

TRANSFORMER OIL DEGRADATION STUDY BY CHROMATOGRAPHY, SPECTROSCOPY AND DISSOLVED GAS ANALYSIS

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Abstract

Transformer oil is a very important component of the transformer. The oil acts as an insulator and heat exchanger. This paper compares and evaluates the analytical observations of two transformer oils. The two transformer oils taken as samples for the study are; one a non-used transformer oil of the make year 1997 and another a fresh transformer oil of 2017 make. The transformer oil used in India is paraffin based having long chains of hydrocarbon, with general chemical formula, C_nH_{2n+2} . In the present study, gas chromatography – mass spectrometry (GC-MS) technique was employed to determine the compositional constituents of both the oils. The Fourier transformed infrared (FTIR) and ultra violet – visible (UV-Vis) spectroscopy techniques were employed to characterize both the oils. Dissolved gas analysis (DGA) technique was employed to analyze the oils conditions. The obtained results for the old and new oils have been deliberated and compared in this paper.

Keywords: Transformer oils; GC-MS; FTIR; UV-VIS spectroscopy; DGA.

1. Introduction

Transformer oils are highly refined mineral oil possessing excellent insulating properties. It also works as a coolant and as a heat exchanger when in operation in a transformer. The transformer oil is of two types, the naphthenic based and the paraffinic based oil. In India the transformer oil generally used is paraffin based and is labeled as IS-335:1993. The transformer oil contains long chains of hydrocarbons possessing general chemical formula as C_nH_{2n+2} , where n varies from 11 to 44.

The working of transformer leads to degradation of the transformer oil. Due to degradation, it loses its insulating property. This degradation is due to hydrogenation and oxidization [1-2]. It has been observed that high voltage and temperature of operation hastens the deterioration of the transformer oil. This deterioration results into the change in the chemical composition of the oil which ultimately results into the generation of new degradation by-products such as carbon monoxide (CO), aldehydes, ketones, etc. [3]. As a result of the change in the chemical composition of the oil, the different gases are evolved and are responsible for the worsening of the insulating property of the oil [4-7]. There are also changes in the physical properties like the color of the oil, density, viscosity and flash point due to its aging process. Because of the changes in the chemical and physical composition of the insulating oil, there is furthermore a change in the electrical property of the insulating oil. These changes affect one of the important parameters, its break down voltage (BDV). Hence one can say owing to working of transformer there is an overall change in the physical, chemical and electrical properties of the insulating transformer oil. As the transformer oil properties change with the operation, there is always a possibility of the oil to alter its properties with the passage of time [8-9]. Sensing to the possibility of transformer oil properties modification with the passage of time the authors studied the properties of two transformer oils of different ages.

The authors were fortunate to have an unused transformer oil of the year 1997 make, which was used as one sample. The 20 years old transformer oil was compared with new transformer oil of 2017 make. Thus, the new transformer oil was the second sample.

There are various techniques to analyse insulating oil, but the methods are costly, laborious and time-consuming. Therefore, the authors employed simple spectral analytical techniques like gas chromatography – mass spectrometry (GC-MS), Fourier transformed infra-red (FTIR) spectroscopy and UV-Vis spectroscopy to characterize the two transformer oil samples.

This paper highlights the chromatographic, spectral and dissolved gas analysis data of the two transformer oils. The effort has been made to compare and analyse both the data.

2. Experimental

An old transformer oil of the year 1997 make was labeled as T1 and was used without any purification or treatment for analysis and study. Similarly, the fresh, pure transformer oil of 2017 make was labeled as T2 and was procured from the local market; APAR Industries, Vadodara, Gujarat, India. Both are branded in India market as IS-335:1993. The photographs of both the samples are shown in Figure 1.

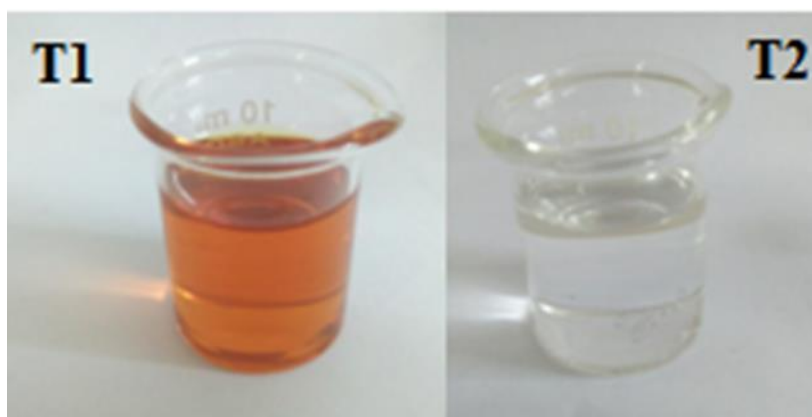


Figure 1. Photography of transformer oils T1 and T2

The photography of the oils, Figure 1, shows that the old oil T1 appears to be darker than the new oil T2. The visual observation seems to indicate that the old oil T1 has colloidal suspension due to degradation. The new transformer oil T2 appeared colorless and transparent.

The chemical composition determination of T1 and T2 oil samples were done by Gas-Chromatography attached with Mass Spectrometry (GC-MS) technique. In this GC-MS analysis, Perkin Elmer Auto system XL GC with Turbo mass was employed. Reason for selection of this technique was the ease and simplicity of analysis. The GC-MS analysis gives instantaneousness, efficient identification, and quantification of oil components and compositions [10-11].

The different chemical bonds present in the T1 and T2 samples were studied by Fourier transformed infra-red (FTIR) technique. The Shimadzu FTIR – 8400S was employed for the analysis of both the transformer oil T1 and T2 samples.

The ultraviolet – visible (UV-Vis) spectroscopy was carried out on T1 and T2 oils using Sytronics Double beam UV-Vis Spectrometer 2202. The UV-Vis Spectroscopy measurement was done in the wavelength range of 200nm to 600nm. In general practice, the UV-Vis spectroscopy is employed as an on-line diagnostic tool to detect early abnormalities in transformers [12-18].

The dissolved gas analysis (DGA) is one of the basic and best techniques to determine the degradation of the oil. The transformer oil composition undergoes lots of chemical changes under the influence of operating temperature and high voltage. Gases evolve due to excessive thermal or electrical stress. The generated dissolved gases are in low concentrations (ppm), and its proper analysis can allow the early intervention before the degradation of the oil sets in and lead to failure of the electrical apparatus. The level of these generated gases will decide the incipient fault [19]. The DGA for both the samples T1 and T2 was performed employing

Perkin Elmer, ARNEL CLARUS 580. The break down voltage (BDV) and moisture content of the oil samples were also determined.

3. Results and discussion

The obtained GC-MS spectra of both the transformer oil samples, T1 and T2, are shown in Figure 2(a, b). The analysis of the GC-MS spectra shows that the sample consists of hydrocarbon with different units of carbon. The thorough analysis of the spectra showed that both the transformer oil samples are liquid paraffin based having chemical formula as C_nH_{2n+2} . The analysis showed that the value of n ranges from 11 to 45 for the analyzed sample T1 (old), whereas in the case of sample T2 (new) it ranges from 14 to 44. The mass spectroscopy of gas chromatography of the sample T1 showed a prominent peak having a retention time of 10.23 minutes. This peak is due to the presence of sulfurous acid, 2-ethylhexyl nonyl ester having molecular formula $C_{17}H_{36}O_3S$. The analysis by GC-MS corroborates the presence of sulphurous acid in T1. This proves that the sulphur content of T1 oil sample has converted to acid. While in the case of T2 no sulfurous compound was observed in the GC-MS analysis.

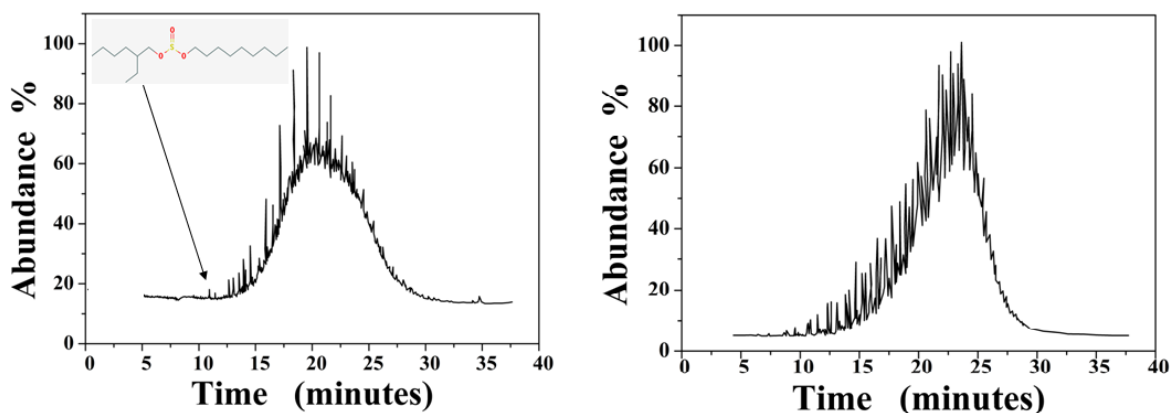


Figure 2. The GC-MS spectra of (a) transformer oil T1 and (b) transformer oil T2

The FTIR spectra recorded for transformer oil samples T1 and T2 are shown in Figure 3(a, b). The FTIR spectra give the qualitative measurement, and the peak sizes directly indicate the specific chemical bonds present in the sample.

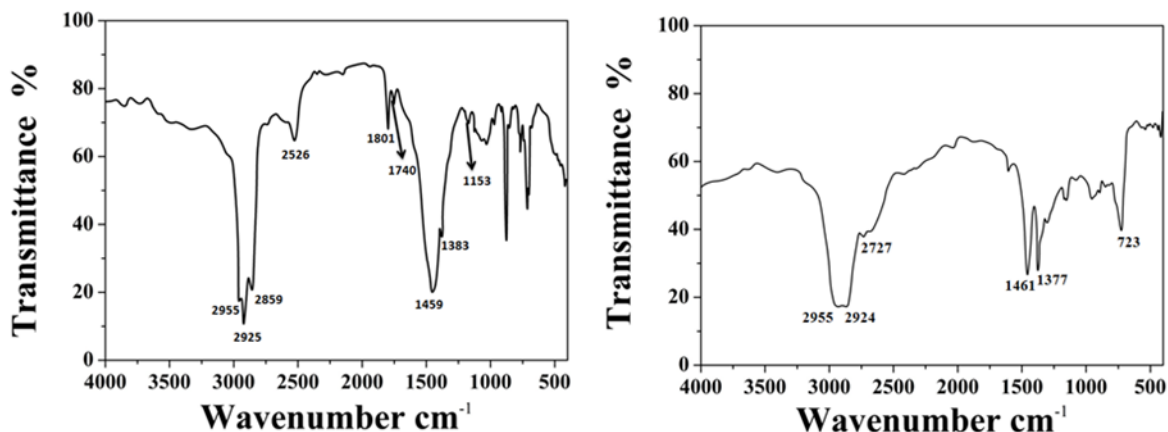


Figure 3. FTIR spectra for (a) transformer oil T1 and (b) transformer oil T2

The observed peaks in recorded FTIR of T1 and T2 samples were assigned bonds [20]. The vibrational and stretching bonds assigned to the observed FTIR peaks of the samples T1 and T2 are tabulated in Table – 1(a, b) [21].

Table 1(a). The FTIR peaks and assigned bonds of transformer oil sample T1

FTIR peak position (cm ⁻¹)	Assigned Bonds
2955	=C-H stretching of the carbon-carbon double bonds
2925 and 2859	CH stretching, CH ₃ methylene group
1801	-C=O stretch
1740	Oxidation of oil (carbonyl group, ketones)
1469	C-H symmetric bend
1373	CH ₃ bend
1153	Sulphonation of the oil
900 -680	Aromatic compounds. Shows the position of the benzene ring.

Table 1(b) The FTIR peaks and assigned bonds of transformer oil sample T2

FTIR peak position (cm ⁻¹)	Assigned Bonds
2955	=C-H stretching of the carbon-carbon double bond
2924 and 2727	C-H stretching of the saturated carbon – carbon bonds
1461	C-H symmetric bending (alkanes) methyl and methylene
1377	C-H bending of the alkanes (iso-propyl split)
733	C-H out of the plane stretching of the standard carbon – carbon bond.

The analysis of Table 1(a, b) shows that many observed peaks remain common in both the samples T1 and T2. The common FTIR peaks of the samples T1 and T2 lies near to wave-number positions 2955, 2924, 2727, 1461, 1373 cm⁻¹. These peaks are present in the old sample T1 and new sample T2, stating them to be standard peaks arising due to a paraffinic compound of which the oils are composed. All these peaks have been assigned with various bonds.

The table shows three extra peaks in the old transformer oil sample T1. They lie at the wave-number positions 1801, 1740 and 1153 cm⁻¹. The peak at wave-number 1801 cm⁻¹ is due to -C=O stretch, thus stating oxygen reacting with the oil and forming a bond. The peak observed at wave-number 1740 cm⁻¹ is due to the oxidation caused by the carbonyl and carboxyl compound [22-24]. The transformer oil modification also leads to an increase in acidic and aromatic (pungent) content. This increase in acidic and aromatic content increases the C=O and C=C double bond. The thermal aging of a paraffinic compound of the transformer oil dehydrogenates and forms naphthenic compounds. These naphthenic compounds get further dehydrogenated and form conjugated C=C double bond [24-25].

The peak observed at wave-number 1153 cm⁻¹ arises due to the sulphonation of the oil. The introduction of sulphur increases the sludge formation and leads to degradation of the oil. They reacted with water to produce powerful inorganic acids such as sulfuric acid (H₂SO₄) [21]. This states that water content in the oil has increased leading to the formation of sulphuric acid. The presence of the sulphuric acid compounds was also confirmed by the GC-MS analysis. The FTIR analysis substantiates that with the passage of time, the transformer oils undergo oxidation as well as sulphonation. The oxidation leads to an acid formation that can corrode the transformer. The sulphonation increases sludge formation which leads to sedimentation and degradation of transformer operation.

Along with the FTIR spectroscopy, the UV-Vis spectroscopy is employed for the study of T1 and T2 transformer oils. The obtained spectra for T1 and T2 oils are shown in Figure 4.

The UV-Vis spectra show that T2 oil has lower absorbance compared to T1 oil. Lower absorbance in T2 oil means more transparency in T2 oil compared to T1 oil. The higher absorbance in T1 clearly shows the oil is less transparent compared to T2. This UV-Vis spectra analysis of less transparency of T1 oil compared to T2 oil substantiates the visual observation of the oil, Figure 1. The decrease in transparency in T1 is due to sludge formation as observed in FTIR spectroscopy analysis. The UV-Vis spectra clearly corroborate the FTIR observations. The higher absorbance indicates the variation in the oil which is due to the increased dissolved decay products as well as the impurities in it due to its ageing [26-27].

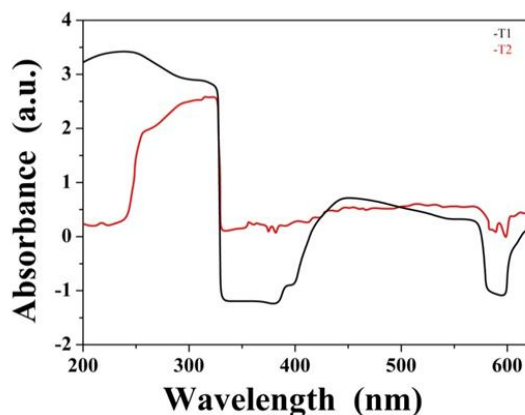


Figure 4 The UV-Vis NIR for the sample T1 and T2

The obtained results of the DGA analysis of both the transformer oil samples T1 and T2 are tabulated in Table 2.

Table 2. The DGA analysis data for T1 and T2 oil samples

Sr. No.	Name of the gas	T1 (old) oil(ppm)	T2 (new) oil(ppm)
1	Hydrogen	5	Traces (<1)
2	Methane (CH ₄)	8	Traces (<1)
3	Ethylene (C ₂ H ₄)	Traces(<1)	Nil
4	Ethane (C ₂ H ₆)	Nil	Nil
5	Acetylene (C ₂ H ₂)	Nil	Nil
6	Carbon dioxide (CO ₂)	633	53
7	Carbon monoxide (CO)	45	4
8	Oxygen (O ₂)	7 774	6 893
9	Nitrogen (N ₂)	24 091	18 350

The analysis of DGA data, Table 2, firstly confirms the non use of both the oils. This is confirmed by the absence of ethylene, ethane, and acetylene in case of both the transformer oil samples. This ethylene, ethane and acetylene hydrocarbon compounds get formed due to the high temperature of the transformer oil. Since the oils are non used samples, the temperature has never increased, and thus ethylene, ethane, and acetylene hydrocarbon compounds have not been formed.

More amount of carbon dioxide (CO₂) and carbon monoxide (CO) in old oil sample T1 compared to new oil sample T2 is due to over exposure of T1 to the atmosphere. Due to the exposure to the atmosphere, the C-C single bond breaking in the hydrocarbon chains of the sample T1 takes place, which further leads to the formation of CO₂ and CO. On the other side the sample T2 is fresh oil and is not exposed more to the atmosphere leading to less formation of CO₂ and CO. The DGA analysis furthermore revealed that oxygen (O₂) and nitrogen (N₂) content is more in T1 oil compared to T2 oil. This further confirms over exposure of T1 oil sample to the atmosphere. The exposure leads to percolation of atmospheric oxygen and nitrogen into the oil.

Other than the chemical constituents present in the oil samples, the standard basic data like break down voltage and moisture content of both the samples were evaluated and are tabulated in Table 3.

Table 3. Basic data of T1 and T2 transformer oils

Sr. No.	Parameter	Test method	T1 (old) oil	T2 (new) oil
1	Break down voltage (BDV)	IS: 6792: 1992	28 kV	60 kV
2	Water content	IS: 13567: 1992	90ppm	< 30ppm

The analysis of the data of Table 3 shows that the BDV value has decreased more than half in case of old transformer oil T1 compared to new oil T2. This corroborates the degradation of transformer oil over time. Similarly, the water content data shows nearly three times more water content in old transformer oil T1 compared to new transformer oil T2. This further confirms the degradation of transformer oil with the passage of time. The water content increase is due to long exposure of old transformer oil to the atmosphere leading to hydration of the oil.

4. Conclusion

Two paraffinic based transformer oils, one of make year 1997 that is 20 years old and another of make year 2017 that is a fresh oil were comprehensively characterized. The visual observation of the oil showed the old transformer oil to be yellowish brown colloidal compared to the new oil which was near colorless transparent. The GC-MS analysis showed the presence of the sulphurous complex in old oil, whereas in new oil no such amalgam was observed. The FTIR analysis further confirmed the presence of the sulphurous complex in the old oil. The old oil was found to be less transparent compared to the new oil analyzed by the transmission spectra analysis employing UV-Vis spectroscopy. The DGA analysis of the transformer oils showed the presence of atmospheric gases in the old oil. The DGA observations clearly stated over exposure of old oil to the atmosphere. The determined standard parameters of the studied transformer oil samples showed that water content has increased in the old oil compared to the new oil. Even the BDV has decreased to more than half in case of old transformer oil, whereas BDV of new transformer oil remained satisfactory. All these observations clearly state that the old transformer oil has degraded due to over exposure to the atmosphere. The degradation is by the formation of different unwanted complexes, leading to colloidal oil and impoverished standard parameters.

Acknowledgments

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References

- [1] Cackova V, Dedinska L, Kvakovsky M. Degradation mechanism in transformer oil. 9th Scientific Conference of Young Researchers, FEI Tu of Kosice (2010).
- [2] Wang M, V Andermaar AJ, Srivastava KD. Review of condition assessment of power transformer in service. *Electrical Insulation Magazine, IEEE* (2002) 12- 25.
- [3] Chernozhukov NI, Krein SE, Losikov BV. Oxidizability of Mineral Oils. *Gostoptekhizdat, Moscow* (1955) 121-126.
- [4] Duval M. Dissolved gas analysis: It can save your transformer. *Electrical Insulation Magazine IEEE* 5 (1989): 22-27.
- [5] Pandey R, Deshpand MT. Dissolved gas analysis (DGA) of mineral oil used in transformer. *Int. J. of Appl. or Innovation in Engg. & Management ;1*: 208-212.
- [6] Kelly J. Transformer fault diagnosis by dissolved gas analysis. *Transactions on Industry Applications IEEE, 1980; 16*: 777-782.
- [7] Hussain K, Karmakar S. Dissolve gas analysis of aged transformer oil: a case study. *J. of Elect. Engg., 2015*: 1-10.
- [8] Missas S, Danikas MG, Liapis I. Factors affecting the ageing of transformer oil in 150/20kV transformers. *Int. Conf. on Dielectric Liq. IEEE* (2011).
- [9] Liapis I, Danikas MG. A study of parameters affecting the ageing of the transformer oil in distribution transformer. *Int. Conf. on Dielectric Liq. IEEE* (2011).
- [10] Blomberg J, Schoenmakers PJ, UA Th. Brinkmanc. Gas chromatographic methods for oil Analysis, *J. of Chromatography A, 2002;972*: 137-173.

- [11] Kaplan IR, Rasco J, Lu. Shan Tan. Chemical characterization of transformer mineral insulating oils. *J. Environmental Forensics*, 2010; 11: 117-145.
- [12] Palmer JA, Wang X, Shoueshi RA, Mander A, Torgerson DRC. Effect of aging on the spectral response of transformer oil. *Electrical Insulation, Conference Record of the 2000 IEEE International Symposium on Electrical Insulation*. Anaheim, CA, USA (2002)
- [13] Siada AA, Lai Sin SP, Islam S. Remnant life estimation of power transformer oil using UV-Vis spectral response. *Power Systems Conference and Exposition, IEEE/PE Conference, Seattle, WA, USA (2009)*.
- [14] Lai SP, Siada AA, Islam SM., Lenc G. Correlation between UV-Vis spectral response and furan measurement of transformer oil. *International Conference on Condition Monitoring and Diagnosis, Beijing, 2008*.
- [15] Karthik R, Raja T, Shunmugam S. Performance evaluation of transformer oil using UV-Vis spectrophotometer. *Acta Scientiarum Technology*, 2014; 36: 245-250.
- [16] Gafiyatullina LG. UV Spectroscopy of GK Transformer Oil. *Opt. and Spect.*, 2010; 109: 97-100.
- [17] Hussain K, Karmakar S. Condition assessment of transformer oil using UV-Visible spectroscopy. *Power Systems Conference, IEEE, (2014) 1-5*.
- [18] Malika H. UV/VIS response based fuzzy logic for health assessment of transformer oil. *Procedia Engineering*, 2002; 30: 905-912.
- [19] Duval M. A review of faults detectable by gas in oil analysis in transformers. *electrical insulation magazine. IEEE*, 2002; 18: 8-17.
- [20] Drago RS. *Physical method in inorganic chemistry (Chapter 7)*. East-West Press Pvt. Ltd., New Delhi (1968).
- [21] <http://machinerylubricationindia.com/magazine/108-2015/sep-oct/302-benefits-of-ftir-oil-analysis>"
- [22] Georgiev A, Karamancheva I, Topalova L. Determination of oxidation products in transformer oils using FT-IR spectroscopy. *J. of Mol. Structure*, 2008; 872: 18-23.
- [23] Mihalcova J. Study of degradation of mineral oils product by FTIR Method. *Chem. pap.*, 2003; 57: 211-215.
- [24] Zakharich MP, Zaitsev II, Komar VP, Nikonovich FN, Ryzhkov MP, Skornyakov IV. Analysis of transformer oil using IR analyzers. *J. of Applied Spectroscopy*, 2001; 68: 61-65.
- [25] Benounis M, Aka-Ngnui T, Jaffrezic N, Dutasta JP. NIR and optical fiber sensor for gases detection produced by transformation oil degradation. *Sensors and Actuators*, 2008; 141: 76-83.
- [26] Karmakar S, Roy NK, Kumbhakar P, Effect of ageing in transformer oil using UV-visible spectrophotometric technique, *J. Optics*, 2011; 40: 33-38.
- [27] Ghalkhani M, Fofana I, Bouaicha A, Hemmatjou H. Influence of aging by-products on the gassing tendency of transformer oils. *Electrical Insulation and Dielectric Phenomena*, 2012: 870-873, DOI: 10.1109/CEIDP.2012.6378919.

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