ABSTRACT

DGA (Dissolved gas analysis) is a chemical method based on chemical measurements of a few dissolved species in insulating liquids (oils). Although most of the users and diagnose-providing sources consider all DGA measurements as equal, it is important to realize that different gas measurements of gases from oil matrices possess different advantages and disadvantages. The calibration is sometimes overestimated for several techniques and sub-estimated for others. Also, the linearity and range of factor response should be observed, known, and estimated before trying to use complex diagnostic models. The extrapolation approach is not recommended for DGA, not for the range, and not for substance, meaning that if a measurement is obtained from one specific matrix, any slight alteration of basic matrix composition may easily affect the DGA measurements.

Although today users may find many types of gas measurements in their DGA system, it is necessary to mention only those that are very specific. Gas chromatography is the only method that is standardized, meaning controlled, and periodically tested. Even in the case of some public standardization, regulations and limited processes, there are those compulsory for the quality of measurements. It is similarly important to stick to regulated processes for all electrical industries such as power supply or any other crucial domain.

KEYWORDS:

phase diagrams, water, organic liquids, boiling temperature, measurement techniques

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Dissolved gas analysis: Gas measurements technologies – Part 1

Introduction – Gases, liquids and solids, and ice between them

As the temperature is increased, there is a corresponding increase in the vigour of translational and rotation motions of all molecules, as well as the vibrations of atoms and groups of atoms within molecules. Experience shows that many compounds normally exist as liquids and solids; and that even low-density gases, such as hydrogen and helium, can be liquified at a sufficiently low temperature and high pressure. A clear conclusion to be drawn from this fact is that attractive intermolecular forces vary considerably and that the boiling point of a compound is a measure of the strength of these forces. Thus, to break the intermolecular attractions that hold the molecules of a compound in the condensed liquid state, it is necessary to increase their kinetic energy by raising the sample temperature to the characteristic boiling point of the compound. In that manner, it is evident in Fig. 1 that even if the temperature remains constant, the substance, water, in this case, may become gas not only by increasing temperature. For large power transformers, it is relevant when the temperature increases even within the normal limits, then some liquids in the power transformer become gaseous and may affect the transformer operation, as activate alarms.

Dissolved gas technology is a technology for measuring substances in the gas phase at ambient conditions

The phase diagrams for hydrocarbons are quite different than for water, yet they are still depending on both pressure and kinetic energy or what we call temperature. A liquid may transform into vapour at much lower temperatures than the boiling point. If one leaves a half-filled open glass with water for several days, the water will vanish, and it will surely become vapour at room temperature.

Also, so-called organic liquids may become vapours or gases at a much lower temperature than the indicated boiling point in literature. Besides the temperatures and pressure, the organic or oil liquids are highly dependent on their exact geometry and even have

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the same number of atoms. In chemistry, these are called isomers, as in Fig. 2.

If the same number of atoms construct a linear shape of molecules, then the boiling point is much higher than for the same molecular weight but in a round shape. For dissolved gas analysis in organic liquids, it means that many gases may appear in addition to those that we are interested in measuring.

Dissolved gas technology is a technology for measuring substances in the gas phase at ambient conditions. The number of potential substances in insulating liquids that may be subject to electrical, mechanical, thermic, magnetic, and other stresses is very large.

Table 1 represents only a partial list of substances that may emerge from insulating liquids. It is important to realize that extraction and especially measurement of those substances are not limited at all for the substances – gases at atmospheric conditions. The other substances (gases) not detected by the classic DGA method may still appear and interfere with the measured gases. In the worst case, they may appear, mask, and even be measured as the expected materials.

The materials stored in insulating oil may be either dissolved by the intermolecular attraction of liquid molecules and foreign substance molecules or between molecules that are derived from the liquid itself. Other types of molecules present in the oil are insoluble materials, such as water emulsions, which may turn into gas in certain conditions.

All liquids, from alcohols to water, oils, and even liquid mercury, develop a certain gas phase above the liquids in concordance with the phase diagram of each liquid and their partial pressures and temperatures.

Specific methods for measuring specific substances that are covered in classical DGA should be able to separate and quantify each specific material (gas) among all potential others. The manufacturers of gas-sensing devices should be able to develop and design detectors that are not only sensitive to what we call the DGA gases. Thus, it is not easy to design a DGA device to cover all DGA gases.

Measurement techniques for dissolved gas in insulating oils (Fig. 3)

- Canaries were used in mines from the late 1800s to detect gases, such as carbon monoxide. The gas is dead-

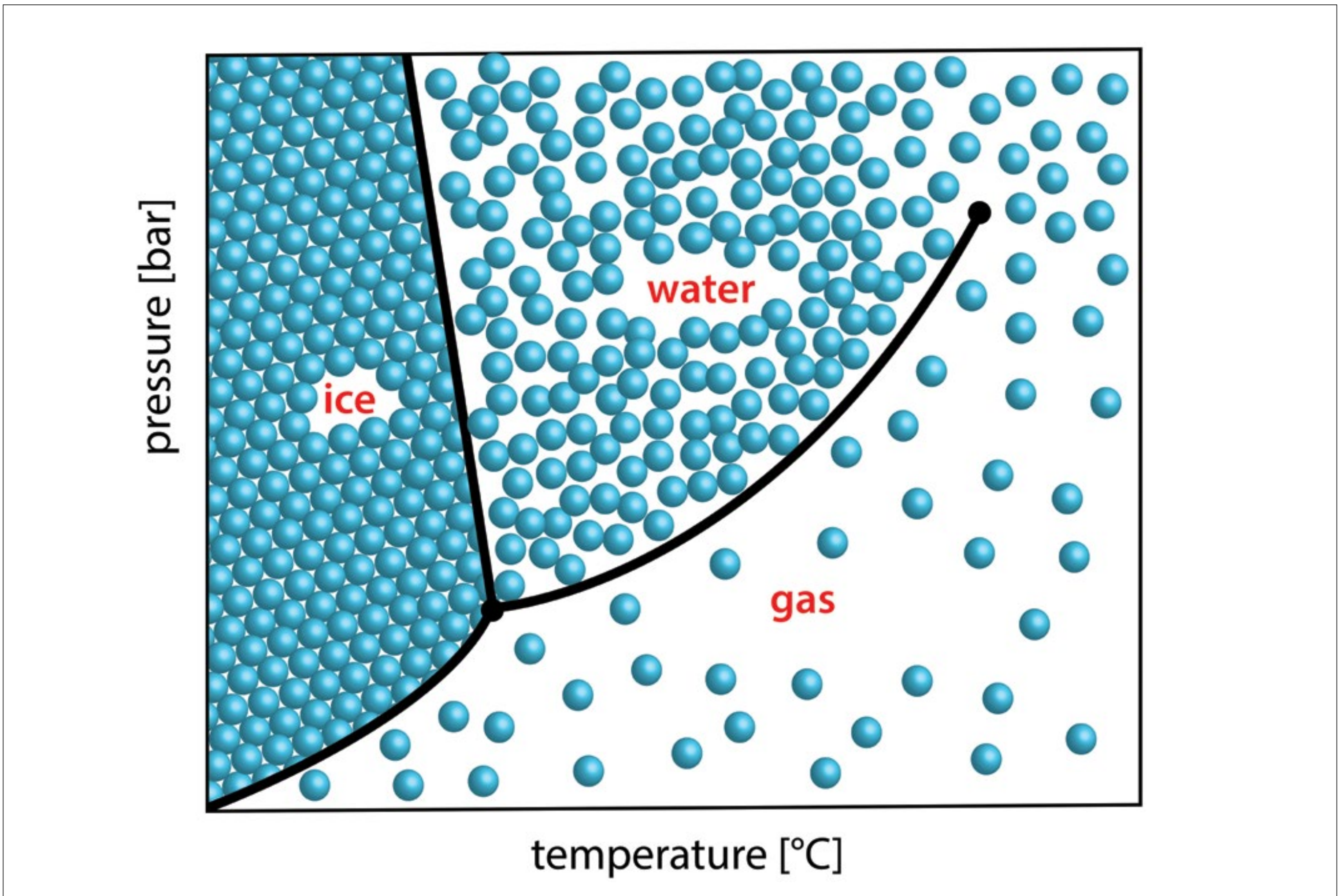
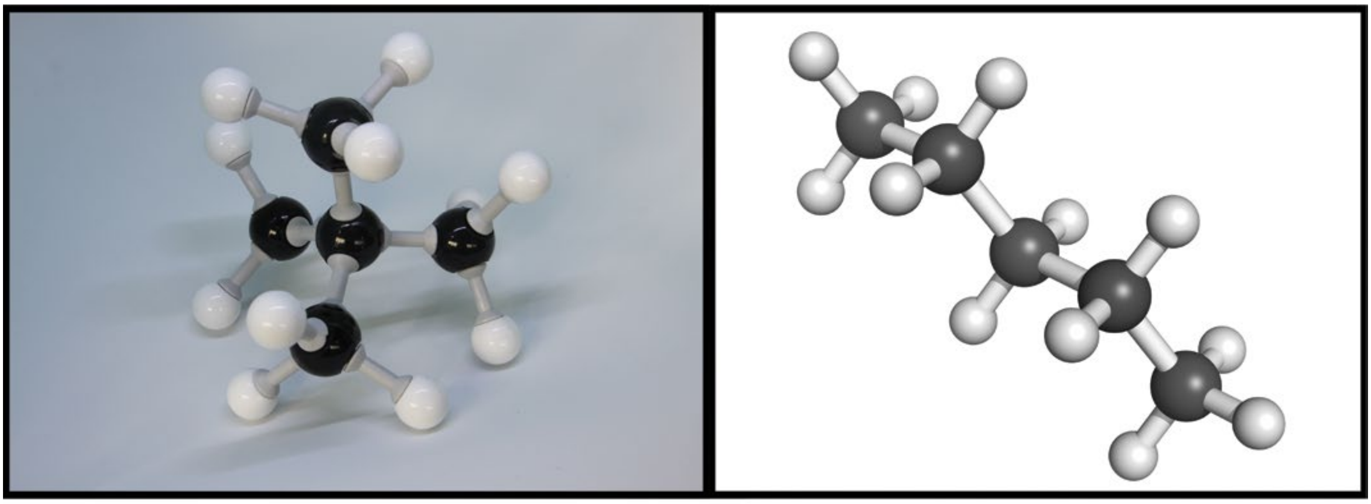


Figure 1. Phase diagram for water. Boiling point dependence on pressure and temperature



Boiling point below 36 °C　　Boiling point below 10 °C

Figure 2. Isomer's shape may influence the intermolecular attractions and the boiling point temperature

ly in large quantities to humans and canaries alike, but canaries are much more sensitive to small amounts of the gas, and they will react more quickly than humans. This was discovered by John Haldane, who was asked to help determine the cause of an explosion at Tylorstown Colliery in 1896. He concluded the explosion was caused by a build-up of carbon monoxide and set out to find a way of detecting the odourless gas before it could harm humans. The result was this cage and its captive canary.

- Open flame by a match. This is the most rudimentary, cheap method used to test the presence of flammable gas dissolved in the oil. However, it is unacceptable from the safety aspect today, although it was one of the most popular methods for detecting combustion gases in oils after a critical event or alarm.

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Table 1. A partial list of materials that may be found dissolved in oils as gases

Boiling point in degrees Celsius at atmospheric conditions	Compound
-269	Helium
-253	Hydrogen
-196	Nitrogen
-192	Carbon Monoxide
-186	Argon
-183	Oxygen
-161.5	Methane
-103.7	Ethylene
-88.78	Ethane
-84	Acetylene
-47.72	Propene
-47.7	Propylene
-42.04	Propane
-11.72	Isobutane
-6.9	Isobutene
-6.25	1-Butene
-0.5	n-Butane
9.5	Neopentane
10.9	1,2-Butadiene

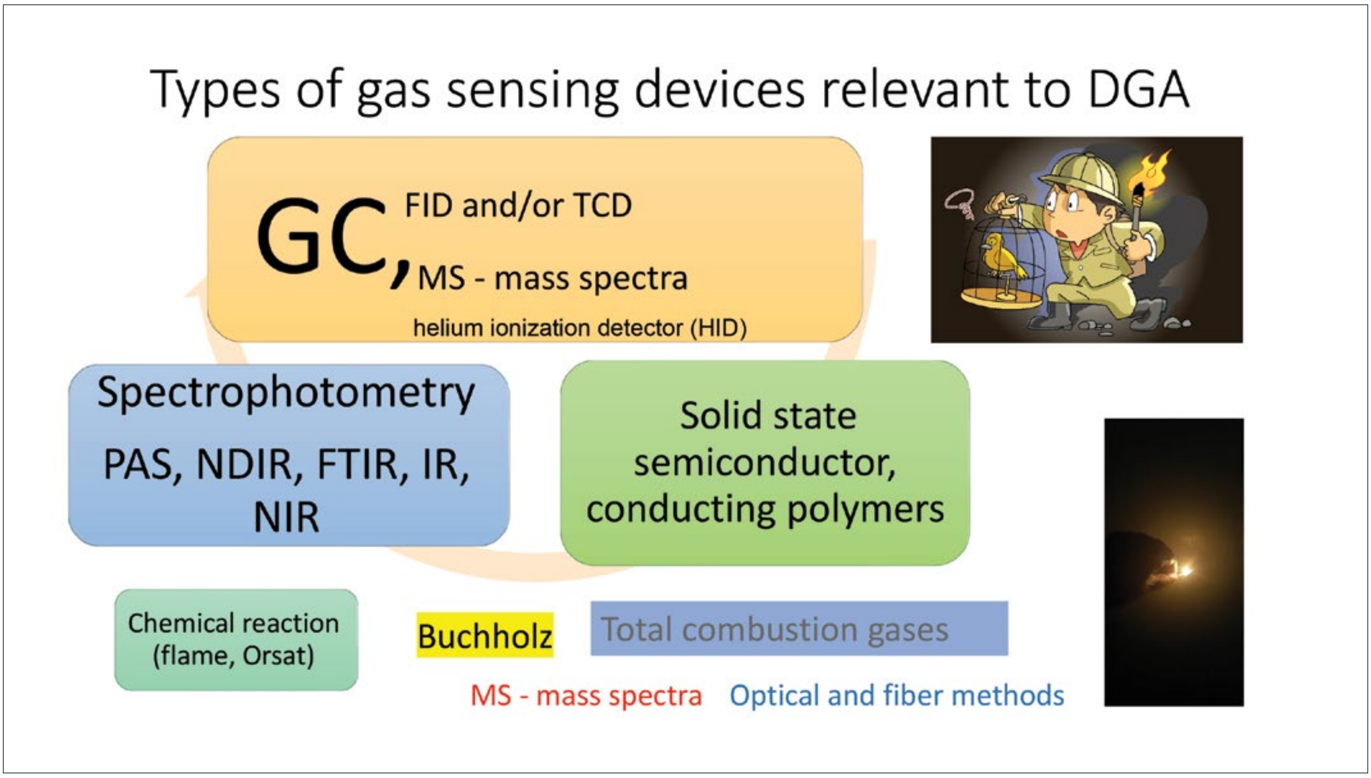

Figure 3. Types of gas sensing devices relevant to DGA

- The chemical reaction by the Orsat method. This is a primary chemical method to detect specific gases by some different chemical reactions adapted to the desired gases. It was mainly designed to measure fuel gases, including oxygen, carbon oxides, and even hydrocarbons.
- Spectrometry. It is probably the most popular technique for out-of-laboratory gas measurements and includes many variations of different techniques such as Laser Absorption Spectroscopy (LAS), Photo Acoustic Spectroscopy (PAS), Chemi-luminescence Detector (CLD) and Non-dispersive Infrared Detector (NDIR). Those techniques need to be carefully adapted and adjusted to gas concentration ranges and matrices. Those methods are excellent for steady-state gas compositions and slight changes in their concentration as air quality monitors on earth or even in outer space. The dissolved gas analysis imposes difficulties in those aspects where the contents may vary from one transformer to another, and the materials that may evolve and be detected or interfere with the desired ones may highly affect the measurement performance and, consequently, the diagnostic capabilities.
- Solid-state gas detection is an attractive method for its price and simplicity, but due to many challenges, it is less accepted for dissolved gas analysis of insulating liquids.
- Total gas measurement methods. This method is used worldwide for most power transformers, and it is called Buchholz relay after its inventor Max Buchholz (1875–1956). It allows the measurement of the gas that evolved naturally from the insulation liquids

Spectrometry is probably the most popular technique for out-of-laboratory gas measurements and includes many different variations

Author

Marius Grisaru holds 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.

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and, according to their volume, induces a signal that even may cause immediate de-energizing of the electrical equipment.

- Total combustion gas detection is an early method to detect those gases in the field during periodic test maintenance or even for portable and first on-line DGA devices.
- Mass spectra. This was the most accurate and capable method to separate and quantify the gas compositions extracted forcedly or naturally from the oil before the gas chromatograph and will probably be a future method for detecting and measuring the most volatile materials evolved from insulating oil in normal service or faulty conditions.

- Gas chromatography method for measuring gases in gases. This is a relatively new version of the classical chromatography method invented more than 100 years ago by Mikhail Semyonovich Tsvet, chromo meaning colour and graph measurements. It separates the colours on solid material pushed by a carrier gas. On the left is the principle of physic separation, where the carrier gas pushes the mixture, and by different affinities, it is separated and eluted at different times. Then the detector measures the amount of the substance and produces the peak. The peak area is proportional to the number of molecules that arrive at the detector. The retention time is the way to identify the molecule, and the peak size or height is the quantity of this gas in a specific volume.

  This is currently (2023) the only standardized method for DGA in power transformers. Transformer manufacturers and most users need DGA results from standardized GC methods to decide the real state of electrical equipment. As far as it may be observed from both ASTM and IEC relevant working groups, none of the earlier gas detection methods will be standardized in the near future.

  DGA users may take advantage of other gas detection methods for fast and continuous transformer monitoring, but for decisive verdicts, only GC technology should be considered.

In the next columns, each gas detection method will be described in detail with its pros and cons. This may allow the transformer users to select the most adequate one for their needs. Even non-standardized methods may be accurate and reliable if one implements specific calibration and maintenance procedures.