ABSTRACT

The most recent IIS reports on comparison tests for the DGA clearly indicate that the participating laboratory on average has not achieved repeatability dictated by both ASTM and IEC standards. This may be seen in the reference IIS report 2020 [11].

Although the headspace extraction method is the most widespread extraction methodology today, other options are favoured by online and portable devices, such as membrane extraction or bubbling. For more reliable, repeatable, and versatile results for different oil types, it is preferred to choose other techniques such as vacuum extraction, total and partial. Mercury vacuum extraction is the most reliable and cost-effective method. Although mercury accidents are very rare, most western laboratories have abandoned them in favour of automatic options. Pros and cons for each option will be described herein.

The gas extraction process is not a process that is in thermodynamical equilibrium, and all the gas transfers from liquid to gas are therefore time-dependent. An exception is the total vacuum extraction by the method described in section 7.2 of IEC60567. ASTM D3612 does not include this procedure.

KEYWORDS:

DGA, extraction, Henry's coefficients, Ostwald's coefficients, standardisation

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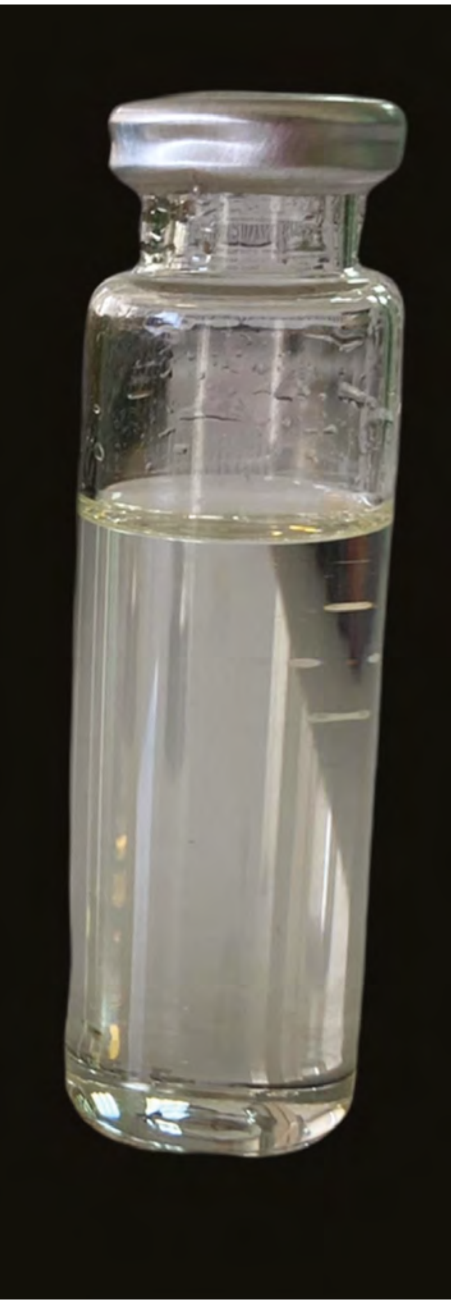

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Gas extractions from insulating liquids – Part I

1. Introduction

Dissolve gas analysis has been one of the most important tests accompanying the transformer industry almost since the transformer has been invented. Transformers are indispensable in our modern lifestyle, and DGA is the best tool for maintaining transformers. The gas extraction stage is the most delicate stage of DGA, and inadequate processing of this stage may induce significant errors in transformer diagnoses. The Buchholz relay invented a hundred years ago is mainly driven by the dissolved gases generated in case of a faulty condition. The gases accumulated in the relay are separated from the oil by one of the two mechanisms:

1. **Kinetic:** In case of a critical failure such as arcing, the gas formation is very rapid, and the gas generated from the oil by the failure energy travel as bubbles on the surface of the liquid, driven by floating potency due to density differences of liquid and gases. In this case, the gases tend to flow through the gas relay, trapped and accumulated there. This will induce an immediate trip and instantly deenergize the transformer. The merit of the Buchholz device is expressed as the fastest reacting DGA online device and as an efficient protection device. In this case, the gases need not be extracted from the oil because they trigger the relay more rapidly than being dissolved in the oil.

2. **Gas saturation:** As shown in Table 1, the gases possess a certain solubility in the mineral oil. The solubility depends, of course, on the chemical interaction between the specific gas and specific liquids. As both species are more comparable in the polarity character and Van der Waals force, gas will be more soluble in the liquid. In our mineral oil and hydrogen case, the interaction will be weaker, and equivalently the solubility. Other hydrocarbon gases are more similar to an organic liquid; therefore, the consequence will be a higher solubility. In case of a slow gas formation in the oil, the volatile species reach their solubility limits and then evolve from the oil as bubbles and again reach the Buchholz relay gas accumulator and induce an immediate trip of the relay. In this case, the transformer may also be tripped by gases that are not correlated with an immediate failure, such as air or water vapour in the case of a non-mineral oil. This situation may also occur during a rapid and abrupt temperature fluctuation that differentially affects the liquid solubility toward a different volatile species. Modern synthetic mineral oils possess a non-polar characteristic. Therefore, polar molecules as carbon monoxide or water obtain a very weak interaction with the liquid non-polar matrix. For the new polar ester liquids, the situation is vice-versa, meaning that non-polar gases interact less with the polar matrix.

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In the case of the Buchholz relay, it is not necessary to intentionally extract the gasses. Although the Buchholz is able to avoid a large percent of dangerous incidents, in some circumstances, the transformer will fail before the Buchholz trip, as shown in Fig. 3. For avoiding such events, it is necessary to extract, analyse, and diagnose the transformer condition. Based on this assessment, the transformer may be saved. The principal purpose of DGA is to save the transformer or to regulate its load.

Table 1. Gas solubility in mineral oil (Pugh & Wagner, 1961)

Gas	Symbol	Solubility in oil, % vol. at 25 °C
Hydrogen	H_2	7
Oxygen	O_2	8.6
Nitrogen	N_2	9
Methane	CH_4	16
Carbon monoxide	CO	30
Carbon dioxide	CO_2	120
Ethane	C_2H_6	280
Ethylene	C_2H_4	280
Acetylene	C_2H_2	400

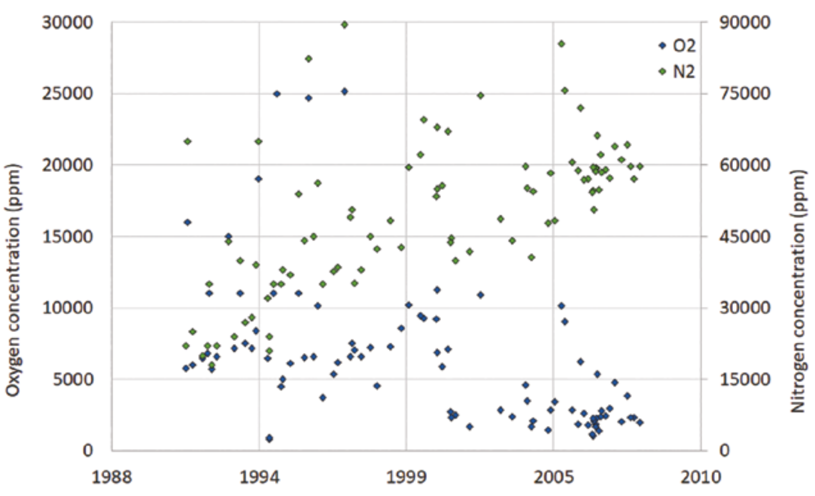

Figure 1. Oxygen and nitrogen by laboratory gas extraction (S. Leivo, 2020)

2. Gas extracting techniques for dissolved gas analysis in power transformers

For being able to measure a gas concentration dissolved in the oil, we may measure the gas concentration in the headspace above the liquids. The correlation between those two concentrations is defined by Henry's law. It states that the concentration of dissolved gas is directly proportional to the partial pressure of that gas above the solution and may be described by a formula as:

$Pa= K_h*C_a$

- Pa is the partial pressure of the solute above the solution
- Ca is the concentration of the solute in the solution (in one of its units)
- Kh is the Henry's law constant, which has units such as L·atm/mol, atm/(mol fraction)

Solubility theories

Henry's law also states that the Henry constant is highly dependent on the temperature and overall pressure.

Such a system of liquids contains dissolved gases. The headspace above the liquid contains the same gases above the liquid as described in Fig. 4.

As temperature or pressure fluctuates, the proportion of soluble and insoluble gas molecules varies in accordance with the intermolecular correlation of the gases and liquid matrix. At a certain temperature and pressure, a specific equilibrium of concentrations is obtained.

Henry's law describes an ideal situation. In fact, Henry's law has had deviations as in multicomponent systems or in very low

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concentrations (Rosenberg et al., 2004). This is also the situation in many cases of DGA where gases are in very low concentrations, such as acetylene, and the liquid matrix consists of many components. Some volatile species are not detected and measured, and in this case, it is impossible even to evaluate their effect on Henry's law deviation.

Friedrich Wilhelm Ostwald (1853 –1932) was a Baltic German chemist and philosopher (Wikipedia). He received the Nobel Prize in the field of chemistry in 1909 "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction."

Ostwald coefficient is the most common parameter describing the gas solubility and gas content in liquids. Another coefficient for this purpose is the Bunsen coefficient, and it takes into consideration the gas volume dissolved in the liquid volume at 0 °C and 760 mmHg. The Ostwald coefficient is expressed by equation (2) for the concentration in liquid and gas space (Battino et al., 1984).

$$Lc0 = (CgL/CgV)\ \text{equilibrium} \qquad (2),$$

where:

- CgL is the concentration of the gas in the liquid phase in units of molarity (moles per litre of solution),
- CgV is the concentration of the gas in the vapour phase in units of molarity,
- The concentrations are determined at a specified temperature and the total pressure of the measurement.

Solubility is a quite complex and even philosophic concept, as the later occupation of Professor Ostwald. Are the solutes a part of the solution? In our case, for DGA, the most relevant question is–have the gases evolved from oil originated before or during the extraction process? This

Figure 2. Buchholz relay, the first DGA sensing unit

Figure 3. A failed transformer, not deenergized by any trip before the critical event

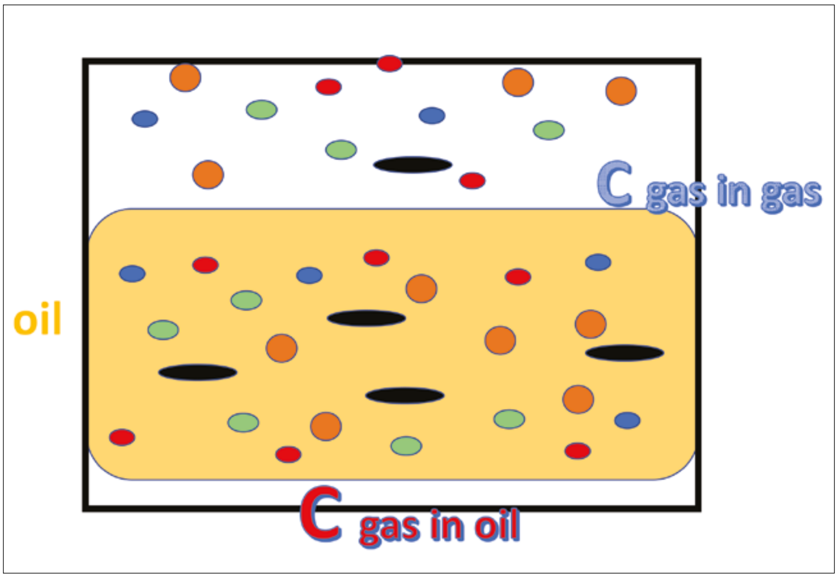

Figure 4. A schematic representation of liquid, space above the liquid and the dissolved gases

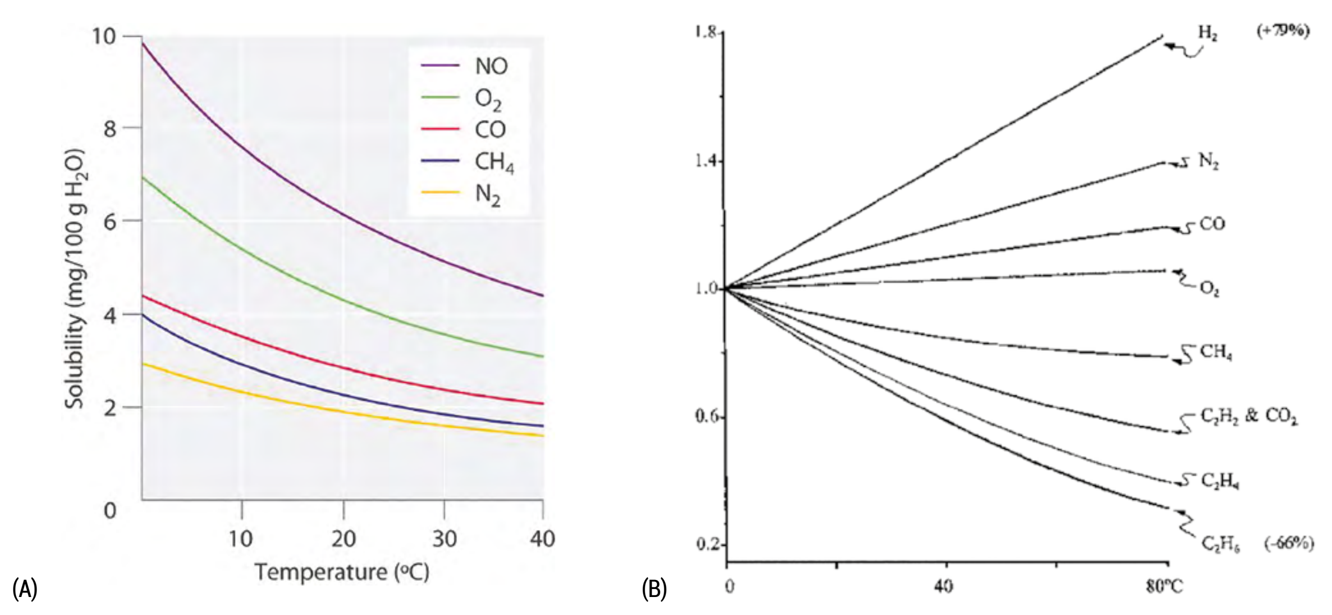

Figure 5. Ostwald coefficients of gases in water (A) (https://chem.libretexts.org/Bookshelves/General_Chemistry) and in oil (B) (Morgan 1973, Di Giorgio 2005)

The actual oil inside the transformer is aged oil that may be different from the oil in a sample, which means that the accumulative accuracy error for the final measurement of the amount of the dissolved gas concentration may be significant

Table 2. Effect of oil temperature on oil solubility Ostwald coefficient (redacted from ASTM D3612 & Baker, 1979)

Coefficient, Ostwald solubility, 760 mmHg			
	25 °C	60 °C	Difference %
Hydrogen	0.0558	0.077	-28
Nitrogen	0.0968	0.119	-19
Carbon monoxide	0.133	0.152	-13
Oxygen	0.179	0.198	-10
Methane	0.438	0.426	3
Carbon dioxide	1.17	0.982	19
Acetylene	1.22	1.06	15
Ethylene	1.76	1.42	24
Ethane	2.59	1.97	31
Propane	11.0		
Reference: ASTM D3612, Baker 1979			

may be an aspect of the stray gas phenomena. Has the extraction of gases from a certain oil extract accumulated dissolved gases in the oil or generated the gases during the extraction process?

Fig. 5 shows the Ostwald coefficient dependency on temperature for two different liquids: (a) water and (b) insulating mineral oil. Oxygen and nitrogen solubility increases with the temperature increase in mineral oil and decreases in water.

In addition to chemical characteristic of the liquid-gas interaction, the physical oil condition also has an important impact of the values of Ostwald coefficients.

Tables 2 and 3 show the Ostwald coefficients for insulating mineral oil with a naphthenic character oil and with 12 % of aromatic carbon content (test method ASTM D2140) and a negative gassing tendency (Voltesso 35). Those oil categories have been almost impossible to obtain in the market for at least two decades, only for special cases. Along with the column of coefficients at 25 °C, as published by ASTM D3612, it shows the Ostwald coefficients at 60°C for the same oil. Table 3 shows the coefficient values calculated at

The DGA users should validate their partition coefficients for the DGA measuring device and use only correctly updated Ostwald coefficient, specific to their oil and gases current characteristics

different oil densities. The actual oil inside the transformer is aged oil that may be different from those density and temperature values. It means that the accumulative accuracy error for the final amount of the dissolved gas concentration may be significant.

Three more recent studies have also indicated significant discrepancies among available sources for those solubilities' coefficients and their own measurements. They are shown in Table 4 and Fig. 6

Those recent studies emphasise the necessity of applying only the actual updated Ostwald coefficient for any gas partition estimation; in the transformer headspace and for calculated gas in oil concentration, based on gas-in-gas measurements. The DGA users should validate their partition coefficients for the DGA measuring device and use only correctly updated Ostwald coefficient, specific to their oil and gases characteristics. As shown in tables 2 to 4, those very large variations in the coefficient may be attributed to different compositions of new oils versus the old Voltesso 35 oil with 12 % of aromatic carbon content. New oils have a very different composition, and this highly influences the oil-gas partition space composition. The intermolecular effects on gas-in-oil solubility have

Table 3. Effect on oil density on oil solubility Ostwald coefficient (redacted from Baker, 1979)

Coefficient, Ostwald solubility, 760 mmHg			
Oil density			
	0.86	**0.89**	**Difference %**
Hydrogen	0.052	0.04	30
Nitrogen	0.090	0.07	29
Carbon monoxide	0.123	0.093	32
Oxygen	0.165	0.13	27
Methane	0.410	0.31	32
Carbon dioxide	1.08	0.82	32
Acetylene	1.13	0.86	31
Ethylene	1.63	1.23	33
Ethane	2.40	1.81	33
Propane	11.0		
Reference: ASTM D3612, Baker 1979			

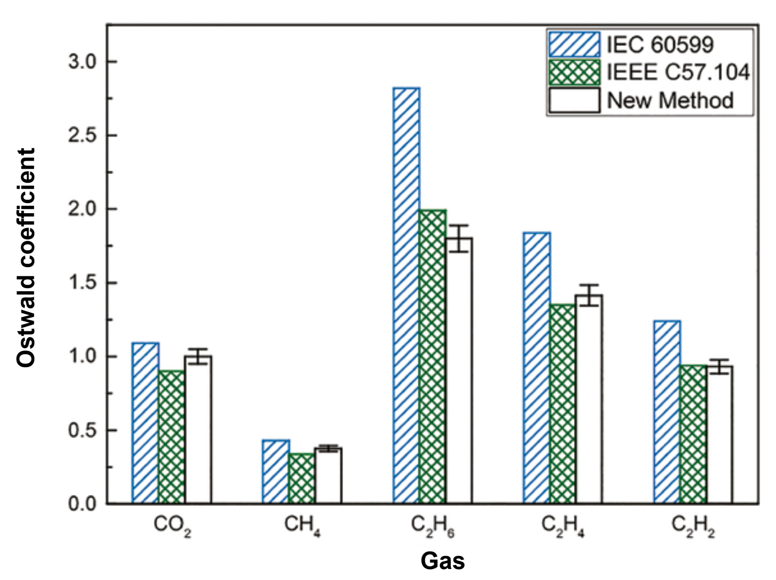

Figure 6. Comparison between results of Ostwald coefficients (Werle et al., 2017)

Table 4. Differences of Ostwald coefficients among two recent studies and standards values

Source	Gusti, 2020	IEC 60567	IEEEC57.104	Gomez, 2014
Oil density	0.86	0.88	0.88	0.88
Methane	0.771	0.429	0.337	0.375
Ethane	3.088	2.82	1.99	1.8

been extensively studied by Jalbert et al., 2003, for naphthenic, paraffinic, and vegetable-based oils. They confirm the theoretical correlation of the solubility of individual gases that decreases with the matrix density. Other factors such as polarity characteristic, molecular size and ageing state have been found to affect the magnitude of the Ostwald coefficients for all the gases.

The article is to be continued in the next issue of Transformers Magazine.

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Marius Grisaru has an MSc in Electro-Analytical Chemistry from the Israel Institute of Technology. He has almost 30 years of intense experience in almost all transformer oil test chains, from planning, sampling and diagnosis to recommendations and treatments, mainly in Israel but also in other parts of the world. He is responsible for establishing test strategies and procedures and creating acceptance criteria for insulating liquids and materials based on current standardization and field experience. In addition, he trains and educates electrical staff on insulating matrix issues from a chemical point of view. He is an active member of relevant Working Groups of IEC, CIGRE, and a former member of ASTM. He is also the author and co-author of many papers, CIGRE brochures, and presentations at prestigious international conferences on insulation oil tests, focusing on DGA, analytical chemistry of insulating oil, and advantageous maintenance policy for oil and new transformers.