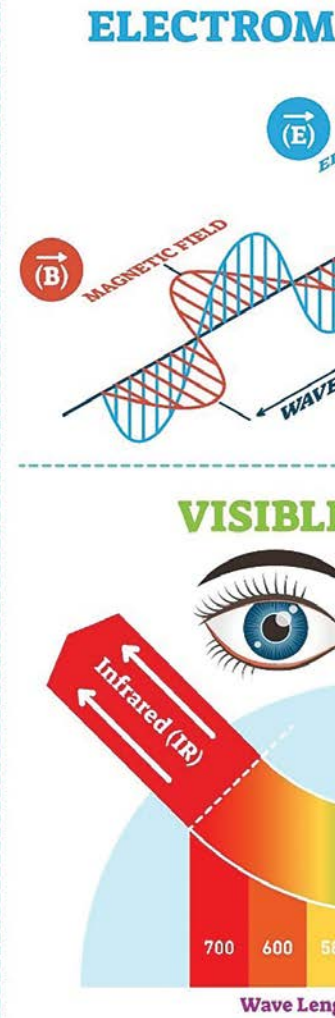
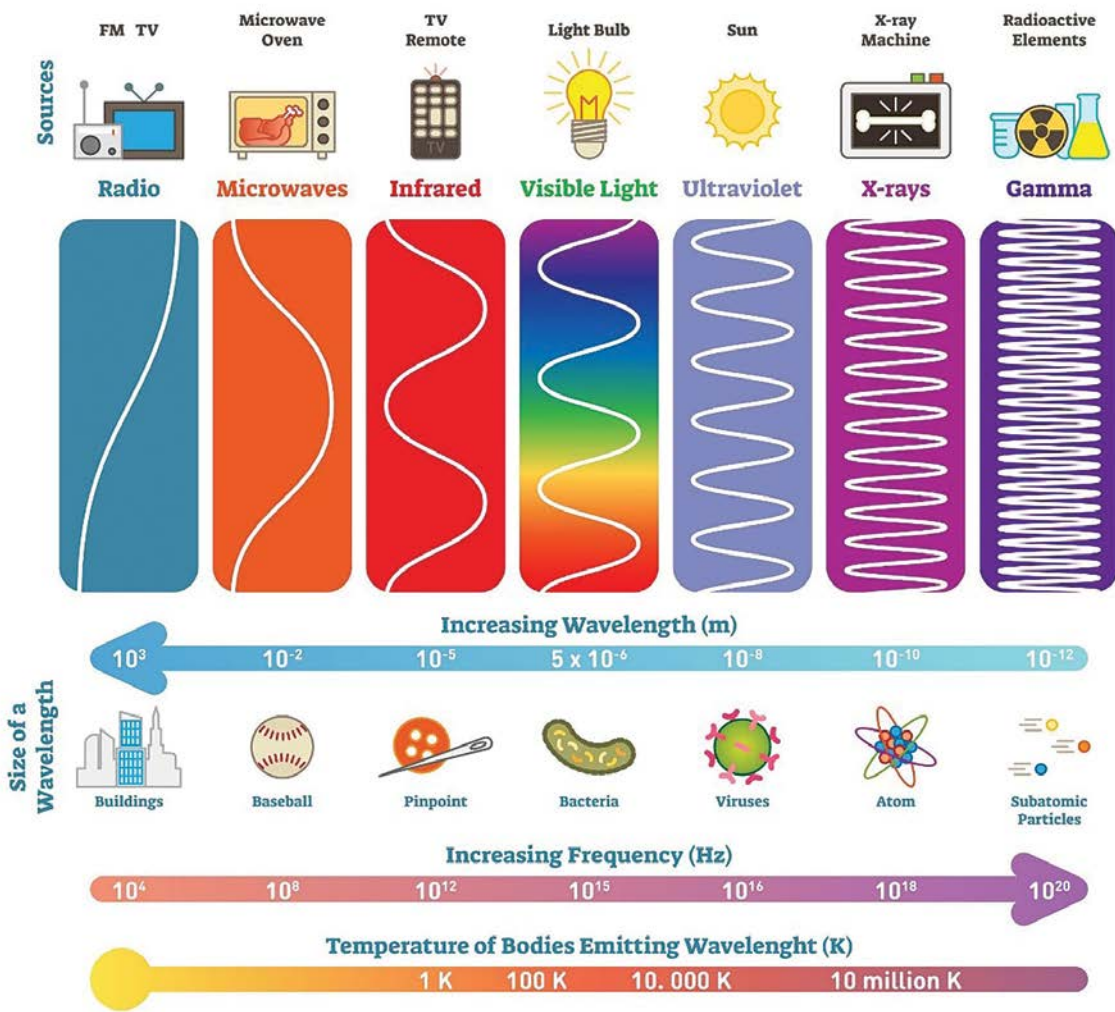


ELECTROMAGNETIC SPECTRUM



Spectrometric methodology for dissolved gas analysis

ABSTRACT

In previous columns, gas chromatography and electrochemical approaches for dissolved gas measurement were described. In this column, the oldest and emerging method, spectrometry, is described. It is an applicable method for most online and

portable devices, and it may reappear in laboratories as reliable and standardized. It can be said that the first DGA analysis was performed using the spectrometric principle, while today, the majority of DGA tests are performed by instruments that issue the final results using the spectrometric methodology.

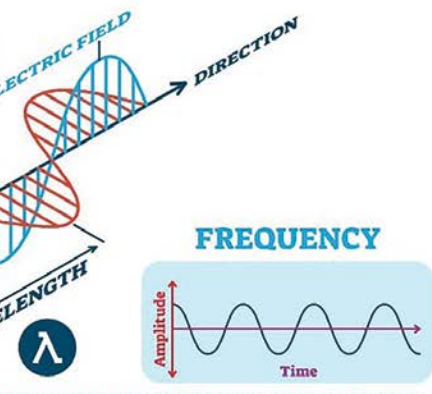
In this column, the pros and cons of spectrometric gas detection for DGA will be described.

KEYWORDS:

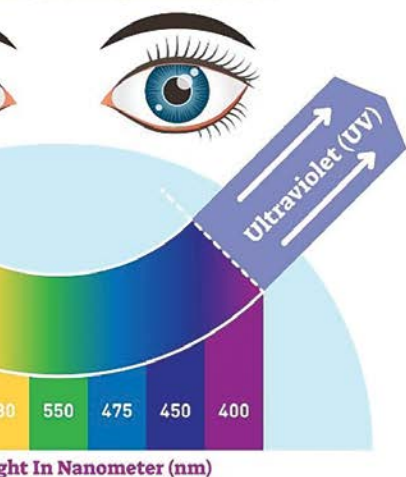
DGA, spectroscopy, analytical spectroscopy, nonlinearities, comparative study

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MAGNETIC WAVES



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Introduction

As described in the previous part of the column, dissolved gas analysis is neither an electrical measurement nor a mathematical or software methodology. Dissolved gas analysis is a pure chemical method that belongs to the category of analytical chemistry.

Spectroscopy is related to the interaction of molecules with electromagnetic radiation.

The invention and evolution of spectroscopy as a scientific discipline involved the collective efforts of numerous scientists across different time periods and regions. It started with the Newton prism in the 17th century, through Joseph von Fraunhofer and Gustav Kirchhoff in the 19th

The important fact for understanding the difference between all spectroscopic methods and other analytical methods for DGA is the existence of photons and energy at discrete levels

century, until the quantum mechanics of Bohr, Einstein, Heisenberg and others. It continues to be a vibrant and interdisciplinary field, with applications ranging from astronomy and chemistry to materials science and biochemistry.

This column will not explain the basic theories of spectrometry, which are, of course, based on quantum physics. The important fact for understanding the difference between all spectroscopic methods and other analytical methods for DGA is the existence of photons and energy at discrete levels.

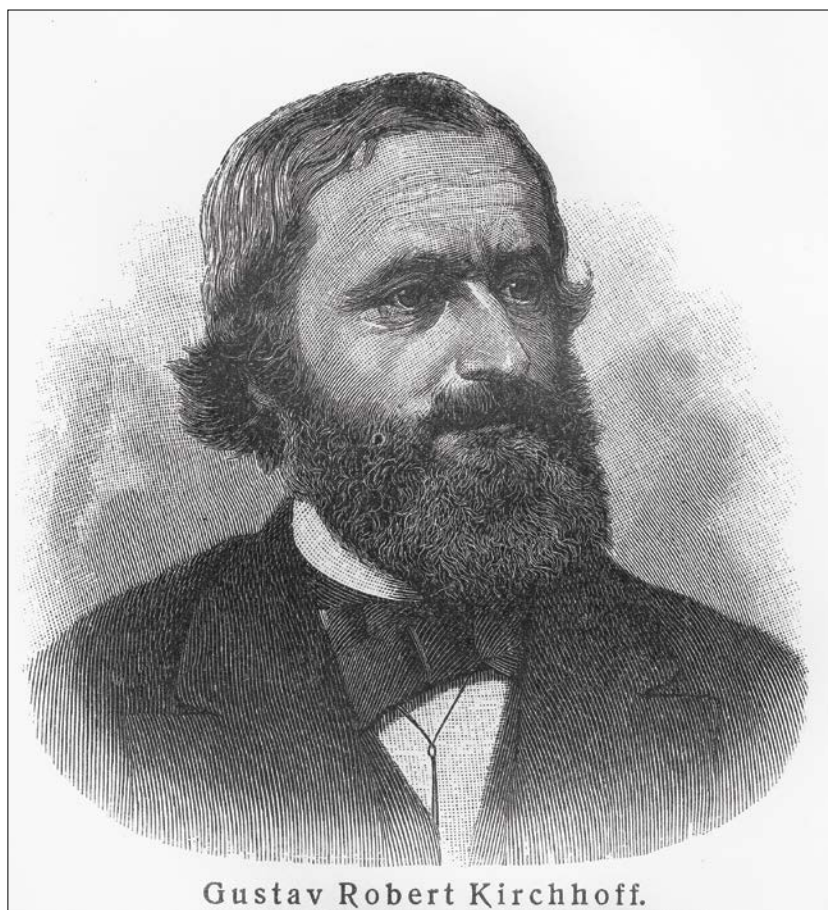
Photons are fundamental particles of light. They are the smallest units or quantum of electromagnetic radiation, includ-

ing visible light, ultraviolet light, infrared radiation, radio waves, microwaves, and X-rays. Photons have both wave-like and particle-like properties, exhibiting characteristics of both waves and particles according to the principles of quantum mechanics.

Electromagnetic interactions

Photons interact with specific particles through electromagnetic force. They can be absorbed, emitted, or scattered by charged particles, leading to phenomena such as absorption, emission, and reflection of light.

The interactions of electromagnetic energy waves with any atom, molecule or



Gustav Robert Kirchhoff.

Analytical spectroscopy is a branch of spectroscopy that focuses on using spectroscopic techniques to analyze and quantify the chemical composition of substances

substance have a different specific pattern. This is the basis of analytical spectroscopy.

Analytical spectroscopy is a branch of spectroscopy that focuses on using spectroscopic techniques to analyze and quantify the chemical composition of substances. It involves the measurement and interpretation of the absorption, emission, or scattering of electromag-

netic radiation by molecules or materials to obtain information about their chemical composition, structure, and properties.

Analytical spectroscopy for DGA mainly encompasses **absorption spectroscopy**. In absorption spectroscopy, the amount of light absorbed by a sample at specific wavelengths is measured. This can provide information about the presence and

concentration of particular chemical species in the sample.

Pros and cons of spectrometric gas detection for DGA

Advantages:

- “Black box” for users
- Friendly user interface

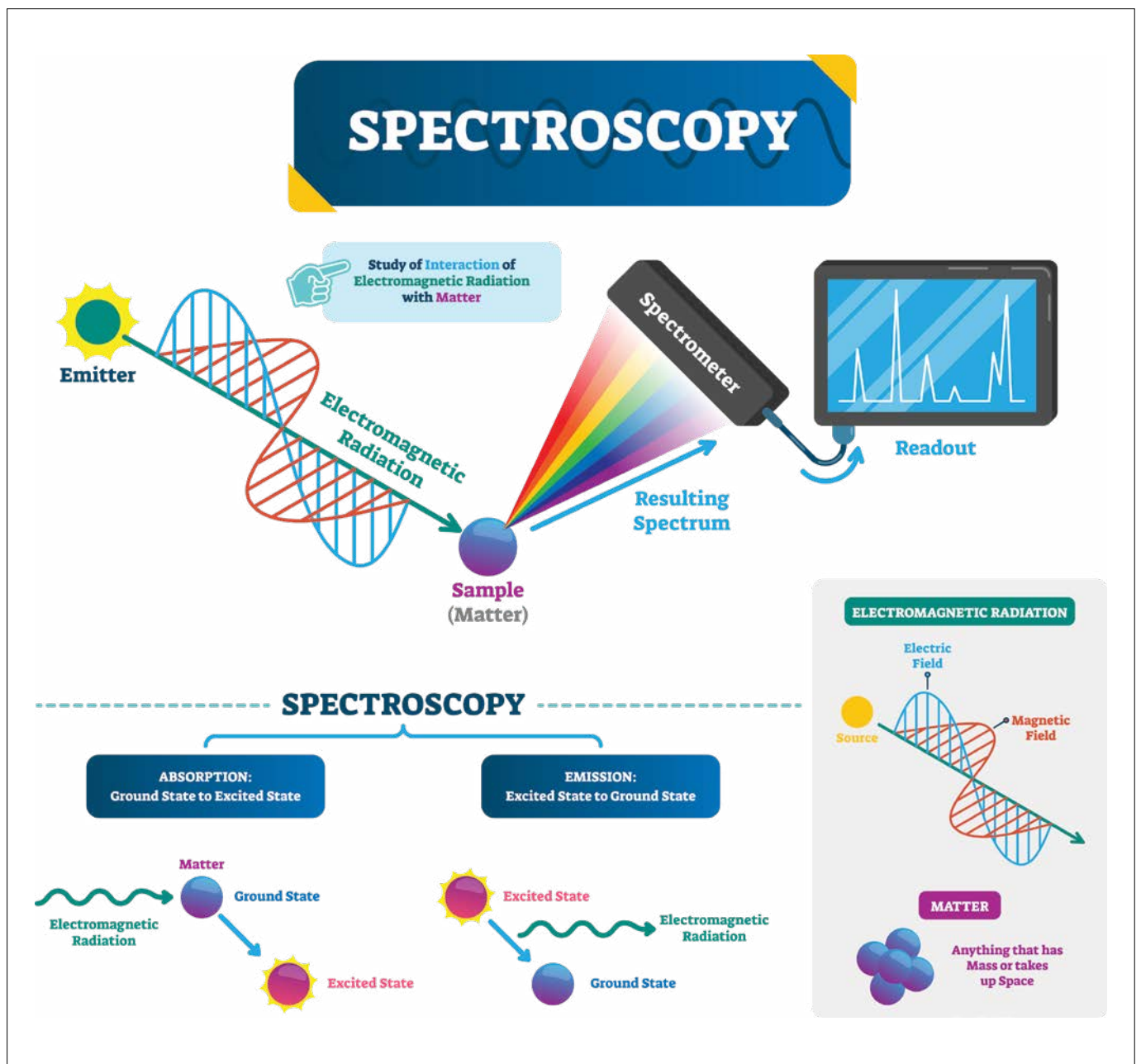


Figure 1. Spectroscopy principles of interaction of electromagnetic radiation with matter

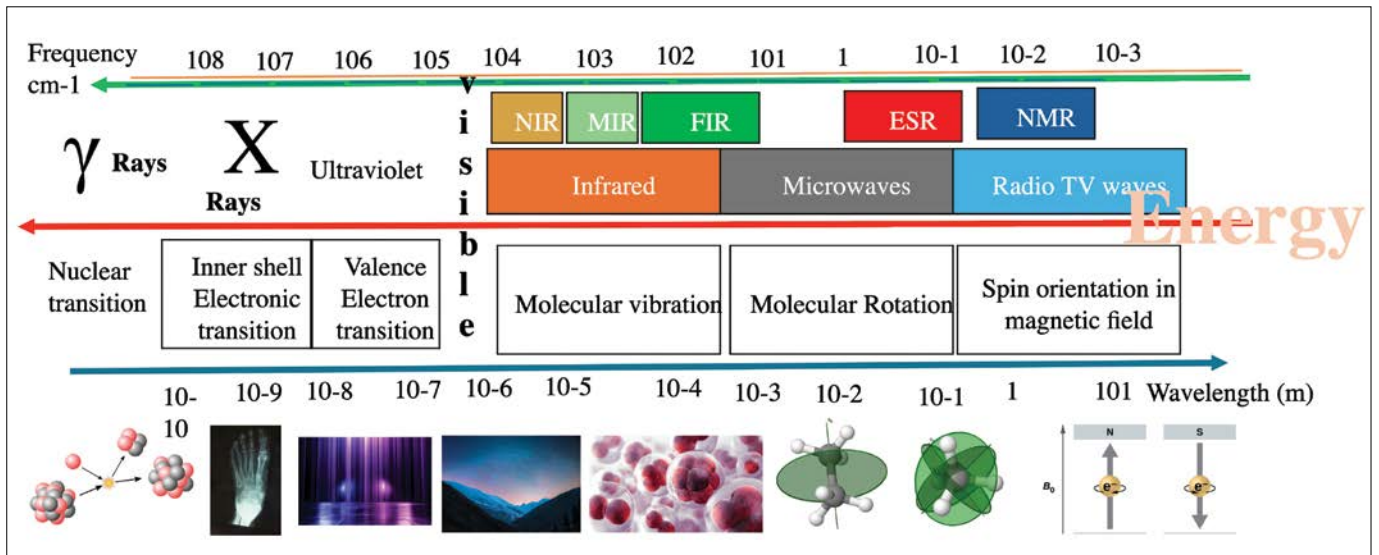


Figure 2. Electromagnetic spectra and relevant regions with main phenomena

Analytical spectroscopy for DGA mainly encompasses absorption spectroscopy, where the amount of light absorbed by a sample at specific wavelengths is measured

- Affordable price compared to gas chromatography devices
- Theoretically maintenance-free, no spare parts or consumables
- No need (permit) to be calibrated by users
- Leading technologies are well established, very robust, and reliable
- Fast and immediate identification of gases in the gas phase
- Intensely researched and emerging gas detection method for multiple applications including DGA

Disadvantages:

- Needs more than one detector type to measure all DGA gases
- Relatively high detection limits and low range of concentration response – limited linearity range

- Sensitive to external environmental conditions, such as pressure, moisture, noise, pollution
- Affected by internal interference and the memory effect
- Allows only factory maintenance, calibration, and replacement – time and transportation costs need to be considered if any type of maintenance is required
- Relatively new approaches for these applications and not standardized for DGA with all consequences – users should always take the results with a grain of salt

Because none of the spectrometric methods is standardized, a careful user prefers not to make any important decisions based on them. The

main problem is that the obtained output (i.e. voltage signals in mV) are not linearly related to the concentrations in the common ranges. The user needs to understand the method's principles, limitations, and performance very well to be able to rely on them. There is a large difference in the quality and stability between different manufacturers. Usually, all repairs and maintenance are done at the factory, and the devices need to be transported a long way by air. The cost of transportation needs to be taken into consideration.

The analytical methodology for DGA spectroscopy employs the vibrational measurements of molecules, as seen in Figure 3.

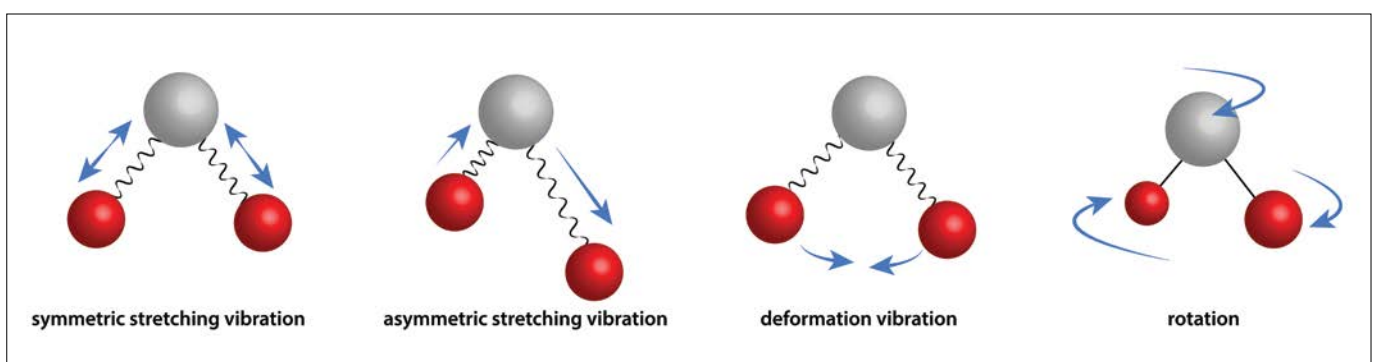


Figure 3. Molecule types sensitive to electromagnetic energy

Hydrogen also has the lowest molecular weight, which makes it almost impossible to detect by IR absorption interaction

Asymmetrical molecules absorb discrete energy levels at significant intensity due to the multiple vibrations. Symmetric molecules such as oxygen and nitrogen have relatively weak absorption bands in the infrared region. Their absorption spectrum of nitrogen primarily involves rotational-vibrational transitions, which may not be as intense or distinct as those of other gases. This can make it challenging to detect and quantify nitrogen and oxygen using conventional IR spectroscopy techniques, especially at low concentrations. Hydrogen also has the lowest molecular weight, which makes it almost impossible to detect by IR absorption interaction.

In principle, analytical spectroscopy consists of three main parts:

1. Energy source for exciting a specific molecule in the gas sample
2. Gas sample – gases should be extracted and purified before measurement
3. Detection of signals evolved from the interaction of electromagnetic waves with specific materials – those feedback signals may consist of electromagnetic energy or acoustic reactions

All the spectroscopy systems should be calibrated for the correct identification of specific species and for their quantification. This requires careful wavelength selection to be as unique as possible to the desired species and with maximum absorbed energy intensity.

The quantification of each species is obtained by the application of the

Beer-Lambert law.

$$A = \epsilon \cdot c \cdot l$$

- A is the absorbance (dimensionless, since absorbance is a logarithmic ratio),
- ϵ is the molar absorptivity or extinction coefficient of the absorber at a given wavelength ($L \cdot mol^{-1} \cdot cm^{-1}$),
- c is the concentration of the absorbing species in the solution ($mol \cdot L^{-1}$),
- l is the path length of the light through the solution (cm).

Formulation by German mathematician and chemist August Beer in 1852 states that the absorptive capacity of a dissolved substance is directly proportional to its concentration in a solution.

The Beer-Lambert Law assumes that the absorption of light by each layer of molecules in the solution is independent of the concentration of the molecules in other layers and that the absorbing medium does not scatter the light. It is widely used in quantitative spectroscopy for applica-

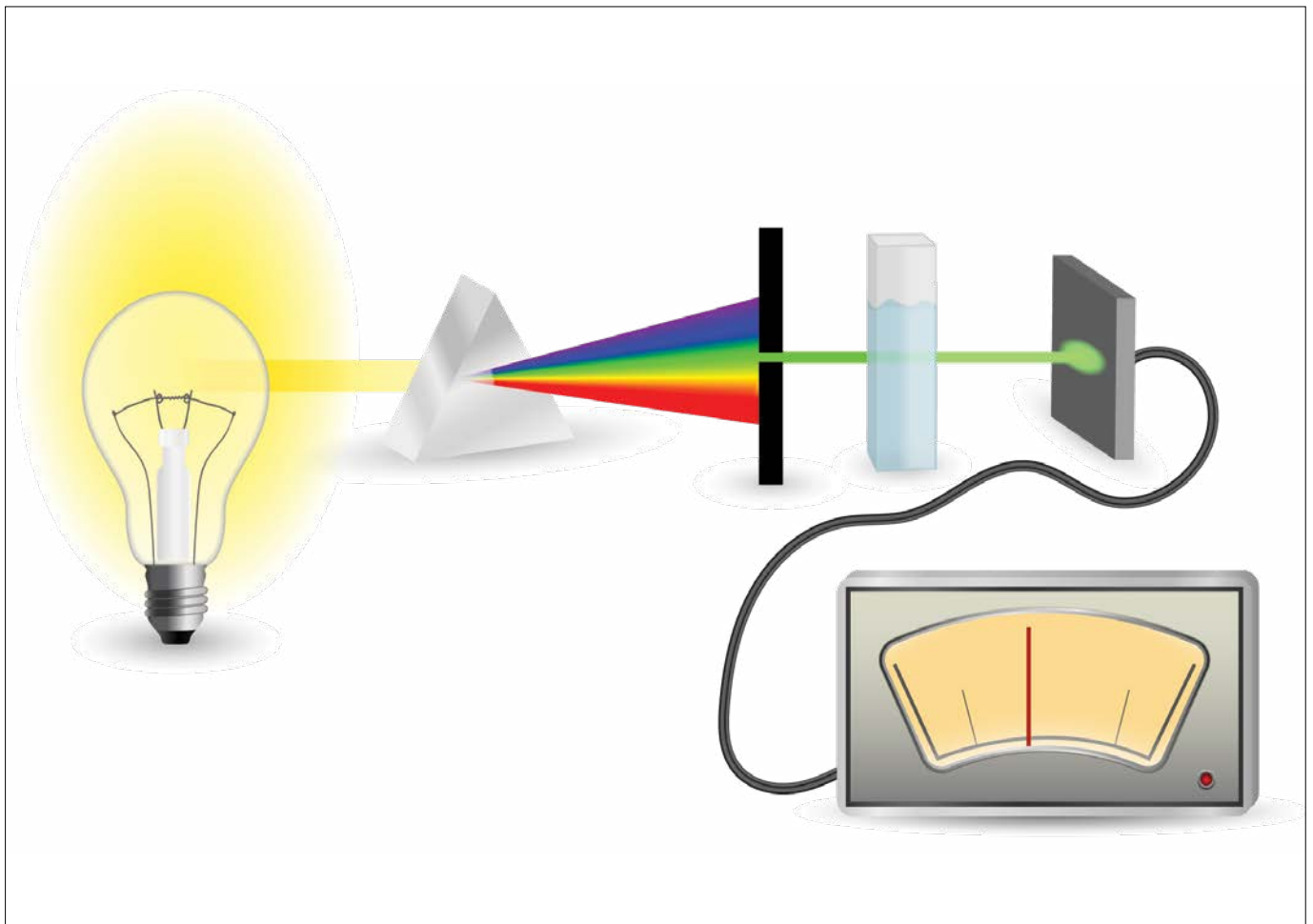


Figure 4. Basic spectrometer

Formulation by German mathematician and chemist August Beer in 1852 states that the absorptive capacity of a dissolved substance is directly proportional to its concentration in a solution

tions ranging from the determination of concentrations of solutions in a lab to the monitoring of gases in the atmosphere.

The key points to remember about the Beer-Lambert Law include its limitations, such as its applicability mainly to dilute solutions (to avoid intermolecular interaction effects that can alter absorbance) and to solutions where the absorber does not change its chemical state upon absorbing light. Additionally, deviations can occur at high concentrations due to changes in refractive index and at wavelengths where the absorbent undergoes saturation.

Although it should theoretically be a linear dependence, it is such in a quite limited range, significantly lower than the linearity range for gas chromatography, as seen in Figure 3.

This means that the measurement depends on the sample box size and the concentration of the specific gas. The target is to have a longer path with high concen-

tration for absorbance at higher energy levels.

The main challenges of DGA spectroscopy are:

1. Excitation part: Selection of specific energy (wave frequency) to be as much positive selective, seen in Figure 6. The spectrum of each gas appears at a different range of the spectrum due to different molecular vibrations. The spectrum itself consists of discrete lines and very accurate wavelengths, not, as sometimes presented, smooth curves. This means that the exciting energy should be very accurate and remain stable at a very specific energy. Otherwise, other species may be erroneously identified.
2. Test cell internal interferences – water; Gases should be present in the cell and be as purified as possible. The main interference is water vapor. Water appears in many parts of the spectrum at very high intensity due to its molecular structure. Water concentration is

also, in almost all cases, at the highest concentration, therefore, it seriously interferes with most of the gases. Algorithms are used in most cases to calculate the moisture content and subtract from the obtained absorbances of specific gases. Because water concentration in the liquid is estimated by using theoretical solubility coefficients, and in the majority of cases, the estimate is erroneous, and it may cause inaccurate important gas determination. For example, as the liquid ages, it dissolves more water, meaning less water vapor is present, so a spectroscopic DGA device may display increased values of gases only because the amount of water in the gas phase has decreased, while in reality, the gases have remained stable. A few transformers around the world were diagnosed incorrectly as possessing increased gas trends of ethylene and even acetylene because the online DGA spectrometric device displayed an increased amount of such gases only because the oil was aged. Aged oil cannot be monitored just by the total acid number.

3. Measurement element: Some spectroscopic methods are sensitive to the environment, as described above. It is also important to reduce the signal-to-noise ratio. For example, acoustic signals are a solution in specific cases where only the excited molecule produces sounds, and it is easier to distinguish low concentration relative to other existent mixtures, providing that the background is quiet and dry.
4. Stability: All spectrometric devices consist of a source of energy that excites the substances for testing. This source of energy is one of the main stability concerns. Normal ageing due to heating and improper usage may considerably decrease the lifespan of their sensors to several years, possibly even less. Detector units, such as the collection diode for energy feedback or microphones, may also degrade. Of course, the filters that protect the sample cell may be affected by too much-contaminated liquid, such as very old or originating from the OLTC compartment.

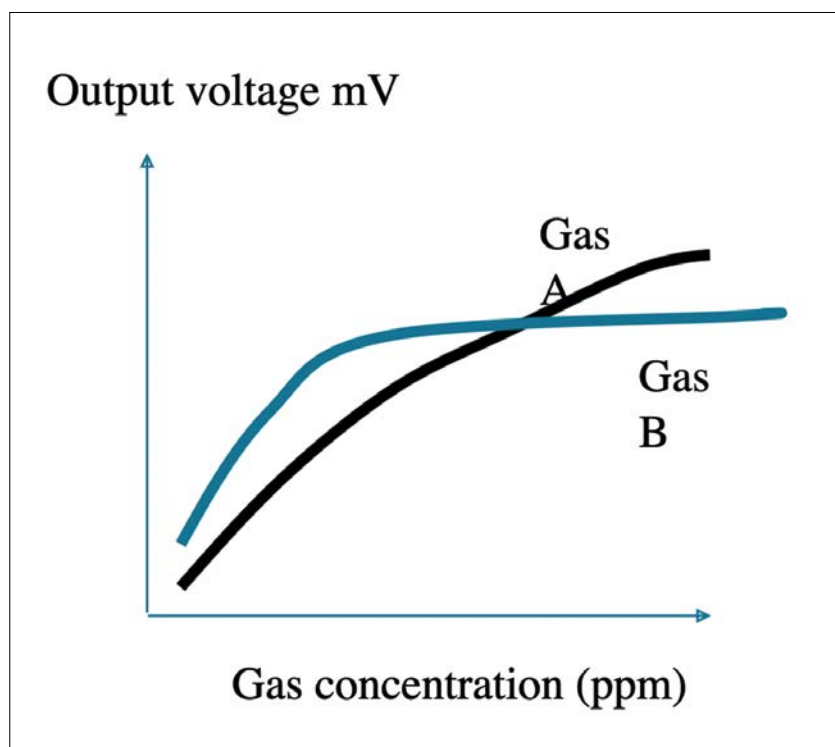


Figure 5. Limited linearity range for spectrometry determinations

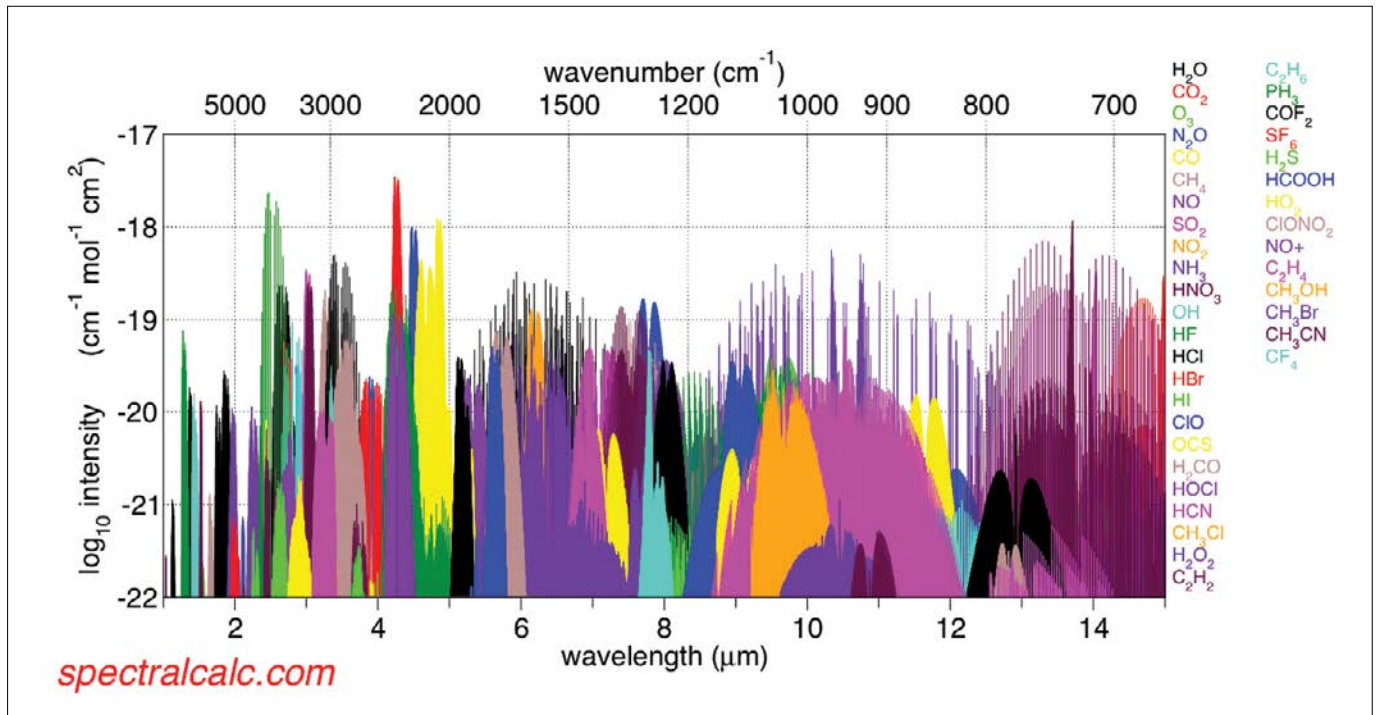


Figure 6. Spectra lines of gas mixtures [1]

Because of limitations and issues, the DGA spectrometric domain is quite dynamic, with many appearances and disappearances

5. Cost: A very reliable device with high selectivity and long-term stability for all the available gases for spectrometry detection (without hydrogen, oxygen, and nitrogen) may be obtained but at prices that most DGA users cannot afford, and higher than alternatives such as gas chromatography. As usual, this product is also a compromise between cost and performance for the power transformer industry. For other applications, such as in the environment or space exploration, those ideal devices may be found.

Because of all these limitations and issues, the DGA spectrometric domain is quite dynamic, with many appearances and disappearances. At least three main models were developed over the years and vanished from the market after a few years due to them.

Those were ATOM by ConEdison, TNU by Syprotec and GE and SmartDGA by Lumasense. The three were launched in the past and are not available anymore. Hopefully, lessons were learned, and the new generation of devices will probably remain on the market longer.

In the next part of the column, the excited DGA spectroscopy measurement and its

pros and cons will be described. Certainly, the products available today for this application are not final, and improvements are expected in the future. Those potential enhancements will be evaluated and anticipated for both users and manufacturers.

Disclaimer: This column is not a recommendation to use spectroscopic or any other technology for online DGA mea-

surement. Each transformer user should consider the most adequate needs for on-line DGA based on their specific needs, budget and experts' recommendations.

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Author



Marius Grisar 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.