Gas chromatography is an analytical chemical method of measuring gases in gases, which is a relatively new version of the classical chromatography method invented more than 100 years ago

Dissolved gas analysis: Gas measurements technologies – Part 2 – Gas Chromatography (GC)

ABSTRACT

This is the second part of the column "Gas measurement technologies for DGA". In Part 1, the principles and problematics of DGA (dissolved gas analysis) were presented as a chemical method based on chemical measurements. The column is mainly intended for non-chemists who are interested in understanding the basics and the main weaknesses of the most popular method for monitoring power transformers, GC-DGA.

Introduction

In previous columns, the intention was to explain one of the problematic aspects of DGA, the differentiation between species (molecules) that are valuable for contemporary transformer health assessments and other volatile compounds in mineral oil and all other insulating liquid types.

An additional "stray" volatile gas that may be found in oils and liquids from electrical devices is SF6 (sulfur hexafluoride). This synthetic gas, still used in many electrical applications near power transformers, may greatly affect DGA results, and all users should be aware of its presence and effects.

A second important purpose of DGA next to the detection and quantification of the well-known 11 gases is the isolation and exclusion of all other volatile species that may be present. The undesirable molecules for non-mineral liquids are different or possibly in significantly different quantities than for classic mineral oils. An example is water vapor.

With the appearance of commercial gas chromatographs in the 1960s, new analytical techniques made the identification and quantification of gases much simpler

Generalities of gas chromatography

Gas chromatography is an analytical chemical method of 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, with *chromo* meaning color and *graph* meaning measurements. The original method separates colors on solid material, pushed by an additional carrier force.

As seen in Fig. 1, analytical gas chromatography includes at least four compulsory stages.

Classic historical chromatography refers mainly to the separation principles of different substances with different properties. This was the first application of separation of materials based on the interactions of species from the mixture to be separated (mobile phase) with static phase. This is classic qualitative chromatography, where the task is to separate a mixture of substances into their single fractions based on different properties. For this, only the retention times of different species are important. For these parameters, the user should understand the chemical nature of both the mobile and static phases. To identify a certain species, a standard sample is compulsory for comparing retention times. This is the first purpose of calibrating any chromatographic technique.

The mobile phase is driven by a particular force, which may be a capillary used in the historical chromatograph invented by Tsvet or another inert substance that advances the mobile one.

Analytical chromatography should, therefore, contain a detector that may also quantify the quantity of substances that were separated by the interactions between mobile and static phases.

The quantification itself is also performed by using a standard material. This is the second calibration stage, mandatory for GC for DGA. For this stage, it is compulsory to know the exact concentrations of materials in the standard sample. By comparing the signal from a certain amount of standard material with the signal from the measured molecule or atom, it is possible to calculate the actual amount of the former separated species.

For analytical chromatography, standard materials are obligatory for identification and for quantification.

Varieties of chromatographic techniques and gas chromatography.

Today, GC is well-developed and used for several purposes, such as in the environment, food quality industry, pharmaceutical industry, astronautics, research, and other industries. It is a versatile and established method to identify most substances. The great majority of commercial, industrial and research laboratories have chromatographs.

In this column, the goal is to explain the principle of this basic analytical chemical technique, which is relevant to power transformer life assessment, to electrical personnel.

The first widespread introduction of classic gas chromatography was made in 1951 by Anthony T. James and Archer J. P. Martin of the National Institute for Medical Research, in London. Commercial applications soon followed. The technique was built on earlier chromatography research by multiple scientists, including work that earned Martin and Richard L. M. Synge the 1952 Nobel Prize in Chemistry.

Also, Dr Cremer, an Austrian scientist, contributed to gas chromatography development in the 1940s, while her student, Dr Prior, published the first separation of acetylene and ethylene in 1947.

GC is differentiated from other chromatographic techniques by the nature of inert substances that cause the mobile phase to move on and between the static phases. These inert substances are gases.
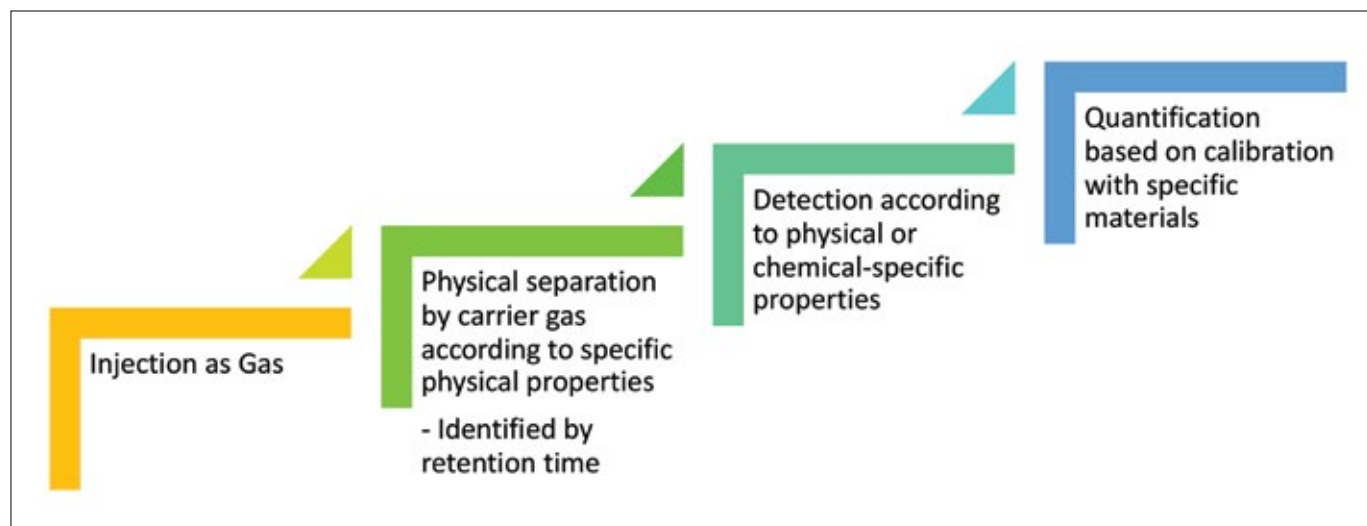

Figure 1. Schematic gas chromatograph central stages

The mobile phase is also introduced as a gas phase by converting to gas if it is originally liquid or even solid. In our case, the gases are mainly extracted from the liquid phase but are not excluded. The same vapor of the liquid phase is also introduced in gas measurement manifolds. Those vapors may contaminate and wreck GC internal parts such as columns, valves, detectors, etc.

Prior to the invention of GC, gases produced in transformers were separated and measured by mass spectra devices Vora and L. C. Aicher [2].

With the appearance of commercial gas chromatographs in the 1960s, new analytical techniques made the identification and quantification of gases much simpler.

Looking back in history, it should be mentioned that the gases used today to diagnose transformer health conditions were determined by the analytical performances of the primer (first) GC. If other gases had been measured 60 years ago, different diagnostic concepts might have emerged. For example, if MS had remained the major DGA technique, acetone would also have been used for diagnosis.
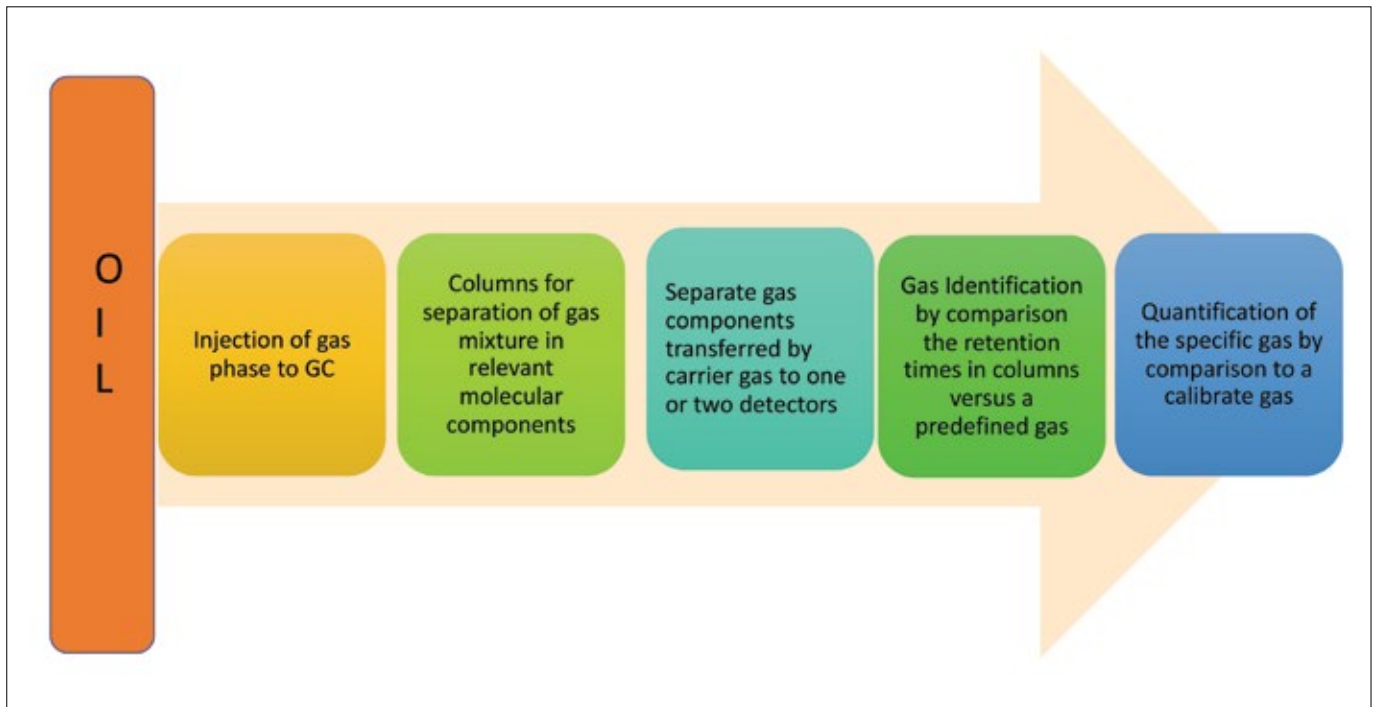

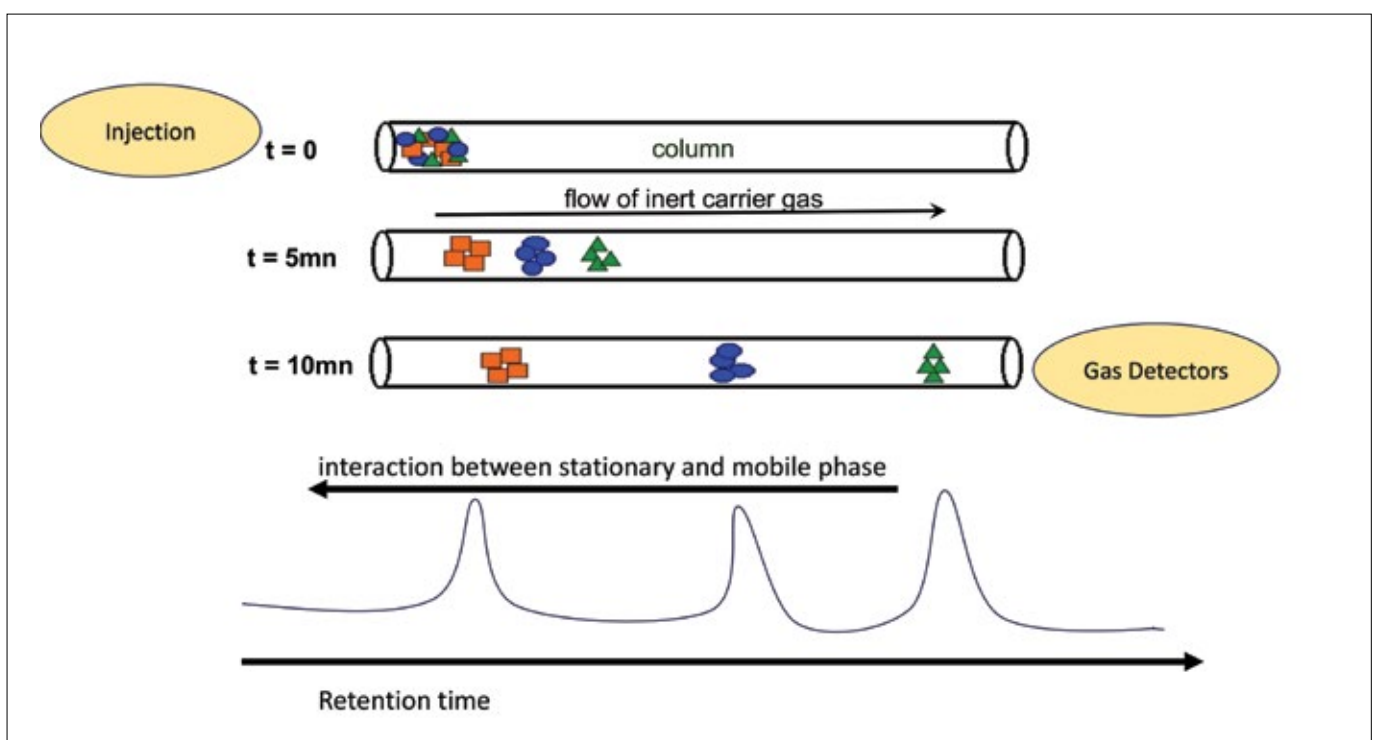Figure 2. The components and actions of gas chromatography for DGA

Figure 3. Principle of the separation of molecules in the chromatograph column and peak formation

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 injected volume

Fig. 3 represents the principle of the physical separation of species from a mixture by the carrier gas that pushes the mixture along the stationary phase, and the different affinities between the molecules in the mobile phase and stationary phase lead to separated and eluted at different times. Each molecule then causes the detector to react, and all molecules of each species form a peak that represents the amount of each substance. Therefore, the peak area (or peak height) 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 injected volume.

DGA by gas chromatography

DGA was not conducted with gas chromatography before 1970. The principal method for DGA was then mass spectra (MS) and other spectrometric techniques. Because GC became easier to manipulate and much cheaper than mass spectra, chromatography became the main technique for DGA. Today, it is on the decline once again due to other gas measurement techniques which are simpler and more affordable. Those techniques will be described in the following columns and, of course, in the Transformers Academy DGA course.

Gas chromatography is still the only method tested and approved by ASTM and IEC standards, as ASTM D3612 [4] and IEC60567 [3]. Until now, no other gas measurement technique has even been suggested for standardization, meaning verification as a reliable DGA method by ASTM or IEC committees. The reason why most of the other techniques are not standardized is not related to reliability, and it will be explained in the next columns. Gas chromatography is now the reference method for all other DGA methodologies.

Because of this, it is imperative to clarify all aspects of GC for DGA.

Gas chromatography for DGA, especially for modern DGA as the headspace technique, is probably one of the most sophisticated and complicated gas chromatography applications. Modern DGA imposes additional difficulties compared to earlier DGA methods because the quantity of gas molecules extracted from transformer oil is at least ten times smaller than by vacuum extraction. The solution for this additional restriction is to use smaller volumes for the separation system, while for detection, the implementation of capillary columns and

As of 2023, the only standardized method for DGA in power transformers is gas chromatography

Figure 4. Illustration of main components of a classic gas chromatograph

more sensitive gas detectors is necessary. Furthermore, the modern non-free-breathing transformer design induces less total gas volume or lower gas-in-oil concentrations.

As of 2023, the only standardized method for DGA in power transformers is

gas chromatography. Not all GC-DGA systems on the market today are suitable for the standard DGA method. Transformer manufacturers and most users are required to obtain DGA results from standardized GC methods to evaluate the real state of electrical equipment. Of course, users should apply the current

ASTM D3612 [4] and IEC60567 [3] standards for their gas chromatograph.

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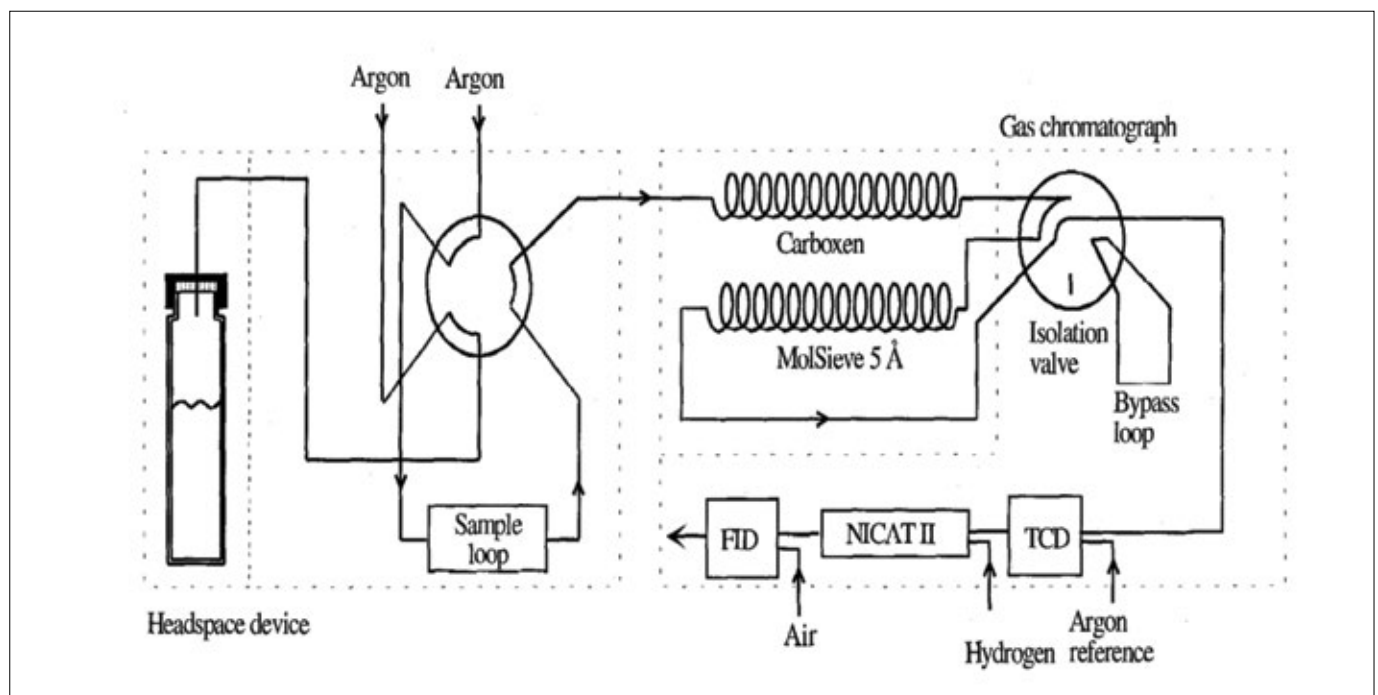

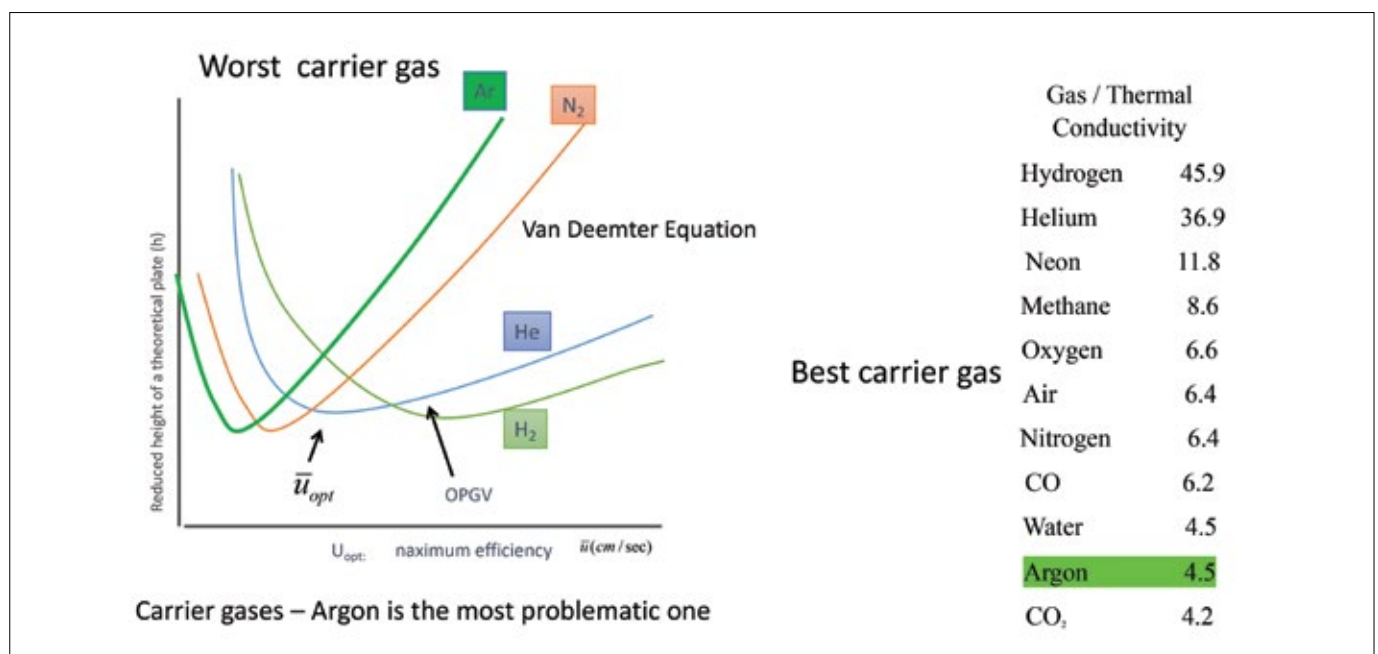Figure 5. Headspace GC configuration, 2 columns, two valves and two detectors [3]

Figure 6. Carrier gases problematic for gas chromatographic technique for DGA

Standard ASTM D3612 allows the implementation of two detectors: a flame ionization detector and a thermal conductivity detector

Nitrogen, helium, and hydrogen are the most common carrier gases used with capillary GC columns. Argon is used as a necessity in DGA application because the helium hides the hydrogen in the measured gas sample. Therefore, hydrogen and nitrogen cannot be used as carrier gases if they are also being measured. It is difficult to detect hydrogen in helium due to:

- The retention times of hydrogen and helium are similar because they have a similar molecular size. They are adjacent elements in the periodic table.
- GC configurations use a TCD where the thermal conductivity of carrier gas and measured gas is compared, and they are also quite similar because they possess similar thermal conductivity.

Despite those difficulties, there are portable and online applications that use helium as a carrier gas by using a sensitive TCD and special separation. Helium as a carrier gas allows for a significant increase in TCD sensitivity for all other gases. Due to safety reasons, it is almost impossible to use FID detectors for field chromatography.

Gas detectors for DGA gas chromatography

Standard ASTM D3612 [4] allows the implementation of two detectors: a flame ionization detector (FID) and a thermal conductivity detector (TCD).

Standard IEC60567 [3] also allows a helium ionization detector (HID), which may replace both an FID and a TCD. Although HID has important advantages over FID and TCD, in theory, it may be found in a few gas chromatographs for DGA, but the reasons for this are beyond the scope of this column.

The operation of an FID is based on the detection of ions formed during the combustion of organic compounds in a hydrogen flame. The generation of these ions is proportional to the concentration of organic species in the sample gas stream.

FID measurements are often measured as total volatile hydrocarbon content as hydrocarbons which have condensed out are not detected. There are many species of hydrocarbons that are extracted, some of them reach the FID detector, while others are condensed on internal tubes of the system of the detector. Those are not detected together with the volatile hydrocarbons of the specific measurements, but may appear in further measurements and therefore interfere with the others.

To detect these ions, two electrodes are used to provide a potential difference. The positive electrode serves as the nozzle head where the flame is produced. The negative electrode is positioned above the flame. The ions are attracted to the collector plate and induce a current upon hitting it. This current is measured with a high-impedance picoammeter and fed into an integrator. The final data is displayed on the computer and software. Usually, a graph with time on the x-axis and total ions on the y-axis is displayed.
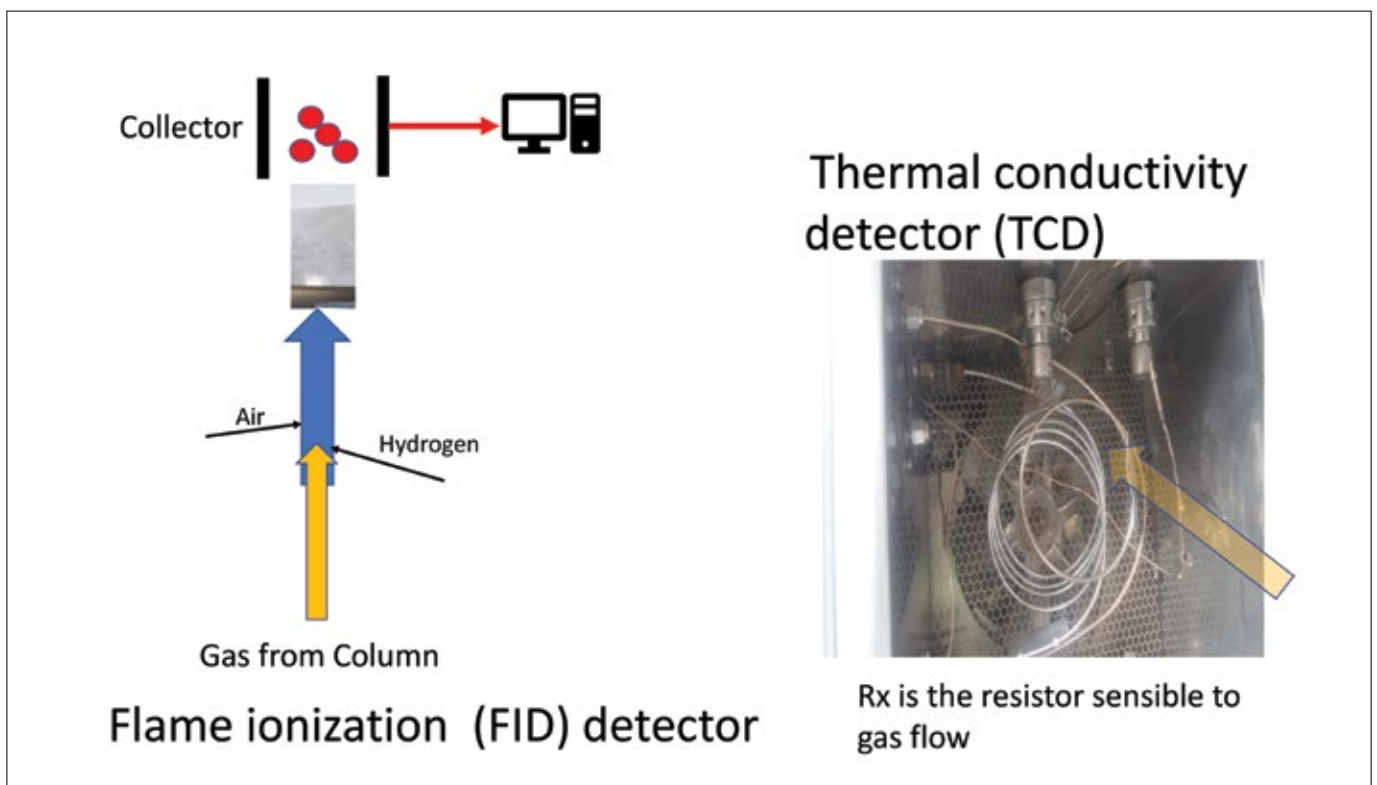

Figure 7. Gas detectors for DGA

> **A standard DGA chromatograph requires temperature programming to produce a well-defined chromatogram with distinct peaks in a reasonable time frame**

A TCD consists of an electrically heated filament in a temperature-controlled cell. Under normal conditions, there is a stable heat flow from the filament to the body of the detector. When an analyte elutes, and the thermal conductivity of the column effluent is reduced, the filament heats up and changes resistance. This resistance change is often sensed by a Wheatstone bridge circuit, which produces a measurable voltage change. The column effluent flows over one of the resistors, while the reference flow is over a second resistor in a four-resistor circuit.

As mentioned above, some online and portable GC systems used for DGA only used a special TCD. Even though a special TCD is more sensitive than a regular TCD, an FID remains superior compared to any TCD for the detection of low gas concentrations and, more importantly, for a high range of linearity. The user must dilute the gas sample prior to injection when using a TCD.

Additional elements and considerations for gas chromatography for DGA

As shown in Fig. 5 and Fig. 6, gas chromatography for DGA is not a simple method, and it is not just because of the complexity of building such a gas chromatograph nor due to integrating and computing the results.

In Fig. 5, it can be seen that, besides the columns and detectors, there are also valves that switch several times during a chromatogram cycle. The columns are in an oven with pre-programmed temperature (see Fig. 7). A standard DGA chromatograph requires temperature programming to produce a well-defined chromatogram with distinct peaks in a reasonable time frame. This improves the detection limit and linearity range for gas peaks. Temperature gradients are also important for purging unwanted materials from the system. Most GCs for DGA also consist

of a device called a methaniser, which is necessary for improving the detection limit of carbon oxides by converting them to methane, which is then detected by the more sensitive FID. This device requires a continuous flow of make-up gas hydrogen. Another challenge for chromatograms is the integration stage. Although there are many programs used for peak integration, most labs that operate a GC for reliable and sensitive measurement perform manual integration. As shown in Fig. 8, manual integration is the preferred approach in cases of an unstable baseline for achieving repeatable gas peaks integration. DGA accuracy and repeatability are superior in laboratories performing manual integration.

This is the main obstacle to using GC for DGA outside laboratories where manual intervention is minimalized. Even in laboratories, skilled chemists should be responsible for overseeing the gas chromatograph operation.
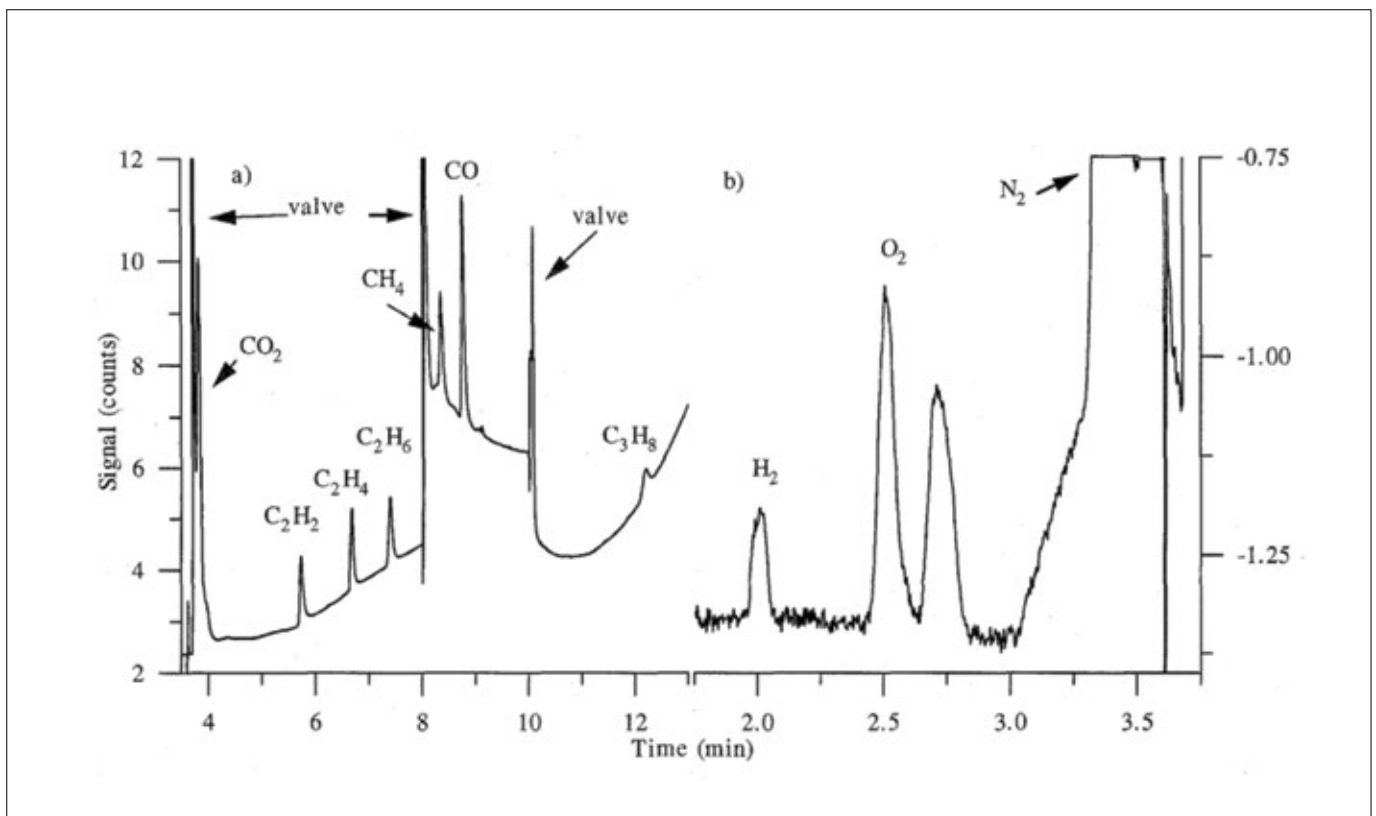

Figure 8. Real chromatogram of DGA gases. [4]

> **Like several other special GC applications, the application of GC for DGA also needs deep knowledge and practical experience to meet expectations**

Conclusion

Advantages of GC for DGA:

Gas chromatography is the most sensitive DGA technique with the largest linearity range for concentration-response.

- GC systems allow for three calibration levels (extraction, identification, quantification), making it the most repeatable, precise and accurate DGA systems.
- Gas chromatographs are manufactured by many companies, which allows for competitive prices and continuous improvements.
- Gas chromatographs are almost completely independent of environmental influences, unlike other DGA methods. GC also includes physical gas separation in the columns with specific detectors.
- GC-DGA is the only standardized method recognized as such by ASTM [4] and IEC [3] standardization organizations.

Drawbacks of GC for DGA:

- It is usually the most expensive method for detection of gases dissolved in oil. The equipment is sophisticated and requires special care and continuous human supervision.
- Gas chromatography is an analytical chemical methodology highly dependent on continuous multistage and multi-level calibrations. Reducing the levels, points and intervals of calibrations may seriously affect gas identification, gas quantification and transformer life assessment.
- Most advantages listed above depend on the operating technician's education and performance. With a gas chromatograph being an analytical chemical device, it is recommended that the technician be an analytical chemist. Without highly professional management, gas chromatography will be inferior to most other DGA techniques.
- Gas chromatography requires several components which have to be replaced periodically, such as up to 6 pressurized gas cylinders, delicate internal columns, lines, and other internal parts. The entire system should be monitored daily, controlled, purged or repaired if necessary. The pressurized cylinder needs special care due to safety conditions associated with high pressure and flammable gasses such as hydrogen. Furthermore, using a hydrogen generator does not eliminate the explosion potential in the GC environment, and such cases of explosion of hydrogen cylinders or hydrogen from generators have been recorded worldwide.
- The full calibration option is complex because in-house gas-in-oil standard mixtures are relatively complicated to prepare and require special manifolds and expensive materials. Plus, the only available commercial gas-in-oil mixture is costly for frequent use and possesses a limited shelf-life of a maximum of one
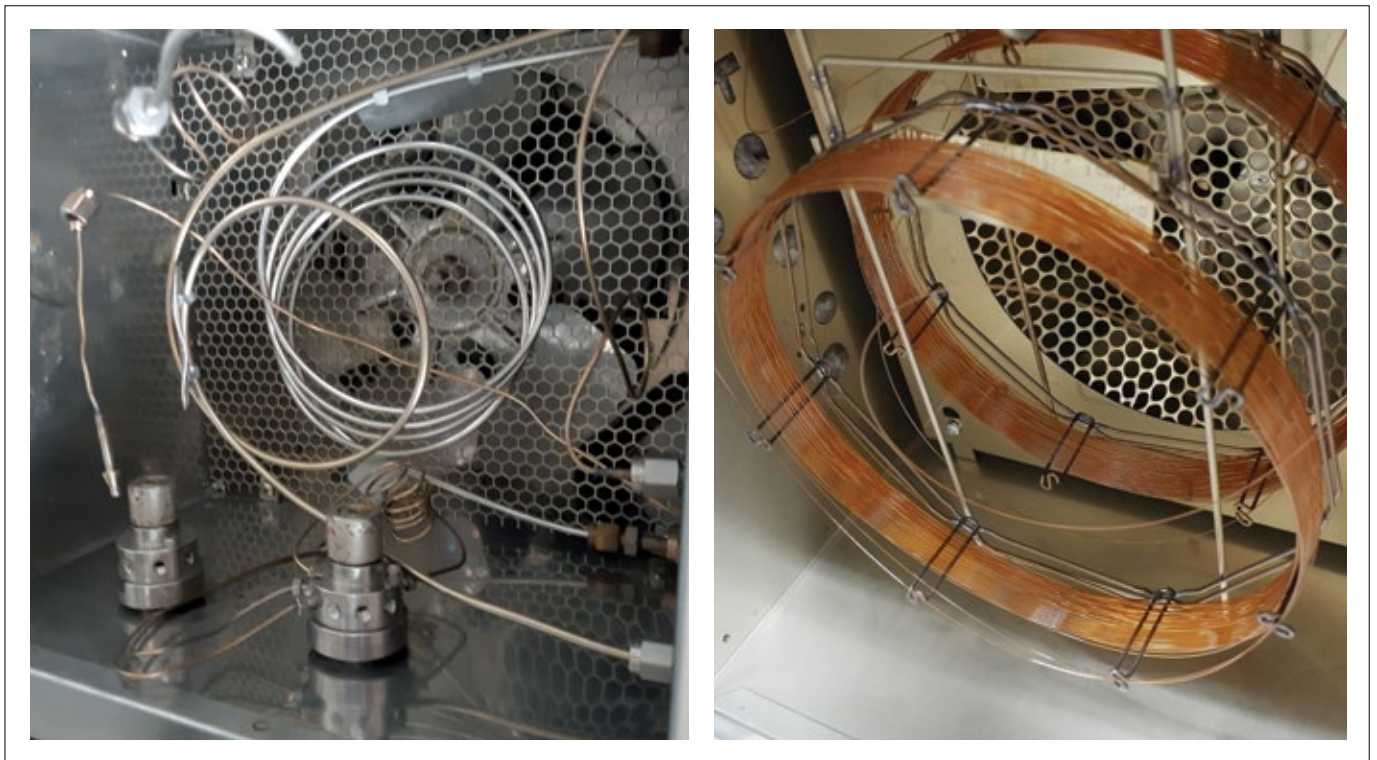

Figure 9. Temperature programmed GC oven with packed columns.

month, meaning that it cannot be stored for longer than 3 weeks. It is problematic to calibrate the entire GC system routine so frequently and on unusual occasions.

This column is not intended to explain gas chromatography techniques as this would require a background in analytical chemistry from the readers.

Like several other special GC applications, the application of GC for DGA also needs deep knowledge and practical experience to meet expectations. Not all GC for DGA techniques and systems are similar, and users should select the adequate approach for their circumstances. Of course, to be able to compare DGA using GC with DGA using different techniques, the awareness of the limitations of each of them is essential to make adequate decisions.

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Author

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