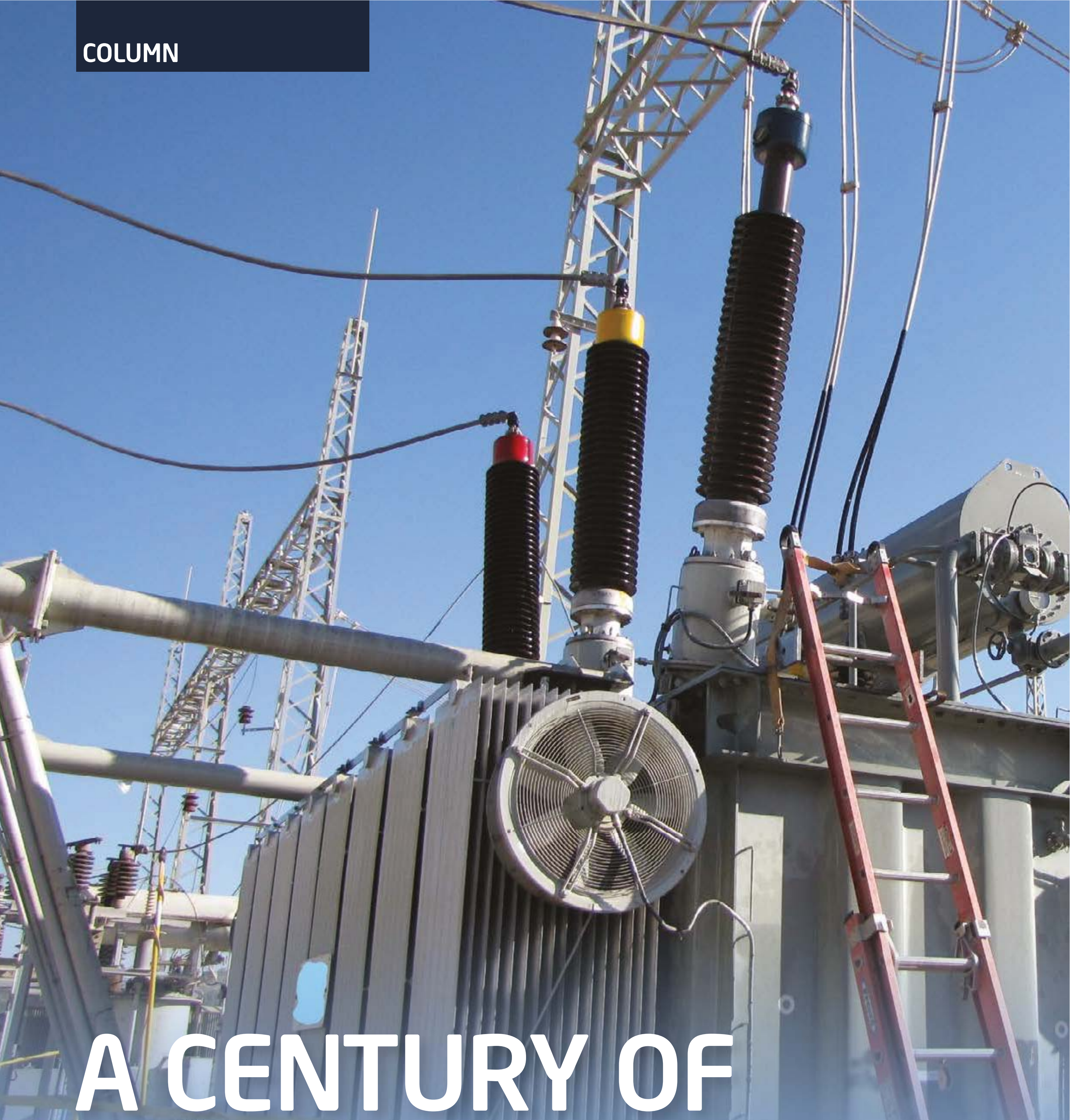


A CENTURY OF DISSOLVED GAS ANALYSIS - PART II

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

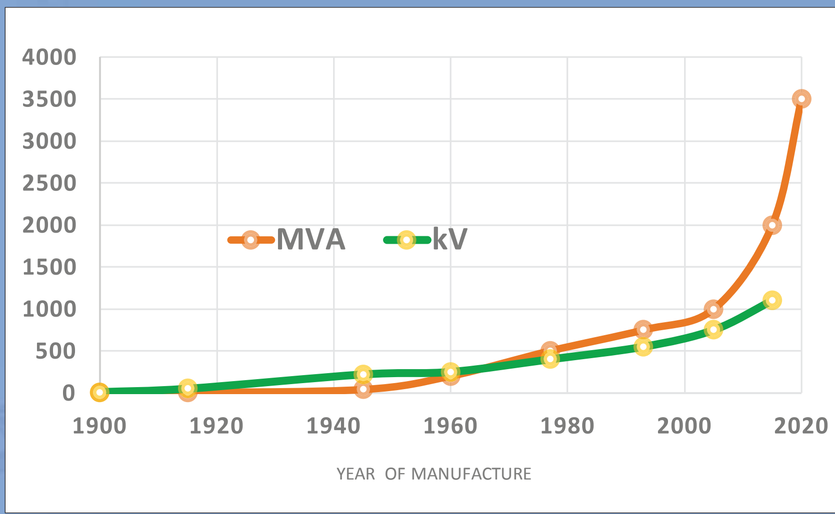


Figure 1. Trends for the transformer power in MVA and voltage in kV vs year of manufacture

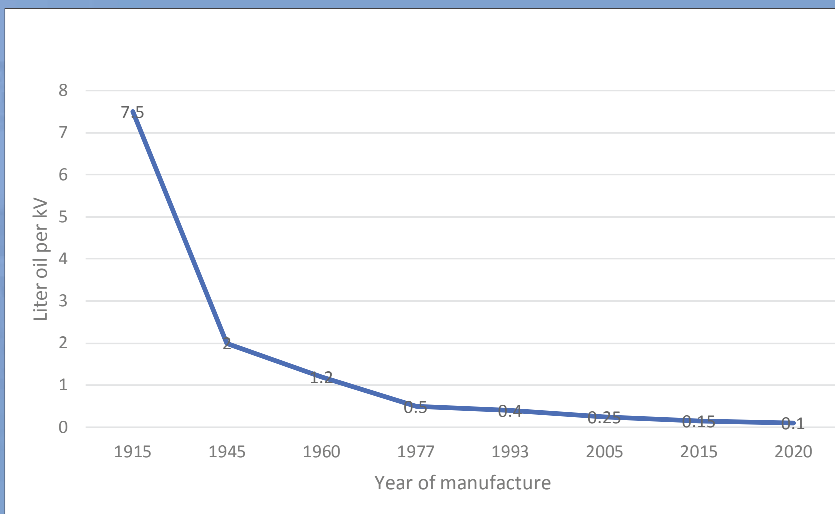


Figure 2. Trends of liter oil per kV vs year of manufacture. Based on SD Myers book, data until 2005

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 concomitant 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.

Figure 4 depicts issues regarding transformer liquids.

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

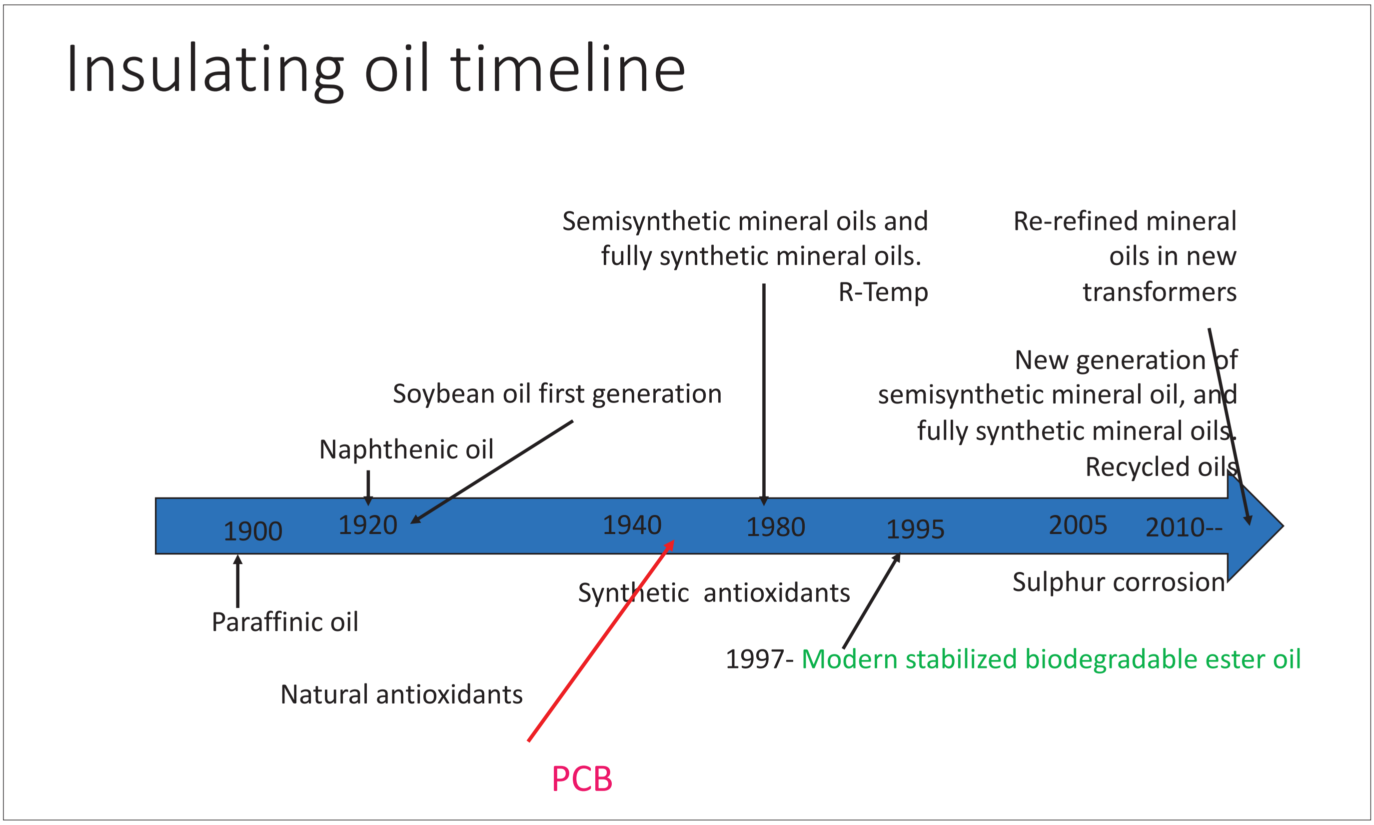


Figure 3. History of insulating oil development

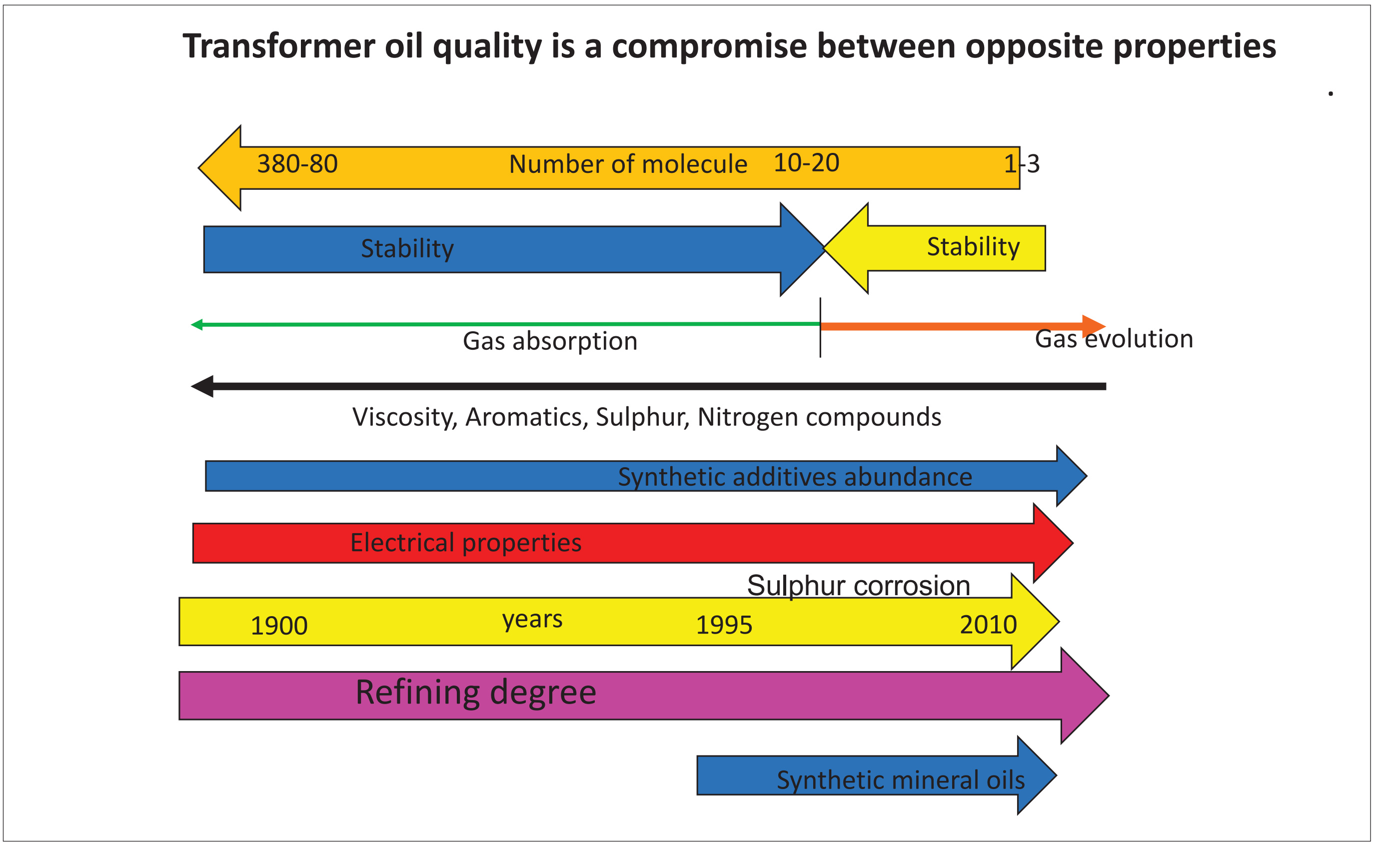


Figure 4. The problematic issues regarding transformer liquids

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. DGA community is alarmed by the very unusual concentrations of dissolved gases that doubtless 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.

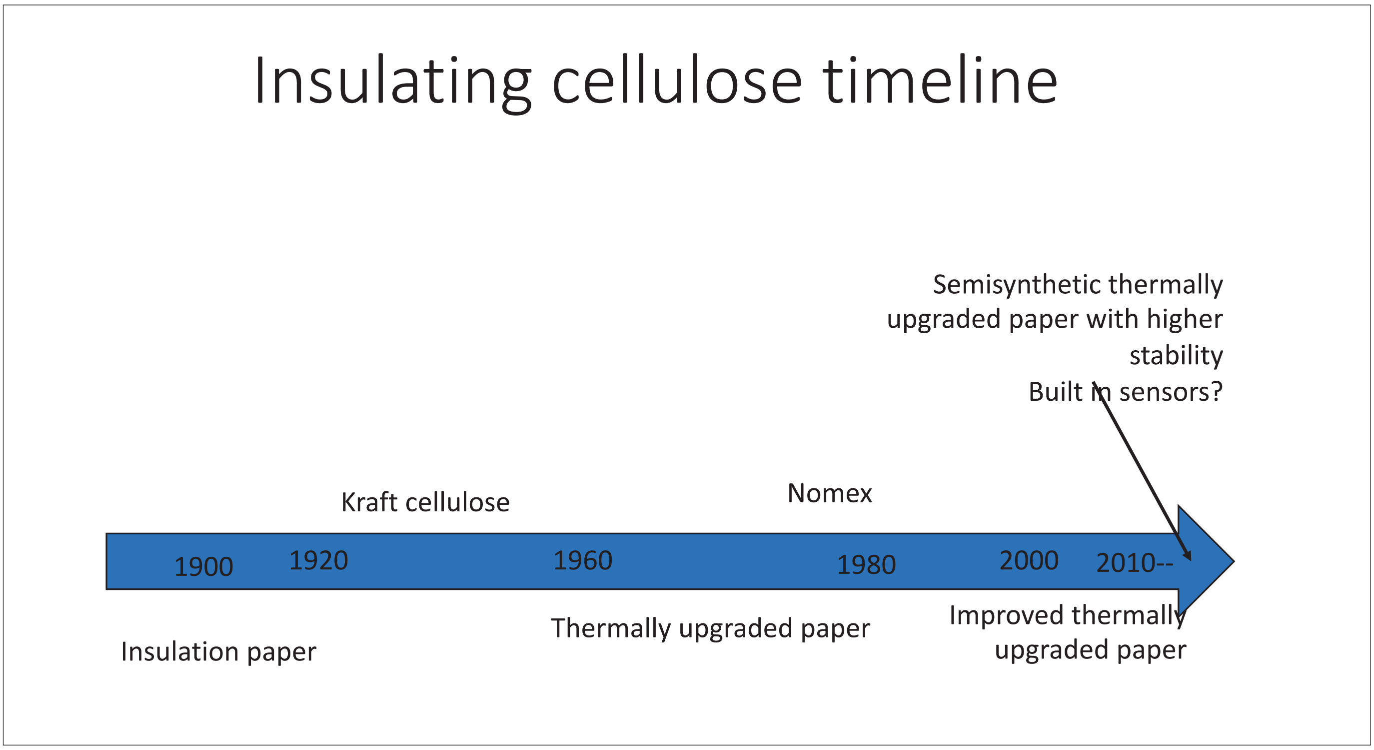


Figure 5. Solid insulating materials as developed through ages

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.

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

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

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].

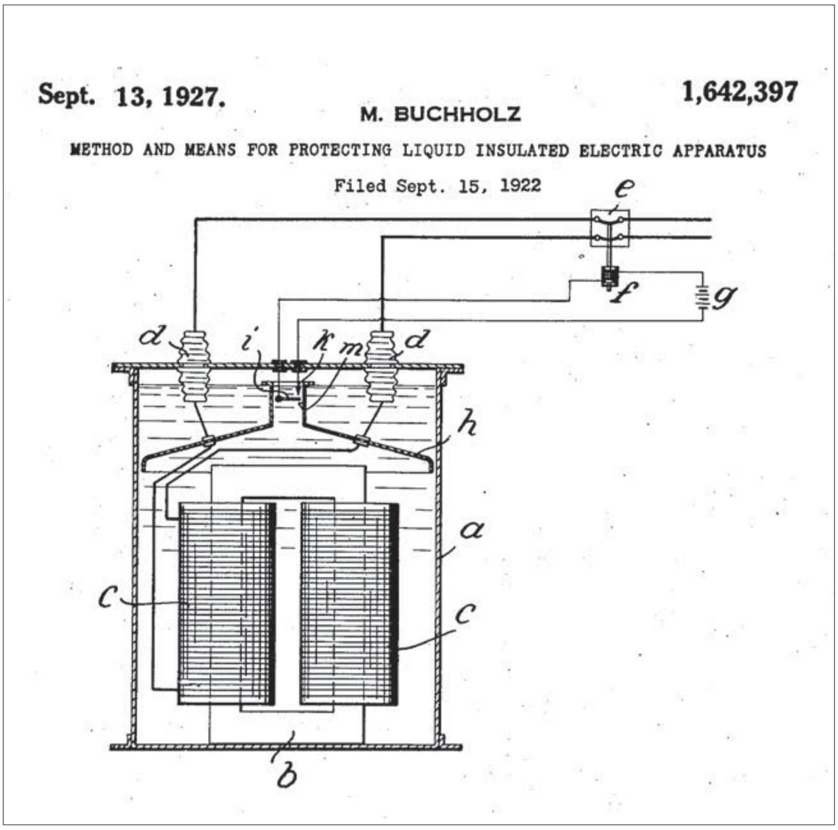


Figure 7. The first and the most reliable DGA online device [9]

1966 - 1970 - Development of vacuum extraction methods with mercury pump for ambient pressure compressor first published in the US in 1966 [15] and Europe (UK) in 1967 [16, 17].

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]

Type of Gas	Analysis by Mass Spectrometer	Combustible Gas Content
Methane	0.1	0.1
Hydrogen	0.1	0.1
Carbon monoxide	0.1	0.1
Argon	0.2	
Carbon dioxide	0.4	
Nitrogen	99.1	
Total	100	
Total combustible gas content*		0.3
*Gas detector reading 0.3 %		

a)

b)

Figure 8 a) and b). Total combustion devices for measuring combustion gases, around 60 years old

Figure 9. Portable device 103B, efficient, cheap and accurate device for DGA

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

or direct in 1990 by S. J. Ferrito [19].

1977 - Online measurement of a single gas composite including hydrogen and carbon monoxide based on membrane separation and detected by the fuel cell. [20] 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.

1980 - Automatic Field Monitoring of dissolved gas in transformer oil, Yamada et al., Japan 1980. Separation of gases from oil by automated Torricelli pump with mercury. Detection of gases by GC with standard detectors [21].

1989 - 1994 - Headspace separation developed through the collaboration of GC companies. Perkin Elmer and HP [22, 23, 24, 25].

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

1992 - Online detector by EPRI - Micromonitor 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 [26].

1997 - New multi-gas online detector named TNU [27] 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.

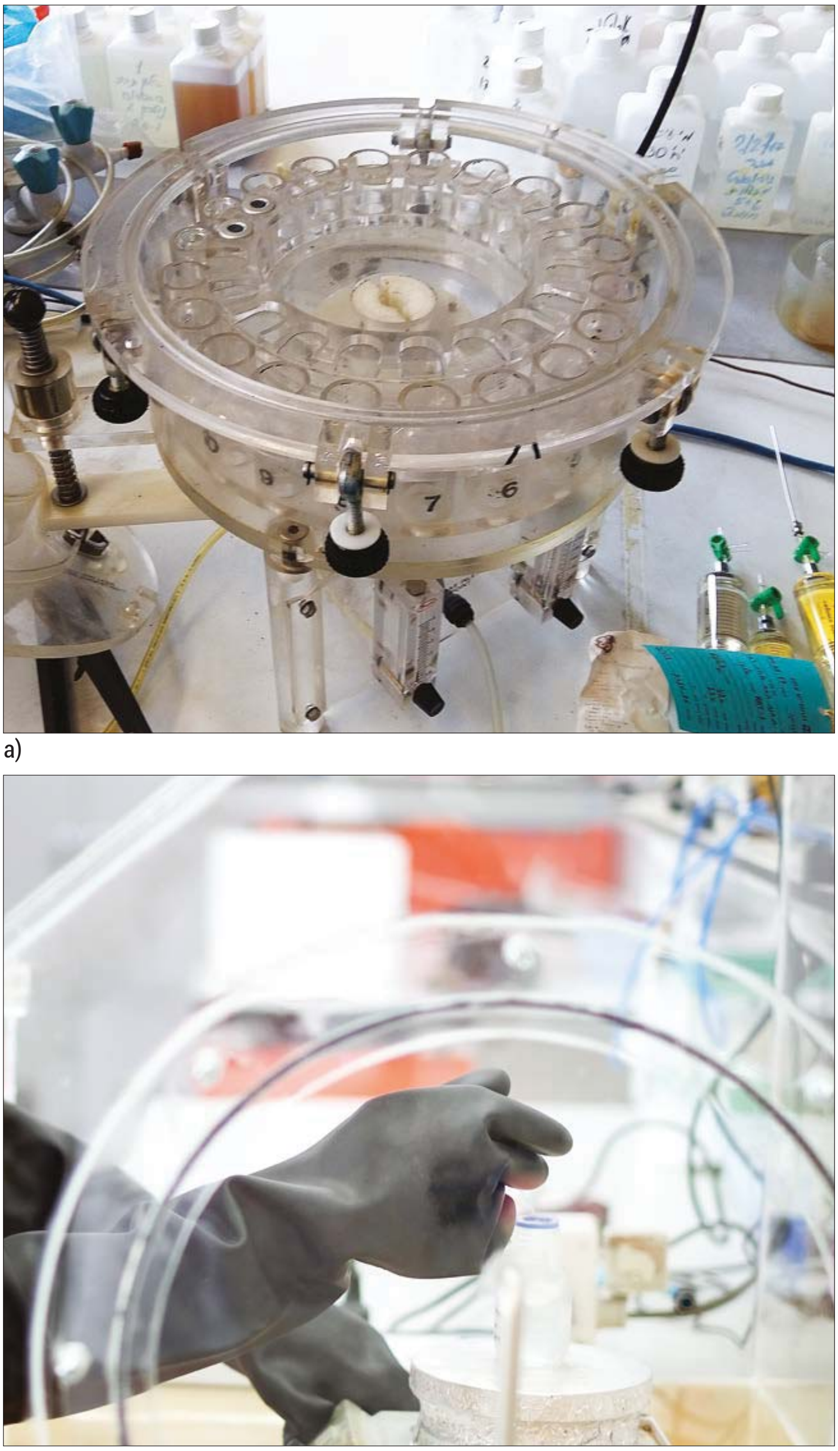
2000 – 2005 - Non-mercury vacuum extraction units, partial and total extraction. The first one was designed and built in Argentina.

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



a)

b)

Figure 12. a) and b) Glove boxes used to fill the vials with oil for headspace analysis without punching the septa according to IEC60567

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 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 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

References

[1] J. B. Williams, *Oil versus air as an insulating medium*, Transactions of the American Institute of Electrical Engineers, Volume 9, Issue 1, January 1892

[2] H. W. Tobey, *Dielectric Strength of Oil*, Transactions of the American Institute of Electrical Engineers, Volume 29, Issue 2, 1910

[3] H. A. Ambrose, *Chemical progress on insulating oils*, Digest of Literature on Dielectrics, 1939

[4] A. R. Everest, *Insulating oils: A review of research work in Great Britain*, Journal of the Institution of Electrical Engineers, Volume 65, Issue 367, 1927

[5] V. Oommen, C.C. Claiborne, *Biodegradable insulating fluid from high oleic vegetable oils*, International Council on Large Electric Systems (CIGRE) Paris Session, 1998

[6] G. T. Kohman, *Insulating paper*, Digest of Literature on Dielectrics, Volume 3, 1938

[7] H. W. Fisher; R. W. Atkinson, *The effect of heat on paper insulation, Journal of the American Institute of Electrical Engineers*, Volume 40, Issue 3, 1921

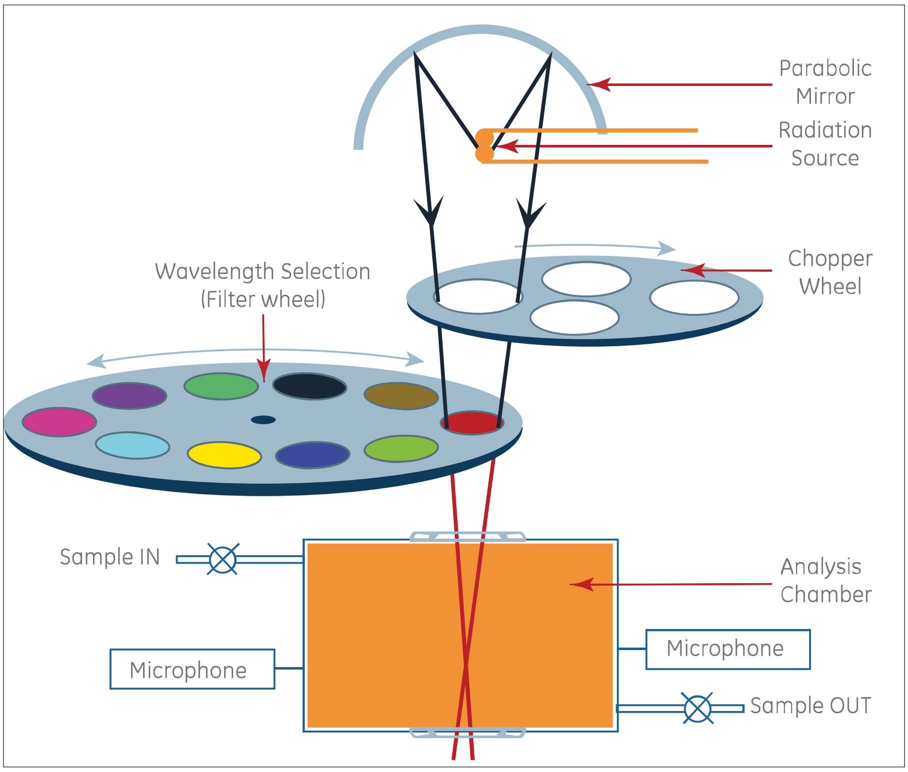
[8] O. H. Eschholz, *Some Characteristics of Transformer Oil*, The Electric Journal, page 75, February 1919

[9] *Method and means for protecting liquid-insulated electric apparatus*, German patent dated 1921 owned by M. Buchholz

a)

b)

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



a) b)

Figure 14. a) and b). Portable device from Kelman, (now GE) - the operation principle

List of commercial gas-in-oil monitors

Company	Model	On-line	Portable	Gases detected	H_2O	Gas Extraction	Detector	North American cost, 2006 US $
Morgan Schaffer	Calisto	x		H_2	x	PTFE	TCD + IC	11,000
Morgan Schaffer	Myrkos		x	7 (not O_2, N_2)		Headspace	TCD	35,000
GE-Energy	Hydran 103B		x	(H_2 + CO)	x	PTFE	FC	9,000
GE-Energy	Hydran M2	x		(H_2 + CO)	x	PTFE	FC	9,000
GE-Energy	Hydran 2010	x		C_2H_2, H_2	x	PTFE	FC	13,000
GE-Energy	TNU	x		7 (not O_2, N_2)	x	Membrane	FTIR + FC	88,000
Serveron	TM8	x		9 (N_2 calculated)	x	Membrane	GC, TCD	33,000
Serveron	TM3	x		3 Triangle gases	x	Membrane	GC, TCD	18,000
Kelman	Transport-X		x	7 (not O_2,N_2)				32,000
Kelman	Transfix	x		9 (N_2 calculated)	x	Headspace +stripping	PA/IR +filter + IC	
Kelman	Mini Trans	x		(H_2+C_2H_2+CO)				
Big Dipper	4810	x		7	x	Headspace	Laser IR	
Unisensor	E 200	x		10 (not O_2, N_2)	x	Vacuum	IR + FC	74,000
Energy Support	Mobile GC	x	x	11		Vacuum	TCD + FID	50,000
Gatron	TGM	x	x	H_2, CO, CO_2, O_2 (N_2 calculated)	x	Headspace	TCD, IR, Press.,Magn.	55,000
EMH	HydroCal	x		H_2, CO		Membrane		
SRI	Mobile GC		x	9		Membrane	TCD + FID	18,000
Buchholz Relay				All		Alarm gases	Gas volume	varies

TCD = Thermal conductivity ; FC = Fuel cell ; IR = Infrared ; GC = Gas chromatograph;
FTIR = Fourier transform infrared ; PA/IR = Photo-acoustic infrared; IC = solid-state sensor;
FID = Flame ionisation; Hydran M2 , 201i and 201T1 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: H_2, CH_4, C_2H_4, C_2H_2, C_2H_6, CO and CO_2. The "9" gases are the "7" gases + O_2 and N_2. The "10" gases are the "7" gases + C_3H_6, C_3H_8 and C_4H_{10}. The "11" gases are the "7" gases + O_2, N_2, C_3H_6 and C_3H_8. The "3" Triangle gases are CH_4, C_2H_4 and C_2H_2.

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

[10] G. W. Nederbragt, *Generation and absorption of gas in insulating oils under the influence of an electric discharge*, IEE, Volume 79, Issue 477, pp. 282 – 290, September 1936

[11] M. Clark, *The Role of Dissolved Gases in Determining the Behavior of Mineral Insulating Oils*, Journal of Franklin Institute, Volume 215, pp. 39, January 1933

[12] D. J. Thomas, *Combustible Gas in Power Transformers*, Doble Engineering Company 1966

[13] Toat et al., *Gas Evolution from Transformer Oils Under High-Voltage Stress IEEE Transactions*, March 1967

[14] P. S. Pugh, H. H. Wagner, *Detection of Incipient Faults in Transformers by Gas Analysis*, AIEE Transactions, Volume 80, pp. 189-195, 1961

[15] L. B. Baranowski, *New method for dissolved gas content of insulating liquids*, Doble Conference 1966

[16] E. Dornenburg, O. E. Geber, *Analysis of dissolved and free gases for monitoring performance of oil filled transformers*, The Brown Boveri Review, No 54, 1967

[17] F. B. Waddington and D.J. Allan, *Transformer Fault Detection by Dissolved Gas Analysis*, Electrical Review, May 1969

[18] Transformer Fault Detection, patent no. 4 4,112,737 dated 1978 owned by J. Morgan

[19] S. J. Ferrito, *A comparative study of dissolved gas analysis techniques: the vacuum extraction method versus the direct injection method*, IEEE Trans. Power Deliv., Volume 5, Issue 1, pp. 20–25, 1990

[20] M. Duval, *Dissolved Gas Analysis: It Can Save Your Transformer*, IEEE Electrical Insulation Magazine, Volume 6, Issue 6, pp. 22-27, 1989

[21] H. Yamada, Y. Nomura, Y. Katayma, T. Ishii, O. Imamura, and K. Isuchiyama, *Automatic field monitoring of dissolved gas in transformer oil*, IEEE Transformer Power Apparatus and Systems, Volume PAS-100, Issue 4, pp. 1538–1544, April 1981

[22] J. V. Hinshaw and W. Seferovic, *Analysis of dissolved gases in transformer oils by simultaneous dual-channel headspace gas chromatography*, in Proc. 1989 Analytical Chemistry Conference, Paper 279, Pittsburgh, 1989

[23] T. J. McGarvey, *An automated system for analysis of gases dissolved in electrical insulating oil by headspace gas chromatography*, Minutes of the 1990 Doble Engineering Conferences, 57AIC90, pp. 10-8.1 / -8.15, 1990

[24] Y. Leblanc, R. Gilbert, M. Duval, and J. Hubert, *Static headspace gas chromatographic determination of fault gases dissolved in transformer insulating oils*, J. Chromatography, Volume 633, pp. 185-193, 1993

[25] J. Jalbert, R. Gilbert and S. Brillante, *Dissolved Gas Analysis of Transformer Insulating Oils by Headspace/Capillary Gas Chromatography*, Hewlett Packard Application Note, pp. 228-310, 1995

[26] *Power Transformer Asset Management On-Line DGA - The New Ballgame*, EPRI Substation Equipment Diagnostics Conference XI, 2003

[27] R. J. Heywood, *Condition assessment of supergrid transformer using a Hydran ® and transformer nursing unit (TNU™)*, Proceedings of the 2001 International Conference of Doble Clients, April-May 2000

[28] J. Jalbert and R. Gilbert, *Decomposition of transformer oils: A new approach for the determination of dissolved gases*, IEEE Power Engineering Society Meeting, Paper 96, SM 407-7 PWRD, 1996

[29] P. Lazarski, M. Cyr, *Improving the assessment of transformer condition by enhancing laboratory accuracy using dissolved gas in oil standards*, 75th Annual International Doble Client Conference, 2008

[30] D. Bates, *DGA in a box, a utility's perspective*, Alabama Power Company

[31] V. Lakhotia, *H2Scan*, 2010, http://pdf.directindustry.com/pdf/h2scan/gridscan-brochure/40428-168323.html

[32] Technical Brochure 409, *Report on Gas Monitors for Oil-Filled Electrical Equipment*, CIGRE WG D1.01 (TF 15), February 2010

[33] S. Karmakar, *Dissolve gas analysis of aged transformer oil: a case study*, Journal of Electrical Engineering, Romania

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

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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.