A CENTURY OF DISSOLVED GAS ANALYSIS - PART II

William Stanley once wrote: “I have a very personal affection for a transformer.”
Permanent pressure put on the development of transformer materials is to decrease the transformer size and increase the operating temperature.

Introduction

With time, the size of the transformer increased exponentially both in power and voltage, Figure 1. Although huge improvements have been made regarding the magnetic core and the decrease of core losses, a transformer is now producing much more heat due to the design optimisation and size reduction.

Heat reduces the insulating properties of the insulating matrix, reducing the conducting properties and accelerating all chemical reactions including ageing and corrosion.

The stresses from the insulation materials increase gradually. In the last century, the ratio of oil volume to the transformer power decreased substantially, Figure 2, and concomitantly with this trend, the transformer power and voltage increased. This means less cooling and less insulation for each MVA and kV. The transformer's efficiency increased as well, mainly due to the development of new core material alloys. Also, the thickness of the core plates gives assistance in reducing no-load losses.
The percentage, declared or not, and diversity of the oil types will increase due to additives, and each transformer size and type will probably have a specific oil type used.

**Insulation oil history**

The history of insulating oil development is depicted in Figure 3.

1892 - Mineral refined oils [1].

1906 - First insulating oil tests [2], development of breakdown voltages.

1900 - 1920: Refined oil consists of mixed hydrocarbon molecules, with oxygen, sulfur, and other components found in crude oil. Main insulating oils are naturally inhibited by aromatic anti-oxidant molecules and different sulfur compounds.

1923 – Intensive oil tests of breakdown voltage, gas in oil and other parameters [3,4]. Soybean oil used as insulating oil since 1920 [4].

1990 - Modern stabilized biodegradable ester oil [5].

2005 – Sulfur arises as potential issue. Although there are still some experts that do not consider this an issue, sulfur issues disrupted not only transformer oil production and insulation capabilities of the new high voltage and high loaded transformer but also the whole transformer industry. The rapid development of the new IEC62535 standard for detecting corrosive sulfur species began. New specifications in IEC60296 imposed high demands for stability and performance. Most of the not inhibited oils disappeared from the market. More refined oils allowed improving electrical properties on account of the oxidation stability. In fact, insulation oil manufacture process has changed. From this period on, insulating oils became more chemically processed due to synthetic procedures than refined oils. The internal molecular structure became more uniform, the dependence on origin of crude oil almost disappeared, and with it, the naphthenic and paraffin definitions disappeared.

2010 - The industry is moving to more synthetic oils such petroleum, isoparaffinic, GTL, synthetic insulating oils made from "one molecule type". The question of recycling used or old oil became more and more current, and the new IEC and ASTM standards will probably allow using the oils as well.

2010 - Abundance of stray gas phenomena, as a byproduct of new oil types and origin. Some speculations attribute these phenomena to the hindered additives, used to meet the very stringent performance.

Future options:

- The percentage of additives, declared or not, will increase and diversify the oil types, as is the case with motor oils. Each transformer size and type will...
DGA community is alarmed by the very unusual concentrations of dissolved gases that doubtlessly causes many transformers to be taken out of service in vain.

2010 - appearance and development of many versions for thermally upgraded paper, adapted to 110°C that allow increased loading without affecting the ageing rate of the transformer and insulation system.

Future perspectives:
- New solid insulation will be thermally upgraded for the majority of transformer types.
- Malleable solid insulation will permit a wide usage of improved temperature upgrade. The goal will be to increase the operating temperature and also decrease the transformer size.

probably have a specific oil type used. The side effects, including influence on the DGA, will be observed in retrospect.

- The insulation oil will no longer be a direct derivate of crude petroleum. Synthetic or semi-synthetic oil will be manufactured by existent or new companies and will replace the old refined mineral insulating oil. The absence of any sulfur compound or other natural antioxidants will increase the usage of more synthetic additives to stop oxidation. The life of the transformer will depend on the life of all the additives, and the importance of tests for additives will increase dramatically.

- New mixtures of biodegradable oil will be available from the new suppliers. The industry will prefer mixability properties for new liquids.

- Re-refined oil and recycled oil will compete with the new insulating oils, but they will probably be only used in low voltage equipment or in used units. The biodegradable liquids will be preferred due to the environmental reasons.

The life of the transformer will depend on the life of all the additives and the importance of additives testing will increase dramatically.

Cellulose:
1900 and before - Insulation paper [6], impregnated paper or cotton with insulations oils.

1920 - Cellulose test and development [7].

1960 - Thermally upgraded paper, standards for 65°C temperature rise inside transformers.

1980 - Synthetic solid materials, such as aramid, for special cases.

1990 - New special design windmill transformer has special needs including high peaks and very high loading in a short time. They don’t operate under continuous load at all. The insulation consists of solid synthetic insulation impregnated with non-mineral liquid.

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- New solid insulation will be thermally upgraded for the majority of transformer types.
- Malleable solid insulation will permit a wide usage of improved temperature upgrade. The goal will be to increase the operating temperature and also decrease the transformer size.
The new insulation conglomeration of the new liquids with special design to impregnate new solid materials. The different impregnation and drying procedure will be more sophisticated and improved.

Development of solid insulating materials through ages is depicted in Figure 5.

**Biodegradable liquids will be preferred due to the environmental reasons while synthetic or semi.synthetic oil will replace old refined mineral insulating oil**

- Specially upgraded paper, such as smart paper, with fiber optics or another kind of probes that will provide online ageing parameters monitoring or even real-time loading feedback, is a probability.

- The new insulation conglomeration of the new liquids with special design to impregnate new solid materials. The different impregnation and drying procedure will be more sophisticated and improved.

**DGA measurement and transformers history facts relevant to gassing issues**

1836 - 1885 - transformer was invented in Europe and in the US.

1900 - Gas chromatography invented by M. S. Tsvet in Russia; photoacoustic technique discovered by Alexander Graham in 1880.

1919 - First observation of combustion gas evolving from insulating oil under electrical stress [8]. The gases were found to be different from oil vapor, they were separated, identified correctly and attributed to the faulty condition as electrical discharge.

The oldest and the most dangerous method for detecting the presence of combustion gas above the oil in the
headspace compartment was igniting the gas, Figure 6.

1916 - Transformer equipped with expansion conservator elevated above the main tank.

1921 - The Buchholz relay was invented in Germany by Max Buchholz, Figure 7. Until 1940, it was very widely used in most of the transformers [9].

1930 - 1936 - Oil composition and electrical stress was related to gas pressure and solubility. Hydrogen was again correlated to electrical discharges. Nederbragt [10] and F. M. Clark [11] were the first to observe gas tendency and aromatic nature of oil.

1947 - The gases accumulated in the protective relay or above the oil were classified and the hydrogen was attributed to electrical discharge [8].

1960 - Measurements of the nature of gas in the protective relay was done by one of the available methods: Orsat Analysis [12], Infra-Red Spectrophotometry [13], Gas Chromatography or Mass Spectrometry, Table 1 [14].

1965 - Portable TCG transformer fault detector used mainly for characterizing the gas in a relay or above the oil, Figure 8, instead of the match flame [14].


1974 - Morgan Schaffer developed the first hydrogen online monitor [18].

1977 - IEC standard for DGA measurement IEC567.

1979 - ASTM developed the first standard for DGA sampling and testing D3612.

1980 - Attempts at different extraction methods, such as bubbling, membrane

Table 1. Analysis of gas sample taken from nitrogen cylinder in warehouse stock, per cent volume, measurement and identification of gases above the oil by MS [14]

<table>
<thead>
<tr>
<th>Type of Gas</th>
<th>Analysis by Mass Spectrometer</th>
<th>Combustible Gas Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Argon</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>99.1</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Total combustible gas content*</td>
<td></td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Gas detector reading 0.3%
Re-refined oil and recycled oil will compete with the new insulating oils, but they will probably be only used in low voltage equipment or in used units.

1977 - Online measurement of a single gas composite including hydrogen and carbon monoxide based on membrane separation and detected by the fuel cell. The instrument was manufactured by Syprotec Canada and it is the most simple and accurate portable instrument, Figure 9. This is probably the most rentable device for monitoring dissolved gas and transformer conditions.


1989 - 1994 - Headspace separation developed through the collaboration of GC companies. Perkin Elmer and HP.

1995 - Morgan Schaffer developed the first multi-gas portable device based on shaking separation and micro GC.

1992 - Online detector by EPRI - Micro-monitor based on direct measurement of oil in contact with an array of metal insulated semiconductor (MIS) silicon-chip sensors. In 1997 the company became Serveron and switch to multi-gas GC online detector. In 2015 Serveron added a multi-gas monitor based on PAS technique to their portfolio.

1997 - New multi-gas online detector named TNU developed by Syprotec and based on FTIR gas measurement. It will disappear in 10 years after GE acquires Syprotec. Spectrum interference and cross-influence reduce reliability.
Offline DGA in standard laboratories will gradually disappear as a routine test and transformer without online DGA will be tested by simple portable devices

2000 - today: Continuous DGA expert groups, as those convened by D. M. Duval at CIGRE, published several informative and state of the art materials on the subject. JTF D1.02/A2.11, 2006 and continuing WG D1.32, 2010 and WG D1.01, 2010. Recently, two new technical brochures were published with the most up to date data regarding all the aspects of DGA including online monitors and new diagnosis techniques for all insulating oil types. They will introduce important modification to headspace technique for the new IEC60567 and will also introduce gas in oil standards to calibrate the DGA measurements, without the need of partition coefficients, nor filling the vial with oil only in argon ambient [28]. Dedicated glove box revolving table manufactured by Sea Marconi in Italy.

2002 - First and, still, only set of gas in oil standard from Morgan Schaffer [29].

Around 2004 - Kelman from North Ireland introduced a new DGA detection method based on PAS method. The company issued portable online device for 8 gases except for hydrogen, which cannot be tracked by PAS [30]. Later on, the GE bought the company.

2000 – 2005 - Non-mercury vacuum extraction units, partial and total extraction. The first one was designed and built in Argentina.

2004 - H2Scan Pd solid state sensor became a cheap and reliable method for online hydrogen detection in many different companies [31].

2010 - Report on gas monitors for oil filled electrical equipment [32]. The second customer review of the online device.

Figure 10. Modern micro GC with shaking device

Figure 11. First attempt to directly measure gases in oil, despite the EPRI reputation, was not successful and the company that developed it in 1992, later known as SERVERON, adopted GC technology and, recently, switched to their version of PAS for DGA
Technologies and at least four new devices appeared. When users consider buying a new online device, they have to be aware of the instability of this market. On top of it all, the most successful companies were acquired by the big concerns, since GE bought Kelman and Doble bought Morgan Shaffer.

2015 - Several non-chromatographic methods for online DGA, most of them based on spectroscopy, IR or near IR or PAS.

Future scenarios for DGA technologies

Few alternatives:

- Most of the transformers will be monitored by cheap and reliable online monitors for one, two or multiple gases. Offline DGA in standard laboratories will gradually disappear as a routine test and the transformers without online DGA will be tested using simple portable devices. The online sensors will then be monitored from a central control room with a sophisticated artificial intelligence in an effort to predict failures. The offline DGA in laboratories will still be used, mainly for calibration. The routine DGA in labs will be reduced gradually due to the complexity of sampling, transport and tests. All those processes are susceptible to operator’s and technician’s errors and the air transport increases the measurement uncertainty of gas concentration dissolved in oil. Portable devices are also very useful for emergencies or after hydrogen monitoring or any protections relays.

- When it comes to lab measurements, the GC headspace extraction method will disappear due to the low accuracy of the method, and the automated mercury free extraction will become the most popular extraction technique. More companies will provide cheaper apparatus, that will be easier to handle and will have higher productivity rate.

- Gas chromatography will be replaced by a modern version of older principle such as spectroscopy or MS as presented in [33, 34].

The online sensors will be monitored from a central control room with a sophisticated artificial intelligence in an effort to predict failures

From eighteen devices listed in the last CIGRE report published in 2010 which summarized the online monitors from 2002 to 2009, one third of them is no longer in business. Out of the remaining companies, three changed their technology and at least four new devices appeared. When users consider buying a new online device, they have to be aware of the instability of this market. On top of it all, the most successful companies were acquired by the big concerns, since GE bought Kelman and Doble bought Morgan Shaffer.
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References


Figure 13. Two non-mercury vacuum extraction systems a) partial, b) a scheme of multi-stroke complete extraction; the present alternatives to previous Torricelli, Toppler and McCleod devices
Figure 14. a) and b). Portable device from Kelman, (now GE) - the operation principle

### List of commercial gas-in-oil monitors

<table>
<thead>
<tr>
<th>Company</th>
<th>Model</th>
<th>On-line</th>
<th>Portable</th>
<th>Gases detected</th>
<th>H₂O</th>
<th>Gas Extraction</th>
<th>Detector</th>
<th>North American cost, 2006 US $</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morgan Schaffer</td>
<td>Calisto</td>
<td>x</td>
<td>Portable</td>
<td>H₂</td>
<td>x</td>
<td>PTFE</td>
<td>TCD + IC</td>
<td>11,000</td>
</tr>
<tr>
<td>Morgan Schaffer</td>
<td>Myrkos</td>
<td>x</td>
<td>Portable</td>
<td>7 (not O₂, N₂)</td>
<td>x</td>
<td>Headspace</td>
<td>TCD</td>
<td>35,000</td>
</tr>
<tr>
<td>GE-Energy</td>
<td>Hydran 103B</td>
<td>x</td>
<td>Portable</td>
<td>(H₂ + CO)</td>
<td>x</td>
<td>PTFE</td>
<td>FC</td>
<td>9,000</td>
</tr>
<tr>
<td>GE-Energy</td>
<td>Hydran M2</td>
<td>x</td>
<td>Portable</td>
<td>(H₂ + CO)</td>
<td>x</td>
<td>PTFE</td>
<td>FC</td>
<td>9,000</td>
</tr>
<tr>
<td>GE-Energy</td>
<td>Hydran 2010</td>
<td>x</td>
<td>Portable</td>
<td>C₂H₂, H₂</td>
<td>x</td>
<td>PTFE</td>
<td>FC</td>
<td>13,000</td>
</tr>
<tr>
<td>GE-Energy</td>
<td>TNU</td>
<td>x</td>
<td>Portable</td>
<td>7 (N₂ calculated)</td>
<td>x</td>
<td>Membrane</td>
<td>FTIR + FC</td>
<td>88,000</td>
</tr>
<tr>
<td>Serveron</td>
<td>TM8</td>
<td>x</td>
<td>Portable</td>
<td>3 Triangle gases</td>
<td>x</td>
<td>Membrane</td>
<td>GC, TCD</td>
<td>33,000</td>
</tr>
<tr>
<td>Serveron</td>
<td>TM3</td>
<td>x</td>
<td>Portable</td>
<td>3 Triangle gases</td>
<td>x</td>
<td>Membrane</td>
<td>GC, TCD</td>
<td>18,000</td>
</tr>
<tr>
<td>Kelman</td>
<td>Transport-X</td>
<td>x</td>
<td>Portable</td>
<td>7 (not O₂, N₂)</td>
<td>x</td>
<td>Headspace + stripping</td>
<td>PAIR ±filter + IC</td>
<td>32,000</td>
</tr>
<tr>
<td>Kelman</td>
<td>Transfix</td>
<td>x</td>
<td>Portable</td>
<td>9 (N₂ calculated)</td>
<td>x</td>
<td>Headspace</td>
<td>Laser IR</td>
<td>27,000</td>
</tr>
<tr>
<td>Kelman</td>
<td>Mini Trans</td>
<td>x</td>
<td>Portable</td>
<td>(H₂+CO₂+CO)</td>
<td>x</td>
<td>Headspace</td>
<td>Laser IR</td>
<td>32,000</td>
</tr>
<tr>
<td>Big Dipper</td>
<td>4810</td>
<td>x</td>
<td>Portable</td>
<td>7</td>
<td>x</td>
<td>Headspace</td>
<td>Laser IR</td>
<td>27,000</td>
</tr>
<tr>
<td>Unisensor</td>
<td>E 200</td>
<td>x</td>
<td>Portable</td>
<td>10 (not O₂, N₂)</td>
<td>x</td>
<td>Vacuum</td>
<td>IR ± FC</td>
<td>74,000</td>
</tr>
<tr>
<td>Energy Support</td>
<td>Mobile GC</td>
<td>x</td>
<td>Portable</td>
<td>11</td>
<td>x</td>
<td>Vacuum</td>
<td>TCD + FID</td>
<td>50,000</td>
</tr>
<tr>
<td>Gatron</td>
<td>TGM</td>
<td>x</td>
<td>Portable</td>
<td>H₂, CO, CO₂, O₂</td>
<td>x</td>
<td>Headspace</td>
<td>TCD, IR, Press., Magn.</td>
<td>55,000</td>
</tr>
<tr>
<td>EMH</td>
<td>HydroCal</td>
<td>x</td>
<td>Portable</td>
<td>H₂, CO</td>
<td></td>
<td>Membrane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRI</td>
<td>Mobile GC</td>
<td>x</td>
<td>Portable</td>
<td>9</td>
<td>x</td>
<td>Membrane</td>
<td>TCD + FID</td>
<td>18,000</td>
</tr>
<tr>
<td>Buchholz Relay</td>
<td>All</td>
<td></td>
<td></td>
<td>All</td>
<td></td>
<td>Alarm gases</td>
<td>Gas volume varies</td>
<td></td>
</tr>
</tbody>
</table>

TCD = Thermal conductivity; FC = Fuel cell; IR = Infrared; GC = Gas chromatograph;
FTIR = Fourier transform infrared; PAIR = Photo-acoustic infrared; IC = solid-state sensor;
FID = Flame ionisation; Hydran M2, 2011 and 2011T1 in this report refer to different versions of the same monitor.
Serveron TM8 and True Gas also refer to different versions of the same monitor.
The "7" gases mentioned above are: H₂, CH₄, C₂H₆, C₂H₄, C₂H₂, CO and CO₂, The "9" gases are the "7" gases + O₂ and N₂. The "10" gases are the "7" gases + C₂H₂, C₂H₄ and C₂H₆. The "11" gases are the "7" gases + O₂, N₂, C₂H₂, C₂H₄, and C₂H₆. The "3" Triangle gases are CH₄, C₂H₆ and C₂H₄.

Figure 15. From 2010 until 2018 one third of the brands disappeared and two were replaced while many new ones appeared.


[18] Transformer Fault Detection, patent no. 4,411,737 dated 1978 owned by J. Morgan


[34] X. Liu, Y. Liu, L. Yue, Online monitoring of dissolved gas-in-oil with FTIR spectra

Author

Marius Grisaru has a M.SC. on Electro-Analytical Chemistry from the Israel Institute of Technology. Marius has almost 30 of intense experience on almost all transformer oil tests chain, from planning, sampling, diagnose, recommendations and treatments mainly in Israel but also in other parts of the world as well. He is responsible for establishing tests strategy and procedures, and for creating the acceptance criteria for insulating liquids and materials, based on current standardization and field experience. 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 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, focused on DGA, analytical chemistry of insulating oil and advantageous maintenance policy for oil and new transformers.