



ABSTRACT

Although the headspace extraction method is the most widespread extraction methodology today, it has many commercial advantages for both test providers and users, and it is the most sensitive technique regarding the chemical and physical properties of the mixture. This technique was developed about 30 years ago when the oil type was mainly naphthenic. Nowadays, the number of available oil types has highly increased even in the mineral oil group. Of course, non-mineral oils are com-

posed of completely different atoms and species and their formulae impose a different treatment.

Commercial gas-in-oil standards are indeed indispensable for the performance verification but it must not be used for routine calibration of any type of gas extraction. DGA online and offline devices should be calibrated with gas in oil mixture containing all the range of concentration all measured gases, especially nitrogen and oxygen, which have become crucial gases for modern sealed transformers, especially those

using non-minerals liquids. Total gases measured by gas detection devices should not be confused with either total gas concentration or total volatile concentrations measured by vacuum extractions. Examples of such calibration curves for total volatile versus total measured gases are presented in this article, as well as calibration curves for acetylene in different oil types.

KEYWORDS:

DGA, extraction, vacuum, stripping, headspace, calibration curves

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Gas extraction from insulating liquids - Part III

The ASTM permits filling the vials by punching the septa, as shown in Fig. 1. Majority of laboratories following the ASTM procedure use this method. It can be seen that this filling practice may create different turbulence and bubbling state. This phenomenon alters the non-equilibrium thermodynamic extraction of gas.

The second issue of the ASTM methodology consists in the usage of a partitioning factor, as appears in the last version of ASTM D3612, shown in Table 1. It has already been proven that the partition coefficients obtained with Voltesso 35 are not relevant to most contemporary oils. The second option offered by ASTM is to calculate the partition value for a specific system, as shown in Fig. 2.

Table 1. Partition coefficients of gases in Voltesso 35 at 70 °C (ASTM D3612)

Gas	K
H ₂	0.074
O ₂	0.17
N ₂	0.11
CH ₄	0.44
CO	0.12
CO ₂	1.02
C ₂ H ₂	0.93
C ₂ H ₄	1.47
C ₂ H ₆	2.09
C ₃ H ₆	5.04
C ₃ H ₈	5.37
C ₄ H ₆	10.10



Figure 1. Filling vials according to ASTM D3612

It is recommended to prepare gas-in-oil standards for the whole gas-in-oil range, from 1 to 1000 PPM

The linearity of the graph in Fig 2 does not always exist. In the case of extreme concentrations, low and maximum volume for several gases may be a plateau for several headspace extraction systems. The laboratories should explore all their ranges, including extremities. For example, the graph in Fig. 3 should be a flat straight line, but in reality, it is bent at extremities, as Henry's law has been found to deviate from ideal, as demonstrated by Battino in 1984.

Another not assumed behaviour of gas extraction into a 7-ml space above 15 ml of oil in a 22 ml vial is presented in Fig. 4. Here, it is shown that the optimum oil volume for detecting acetylene of 500 PPM in oil is around 7 ml of oil and the optimum for hydrogen is almost a maximum of 15 ml of oil. The same studies need to be performed at varying temperatures and shaking times. Each gas will display a different value, and, of course, the oil condition matters.

For avoiding most of these complications, it is recommended to prepare gas-in-oil standards for the whole gas-in-oil range, from 1 to 1000 PPM. The in-house gas-in-oil preparation procedures allow to prepare them in the actually tested oil. Fig. 5 shows an example of eight gas calibration curves obtained in four oil types, aged mineral naphthenic oil, new naphthenic oil, synthetic and natural esters. For each gas, each oil matrix and each extraction system, such calibration must be performed. The gas-in-oil commercial standards, as those existing today, have been developed by Morgan Schaffer, named TrueNorth (M. Cyr, 2008).

Table 3 displays all dissolved gas conversion factors for nine gases in eight different insulating oils (liquids). Of course, each oil may be further classified according to its ageing state. Those figures are suitable for one test method, and each DGA instrument or laboratory must calculate those periodically for an accurate diagnosis of the transformer's capability.

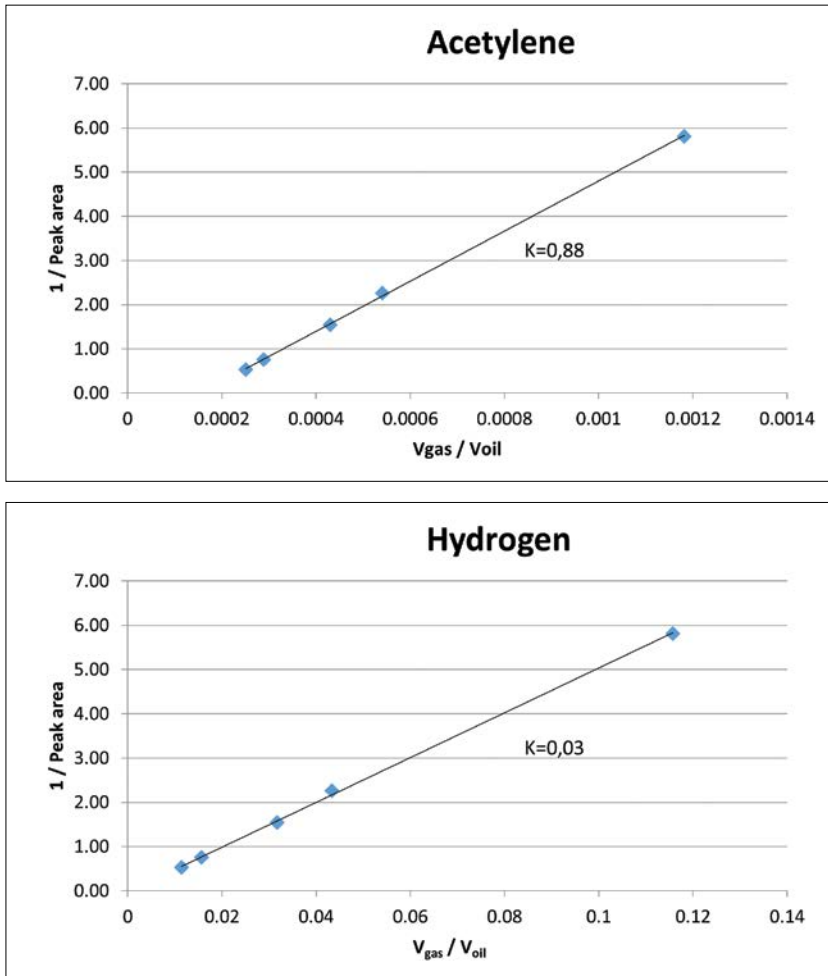


Figure 2. An example of linear behaviours of reciprocal calculation for partition coefficient for acetylene and hydrogen

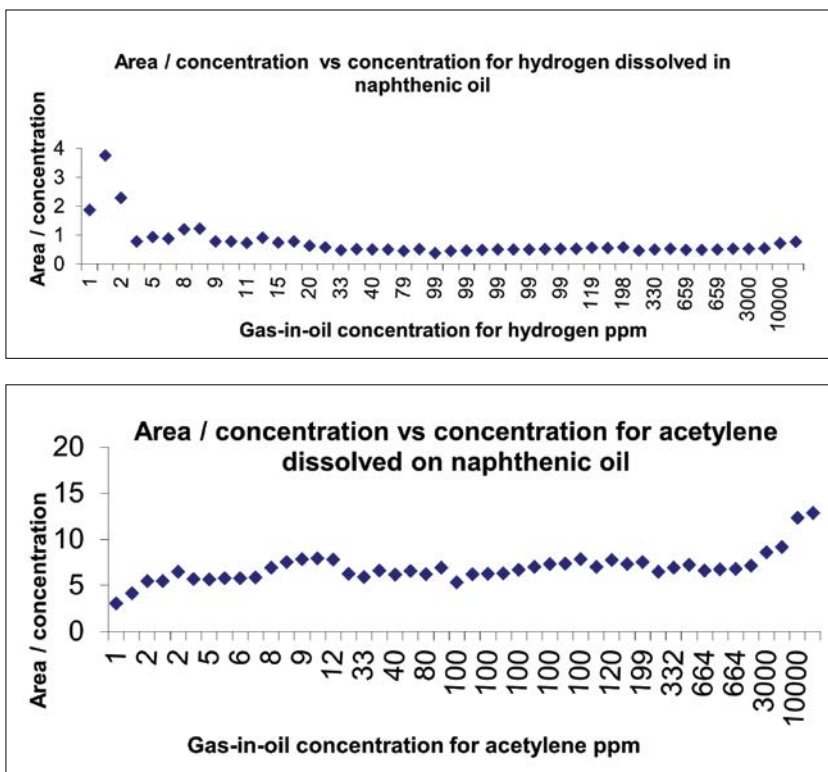


Figure 3. A graph of peak area divided into concentration versus concentration for hydrogen and acetylene

In-house gas-in-oil standards allow calibration of oxygen and nitrogen dissolved gases which can be very important for modern sealed transformers where an air leak may be considered as an actual failure.

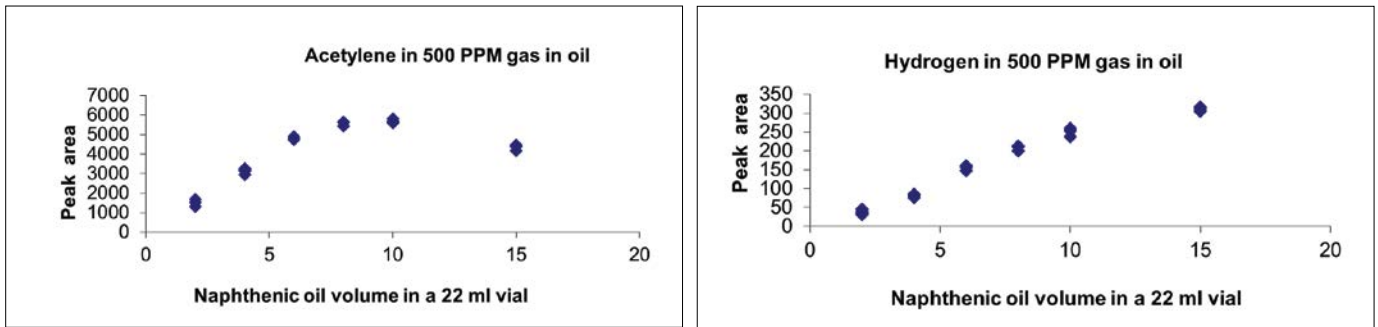


Figure 4. Yield dependence of gas extraction versus oil volume and the gas itself in a 22 ml vial

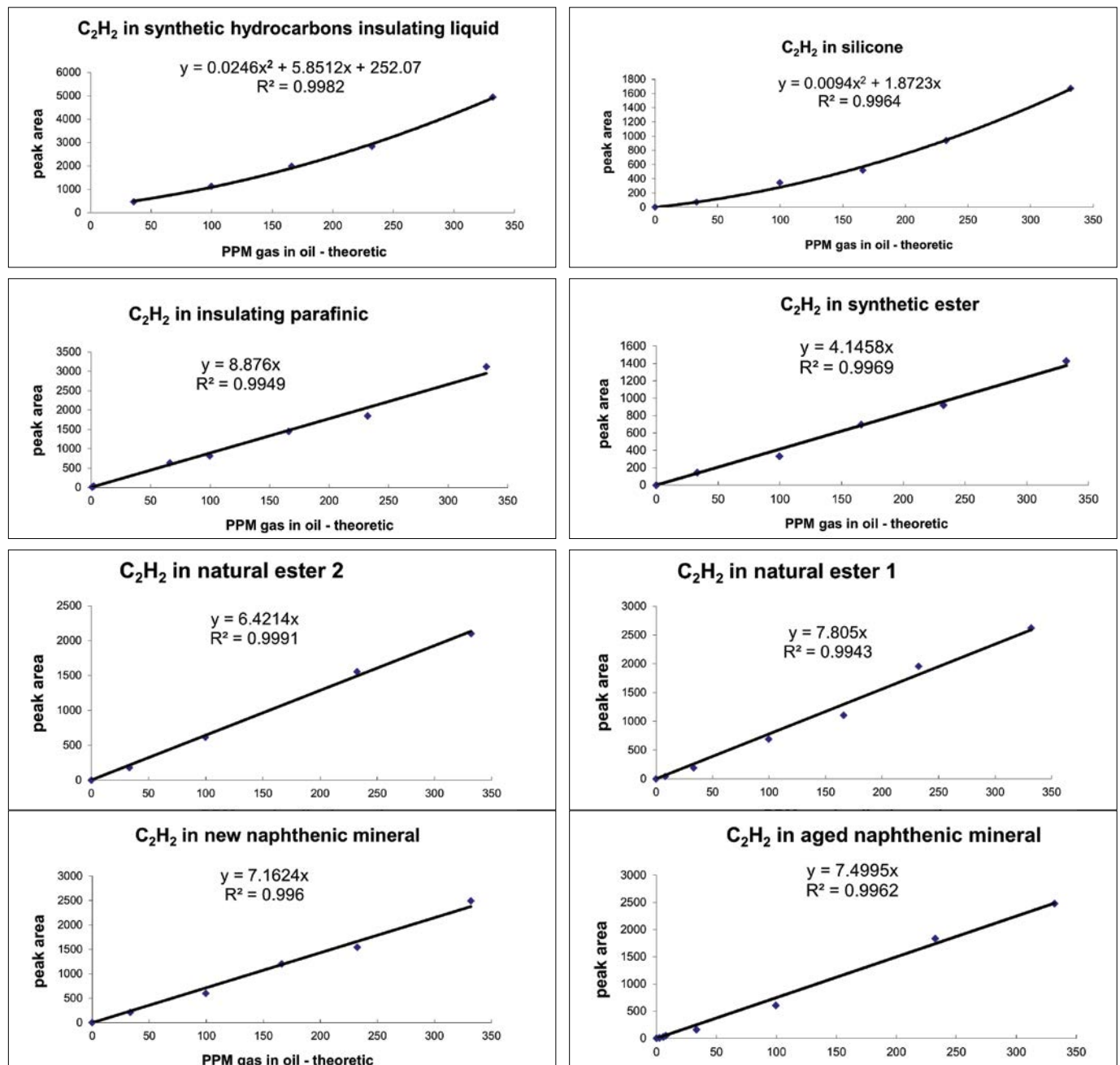
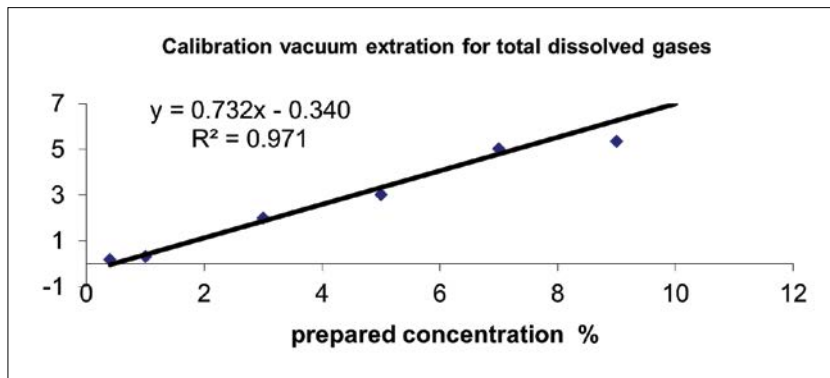
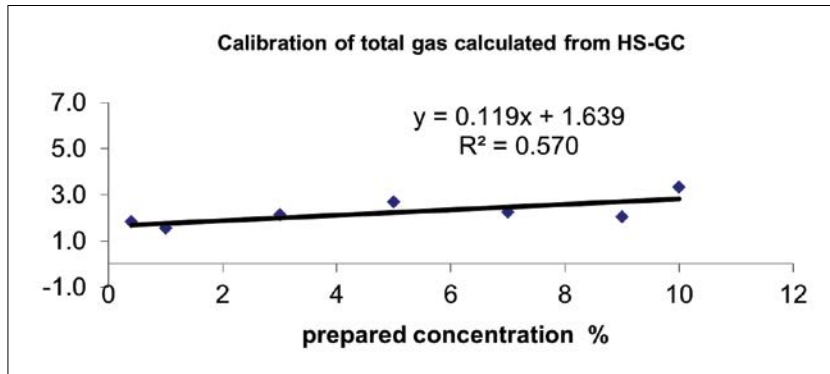


Figure 5. Gas-in-oil standards prepared in-house for acetylene in eight oil types



Total gas calibration % obtained by vacuum extraction



Total gas calibration by sum of gases concentrations from headspaces

Figure 6. Importance of in-house gas-in-oil standards in the aspect of oxygen-nitrogen calibration for different extraction methods

Table 2. A list of extraction methodologies implemented by online and portable devices, (redacted from CIGRE TB409)

Company	Model	Gases detected	Gas extraction
Morgan Schaffer	Calisto	H ₂	PTFE
Morgan Schaffer	Myrkos	7 (not O ₂ , N ₂)	Headspace
GE-Energy	Hydran 103B	(H ₂ + CO)	PTFE
GE-Energy	Hydran M2	(H ₂ + CO)	PTFE
GE-Energy	Hydran 2010	C ₂ H ₂ , H ₂	PTFE
GE-Energy	TNU	7 (not O ₂ , N ₂)	Membrane
Serveron	TM8	9 (N ₂ calculated)	Membrane
Serveron	TM3	3 Triangle gases	Membrane
Kelman	Transport-X	7 (not O ₂ , N ₂)	Headspace +stripping
Kelman	Transfix	9 (N ₂ calculated)	
Kelman	Mini Trans	(H ₂ +C ₂ H ₂ +CO)	
Big Dipper	4810	7	Headspace
Unisensor	E 200	10 (not O ₂ , N ₂)	Vacuum
Energy Support	Mobile GC	11	Vacuum
Gatron	TGM	H ₂ , CO, CO ₂ , O ₂ (N ₂ calculated)	Headspace
EMH	HydroCal	H ₂ , CO	Membrane
SRI	Mobile GC	9	Membrane
Buchholz relay	All	All	Alarm gases

Diagnosis by online devices can be erroneous, and the consequences may be devastating for a transformer, but the situation can be improved by special extensive calibration

In-house gas-in-oil standards allow calibration of oxygen and nitrogen dissolved gases. This option does not exist for the commercial gas in standard, but it has become very important for modern sealed transformers where an air leak may be considered as an actual failure. The tightness of the transformer has also become crucial for some non-mineral liquids as natural esters. Here, an undetected air leak may endanger the transformer operation in the very short term, as for mineral oil in the long term. Different calibrations may be obtained for different gas extractions, as shown in Fig. 6.

Online devices implement other extraction types according to Table 2 from the CIGRE TB 409, 2010. The user should demand from the manufacturer, or perform by themselves, similar studies as explained above. Otherwise, the diagnosis by online devices can be erroneous, and the consequences may be devastating for a transformer, such as unnecessary costly maintenance, or unnoticeable failure. This situation will be improved if standardisation or calibration of the online and portable DGA devices is initiated and accomplished in order to develop quality methods.

Conclusion

Gas extraction from oil is a critical phase in a DGA diagnosis. This stage of DGA affects the values of gas concentrations. In the past, when all the laboratories implemented partial vacuum extraction, and there were only one or two types of mineral oils available in the market, it was correct to use a literature set of figures for the calculation of the gas-in-oil concentration from gas-in-gas measurements. In our day, there is a wide variety of oil types and a variety of options for obtaining gases in the

gas space dissolved in the different liquids. Therefore, the usage of one or even two sets of partition coefficients may be erroneous and lead to catastrophic consequences for the transformer life assessment. This situation is even more important for non-standardised methods implemented in different online and portable DGA devices. Also, the new insulating oil types, whether mineral, bio-based or vegetable, impose additional challenges in the estimation of each gas extorted from each oil type at different stages in the liquid life.

The solutions for those difficulties are available and achievable as indicated in the most recent DGA CIGRE brochures, but for most online DGA devices and even a few laboratories, they are currently not routinely applied. Probably because they are not effortless.

For correct partition coefficients, it is imperative to calculate the exact partition coefficients for each oil type, each extraction system, for each individual gas, and in different matrices. Because the Henry and Ostwald coefficients are driven by total volatile material in the liquids and in gas space, it is necessary to perform the experiment as real possible matrices, e.g., it is not enough to prepare a liquid-gas mixture synthetically, only with measured gases.

For gas-in-oil standards, it is very useful and important to prepare a gas-in-oil mixture for all gas ranges, from 1 PPM up

to 1000 PPM, separately for each type of liquid at different ageing states. The gas extraction system also highly affects the slope and linearity range of the calibration curves. The in-house gas-in-oil mixtures are indispensable for oxygen, nitrogen (see Fig. 6), and other volatile materials not included in the commercial gas-in-oil standards (GIOS). Those GIOS are necessary for the verification, as internal or external Round Robins may be used.

Laboratories and organisations need to reconsider their approach to vacuum extraction methods, especially to total degassing types. This is the only method that permits the calculation of the gas-in-liquid concentrations without using partition coefficients or even calibration curves. In this context, it is recommended to reconsider and readjust the cost-effective mercury vacuum extractions. Chemists and laboratories have utilised hazardous materials and mercury should not be an issue for trained chemists. Even today, it is possible to have a closed-type system that reduces any hazard to a minimum. If mercury is prohibited for at-home use, such as thermometers, it should not be the

same case for professional chemists in the industrialised environment.

DGA must be adapted to new transformer types, new requirements for electrical device sealing, new liquid types and demands for accuracy and repeatability of DGA. Those new appreciated developments in the transformer industry should reflect not only on DGA diagnostics but in the first place on DGA extraction and measurement techniques. Accordingly, to increase the demand for diagnostic accuracy, extra attention should be devoted to gas extraction method, and calibration should be considered as the single option for determining gases in different oil concentration. Each laboratory or DGA device should be able to provide to their customers and clients a table with values for tested oils, such as Table 3, along with linearity ranges and all major matrices effects.

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Table 3. Calibration curve slopes values for different insulation oil liquids in typical headspace extraction manifold

		H ₂	O ₂	N ₂	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	CH ₄	CO
Natural ester 1	slope	0.7	152.3	104.4	8.6	6.9	10.8	9.3	11.5	16.1
	standard deviation	0.2	176.1	125.4	2.8	1.1	1.1	1.0	1.5	3.1
	levels number	6	6	6	6	6	6	6	6	6
New naphthenic mineral	slope	0.4	171.8	126.1	5.6	6.8	7.1	5.2	7.3	9.9
	standard deviation	0.1	224.5	145.3	0.8	0.6	1.2	1.3	1.0	0.5
	levels number	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Aged naphthenic mineral	slope	0.5	113.5	81.6	7.8	6.0	6.7	4.9	7.3	12.2
	standard deviation	0.1	126.2	90.4	3.9	1.6	1.2	1.1	1.3	3.6
	levels number	8	8	8	8	8	8	8	8	8
Natural ester 1	slope	0.7	92.1	141.5	6.7	6.2	9.6	8.3	10.3	13.9
	standard deviation	0.0	91.1	134.6	0.6	0.5	0.7	0.5	0.3	0.5
	levels number	4	4	4	4	4	4	4	4	4
Synthetic ester	slope	0.6	235.4	155.3	5.1	4.0	8.2	9.2	9.0	12.2
	standard deviation	0.1	307.8	197.4	1.3	0.4	1.1	2.8	1.2	1.5
	levels number	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
New mineral paraffinic	slope	0.5	212.1	126.2	5.0	8.8	8.6	6.6	8.7	11.1
	standard deviation	0.0	186.7	112.4	0.1	0.7	0.6	0.5	0.5	0.6
	levels number	5	5	5	5	5	5	5	5	5
Insulating silicone oil	slope	0.3	103.5	56.9	3.0	3.6	4.1	3.3	4.6	7.3
	standard deviation	0.1	29.5	18.7	0.5	1.0	1.0	0.8	0.8	1.2
	levels number	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Synthetic hydrocarbon liquid	slope	0.7	217.5	205.9	10.7	12.6	12.5	10.5	10.9	13.1
	standard deviation	0.2	198.6	152.1	2.4	1.4	1.5	1.1	1.1	1.6
	levels number	5	5	5	5	5	5	5	5	5

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Author



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.