ABSTRACT

As widely described in the first part of the column, all types of partition coefficients between liquid and gas phase are highly dependent on the physical and chemical properties of materials and process involved. In this second part, the large variation of extraction methodology will be described. Although most laboratories follow current standards (ASTM D3612 and IEC60567), the standards themselves allow for a large variation and laboratories also allow themselves too much leeway. The situation is even more complicated and challenging with the portable and online DGA device that does not at all calibrate the extraction stage for different gases and physical conditions. This crucial calibration stage is solely the users' responsibility, and it is described in the most recent CIGRE DGA brochures. Unfortunately, few users actually perform it, and this is one of the main drawbacks of all online devices. These situations have lead to many unnecessary maintenance episodes or, even worse, undetectable faults causing forced deenergising, and finally the loss of credibility for those users.

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 composed of completely different atoms and species and their formulae impose different treatment.

KEYWORDS:

DGA, gas extraction methodologies, IEC, ASTM, standardisation

Two major international standards for DGA, IEC60567 and ASTM D3612, differentiate three main categories of gas extractions: vacuum, striping and headspace

Gas extraction from insulating liquids – Part II

Dissolved gas analysis extraction for DGA

Presently, two major international standards for DGA, IEC60567 and ASTM D3612, differentiate three main categories of gas extractions: vacuum, striping and headspace. Besides the vacuum partial degassing method, all other methods mentioned by both standards are different. Both international standards allow for a great variety of options for each main technique. This is true especially for the most popular headspace extraction method that possesses an almost infinite number of variants. As visiting many oil laboratories around the world, I have observed that there are probably not even two different laboratories that perform DGA by a similar procedure. Each alternative has its advantages and disadvantages and its reasons to be preferred in each specific case. This reality imposes a real change for analytical parameters such as inter-laboratory reproducibility as reflected in international and local round-robin studies.

Besides those three main categories and their large degree of freedom, each of the portable and online devices uses totally different extraction methods. Those are variants of diverse methods such as separation through property membranes, bubbling, or different vacuum approaches. A large majority of the extraction methods appearing in portable and online devices are not accepted as standard methodologies. Some online device manufacturers even claim that their devices comply with the standards because the gas detection is achieved by one of the standard methods, but the separation of gas from oil should be taken into consideration as well. The

The stripping method is challenged with a high detection limit (unable to detect low gas-in-oil concentrations), and therefore, it is less useful for modern oil and transformer

Table 5. Extraction of gases from oil by ASTM D3612 and IEC60667

DGA method	Computation by	IEC 60567	ASTM D3612
Vacuum extraction by partial degassing	Ostwald coefficients gas-in-oil and gas peaks calibrated by gas-in-gas	7.3	A
Stripping extraction method	Efficiency coefficients and gas peaks calibrated by gas-in-gas	7.4	B
Multi-cycle vacuum extraction using Toepler pump apparatus	Absolute volume of gases and gas-in-gas calibration	7.2	No
Headspace method	IEC calibrated by gas-in-oil standards or partition factor ASTM by calculated partition coefficients and gas peaks calibrated by gas-in-gas	7.5	C

The main disadvantages of the vacuum extraction method in comparison with other extraction approaches are the overall price and their comparably lower productivity versus the headspace equivalent

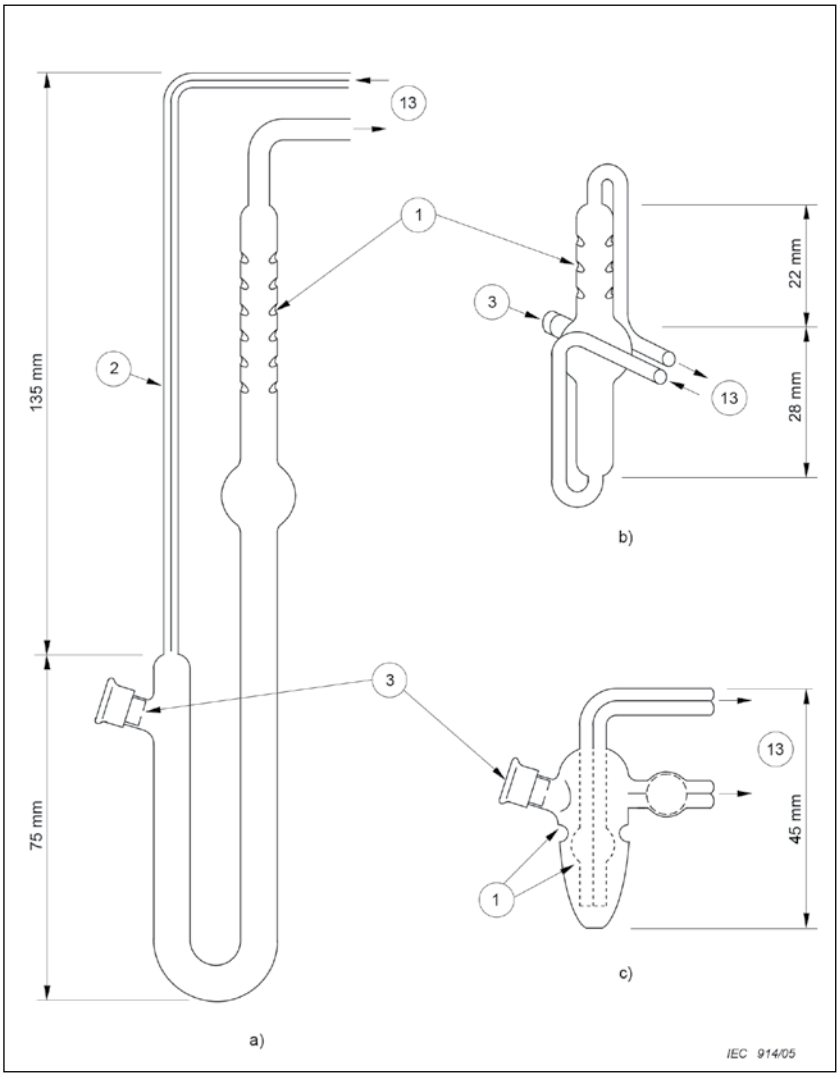

Figure 7. Stripping manifold for DGA. IEC60567

nonstandard performances are not verified and proven as accurate, reliable and repeatable, and may even be hazardous for transformers. The responsibility of accuracy, long-term stability and all other analytical parameters is shifted from device manufacturers to end-user. This is one of the reasons that online devices are not a completely concern-free approach. This is true even for those for which there are existing gas standards. It is only about calibrating the peak identification and less the extraction efficiency or interference of gases from actual oil samples.

Standard extraction methods

Method B – stripping

In ASTMD3612, it is method B, and in IEC60567, method 7.4. This method is quite similar in both standards, but since it is less utilised than the other two alternatives in laboratories, it is rather popular in portable and online DGA devices. By this method, the dissolved gases are extracted from a sample of oil by sparging the oil with the carrier gas on a stripper column containing a high surface area bead. By the IEC60567 approach, the extraction of dissolved gases is carried out by the carrier gas itself, bubbling through a small volume of oil. The gases are then flushed from the stripper column into a gas chromatograph for analysis. This is accomplished by a manifold described in Fig. 7.

The stripping method is challenged with a high detection limit (unable to detect low gas-in-oil concentrations), and therefore, it is less useful for modern oil and transformer. Recently, few gas chro-

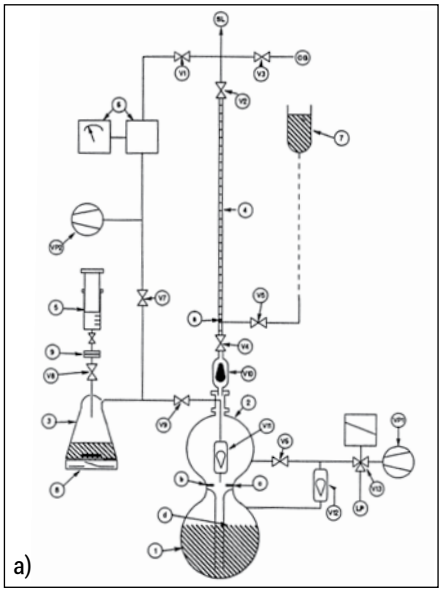

Figure 8 a) Schematic Toepler pump for partial and total gas extraction IEC60567;
b) a really old Toepler pump for partial and total gas extraction. The metal curtain is installed for protection against glass breakage.
Figure 8 c) Modern vacuum gas extraction with mercury, courtesy of Dakshin India

matograph manufacturers have tried to design-improve the devices also to permit gas detection at low limits. One of the main advantages of this method is the simplicity of extraction devices. Two other alternatives involve large supplementary equipment only for the extraction process, adjacent to the gas detector itself.

Vacuum extraction methods

In ASTM D3612, it is titled method A for partial degassing. The equivalent in IEC60567 is 7.3. This method uses a Toepler pump filled with mercury. Fig. 8 shows both schematic and two real glass manifolds for such purposes. Most glass-mercury arrangements have disappeared from the market despite their high analytical performance and reliability and a very low price compared to other options. The main cause is the mercury spill hazard. The remaining laboratories allowing this method still successfully take advantage of them as those using Dakshin manifolds displayed in Fig. 8(c). Of course, this glass-mercury system may be built at any experienced glass shop for a much lower price than non-mercury alternative vacuum systems.

A non-mercury vacuum extraction system may be found commercially at two main suppliers, displayed in Fig 9(c). The 9 is a very simple and reliable system that has been successfully manufactured in Argentina, but it is no longer

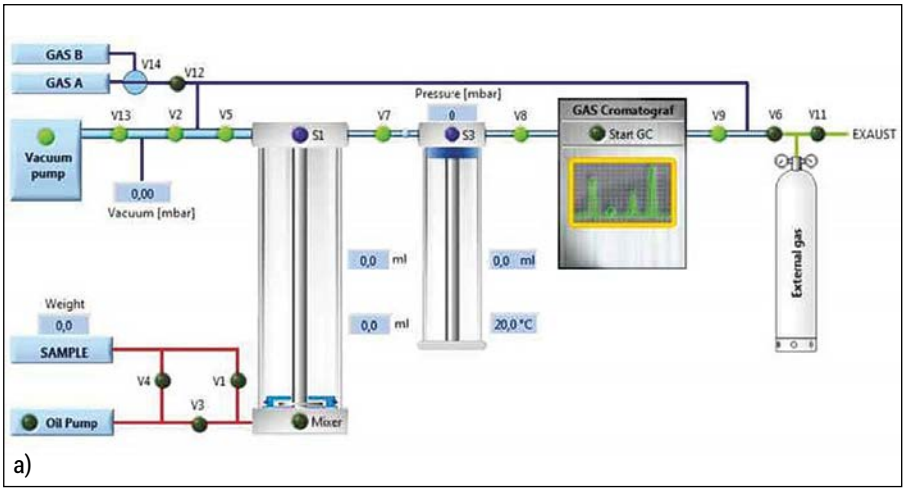

Figure 9(a). A total non-mercury extraction system for DGA by Merel
Figure 9(b). Non-mercury vacuum extraction for DGA by Energy Support
Figure 9(c). Partial degassing non-mercury system, not manufactured

The advantage of the total degassing system is not using any partition coefficients such as Ostwald because the assumption is that all the gases are extracted

available. Entrepreneurs are challenged to manufacture it. The other two available options are reliable and accurate systems, which may be easily operated and software controlled, but they are much more expensive than vacuum extraction by a glass-mercury system. The main disadvantages compared with other extraction approaches are the overall price and their comparably lower productivity versus the headspace equivalent.

Total gas extraction

Total gas extraction is method 7.2 in IEC60567, and it does not appear in the ASTM DGA standard. The advantage of the total degassing system is not using any partition coefficients such as Ostwald because the assumption is that all the gases are extracted. Users who may need to comply with ASTM standards need not use this type of extraction.

Headspace extraction

It is known as method C in ASTM D3612, and at IEC60567, it is registered as 7.5. This is inappropriately considered as a single version for both standards, and major gas chromatographs manufacturers, for example, refer to them as a single method. This may be correct from their aspect as gas chromatograph manufacturers are not interested in studying how the gas was obtained. But users and operators in laboratories need to know which percentage of each gas is extracted from specific oil and if is it easily contaminated by air, or some light gases such as hydrogen, which percentage is released into the ambient atmosphere through uncontrolled leakages. As explained and demonstrated in previous paragraphs, the implementation of any partition coefficient for estimating the yield of the extraction procedure is theoretically viable if all the highly influenced parameters of the Ostwald coefficient are identified for each oil type and oil condition versus a specific gas and if they are in intermolecular correlation with all existing volatile species; not only those measurable gases. In this context, it is important to mention the challenge of DGA from non-mineral oil as described by I. Atanasova-Höhlein and C. Schütt, 2020. These novel approaches estimate the impact of the high water content of those non-mineral oils. The volatile vapour interferes and affects the percentage yield of the relevant gas extraction. In mineral oils or oils with very low water and polar gas affinity, this situation may theoretically occur with few species undetectable by common DGA detectors. The insulating oils may contain as much as 50 volatile species that may appear in extracted gas phases but remain hidden do to the gas detector limitations and which will be described in the next lines.

Headspace DGA application was first described first by (Hinshaw & Seferovic 1989), and in the early nineties, it became widely commercially available based on cooperation through a study by (Jalbert et al.,1995) with Hewlett Packard. This was the most utilised DGA system for laboratories in those days. I had the opportunity to experience the third HP manufactured apparatus and was trained by Mr M. Pilon from IREQ, one of the developers of the HP system. In those early days, we confronted the childhood concerns of this new DGA method and tried to solve them with the IREQ staff. For trying to solve some difficulties, it was necessary to contact additional leading European laboratories that had already acquired it, such as Sea Marconi and Laborelec. In cooperation with Mr Daniel Schroyens from Laborelec, the principles of gas-in-oil standards were developed. Mr Schroyens also contributed to the development of the revolving table manifold in cooperation with Mr W. Tumiatti from Sea Marconi. The advanced version of the revolving table is now manufactured worldwide by Sea Marconi as shown in Fig. 12.. The most important advantages of the revolving table are being able to introduce oil inside a vial conveniently without exposing the vials to ambient and without punching the vials as performed by ASTM D3612. It was developed as a dedicated comfortable glove box manifold. The conventional glove box is probably better sealed to prevent air contamination than the revolving table but less convenient for manipulating the syringes and vials. Other more common alternatives to the complex glove boxes are plastic glove sacs, as shown in Fig. 11. The glove sac has been developed, and it is available from US manufacturers that make use of it against anthrax threats. If a laboratory needs the cheapest and still comfortable solution for DGA headspace, it is possible to use this glove sac first.

Those manifolds permit obtaining an unpunched oil-filled vial. The punched vial may leak, and this is critical for the last measurement in a carousel run of the headspace device attached to the gas chromatograph. See Fig. 10 showing a couple of vials with leaking punched septa dipped in water. On the top of each vial, small gas bubbles indicate leaks. ASTM users should perform such tests periodically to randomly gas vials after being punched and filled with oil.

The main disadvantages of the vacuum extraction method in comparison with other extraction approaches are the overall price and their comparably lower productivity versus the headspace equivalent

Figure 10. A Headspace extractor designed to allow gas to leave the liquids and accumulate in the restricted space above the vial;(b) typically filled vials; (c) leaking vials dipped in water

Figure 11. Glove box and glove box back for filling headspace vials

The most important advantages of the revolving table are being able to introduce oil inside a vial conveniently without exposing the vials to the ambient and without punching the vials as performed by ASTM D3612

Figure 12. A revolving table manufactured by Sea Marconi

The conclusion of this article will be provided in its third part, to be published in the next volume of Transformers Magazine.

Bibliography

[1] I. Atanasova-Höhlein, C. Schütt, *Gas-in-oil analysis and evaluation criteria for synthetic esters in offshore and traction transformers*, in IEEE Electrical Insulation Magazine, vol. 36, No. 6, pp. 31-35, Nov.–Dec. 2020,

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

[3] J. Jalbert, R. Gilbert, S. Brillante, *Dissolved gas analysis of transformer insulating oils by headspace / capillary gas chromatography*, Hewlett Packard Application Note, pp. 228–310, 1995

[4] IEC 60567:2011 Oil-filled electrical equipment - Sampling of gases and analysis of free and dissolved gases – Guidance

[5] ASTM D3612-02(2017) Standard Test Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography

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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.