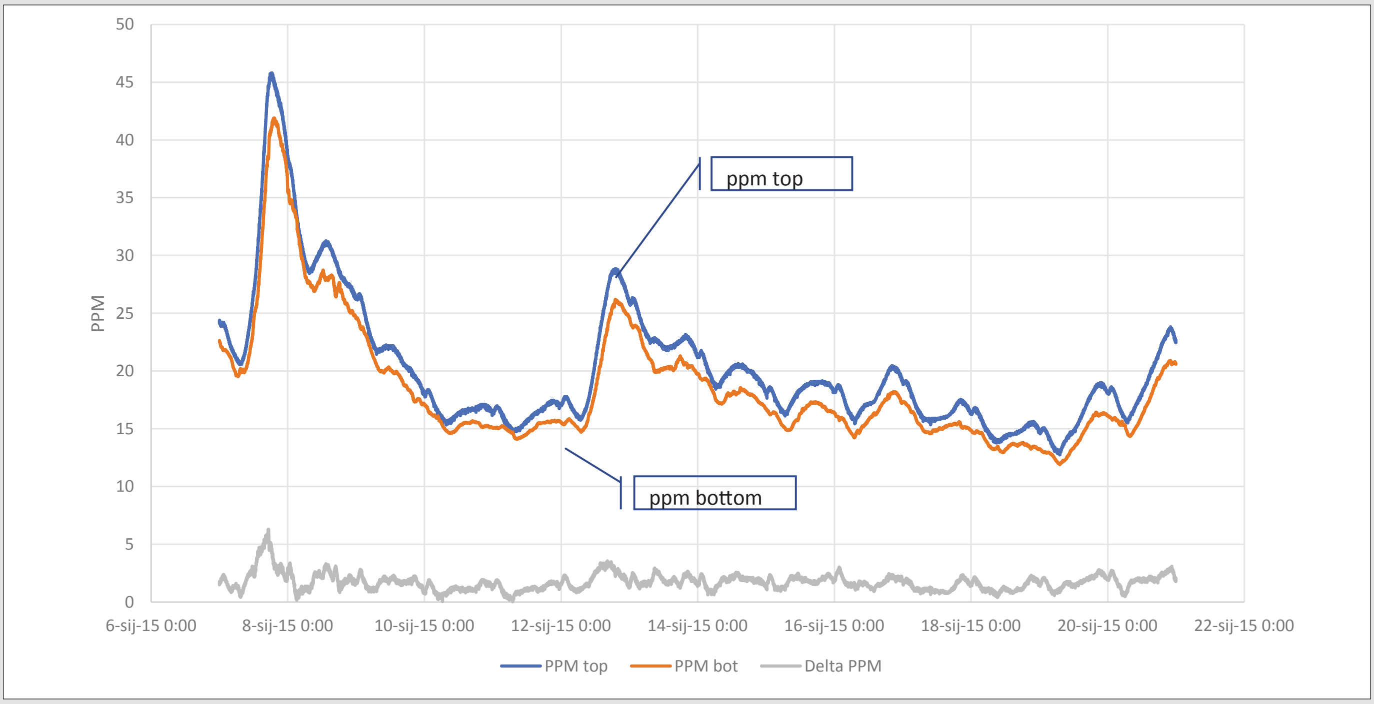

Figure 6: Top, bottom, and residual water content recorded for studied transformer
A = 7.37; *B* = -1662.7 – built in coefficients

> ***LQI*** **has a solid physicochemical background and is very sensitive to change in oil conditions**

In this article we have demonstrated that annual oil sampling may not be adequate for tracking moisture content, which may lead to misdiagnosis and create the real need for online oil quality assessment.

It was also demonstrated that with periodic sampling it is difficult to see any trends in the degradation of the dielectric strength and oil acidity before the oil reaches a condition of severe deterioration.

The proposed Liquid Quality Index (*LQI*) is an integral indicator of oil deterioration, which correlates well with both late oil life acidity and IFT. ***LQI*** has a solid physicochemical background

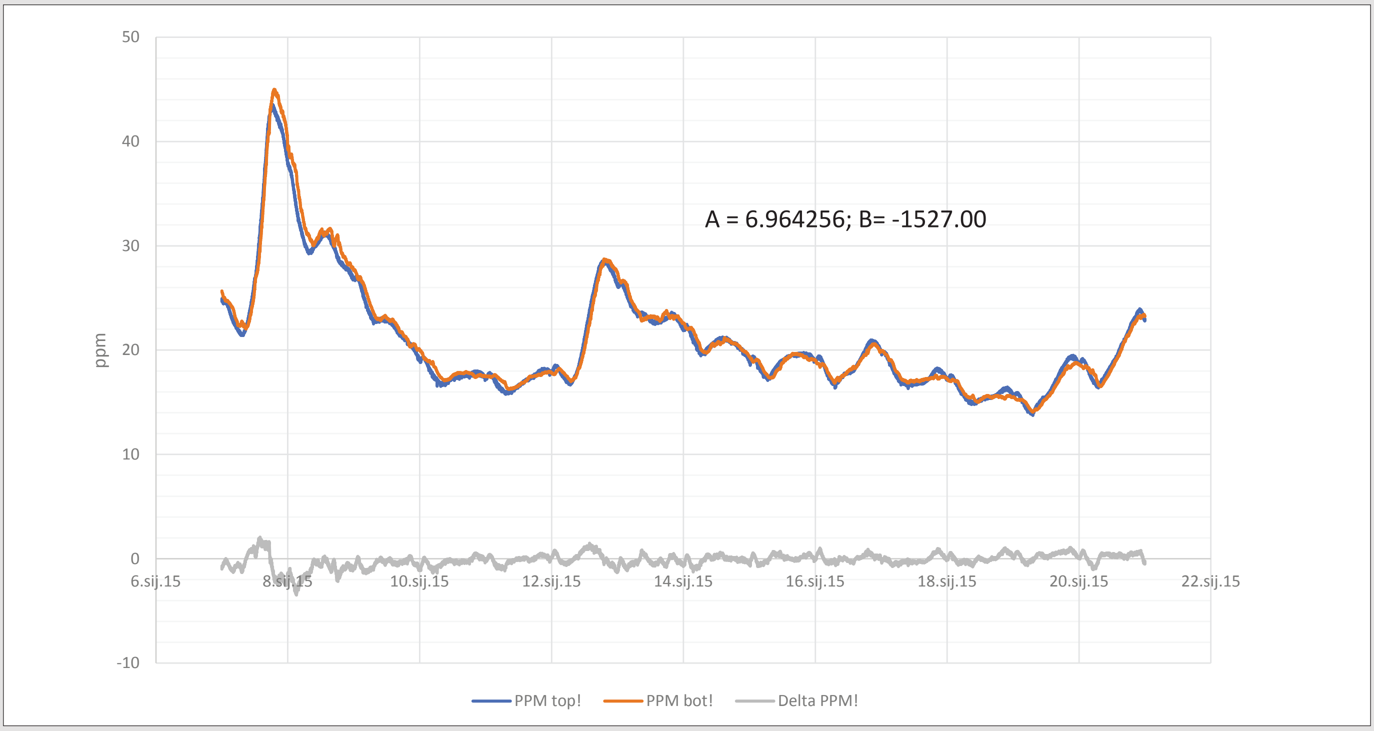

Figure 7: Top, bottom, and residual water content recorded for Trx – B:
A = 6.96; *B* = -1527.0 determined by the proposed method

and is very sensitive to change in oil conditions. It is not the absolute value of ***LQI*** that will find a use for the proposed technique, but the ability to calculate the rate of its change and therefore, the rate of oil deterioration.

We have also shown the way to calculate absolute water content (ppm) based on two sets of relative saturation and temperature sensors.

One of the benefits of a proposed method is eliminating the need for manual oil sampling, thus saving resources on analytical laboratory services.

Another benefit of the proposed method is the simplicity of measuring oil quality with well-regarded and time proven monitoring means such as moisture sensors.

The author believes that a new approach to electrical insulation quality assessment will lay a foundation for new analytical techniques and instruments for more accurate and reliable determination of water in oil parameters, and its effects on the quality of electrical insulating liquids.

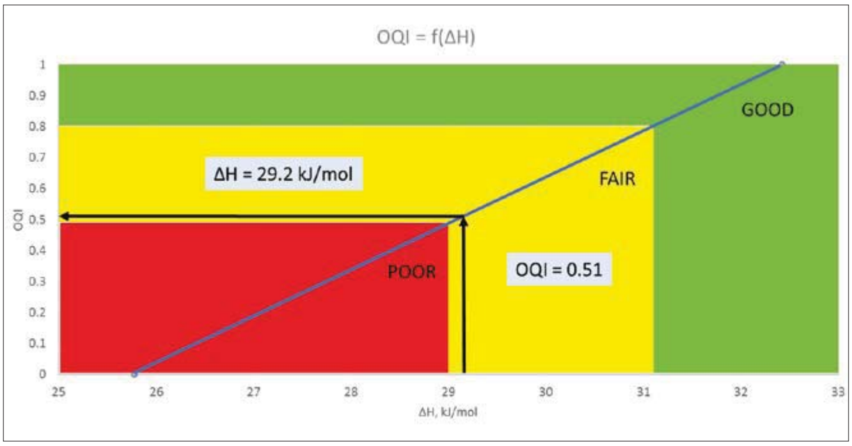

Figure 8: Liquid Quality Index for oil condition online diagnostic

> **It is not the absolute value of *LQI* that will find a use for the proposed technique, but the ability to calculate the rate of its change and therefore, the rate of oil deterioration**

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