

## **EFFECTIVENESS OF METHODS FOR WATER-IN-OIL DETERMINATION IN POWER TRANSFORMERS AND GAS-IN-OIL SOLUBILITY VARIATIONS:**

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### **SUMMARY**

This paper discusses the mechanism of gas-in-oil and water-in-oil solubility, and is supported by experimental data. It was shown that solubility coefficients are not constants but depend on mineral oil content and will change over time, due to the creation of oxidation by-product associated with aging. The paper presents experiences and experiments with; moisture-in-oil determination, including laboratory studies of the impact of aromatic content and oil oxidation by-products on the water-in-oil solubility; evaluation of absorbed (bound) water and its release with increasing temperature; influence of oxidation by-products on results from different methods of moisture determination.

### **KEYWORDS**

**GAS – IN – OIL, MOISTURE – IN - OIL, DGA, TRANSFORMER OIL, INSULATING FLUID**

## Fluid structure

Interaction forces between molecules of a fluid are subjected to Lennard-Jones Potential<sup>1</sup>, declaring that molecules are repulsing while approaching each other to a distance which is comparable with molecular size and attracting while the distance is increasing, however as the distance becomes large, attractive forces asymptotically reduce to zero.

These conditions result in the consolidation of fluid molecules into compact globules (a self-adsorption phenomenon), and fluid can be represented as quasi-solid globules being in continuous sliding motion relative to each other and small-sized spaces between the globules where single molecules will reside and be in motion.

The size of the spaces can be evaluated on the basis of fluid density and its correlation with temperature, which can be expressed as

$$\rho_4^t = \rho_4^{20} - \alpha(t - 20) \quad (1)$$

An essential feature of this correlation is that it is practically linear, i.e. a linear expansion coefficient which corresponds to, for example, mineral oil of a particular density, and is practically independent of temperature in the range of several tens of degrees. About 7% per 100°C change of temperature.

Thus a theoretical model of transformer oil can be considered in the form of mutually sliding particles (globules) and interstices, which make up a substantial (10% or larger for mineral oil) part of the total fluid volume.

Volume of interstices depends on size of globules (the smaller the size of the globules the smaller the volume of the interstices). The mean distance between molecules increases with temperature due to enhancing thermal fluctuation of molecules resulting in the expansion of globules and accordingly the increasing of interstices volume.

All this means that any fluid is a porous substance.

## Solubility of gases in oil

There are two possible states for gas-in-oil:

1. Free arrangement of gas molecules in the space between fluid globules (interstices). Solubility  $B_1$

## 2. Adsorption of gas molecules by molecules of fluid. Solubility $B_2$

Accordingly any expression for solubility coefficient  $B$  should have a form

$$B = B_1 + B_2 \quad (2)$$

## Free gas

Gas in oil is somewhat similar to that of gas outside of oil but with the difference being, gas outside the oil has penetrated into the labyrinths between the oil globules. Gas-in oil concentration ( $A_g$ ) obeys Henry's law and can be described by

$$A_g = B_1 \cdot \frac{p}{P_0} \quad (3)$$

Where  $B_1$  is the solubility coefficient,  $p$  the partial pressure and  $P_0$  normal atmospheric pressure.

If the gas is ideal, the second state is absent (no absorption of gas with fluid molecule as well as no self-adsorption with gas molecules) and dissolved gas is situated only in interstices between fluid globules.

The quantity of gas is determined as a product of the interstices volume and gas concentration. Accordingly solubility coefficient  $B_1$  may be expressed as

$$B_1 = \lambda_0 (1 + \beta t) \quad (4)$$

$\lambda_0$  - equivalent volume of interstices

$\beta \cong 3\alpha$  - thermal expansion coefficient

For non-ideal gases, but when self-adsorption of the gas is negligible,  $B_1$  is just a part of the solubility coefficient associated with gas in the labyrinth found between the globules.

It should be underlined that in this case the solubility coefficient is a linear function and linearly rises with temperature. A typical example is the solubility in oil of Hydrogen (Figure 1). This shows that Hydrogen is weakly absorbed by oil molecules, having a great mobility in the oil.

A positive temperature coefficient of solubility has been observed for  $N_2$ , air, He, CO,  $O_2$  and Ar.

From the aforesaid it follows that increasing oil density results in decreasing solubility.

## Adsorbed gas

Gas that is adsorbed by molecules of fluid make up another part of dissolved gas. This

state is characterized by reducing gas solubility with temperature due to the reversible mode of adsorption and de-adsorption (evaporation) of gas molecules from the globules surface with temperature. i.e. the adsorbed component of the gas solubility coefficient decreases with temperature

Analysis have shown that  $B_2$  depends not only on temperature but on gas pressure or rather on the gas pressure ratio  $\frac{p}{P_0}$

This means that Henry's law is true if the gas solubility is very low (several percent) or in the case of  $p \ll p_0$ . Fortunately for most practical cases gas pressure is substantially less than atmospheric pressure.

The adsorption component of solubility and the decreasing form of the solubility coefficient with temperature is predominant for such gases as  $CH_4$ ,  $C_2H_2$ ,  $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$ , other hydrocarbons, and particularly for  $H_2O$ .

In reality transformer oil is a complex mixture of components. For new oils, the typical "variable" component is the amount of aromatic hydrocarbons. In addition oxidation of transformer oil produces by-products, which add to adsorbing substances. Accordingly the adsorbed component of solubility becomes dependant on the ratio of oil components, the density of the oil and the ratio of relative mass concentrations.

#### Experimental study of gas-in-oil solubility<sup>1</sup>

Solubility of gases was studied for three types of oil (See Table 1 for details of the oils used) at and at four different temperatures 20, 50, 90 and 100°C

Parameters	Type of oil		
	GK	T-1500	Synthetic Y-3
Density @ 20°C, g/cm <sup>3</sup>	0.856	0.869	0.968
Aromatic content, %	1.6	14.0	66.0
Naphtenes, %	40.3	37	0
Paraffines, %	58.1	49	33.5

**Table 1: Details of three oil types used in experiments.** Results of solubility variations with temperature are presented in Figures 1 – 4.

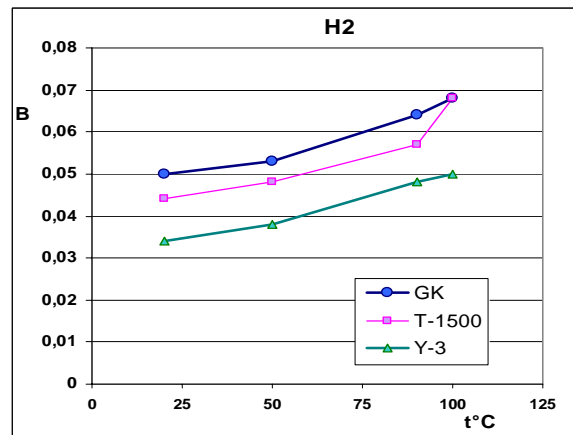
Gases whose solubility in oil increases with increasing temperature show an inclination

<sup>1</sup> Experimental study of gas-in-oil solubility was performed under leadership of Prof. R. Lipstein

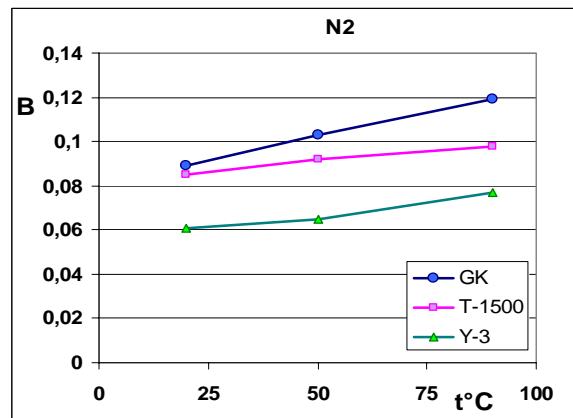
towards decreasing solubility with increasing oil density and aromatic content.

Gases, whose solubility in oil decreases with decreasing temperature show an inclination towards increasing solubility with increasing oil density and aromatic content.

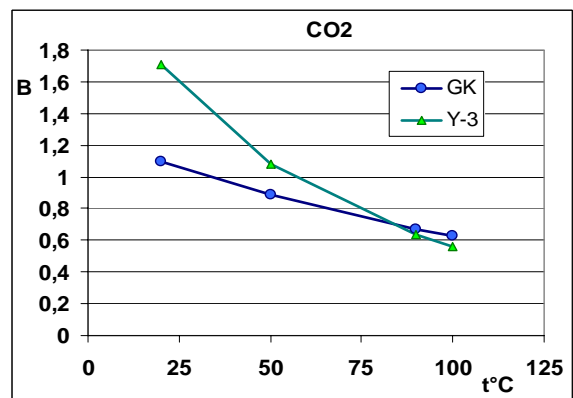
These results strongly indicate that the difference in gas solubility coefficients in mineral oils, in the typical range of relative density variation (0.85-0.90) and aromatic content variation (0%-20%) is substantial and should be taken into consideration.



**Figure 1 : Solubility of Hydrogen**



**Figure 2: Solubility of Nitrogen**



**Figure 3: Solubility of CO<sub>2</sub>**

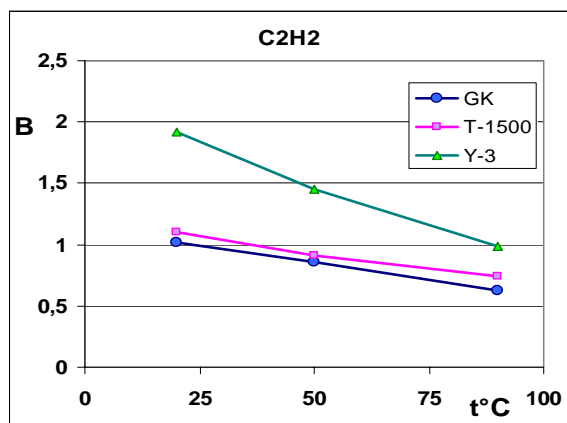


Figure 4: Solubility of Acetylene

## WATER – IN –OIL SOLUBILITY

### Mechanism of Water-in-oil solubility

In contrast to real gases, water is a vapor at room temperature and is subdued to a great extent to self-adsorption, which plays a predominant role in water vapor behavior with changing temperature.

*Self-adsorption* is the phenomenon whereby water molecules are assimilated in groups of two, three or four molecules, and other associations similar to microscopic crystals. That explains an unlimited rise of water-in-oil solubility when nearing saturation.

*Saturation of fluid* with water is a state when self-adsorption of water becomes prevailing, and the formation of large water groups is an irreversible one, resulting in the formation of microscopic drops of water.

Water association and water in the interstices between oil molecules globules (hereinafter referred to as “free” water) determines the relative saturation of oil and is responsible for the water migration process.

Another difference of water from real gas is that water can be adsorbed by “active” molecules of oil e.g. aromatics, in the form of poly-molecular adsorption. Adsorbed-mode water is often considered as being “bound” water because it is subject to physical but not to chemical interconnections.

The presence of the two components of water molecule associations (self-adsorbed water and adsorbed water) results in an increase of the oil dew point, i.e. more water is required to reach saturation level.

The ratio of the dissolved water content in oil and water content in gas media above oil

(head-space) is called water solubility coefficient.

Increasing the temperature mitigates adsorption as well as self-absorption (due to degradation of associations) and more water is required to reach the saturation level.

### Methods for water content and water solubility determination

Three procedures / methods for water determination are used typically:

1. Methods based on the extraction of water and its subsequent measurement by means of an observable / measurable chemical reaction, namely the Karl Fischer Coulometric Titration (KFT) and the Hydride Calcium Method.
2. Methods based on the physical extraction of water into a headspace, until equilibrium, and its subsequent measurement by means of gas chromatograph (GC) or photo-acoustic spectroscopy (PAS).
3. Capacitive probe method, which measures, indirectly, relative saturation of the oil through relevant changes of sensitive film conductivity.

In the present work two of these methods were used, namely the KTF method and the PAS method.

Water-in-oil solubility was determined by means of maintaining a known concentration of water vapor in a gas space over an oil sample until equilibrium is reached. This is achieved by means of the use of a certain concentration of  $H_2SO_4$  thus maintaining a constant vapor pressure in the head space.

### Effect of temperature and aromatic content on water-in-oil solubility

The temperature dependence of water-in-oil solubility of three types of oil (see Table 1 for details of the oils used) were studied at 20, 50 and 90°C by means of maintaining, in a head space, a water vapor pressure of 17.5 mm Hg until equilibrium. Water content was measured by KFT and PAS methods.

The results (Table 2) confirmed a significant influence from aromatic content on water solubility. The adsorbed component of dissolved water can exceed the amount of water dissolved in conventional oil at room temperature by a factor of ten to twenty. On

the other hand increasing temperature results in a significant increase of “free” water

Oil	Water-in oil content, ppm		
	20C/ 100%*	50C/ 19%	90C/ 3.19%
GK	40/40**	32/168	20/627
T-1500	81/81*	64/336.5	33/1035
Y-3	726/726	480/2523	192/6023

**Table 2: Solubility of water in oils.**

\*numerator-oil temperature, denominator-relative saturation;

\*\* numerator – moisture concentration measured under vapor pressure 17.5 mmHg, denominator – moisture concentration corrected to 100% saturation.

### Effect of aromatic content on the water solubility of new and oxidized oils

The water content in oil is directly proportional to the relative water concentration (relative saturation) up to the saturation level. Cigre<sup>(2)</sup> suggested the temperature dependence of the solubility of water in oil ( $W_s$ ) as follows:

$$W_s = W_{oil} \cdot e^{\frac{B}{t+273}} \quad (5)$$

Where  $W_{oil}$  and B are constants. These are different for oils with different aromatic contents.

It's well known also that water solubility increases for aged oil due to the formation of additional adsorbed water and the amount of this increase was also a subject of interest in this series of experiments.

Standard water-in-oil specimens were prepared by means of “wetting” dried oil in a humidity chamber under a relative saturation of 98%. The humidity was maintained by use of a known concentration of  $H_2SO_4$  in the chamber. Five oils having notable differences in aromatic content were selected for study. Each specimen was prepared at a temperature of 15°C and also at 40°C. Note: Water-in-oil solubility close to saturation level was studied (relative humidity in head space 98%).

Oil	Ca	Water-in-oil content, ppm (mg/kg), 98% on saturation				
		15C		40C		
		KFT	PAS	KF	PAS	Ws*
A	4	27	38	83	86,5	97.5
B	8	38	44	102	100	108
C	12	36	44	108	104	128.3
D	14	41	45	103	97,5	
F	19	52	52	126	110,5	162

**Table 3: Water-in-oil saturation level**

\* Saturation level calculated using formula 5 above

The results display a good correlation between solubility of water-in-oil and aromatic content. Water content values measured both by the Karl Fischer method and the Photo-Acoustic method show quite consistent data.

Also, water content values measured by both methods appear to be quite consistent to the theoretical values presented in the table and as calculated by (5)

As an add-on to this experiment, two of the oils (A and D), were artificially oxidized for a period of time in the presence of copper and oxygen resulting in the formation of a notable amount of acids.

Oil A (Ca = 4%) - total acidity = 0.085 mg KOH/g.

Oil D (Ca = 14%) - total acidity = 0.071 mg KOH/g,

Subsequently the solubility of water in these oils was measured under the same conditions as for new oils:

Relative humidity of air media 98%,  
Temperature 15 and 40C.

Oil	Ca	Water-in-oil content, ppm (mg/kg)			
		15C		40C	
		KFT	PAS	KFT	PAS
A	4	38 (27)	39 (38)	88 (83)	85 (86,5)
D	14	59 (41)	47 (45)	155 (103)	103 (97,5)

**Table 4: Effect of oil oxidation of water-in-oil saturation level**

These results show that oxidation of the oil does not change the solubility of water-in-oil when moisture was measured by means of the equilibrium mode Photo-Acoustic method (PAS). Karl Fischer coulometric (KFT) method however showed a 50% increase of water readings for oil D. This is likely to have been associated with the effects of by-products production. Further experimentation was required to prove this hypothesis - see results further on in this paper.

### Migration of absorbed water

The process of moisture adsorption is accompanied with a release of energy from the members of the process. Conversely the process of de-sorption requires supplying external energy.

In order to desorb water, additional compensative energy is required, by means of, for example, heating or prolongation of time. Because of that the time required for adsorption and the time required for desorption can be different.

This phenomena impacts on the results of water-in-oil measurement, by virtue of the process of extraction of the water out of oil, and also the processes of water migration.

The release of adsorbed water was studied by means of heating a sealed sample of oil up to 70 or 100°C for between 2 and 5 hours. Water content was measured prior to heating, after air cooling the heated sample (approximately 30 minutes after heating was stopped) and after cooling and prolonged (19-24 hours) holding of the sample at room temperature.

The results have shown that both unused and to a greater extent service aged oil can contain substantial amounts of adsorbed water, which contribute to the amount of “free” water at a given temperature.

Oil	Water content, ppm (mg/kg)		
	No Heating	Heating, air cooling & immediate analysis	Prolonged cooling (19-24 hours)
GK (new) (Ca = 4%)	20.7	32.2 (100°C, 2hr)	23 (100°C, 2hr)
Nytro 11 GX (new) (Ca = 12%)	19.6	31.4 (100°C, 2hr)	
SHELL Diala AX (new) (Ca = 8 %)	10.4	18 (80°C, 4hr)	10 (80°C, 4hr)
Service aged oil T-750, Ca=19% NN=0.064mg KOH/g; IFT=32 dynes tanδ <sub>90</sub> =5.3%	26.3	85 (100°C, 5hr)	
Service aged oil TKp, Ca=23% NN=0.133 mg KOH/g IFT=23.18dyne s/cm tanδ <sub>90</sub> =10.8 %	25.8	50 (100°C, 4hr)	
Service aged GK, Ca=3.5% NN=0.013 mg KOH/ g	17.7	40.2 (100°C, 2hr)	19 (100°C, 2hr)
Service aged TKp, Ca=23%	30.2	45 (70°C, 4hr)	23.2 (70°C, 4hr)

Table 5 : Temperature releasing of bound water

### Impact of released “bound” water on oil breakdown voltage.

Obviously the supplement of bound water should affect oil breakdown voltage. In order to evaluate the impact of increasing oil temperature and the subsequent release of bound water, oil samples were tested in a sealed cell, well preserved from atmospheric water (Fig. 5).

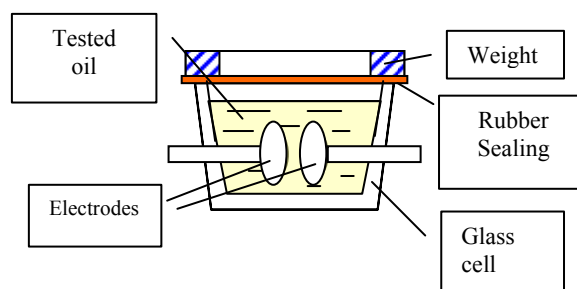


Figure 5: Breakdown voltage apparatus set-up

Sample No.	State	Water, ppm	Ubd, kV
1	Initial	16.9	55.3
	After heating up to 75°C and cooling	42.1	33.4
2	Initial	26	73.6
	After heating up to 75°C and cooling	48	58
3	Initial	27	65
	After heating up to 75°C and cooling	44	42

**Table 6 : Effect of oil temperature on variation of moisture and breakdown voltage**

The results in Table 6 clearly show that transformation of adsorbed water by heating can deteriorate the oil withstand strength substantially. This phenomenon should be considered and monitored.

### Impact of oxidation by-products on water-in-oil measurement.

A comparative measurement study of water content in service-aged oils has shown a systematic overestimation of water content as measured by KFT over the equilibrium-mode PAS method. Some data relating to this is shown in Table 7

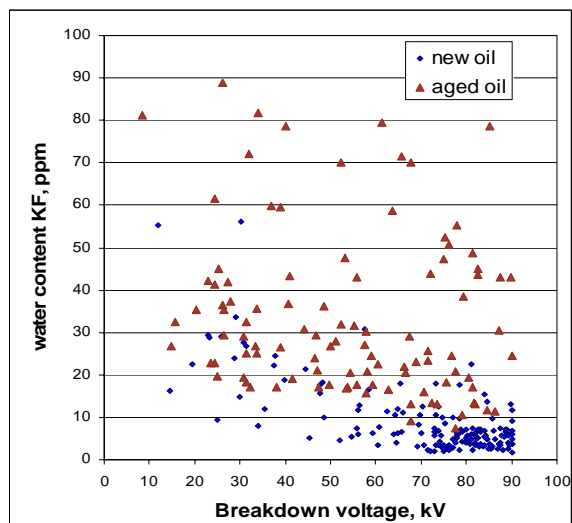
Object	Water, ppm KFT	Water, ppm PAS	$\Delta$ Water	Acidity mgKOH/g
GSU	33,9	35	+2	0.122
furnace unit	33	27	-6	0.078
PT step down	29	22	-7	0.125
PT step down	21,6	29	-7.4	0.087
Bushing	68,5	24	-47.5	0.17
Bushing	74,6	25	-49.4	0.241
Bushing	87,1	26	-61.1	0.241
PT	66,6	60	-6.6	0.127
PT	78,6	28	-50.6	0.157
furnace unit	56	24	-32	0.263
furnace unit	53,3	26	-27.3	0.223
GSU	71,5	31	-40.4	0.243

**Table 7 : Sample data of KFT water-in-oil results and PAS results,**

It is known that the main reason for overestimation of moisture by KTF is associated with the reaction of the Karl Fischer titration solution with conductive by-product of oil oxidation.

Statistical analysis (ZTZ-Service, Ukraine - database) has shown (Fig.6) that the overestimation of water by KFT does not

impact significantly on the breakdown voltage of the oil.



**Figure 6 : Breakdown voltage Vs Water concentration as measured by KFT.**

*New oil -160 samples, acidity <0.004mgKOH/g*

*Aged oil-100 samples, acidity >0.12 mgKOH/g*

### Effect of drying out of an oil on the moisture readings as measured by both the KFT and the PAS methods

Samples of oil, showing elevated moisture content, were subjected to drying out by means of molecular sieve treatment. Two groups of service aged oils were tested:

- Oils that did not show symptoms of notable oxidation.
- Highly aged oils displaying signs of high levels of oxidation.

Treatment involved zeolites at a concentration of 50 g per 125 g of oil for notably aged oils and 20 g per 100g of oil for fairly new oils. The treatment time was 24 hours, which allowed a sufficient duration for the effective drying out of all the oil sample.



### Service oil without symptoms of notable oxidation

		Acidity	Water content ppm	
			KFT	PAS
#1	Initial	0,005	27	30
	After drying out	0,003	9	< 1
#2	Initial	0,004	27	30
	After drying out	0,002	9	< 1
#3	Initial	0,005	15	23
	After drying out	0,004	6	< 1
#4	Initial	0,006	27	33
	After drying out	0,004	4,5	< 1
#5	Initial	0,006	22	25
	After drying out	0,005	4,7	2

**Table 8: Effect of drying out on water-in-oil readings : New Oil**

		Acidity	Water content, ppm	
			KFT	PAS
#1	Initial	0,157	78,6	28
	After treatment	0,065	58,5	< 1
#2	Initial	0,206	94	34
	After treatment	0,131	56	< 1
#3	Initial	0,162	32	17
	After treatment	0,120	27	< 1
#4	Initial	0,103*	32	28
	After treatment	0,120	27	< 1
#5	Initial	0,106	31	27
	After treatment	0,043	14	< 1
#6	Initial	0,090*	30	25
	After treatment	0,030	15	< 1

**Table 9: Effect of drying out on water-in-oil readings : Service oil with symptoms of notable oxidation**

\* Presence of sludge

In all cases drying out of fairly new oils resulted in significant decreases in moisture readings measured by both methods. However the KFT method showed some “residual” moisture, which is most likely associated with something other than the moisture. Drying out of notably oxidized oils did however show a significant reduction of KFT readings confirming impact of factors other than water. Thus an elevated value of water-in-oil, as measured by the KFT coulometric method may indicate substantial oxidation of oil. Real water content may be verified using another method.

### Aging by-products removal, and the effect on water content readings as measured by KFT

Oil reclamation and the removal of oil by-products resulted in the reduction of water content readings as reported by the Karl Fischer titration, confirming that the KFT method result is, to a great extent directly associated with oxidation by-products

Oil	Acidity, mgKOH/g		W, ppm, KFT	
	Oxidized	Reclaimed	Oxidized	Reclaimed
I	0,263	0,006	56	19,7
II	0,223	0,002	53,3	19,1
III	0,243	0,009	71,5	39

More clear evidence of the influence of acids on KFT readings was obtained in the following experiment.

Service aged oil, with an aromatic content of 18%, color-8 and acidity 0.206 mgKOH/g was reclaimed using different quantities on clay (palygorskit).

Using this method 5 specimen were prepared with different acidity; 0.206-0.003 mgKOH/g. These specimens were then placed in the humidity chamber and 50% relative humidity was maintained in the chamber until equilibrium. Water content was subsequently measured by both KTF and PAS methods.

It was found that there was a good correlation between KTF water reading and acidity in reclaimed oils (Fig.7a). Equilibrium-mode PAS method did not show any change of water content with changing acidity (Fig.7b).



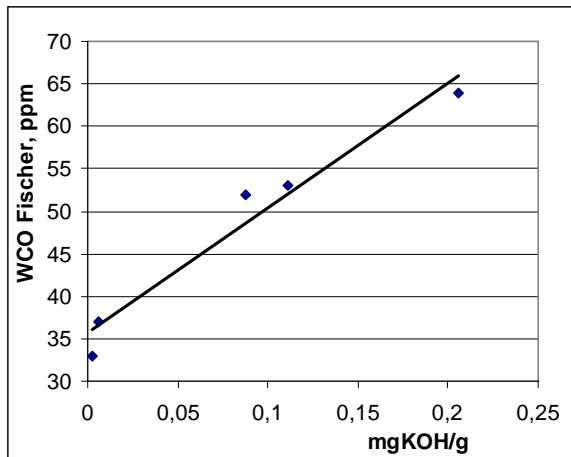


Figure 7a: Correlation between water content measured by KFT and acidity

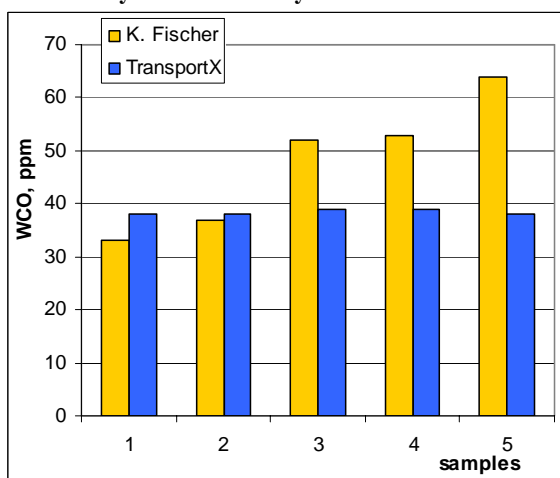


Figure 7b: Comparison of KFT to PAS water-in-oil measurements on acidic oil

### Conclusion

Gas-in-oil solubility is presented in two forms:

- free arrangement of gas molecules in the space between fluid globules.
- adsorption of gas molecules with molecules of fluid.

The difference in gas solubility coefficients in mineral oils, in the typical range of density variation and aromatic content variation is substantial and should be taken into consideration.

In contrast to gases, water is subdued to great extent to self-adsorption, which plays a predominant role in water vapor behavior with changing temperature

Another difference between water and “real” gas is that water adsorbed by “active” molecules of oil e.g. aromatics, can be in the form of poly-molecular adsorption, accumulating to a significant amount of water.

Free water in the interstices between oil molecule globules (real oil component), determines relative saturation of oil and is responsible for the water migration process.

Both unused and, in particular, service aged oil can contain substantial amounts of (often) underestimated adsorbed water. This adsorbed water contributes to the amount of “free” water with changing temperature. This water can seriously deteriorate the voltage withstand strength of the oil. Additional energy, in the form of heating the oil is required to measure full water-in-oil

An alternative method may be on-line water-in-oil monitoring, considering temperature variation.

Finally readings of water-in-oil by KFT method can be affected by oxidation by-products.

An elevated (“false”) amount of measured water-in-oil may indicate on substantially oxidized oil. Real water content may be additionally verified using another method such as PAS.

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